



Diana Filipa Pereira Gaspar

Mestre em Engenharia de Materiais

Active cellulose-based substrates for application in electronic devices

Dissertação para obtenção do Grau de Doutor em
Materiais e Processamento Avançados

Orientador: Doutor Luís Miguel Nunes Pereira
Professor Associado, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa

Co-orientador: Doutor Rogério Manuel dos Santos Simões,
Professor Associado, Universidade da Beira Interior

Júri:

Presidente: Prof. Doutor João Carlos Palma Goes

Arguentes: Prof. Doutor Henrique Leonel Gomes

Prof. Doutora Florinda Mendes da Costa

Vogais: Prof. Doutor Carlos Pascoal Neto

Prof. Doutor Rodrigo Ferrão de Paiva Martins

Prof. Doutora Elvira Maria Correia Fortunato

Prof. Doutor Francisco Miguel Portela da Gama

Prof. Doutor Luís Miguel Nunes Pereira



FACULDADE DE
CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

Julho de 2019

Diana Filipa Pereira Gaspar

Mestre em Engenharia de Materiais

Active cellulose-based substrates for application in electronic devices

Dissertação para obtenção do Grau de Doutor em
Materiais e Processamento Avançados

Orientador: Doutor Luís Miguel Nunes Pereira, Profes-
sor Associado, Faculdade de Ciências e
Tecnologia da Universidade Nova de Lisboa

Co-orientador: Doutor Rogério Manuel dos Santos Simões,
Professor Associado, Universidade da Beira
Interior

Júri:

Presidente: Prof. Doutor João Carlos Palma Goes

Arguentes: Prof. Doutor Henrique Leonel Gomes
Prof. Doutora Florinda Mendes da Costa

Vogais: Prof. Doutor Carlos Pascoal Neto
Prof. Doutor Rodrigo Ferrão de Paiva Martins
Prof. Doutora Elvira Maria Correia Fortunato
Prof. Doutor Francisco Miguel Portela da Gama
Prof. Doutor Luís Miguel Nunes Pereira



Julho de 2019

Active cellulose-based substrates for application in electronic devices

**Copyright © Diana Filipa Pereira Gaspar, Faculdade de Ciências e Tecnologia,
Universidade Nova de Lisboa.**

A Faculdade de Ciências e Tecnologia e a Universidade Nova de Lisboa têm o direito, perpétuo e sem limites geográficos, de arquivar e publicar esta dissertação através de exemplares impressos reproduzidos em papel ou de forma digital, ou por qualquer outro meio conhecido ou que venha a ser inventado, e de a divulgar através de repositórios científicos e de admitir a sua cópia e distribuição com objectivos educacionais ou de investigação, não comerciais, desde que seja dado crédito ao autor e editor.

Acknowledgments

“We must find time to stop and thank the people who make a difference in our lives.”

John F. Kennedy

The quote that I chose to start my acknowledgements may seem like a cliché, but yet true. During this journey, I had the luck to be surrounded by people that made the difference and supported me during this work and to whom I wish to thank.

First, I want to acknowledge my supervisors for their support, advice and guidance.

I am profoundly grateful to Prof Luís Pereira, for providing me the scientific knowledge, encouragement, and help that any PhD student needs during this journey. Without his guidance and motivation, this PhD would not have been achievable.

My sincere gratitude to Prof. Rogério Simões, for your support, patience, comments during the writing period and knowledge. I know that this thesis is better due to your kind help. Also, thank you for receiving me at UBI (I felt so welcome there!), teaching me so much about paper and to let me make my own paper. I never thought that paper and cellulose could be such an exciting field. I also would like to acknowledge to the colleagues from UBI, Patrícia Baptista, Sónia Sousa, Vera Costa and Prof. Ana P. Costa, that helped me so much and made feel part of the group.

To Prof. Rodrigo Martins and Prof. Elvira Fortunato that turned the “*paper electronics*” a hot-topic, for the shared ideas, fruitful discussions that allowed me to progress, for providing me with the tools and allowing the development of this work in the research facilities of CENIMAT-i3N and CEMOP. Also, I am thankful for the confidence by including me in research projects, which allowed me to evolve personally and professionally.

To Prof. Miguel Gama from Minho University that gently offered me bacterial cellulose. A special thank you for Daniela Martins, that had the patience to “feed and take care” of the bacteria in order to produce my special membranes.

To Dr David Guerin, from CTP, for providing paper samples and nanocellulose that I studied and tested during this work.

To Prof. Maria H. Godinho and Dr Susete Fernandes from Soft Materials Group from FCT-NOVA, for the nanocrystalline cellulose membranes that were the beginning of this journey.

To Fundação para a Ciência e Tecnologia and AdvaMTech Program for the fellowship (PD/BD/52627/2014).

To the European Commission under project NewFun (ERC-StG-2014, GA640598), A3Ple (FP7, NMP-2010-SME-4 grant n° 262782) and BET-EU (H2020-TWINN-2015, GA

692373). This work was also supported by the FEDER funds through the COMPETE 2020 Program and the National Funds through the FCT – Portuguese Foundation for Science and Technology under the Project No. POCI-01-0145-FEDER-007688, Reference UID/CTM/50025, project FunPaper, reference EXPL/CTM-NAN/1184/2013, project PapEl, reference PTDC/CTM-NAN/5172/2014, and project SKINCHIP, reference PTDC/BBB-BIO/1889/2014_LISBOA-01-0145-FEDER-016595.

To all my colleagues in the MEON group that, direct or indirectly, contributed to this work: Prof Pedro Barquinha, Prof Rita Branquinho, Prof Joana Pinto, Ing. Alexandra Gonçalves, Ing. Sónia Pereira, Msc. Tiago Mateus, Ricardo Ferreira, Prof. Manuel Mendes, Dr Jonas Deuermier, Dr Asal Kiazadeh, Dr Daniela Gomes, Msc. Tomás Calmeiro, Msc. Jorge Martins (to have so much patience to help me to characterise my devices; I know how that can be challenging), Prof. Ganga Bahubalindrani, Msc. Ana Rovisco, Msc. Emanuel Carlos, Msc. Carolina Marques, Dr Deneb Menda, Dr Ana Pimentel, Msc. João Ribas, Msc. Adriana Costa, Msc. Sara Silvestre and everybody else I don't have room to mention. Thank you all! I learned so much with you all.

A special thank you for my partners of endless clean room work the (1.5 m) *girl squad*: Msc. Ana Santa, Msc. Cátia Figueiredo, Msc. Inês Martins, and Msc. Maria Pereira. I never get bored around you!

To the amazing people that I work every day: Msc. Paul Grey, Msc. Inês Cunha, Msc. Tiago Carvalho, Msc. Raquel Barras, Dr Cristina Gaspar, Msc. Marco Moreira, and Msc. Pedro Claro. It is a great pleasure to share the lab with you!

To former colleagues (but lifelong friends) that help and teach me so much in the begging or during this journey: Ing. Nuno Correia, Dr Gonçalo Gonçalves, Dr António Vicente, Dr Andreia Araújo, and Dr Lúcia Santos.

Also, I would like to extend my gratitude to the administrative support, Sara Oliveira (for the good mood, help and for handling so many issues during this PhD), Sónia Soares, Luís Milhano, Susana Mendes, Valéria Gomes, and Lúcia Mendes.

To all my friends for their comprehension and support. To my long(long)time friends Sophie Fidalgo, Rita Fernandes, and Ana Gaspar, for all the friendship, for keeping “*centred*” in good and bad moments. To Igor and Andreia for the friendship! To Rita and Rodrigo – no words are enough to thank your affection.

Finally, to my family for their support, love, for the patience and comprehension during this last year. To my parents who worked very hard to provide me the conditions and opportunities to follow my path. This achievement is also yours!

Abstract

The market for flexible, hybrid and printed electronics systems, which can appear in everything from sensors and wearables to displays and lighting, is still uncertain. What is clear is that these systems are appearing every day in new commercial applications, enabling devices and systems that can, in a near future, be crumpled up and tucked in our pocket. Although the exciting future foreseen for flexible electronics, it is clear that recyclability and sustainability is a concern due to the expected large number of devices to be disposed.

This PhD thesis aimed to be part of the (r)evolution of “*paper electronics*” that targets to turn cellulose into an electronic material, going beyond of considering it just as a substrate for flexible electronic devices. Functional cellulose-based substrates were developed able to serve both as physical support and gate dielectric layer in field-effect transistors (FETs). Several fibre sources were studied and modified aiming to form paper-like membranes with high electric double layer capacitance, enabling highly stable oxide-based FETs and logic gates. A key point is the ionic “doping” of membranes that was achieved either by chemical modification of the pulp or through impregnation of the formed membranes with alkaline solutions. It was found that the ones consisting of small fibres (nanofibrillated or bacterial cellulose) combined with the addition of sodium (Na^+) ions result in FETs with low operation voltage (-3 to 3 V), mobility above $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, current modulation surpassing 10^5 and negligible hysteresis, with proper dynamic response up to 40 Hz. The excellent performance of the FET on cellulose was also possible due to the optimisation of the oxide layers used (IGZO and IZO) as required due to the specific characteristics of fibre-based substrates. One of the innovations brought by this work was on the understanding of the role of hydrogen incorporation in such oxide layers, capable of resulting in optimal electro-optical properties at low deposition temperatures on paper like membranes.

The demonstration of electronics on and with cellulose went beyond the implementation as dielectric in transistors. New device architecture was introduced consisting of dual gate planar FETs enabling logic operations making use of just one transistor. This new architecture proved to be useful when integrating other devices, such as photodetectors in the same membrane to control the FETs, proving the enormous potential and versatility of such cellulose-based devices.

Keywords: *paper electronics; field-effect transistors; cellulose-based FET; electric-double layer; ionic doping; low temperature.*

Resumo

O mercado para sistemas electrónicos flexíveis, híbridos e impressos, que podem surgir em todos os dispositivos desde sensores e *wearables* a mostradores e iluminação, ainda é incerto. Contudo, o que é certo é que estes sistemas estão a aparecer diariamente em novas aplicações comerciais, possibilitando dispositivos e sistemas que num futuro próximo podem ser dobrados e facilmente guardados num bolso. Apesar do emocionante futuro previsto para a electrónica flexível, há uma constante preocupação com a sustentabilidade e reciclabilidade devido à grande quantidade de dispositivos que serão descartados.

Esta tese de doutoramento ambiciona contribuir para a (r)evolução da electrónica do papel utilizando a celulose como material electrónico ativo, e não apenas como um substrato para dispositivos electrónicos flexíveis. Desenvolveram-se substratos funcionais baseados em celulose que atuam simultaneamente como suporte físico e camada dieléctrica em transístores de efeito de campo (FETs). Foram também estudadas e modificadas diversas fontes de fibras de modo a obter papel com elevada capacidade da dupla camada eléctrica, permitindo produzir FETs baseados em óxidos e portas lógicas com elevada estabilidade. Um parâmetro fundamental é a dopagem das membranas com iões alcalinos que foi efetuada com soluções alcalinas, quer por modificação química da polpa quer por impregnação das membranas já formadas. Verificou-se que membranas compostas por fibras menores (nanofibriladas ou celulose bacteriana) quando dopadas com iões sódio (Na^+) resultavam em FETs com baixa tensão de funcionamento (-3 V a 3 V), mobilidade acima de $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, modulação de corrente superior a 10^5 , histerese negligenciável, e com uma boa resposta dinâmica até 40 Hz.

O excelente desempenho dos FETs em celulose também foi possibilitado pela otimização das camadas de óxidos utilizadas (IGZO e IZO) de acordo com as características específicas dos substratos celulósicos. Uma das grandes inovações deste trabalho foi a elucidação da influência da incorporação de hidrogénio nestas camadas de óxidos que permitiu obter filmes com propriedades eletro-ópticas otimizadas em substratos celulósicos e a baixa temperatura de deposição. A demonstração de electrónica em e com celulose foi para além da implementação como camada dieléctrica em transístores. Foi também implementada uma nova arquitetura consistindo em FETs planares com dois elétrodos de porta, permitindo assim operações lógicas utilizando apenas um transístor. Esta nova arquitetura é extremamente útil quando integrada com outros dispositivos como fotodetectores controlar os FETs, demonstrando o enorme potencial e versatilidade destes dispositivos baseados em celulose.

Palavras-chave: *electrónica de papel; transístores de efeito de campo; FET baseados em celulose; dupla camada eléctrica; dopagem iónica; baixa temperatura.*

Contents

Chapter 1. Cellulose-based substrates for electronic devices	5
1.1. Cellulose-based substrates	5
1.2. Cellulose	5
1.3. Paper and papermaking process	10
1.3.1. Sources: Raw materials	10
1.3.2. Pulping and papermaking processes	11
1.3.3. Paper classification	11
1.4. Micro/Nanofibrillated and Nanocrystalline cellulose	12
1.5. Bacterial Cellulose	15
1.6. Paper as a substrate for electronics and paper-based devices	16
1.6.1. Thermal and electrical properties	20
1.6.2. Field-effect transistors	21
1.7. References	31
Chapter 2. Materials and devices: fabrication and characterisation	43
2.1. Preparation of the cellulose substrates	43
2.1.1. Papermaking process	43
2.1.2. Nanocellulose membranes	47
2.1.3. Nanocrystalline cellulose membranes	48
2.1.4. Bacterial Cellulose	49
2.2. Thin films deposition and device fabrication techniques	51
2.2.1. Thin film deposition	51
2.2.1.1. Magnetron sputtering	51
2.2.1.2. Electron-beam assisted thermal evaporation	52
2.2.2. Field effect transistors	53
2.3. Cellulose substrates and thin-film characterisation	55
2.3.1. Structural, morphological, and compositional characterisation	55
2.3.1.1. X-ray diffraction	55
2.3.1.2. Porosity	56
2.3.1.3. Atomic force microscopy	56
2.3.1.1. Scanning Electron Microscopy	58

2.3.1.2.	X-ray Photoelectron Spectroscopy	59
2.3.2.	Optical characterisation	60
2.3.2.1.	UV-Visible-NIR transmittance spectroscopy	60
2.3.2.2.	Fourier-transform infrared spectroscopy	61
2.3.3.	Electrical characterisation	62
2.3.3.1.	Hall Effect	62
2.3.3.2.	Electrochemical Impedance Spectroscopy	63
2.3.4.	Complementary characterisation techniques	64
2.3.4.1.	Simultaneous Thermal analysis	64
2.4.	Electrical characterisation of cellulose-based transistors	65
2.5.	References	67
 <i>Chapter 3. Functional oxide thin films</i>		 73
3.1.	Transparent conductive and semiconductor oxides	73
3.2.	Hydrogenated TCOs	76
3.2.1.	Hydrogenated Zinc Oxide TCOs	78
3.2.1.1.	Structure and morphology	79
3.2.1.2.	Electrical and optical properties	82
3.2.1.3.	Chemical state and composition	87
3.2.2.	Aluminium-doped zinc oxide and gallium-doped zinc oxide thin films	89
3.2.2.1.	Electrical and optical properties	90
3.2.2.2.	Al and Ga co-doped ZnO thin films	92
3.2.3.	Hydrogenated Indium Zinc Oxide TCOs	95
3.2.3.1.	Structure and morphology	96
3.2.3.2.	Electrical and optical properties	97
3.2.3.3.	Electrical properties of IZO:H on different substrates	100
3.2.3.4.	Chemical state and composition	101
3.3.	Semiconductor oxide thin films	104
3.3.1.	IGZO system	104
3.3.1.1.	Optical and electrical properties	105
3.3.1.2.	IGZO-based FETs	107
3.4.	References	109

Chapter 4. Transistors on paper-like substrates	119
4.1. Substrates from commercial kraft pulp	119
4.2. Influence of the pulp	120
4.3. Fibres' dimension	125
4.3.1. Influence of the water content on the paper's characteristics	125
4.3.2. Paper/semiconductor interface	128
4.3.3. Influence of the water content in the FETs performance	129
4.3.4. I_{On}/I_{Off} ratio dependence with frequency	132
4.3.5. Mechanical Stability	134
4.3.5.1. Bending tests	134
4.3.6. Electrical stability over time	136
4.4. Physical modification of bleached softwood kraft pulp (BSKP) papers	138
4.4.1. Refining and porosity/density influence	138
4.4.2. FETs on BSKP papers	141
4.4.2.1. Influence of the fibres' orientation	144
4.5. Chemical modification	145
4.5.1. Addition of extra ionic species to the micro-nanofibrillated cellulose	146
4.5.1.1. M/NFC papers: morphology, structure, and electrical characterisation	146
4.5.1.2. M/NFC papers as a gate dielectric in field-effect transistors	148
4.5.1.3. FETs stability over time	150
4.5.2. Papers produced with TEMPO-mediated oxidised pulps	151
4.5.2.1. TEMPO-mediated oxidised papers	152
4.5.2.2. Influence of the oxidation level in the FETs' performance	153
4.6. References	156
 Chapter 5. Transistors on modified micro/nanocellulose membranes	 163
Lightweight micro/nanocellulose membranes	163
5.1. Micro/nanofibrillated cellulose	164
5.1.1. Micro/nanofibrillated cellulose and influence of the alkaline ion doping	165
5.1.1.1. Structural and morphological characterisation	165
5.1.1.2. Electrochemical characterisation of the NFC-membranes	169
5.1.1.3. NFC-Membranes as gate dielectric in oxide FETs	174

5.1.1.4.	Shelf time stability of the NFC-gated FETs	177
5.1.1.5.	Flexibility, and electrical endurance of the pristine membranes	179
5.1.1.6.	Recyclability	184
5.2.	Nanocrystalline cellulose	187
5.2.1.	Structural and morphological properties of NCC membranes	187
5.2.2.	NCC-gated FETs	189
5.3.	All-cellulose composites	191
5.3.1.	Structure and morphology	191
5.3.2.	All-cellulose composites as gate dielectric in FETs	193
5.4.	Bacterial Cellulose	195
5.4.1.	Alkali-doped BC membranes	195
5.4.1.1.	Morphological and structural characterisation	196
5.4.1.2.	Application of BC as dielectric in field-effect transistors	199
5.4.2.	Highly pure membranes and pH influence	201
5.4.2.1.	pH influence on oxide-based FETs performance	202
5.5.	References	203
 <i>Chapter 6. Logic operations with transistors on cellulose substrates</i>		 211
6.1.	Dual-gate oxide-based field effect transistors	211
6.1.1.	Architecture and devices' conception	212
6.1.2.	DG-FGFETs electrical characteristics	213
6.1.2.1.	Influence of the electrodes' separation and yield of fabrication	220
6.1.3.	Logics in a single DG-FGFET	223
6.1.4.	Tensile Bending Strain Tests	226
6.2.	Low voltage logic on NFC membranes	227
6.2.1.	NFC-gated dual-gate transistors	228
6.2.2.	Alkali-doped NFC membranes in inverters	230
6.3.	References	236
 <i>Chapter 7. Conclusions and future perspectives</i>		 241
7.1.	Main conclusions	241
7.2.	Future perspectives	247
7.3.	References	249

List of Figures

Figure 1.1 Schematic association of cellulose at the molecular level in the vegetable cell walls [10], [14]–[16].	6
Figure 1.2 Scheme of the general structure of the cell wall of fibre, and respective layers (adapted from [17]–[19]).	7
Figure 1.3 Different cellulose sources in Nature [14], [23]–[26].	8
Figure 1.4 Cellulose polymorphs (adapted from [11]).	9
Figure 1.5 From macroscopic fibres to nanomaterials: Top-down approaches for the preparation of micro and nanoscale cellulosic materials [13].	13
Figure 1.6 a) SEM micrograph of the surface morphology of nanocrystalline cellulose (NCC) membranes obtained from cotton and the corresponding cross section (inset), and b) photograph of the corresponding NCC membrane (adapted from [22]).	14
Figure 1.7 Bacterial Cellulose - a) <i>Komagataeibacter xylinus</i> micrographs and schematic representation from the extrusion mechanism; b) photograph from a dried membrane, c) SEM image from the membrane's surface, and d) corresponding cross section [39].	16
Figure 1.8 a) Bulk resistivity of paper (160 g m^{-2}) as a function of NaCl addition, with RH constant and tested voltages of 10 and 750 V, and b) Conductivity variation with the RH for kraft paper, wood nanofibrillated and algae cellulose (adapted from [88], [90]).	21
Figure 1.9 Schematic representation of a TFT and a MOSFET [93].	22
Figure 1.10 Conventional TFT structures depending on the positioning of layers [93].	22
Figure 1.11 Schematic representation of staggered-bottom gate FETs using cellulose as a gate dielectric.	23
Figure 1.12 Schematic diagram of the device structure and respective charges modulation for a) oxide-based dielectric and b) EDL in cellulose-based dielectric.	25
Figure 1.13 Stern model of the electrical double layer at a negatively charged surface.	26
Figure 1.14 Cross section of an EDL gated devices working in a) electrochemical mode (ECTs), b) field-effect mode, and c) EDL behaviour under a negative and positive V_{GS} , respectively.	27
Figure 2.1 a) PFI mill in UBI and schematic representation of the working principle. b) Schopper–Riegler apparatus [3].	44
Figure 2.2 a) Hand sheet former at UBI facilities, and b) dynamic former.	46
Figure 2.3 a) BBKP and BSEP NFC gel produced at CTP and UBI, respectively. b) NFC dried membranes produced by casting evaporation.	47
Figure 2.4 Bacterial cellulose fermentation in several bioreactors. The BC slab is identified with the blue arrows.	50

Figure 2.5 Schematic representation of a magnetron sputtering deposition system.	52
Figure 2.6 Representation of electron-beam assisted thermal evaporation system.	53
Figure 2.7 Schematic representation of cellulose-based FET deposition steps sequence.	54
Figure 2.8 (a) Representation of a constructive interference according to Bragg's Law. b) Panalytical XPert Pro diffractometer at CENIMAT/CEMOP facilities.	56
Figure 2.9 Asylum MFP3D atomic force microscope system existent in CENIMAT.	57
Figure 2.10 SEM-FIB Cross-Beam Auriga system existent in CENIMAT facilities.	58
Figure 2.11 XPS Axis Supra by Kratos Analytical system existent in CEMOP facilities.	59
Figure 2.12 Thermo Nicolet 6700 Spectrometer equipment used during this work.	61
Figure 2.13 a) Van der Pauw geometry used for the Hall effect measures. b) Biorad 5500PC Hall effect system installed in the CEMOP.	63
Figure 2.14 Electrochemical cell produced for the a) potentiostatic, and b) electrochemical impedance spectroscopy. c) Potentiostat 600TM Gamry Instruments used for impedance measurements of the cellulose samples	64
Figure 2.15 a) Agilent 4155C analyser coupled to a Cascade M150 microprocessor (dark box), and b) microprobe station from Janis Research Company.	67
Figure 3.1 Periodic table where the elements whose electronic configuration is $(n-1)d^{10}s^0$ are highlighted.	75
Figure 3.2 Schematic representation of the conduction band for the covalent amorphous (on the left) and ionic semiconductors (on the right), respectively [8].	76
Figure 3.3 Universal alignment of hydrogen level in semiconductors (adapted from [21]).	77
Figure 3.4 ZnO thin film growth rate variation as a function of H_2 dilution ratio (D_{H_2}).	79
Figure 3.5 a) XRD diffraction patterns of ZnO thin films deposited with different H_2 dilution ratios (D_{H_2}). The patterns show the preferential growth along [001] directions for the highest D_{H_2} ; in the inset the top view of the ZnO crystal for [001] direction is depicted (orange and blue atoms represent O and Zn, respectively). b) and c) detailed view of the (002) reflex shift towards lower 2θ values as D_{H_2} increases.	80
Figure 3.6 Dependence of the crystallite size, and RMS roughness determined by AFM on the H_2 dilution (D_{H_2}) ratio used. (The lines are guide for the eyes.).	81
Figure 3.7 SEM micrographs obtained for ZnO thin films for different D_{H_2} tested: a) 0%, b) 0.5%, c) 1%, d) 1.5% and e) 2%, and AFM images D_{H_2} of f) 0 % and g) 1.5 %.	81
Figure 3.8 Variation of resistivity (ρ) carrier concentration (n), and electron mobility (μ_H) for the ZnO films deposited with different H_2 dilution ratios (D_{H_2}).	82
Figure 3.9 Optical characterisation of ZnO films processed at different H_2 dilution ratios (D_{H_2}): a) Optical transmittance spectra. The inset shows the blue-shift of the absorption	83

edge with D_{H_2} , b) Linear relation of E_{op} vs $n^{2/3}$, corroborating the B-M effect (The line is a guide for the eyes.).

Figure 3.10 Dependence of the figure of merit (FoM) on the H_2 dilution (D_{H_2}). FoM of ITO, FTO, AZO, and GZO are also indicated in the graph using a dashed line only as a guide for the eyes. **84**

Figure 3.11 Temperature dependence of the electrical properties for the ZnO films prepared with D_{H_2} of 0 and 1.5 %: a) Temperature dependence for both μ_H and n ; b) Relation between μ_H and T for $D_{H_2}=0$ % using the grain boundary (degenerated and non-degenerated) and ionised impurities (non-degenerated) scattering models. **85**

Figure 3.12 Schematic band diagram of the possible electronic transitions responsible for the different emissions in ZnO films. **86**

Figure 3.13 Room temperature PL spectra ZnO films deposited without H_2 (dotted line) and with $D_{H_2}=1.5\%$ (solid line). **87**

Figure 3.14 XPS spectra for films processed without (dashed line) and with H_2 dilution ($D_{H_2}=1.5\%$, full line): a) ZnO and ZnO:H Zn 2p XPS spectra; b) O 1s Peak from ZnO and ZnO:H. **88**

Figure 3.15 Doped zinc oxide structure, the substitutional position of the doping atoms is represented by the golden atoms. **89**

Figure 3.16 AZO and GZO growth rate variation as a function of H_2 dilution ratio (D_{H_2}). **90**

Figure 3.17 Electrical properties variation - resistivity (ρ) carrier concentration (n), and electron mobility (μ_H) - for the a) AZO films, and b) GZO deposited with different H_2 dilution ratios (D_{H_2}). (The lines are a guides for the eyes.). **91**

Figure 3.18 Influence of the H_2 dilution ratios (D_{H_2}) on the optical properties of the AZO and GZO films. Optical transmittance spectra of a) AZO, and b) GZO thin films. **92**

Figure 3.19 a) Optical transmittance spectra of AGZO films processed with different power densities; b) Figure of merit (FoM) of the sputtered AZO, GZO and AGZO films in the visible range (solid lines). Reference values of the FoM for ITO, FTO, AZO, and GZO are also indicated in the graph using the dashed line [4]. **94**

Figure 3.20 a) XRD diffraction patterns of AZO (5.5 W cm^{-2}), GZO (2.2 W cm^{-2}) and AGZO ($5.5/2.2 \text{ W cm}^{-2}$) thin films deposited with $D_{H_2}=1.5\%$, b) and detailed view of the (002) reflex peak. c) SEM micrograph of the AGZO ($5.5/2.2 \text{ W cm}^{-2}$) film and respective elementary identification (table). **94**

Figure 3.21 Diffractograms of the sputtered IZO:H films prepared with different D_{O_2} and D_{H_2} . **96**

Figure 3.22 a) SEM micrographs of the IZO thin films produced under different sputtering atmospheres (Ar and five different reactive atmospheres), and b) AFM image of the Ar sputtered IZO film. **97**

Figure 3.23 Influence of the deposition conditions on the IZO:H thin films' electrical parameters: a) resistivity, b) mobility, and c) carrier concentration. **98**

Figure 3.24 a) Optical transmittance of the IZO:H films, and b) E_{op} as a function of the $n^{2/3}$, **99**

according to the Burstein-Moss effect. (The lines are guide for the eyes.)

Figure 3.25 Normalised electrical parameters of IZO:H deposited on glass, nanofibrillated cellulose (NFC), sodium-doped NFC (NFC:Na) and commercial standard paper (CSP) with $D_{O_2}/D_{H_2}=1.44\%/2.87\%$. **100**

Figure 3.26 XPS spectra for IZO:H films processed without and with different H_2 dilution: a) Zn 2p_{3/2}, and b) In 3d_{5/2} XPS spectra. **102**

Figure 3.27 XPS spectra of O 1s peak for IZO produced under atmosphere of a) Ar, b) Ar + O₂, c) Ar + H₂, d) and e) Ar + O₂ + H₂, with $D_{O_2}(\%)/D_{H_2}(\%) = 1.46/1.46$ and $1.42/3.79$, respectively. **103**

Figure 3.28 a) XRD diffractograms of the sputtered IGZO 1:2:2 for the different D_{O_2} tested. b) Micrograph and c) AFM 3D topography of the IGZO 1:2:2 produced with $D_{O_2}=17.6\%$. **105**

Figure 3.29 a) Optical characterisation (optical transmittance and α^2 -E plots) of the IGZO thin films produced with different O₂ dilutions. b) Normalised atomic concentration of zinc, gallium and indium (excluding oxygen) in the IGZO thin films produced with different reactive atmospheres. **106**

Figure 3.30 Arrhenius plot of electrical conductivity dependence as a function of the temperature, used to determine the thermal activation energy the IGZO thin films for the different D_{O_2} . **107**

Figure 3.31 Effect of the D_{O_2} on the transfer characteristics of the IGZO FETs on paper annealed at 150 °C: a) I_{DS} - V_{GS} transfer characteristic, and b) I_{On}/I_{Off} , S, and V_{On} . **108**

Figure 4.1 SEM micrographs of samples of a) commercial paper, b) lab prepared softwood pulp substrates and c) lab prepared hardwood pulp substrates. **121**

Figure 4.2 a) XRD diffractograms of samples produced with different pulp sources and b) ATR-FTIR spectra of the different paper samples (normalised to the intensity of the band at 2900 cm⁻¹). **122**

Figure 4.3 Thermogravimetry analysis (TGA and DTA) of the different paper samples. **123**

Figure 4.4 Capacitance variation with frequency (C_{real} -f) of the three paper samples analysed. The inset shows the structure of the capacitors produced for the EIS measurements. **124**

Figure 4.5 SEM micrographs of a) commercial standard paper (CSP), b) bleached softwood kraft paper (BSKP), and c) micro-nanofibrillated cellulose paper (M/NFC). **125**

Figure 4.6 Electrochemical Impedance Spectroscopy: a) Capacitance variation with frequency (C-f) of the set of paper samples used. (Solid lines represent the capacitance measured at atmospheric pressure, while the open symbols represent the capacitance measured under vacuum after pumping for 15 minutes), b) Phase angle as a function of the frequency, at atmospheric pressure, and c) after under vacuum after pumping for 15 minutes. **126**

Figure 4.7 ATR-FTIR spectra of the bands at 3600-3000 cm⁻¹ and 1635 cm⁻¹ for a) CSP, b) BSKP, and c) M/NFC. The water content variation under vacuum and after recovery was analysed by the changes in the intensity of these bands. d) Thermal analysis of the three different paper samples. **127**

Figure 4.8 SEM of a cross-section of the paper/IGZO surface. The inset shows an artificial colouration of the IGZO for better visualisation, showing a perfect fibre coverage provided by the sputtered layer.	129
Figure 4.9 Transfer characteristics (I_{DS} - V_{GS}) for the IGZO-based paper FETs on the tested paper samples, and schematic representation of the devices.	130
Figure 4.10 I_{DS} - V_{GS} transfer characteristics of the paper gated IGZO FETs ($V_{DS}=15$ V) measured initially at atmospheric pressure (solid line), under vacuum after different times and after recovery at atmospheric pressure.	131
Figure 4.11 Gate leakage current (I_{GS}) variation under vacuum conditions and after recovery at atmospheric pressure.	132
Figure 4.12 I_{ON}/I_{OFF} ratio as a function of the applied frequency to the gate of the paper-based FETs ($V_{DS}=15$ V).	133
Figure 4.13 I_{DS} variation under a square wave of 10 mHz and an amplitude of 40 V (from -20 to 20V). ($V_{DS}=15$ V).	133
Figure 4.14 Bending test of the paper-based FETs: a) photograph of the devices under test, and normalized electrical characteristics of the devices' values ($\mu_{Sat} - \mu/\mu_0$, I_{ON}/I_{OFF} ratio - I/I_0 , and $S - S/S_0$) on b) CSP (The inset shows schematic representation of the bending test), c) BSKP and d) M/NFC papers determined under tensile bending strain (solid symbols) and flat position after the bending (open symbols).	135
Figure 4.15 Transfer characteristics (I_{DS} - V_{GS}) of the fresh and four years aged FETs.	137
Figure 4.16 a) SEM micrographs for the produced BSKP papers, and b) corresponding diffractograms.	139
Figure 4.17 a) Capacitance as a function of the frequency for the papers produced with a beating index of 27°SR and 48°SR (solid and dashed lines, respectively), and b) Cole-Cole plots for the papers produced from pulp with 48°SR	141
Figure 4.18 I_{DS} - V_{GS} transfer curves ($V_{DS}=15$ V) for the FETs produced on the BSKP papers with 27°SR (on the left), and 48°SR (on the right).	142
Figure 4.19 Output curves for the IGZO-FET on calendared orientated paper with a) 27°SR, and b) 48°SR, respectively.	144
Figure 4.20 Preferential orientation of the fibres in respect to the FETs channel: a) schematic representation, b) width-oriented fibres, and c) length-oriented fibres. The dashed lines in b) and c) aim to highlight the fibres' orientation along the channel.	144
Figure 4.21 SEM micrographs of the M/NFC papers produced with: a) pristine fibres, b) alkaline pulp (pH=8.5 adjusted with NaOH addition), and c) acid pulp (pH=5.5 adjusted with HCl addition).	146
Figure 4.22 XRD diffractograms for the prepared M/NFC papers.	147
Figure 4.23 Electrochemical Impedance Spectroscopy of the M/NFC papers. Capacitance and phase as a function of the frequency. The inset shows the Cole-Cole plot to determine the papers' resistance.	148

Figure 4.24 a) Transfer characteristics I_{DS} - V_{GS} , and b) output curves of the M/NFC gated transistors. In the inset a photograph of the FETs produced with the M/NFC papers is shown (from top to bottom: M/NFC pristine pulp, pulp with pH=8.5, and pulp with pH=5.5).	149
Figure 4.25 Aging effect of the M/NFC gated FETs: transfer characteristics I_{DS} - V_{GS} of the devices produced on M/NFC with different pH levels. The solid line represents “fresh” devices (1 st day), while the dotted line stands for the devices aged for four years.	150
Figure 4.26 Schematic representation of the selective oxidation of mainly the C ₆ primary hydroxyl groups to C ₆ sodium carboxylate groups using the TEMPO/NaBr/NaClO system [40].	152
Figure 4.27 Micrographs of the bleached eucalyptus kraft pulp paper with different oxidation levels. a) no oxidation, b) oxidation with 2 mmol of NaClO, and c) oxidation with 4 mmol of NaClO.	153
Figure 4.28 Transfer characteristics of the FETs on BEKP papers with different oxidation grades. On the top right the steps of the preparation of TEMPO-oxidized cellulose and counterion exchange with HCl is depicted.	154
Figure 4.29 ATR-FTIR data of the BEKP papers with different oxidation grades. The inset shows the full spectra acquired with indication of the zoomed region.	155
Figure 5.1 Diagram of the top-down approach to obtain cellulose nanofibrils and cellulose nanocrystals.	164
Figure 5.2 NFC gel produced at CTP (on the left) and UBI (on the right) laboratories.	163
Figure 5.3 NFC membranes produced with bleached birch kraft pulp (BBKP), and bleached sulphite eucalypt pulp (BSEP), from CTP and UBI, respectively.	166
Figure 5.4 XRD diffractograms of the pristine and ion enriched BBKP-NFC and BSEP:NFC membranes.	166
Figure 5.5 FTIR spectra of the pristine NFC and ion doped NFC membranes produced with bleached birch kraft pulp (BBKP – on the left), and bleached sulphite eucalypt pulp (BSEP – on the right).	168
Figure 5.6 EIS of the BBKP-NFC membranes (pristine, Li, Na and K doped): a) C_{real} (solid line) and phase angle (open symbols) as function of the applied frequency, b) Comparison of the C_{real} and C_{eff} as a function of the applied frequency for NFC:Na, and c) Cole-Cole plot of the NFC membranes. The insets show a zoom of the indicated area for low resistance values from the NFC:Li and NFC:Na.	171
Figure 5.7 Cyclic voltammetry of the BBKP-NFC membranes (pristine, Li, Na and K enriched) at different scan rates.	173
Figure 5.8 a) Comparison of the capacitances (C_{real} , C_{eff} and C_{DL}) obtained from EIS and CV measurements. b) CV of the Al/NFC/IGZO/Al structure produced to emulate the electrochemical behaviour in real FETs for a scan rate = 400 mV s ⁻¹ . The inset of b) shows a schematic representation of the cells produced to perform the respective measurements.	174
Figure 5.9 Transfer characteristics (I_{DS} - V_{GS}) with hysteresis of the NFC-gated FETs for	175

$V_{DS} = 1$ V (on the left) and $V_{DS} = 2.5$ V (on the right). The scattered squares stand for the I_{GS} .

Figure 5.10 Output characteristics for the NFC-gated FETs. **177**

Figure 5.11 Transfer characteristics I_{DS} - V_{GS} of the NFC-gated FETs acquired one day, three months and fifteen months after production. **178**

Figure 5.12 Normalized values of the I_{ON}/I_{OFF} ratio (I/I_0), sub-threshold slope (S/S_0), and mobility (μ/μ_0) of the aged NFC-gated FETs. The parameters with the subscript “0” refer to the values determined in the first measurement of the device. **179**

Figure 5.13 Normalized electrical parameters of the I_{ON}/I_{OFF} ratio (I/I_0), sub-threshold slope (S/S_0), and mobility (μ/μ_0) of the device for outward (on the left) and inward (on the right) bending strains. The open symbols represent the variation of the electrical properties after back to flat condition. **180**

Figure 5.14 Transfer characteristic curves of the FETs characterised with a scan rate of 0.4 V s^{-1} . On the left the curves for the initial 900 cycles are represented, while on the right the 200 cycles after 8 hours recovery are plotted. The dash-dot lines are indicative of the 1st and 900th cycle of the FET before resting time. **182**

Figure 5.15 Electrical performance of the NFC-gated FETs for a scan rate of 4 Vs^{-1} . a) and b) transfer characteristics curves of the initial 900 cycles in semi-log and linear scale, respectively. c) devices behaviour after 8 hours of rest and an extra 200 cycles. d) Normalised On current as a function for the first 900 cycles and the following 200 cycles after an 8h recovering period. e) Leakage current (I_{GS}) variation for the 900 first cycles. **183**

Figure 5.16 Normalised electrical parameters (I_{ON}/I_{OFF} ratio - I/I_0 , sub-threshold slope - S/S_0 , and mobility - μ/μ_0) of the devices for 900 cycles (on the left) and 200 cycles after 8 hours of recovery (on the right). The solid symbols represent the scan rate of 0.4 V s^{-1} , and the hollow symbols represent the scan rate of 4 V s^{-1} . **184**

Figure 5.17 Steps involved in the NFC FETs recycling process. a) NFC-gated FETs used for the recycling before soaked in water (b1), and b2) after stirring for a few hours. c1) dried pristine and recycled membranes, also photographed in c2). **185**

Figure 5.18 SEM micrograph of the recycled NFC membrane, and EDX elements identification for the Al, In, and Ga. The inset shows an IZO particle with a large dimension entangled in the NFC fibres. **185**

Figure 5.19 a) EIS characterisation of the NFC membranes (pristine and recycled), b) CV of the devices produced to emulate the electrochemical behaviour of real FETs (scan rate= 0.4 mV s^{-1}) The inset shows a schematic representation of the produced cells. c) I_{DS} - V_{GS} curves of the NFC-gated transistors using pristine and recycled membranes ($V_{GS}=2.5 \text{ V}$). **186**

Figure 5.20 Micrographs of the free-standing NCC membranes produced by shear casting (on the left) and by evaporation. The insets show the corresponding cross-sections. **188**

Figure 5.21 a) Optical characterisation of the NCC membranes reaching an AVT $\approx$ 85% (membranes with $30 \text{ }\mu\text{m}$), and b) photograph of one NCC membrane produced by evaporation. **189**

Figure 5.22 NCC-gated FET's electrical characteristics, a) I_{DS} - V_{GS} transfer and output characteristics of the FETs deposited on b) evaporated and c) shear casting NCC.	190
Figure 5.23 SEM images of the all-cellulose composites, NFC and NCC membranes.	192
Figure 5.24 Specular transmittance of the all-cellulose composites.	193
Figure 5.25 I_{DS} - V_{GS} transfer characteristics of the FETs with all-cellulose composites as gate dielectrics.	194
Figure 5.26 XRD diffractograms of the BC membranes with different metal alkaline ions.	196
Figure 5.27 a) SEM Micrographs of the pristine BC and the alkali-doped membranes. b) FTIR spectra of the BC membranes (pristine and alkali-doped).	197
Figure 5.28 Thermal analysis of the reference BC membrane. The thermogravimetric analysis is represented in the left yy axis, and derivative weight is represented in the right yy axis.	198
Figure 5.29 EIS characterisation of the alkali-doped BC membranes: C_{eff} as a function of the applied frequency (on the left) and determination of the BC resistance (on the right).	199
Figure 5.30 FETs using alkali-doped membranes as the gate dielectric. On the left the transfer characteristics I_{DS} - V_{GS} for a V_{DS} =2.5 V. On the right, saturated output characteristic curves for the FETs on BC:Na.	200
Figure 5.31 a) SEM of pristine BC and of a membrane with pH=11, b) Optical transmittance of the BC membranes with pH=11. The inset shows a photograph of a highly pure dried BC membrane.	201
Figure 5.32 a) Impedance spectroscopy of the membranes produced with pH=11 showing C_{eff} and Phase as a function of frequency. b) Transfer (I_{DS} - V_{GS}) curves of the BC-gated FETs (V_{DS} =2.5 V) and c) respective output characteristics.	202
Figure 6.1 a) Schematic illustration of the architecture of IGZO paper DG-FGFETs using the tracing paper as the gate dielectric. G_1 and G_2 stand for the primary and secondary gate, respectively, while S and D are the source and drain, respectively.	212
Figure 6.2 a) I_{DS} - V_{GS} transfer characteristics of the paper gated IGZO DG-FGFETs at V_{DS} =1 and 15 V (linear and saturation regime). I_{GS} for V_{DS} =1 V and V_{GS2} =0 V is also plotted, b) I_{DS} - V_{GS} transfer characteristics of DG-FGFETs with and without floating gate (V_{DS} =15 V and V_{GS2} =0).	213
Figure 6.3 V_{ON} dependence on V_{GS2} , respectively for a V_{DS} of 1V and 15 V. The variation of V_{ON} follows a linear tendency that was fitted according to the equations presented in the figure.	214
Figure 6.4 Comparison of electrical parameters of the paper-based DG-FGFETs for different V_{GS2} : a) sub-threshold slope (S), and b) mobility (μ_{FE} and μ_{SAT}) (open symbols for V_{DS} =1 V and solid symbols for V_{DS} =15 V) (The lines are merely guides for the eyes.)	215
Figure 6.5 Schematic representation of the operation mode of the paper DG-FGFETs as a function of the V_{GS2} , and its influence on the accumulation of carriers in the channel, showing the depletion region (in orange). The plots depict the Surface Potential Profile (SPP,	217

solid lines) for different $V_{GS1}/V_{DS}/V_{GS2}$ combinations and the resulting Floating Gate potential (V_{FG}) determined for each case (dashed lines). In each situation, a simplified schematic diagram of the ions' distribution in the paper dielectric is presented, aiming to understand better the potential's intensity established at the floating electrode that depends on the balance established by $V_{GS1}/V_{DS}/V_{GS2}$.

Figure 6.6 V_{FG} potential simulation using SILVACO software for a DG-FGFETs with $V_{GS1}=30$ V, $V_{DS}=15$ V, and $V_{GS2}=-5$ V, a) Cross-section of the potential profile, b) Surface potential profile at the interface paper/electrodes and respective V_{FG} for the applied voltages, c) Zoom-in of the region near the electrodes, and d) Detail of the potential variation in the IGZO channel. **219**

Figure 6.7 a) $I_{DS}-V_{FG}$ transfer characteristics of the paper gated IGZO DG-FGFETs at $V_{DS}=1, 6$, and 15 V for different V_{GS2} , b) V_{FG} variation as a function of V_{GS1} and V_{GS2} for different V_{DS} . **220**

Figure 6.8 a) Schematic representation of the separation of the electrodes, and b) respective transfer characteristics for DGFG-FETs for $V_{DS}=15$ V. **221**

Figure 6.9 a) Transfer characteristics for DGFG-FETs with three different distances between S/D and G_1/G_2 (365, 570, and 770 μm) as a function of V_{FG} , and b) respective variation of V_{FG} with V_{GS2} as a function of V_{GS1} ($V_{GS2}=[-15;15]$ V, and $V_{DS}=1$ V). **222**

Figure 6.10 $I_{DS}-V_{GS}$ transfer characteristics of six IGZO DG-FGFETs at $V_{DS}=1$ V. **223**

Figure 6.11 Demonstration of a) AND, and b) OR logic in DG-FGFETs on paper substrates with a single device, for an applied frequency of 20 mHz and 40 mHz in V_{GS1} and V_{GS2} , respectively. **224**

Figure 6.12 Universal logic gates: a) Circuit schematic, b) On-chip implementation, and c) $I_{DS}-V_{GS}$ transfer characteristics DG-FGFETs at $V_{DS}=6$ V. **225**

Figure 6.13 Dynamic response of the universal logic gates: a) NOR functional demonstration from measurements, and b) NAND functional demonstration from measurements. **226**

Figure 6.14 a) Normalized values of μ_{sat} (μ/μ_0), I_{ON}/I_{OFF} ratio (I/I_0) and S (S/S_0) for DG-FGFETs determined after measuring the transfer characteristics under tensile bending strain. The bending radius is presented next to the symbols. Solid symbols represent the values calculated for the flat condition after bending. The inset shows a picture of the FETs being measured under bending conditions. b) SEM magnification of the surface of the DG-FGFET channel after bending with a tensile strain of 0.75% (equivalent to 5 mm radius). **227**

Figure 6.15 a) $I_{DS}-V_{GS}$ curves of the NFC-gated DG-FGFETs with $V_{DS}=1$ V. b) Voltage output for the a-Si:H PD produced on glass and on NCC in the dark and when irradiated with $\lambda=505$ nm. c) Schematic representation of the integration of the DG-FGFETs with the a-Si:H PD. **228**

Figure 6.16 $I_{DS}-V_{GS}$ transfer characteristic curves for the DG-FGFETs using an a-Si:H PD produced on glass (on the left) and produced on NCC (on the right) as external bias at V_{GS2} . **229**

Figure 6.17 Representation of the integration of a DG-FGFET with an a:Si-H photodetector. **230**

Figure 6.18 a) I_{ON}/I_{OFF} ratio as a function of the frequency applied to the gate of the NFC-membrane FETs ($V_{DS}=3$ V). b) Electrochemical characterisation of the NFC membranes - **231**

capacitance and phase as a function of frequency.

Figure 6.19 a) Schematic diagram of the inverter. b) Gain as a function of the applied $V_{DD}=[1;5]$ V (on the left) and as function of the load resistance used for a constant $V_{DD}=3$ V and $-3 \leq V_{in} \leq 3$ (on the right). **232**

Figure 6.20 Voltage transfer characteristics (VTCs) of the resistor-loaded inverters on NFC measured with $V_{DD}=3$ V. In the inset the truth table for the logic operations is shown. **233**

Figure 6.21 Voltage output for high and low states of the different NFC based inverters with a fixed V_{DD} ($V_{DD}=3$ V) and variable load resistances ($R_{Load}=97$ k Ω , 561 k Ω and 1 M Ω). **234**

Figure 6.22 Voltage output of the different NFC based inverter with a fixed V_{DD} ($V_{DD}=3$ V) as a function of the frequency. **235**

Figure 7.1 Developments made along this PhD work towards high-performance cellulose-based field-effect transistors. **241**

Figure 7.2 Photographs of the several steps involved in the production of the NFC membranes, FETs and final circuits on paper for the IPhO2018. **246**

Figure 7.3 Nature Electronics editorial “A lesson on paper” featuring the IPhO2018. **246**

Figure 7.4 a) Transfer ($I_{DS}-V_{GS}$) characteristics measured at $V_{DS}=1$ V for as-deposited devices (solid line) and after 1 minute of O_2 plasma treatment to the IZO floating gate, and b) ΔV_{On} after O_2 plasma treatment (V_{DS} of 1, and 15 V) with different V_{GS2} applied. **247**

Figure 7.5 Schematic representation of reactions occurring between the IZO floating gate and O_2 plasma treatment responsible for the V_{ON} shift. **248**

List of Tables

Table 1.1. Approximate chemical composition of Softwoods and Hardwoods	10
Table 1.2. Summary of oxide-based transistors using paper as the substrate.	19
Table 1.3. Comparison of some properties of mature semiconductor technologies.	24
Table 1.4. Summary of oxide-based transistors using cellulose substrates as a dielectric.	29
Table 2.1 Paper-like substrates used during this work, and respective details.	50
Table 2.2 Nanocellulose samples used during this work, and respective details.	51
Table 2.3. Production details of the cellulose-based FETs layers.	54
Table 3.1 TCOs materials and some dopants (adapted from [2], [5]).	74
Table 3.2 Experimental parameters used for the production of ZnO thin films by rf. sputtering.	78
Table 3.3 Experimental parameters used for the sputtered doped-ZnO thin films.	90
Table 3.4 Properties of the AZO and GZO thin films for different sputtering power densities.	93
Table 3.5 Electrical and optical properties of the AGZO thin films processed at room temperature.	93
Table 3.6 Deposition conditions of IZO thin films by rf reactive magnetron sputtering.	96
Table 4.1 Paper-like substrates used during this work, and respective details.	120
Table 4.2 Characteristics of the paper samples produced with different sources.	121
Table 4.3 Characteristics of the tested paper samples.	125
Table 4.4 Summary of the electrical parameters of the IGZO-based paper FETs.	130
Table 4.5 Dynamic parameters obtained at 10 MHz for paper-based FETs.	134
Table 4.6 Variation of the electrical parameters of the aged non-encapsulated IGZO-based paper FETs.	137
Table 4.7 Characteristics of the tested paper samples.	140
Table 4.8 Comparison of the electrical properties of IGZO based FETs for the different BSKP papers tested as a gate dielectric. For the oriented papers, the preferential orientation of the fibres was placed along the width.	143
Table 4.9 Comparison of the electrical properties of IGZO based FETs for BSKP papers with 48°SR with preferential fibre orientation parallel and perpendicular to the channel.	145
Table 4.10 Summary of the electrical properties of IGZO based FETs for the M-NCF papers tested as a gate dielectric.	149
Table 4.11 Summary of the electrical properties of aged IGZO FETs for the M-NCF mem-	151

branes tested as a gate dielectric.

Table 4.12 Summary of the electrical properties of IGZO based FETs for the BEKP papers tested as the gate dielectric. **154**

Table 5.1 Nanocellulose membranes used during this work, and respective details. **164**

Table 5.2 Properties of the NFC membranes produced with the bleached birch kraft pulp and bleached sulphite eucalypt pulp. **168**

Table 5.3 Summary of the electrochemical and electrical properties of the tested NFCs. **171**

Table 5.4 Electrical properties of NFC-gated FETs for $V_{DS}=2.5$ V. **176**

Table 5.5 Electrical properties of the FETs with cotton-based NCC as gate dielectric. **190**

Table 5.6 Properties of the all-cellulose composites prepared with the different amount of NFC and NCC **193**

Table 5.7 Electrical properties of the FETs with all-cellulose composites as gate dielectrics. **194**

Table 5.8 Summary of the BC membranes' composition and thickness. **198**

Table 6.1 VFG values obtained for the simplified operation mode of the paper DG-FGFETs as a function of the V_{GS2} and the ones obtained using SILVACO software and measured. **218**

Acronyms

a.c. – alternate current

AFM – atomic force microscopy

AOS - amorphous oxide semiconductor

a-Si - amorphous silicon

a-Si:H PD - amorphous hydronated silicon photodetector

ATR - attenuated total reflectance

ATR-FTIR - Fourier-transform infrared spectroscopy with attenuated total reflectance

AVT – average transmittance in the visible range

AZO - aluminium-doped zinc oxide

BBKP – bleached birch kraft pulp

BEKP - bleached eucalyptus kraft pulp

BHKP - bleached hardwood kraft pulp

BSEP – bleached sulphite eucalypt pulp

BSKP – bleached softwood kraft pulp

BC- bacterial cellulose

BW – basis weight

CEMOP – Centre of Excellence in Microelectronics Optoelectronics and Processes

CENIMAT – Centro de Investigação de Materiais

CMOS - complementary metal oxide semiconductor

CNF – cellulose nanofibrils

CNC – cellulose nanocrystals

CNT - carbon nanotubes

c-Si – crystalline Si

CPE - constant phase element

CSP - commercial standard paper

CTP - Centre Technique du Papier

CV - cyclic voltammetry

d.c. – direct current

DG-FGFETs - dual-gate in-plane oxide-based field effect transistors with a back floating gate electrode

DL – diffuse layer

DSC – differential scanning calorimetry

ECM - electric circuit model

ECT - electrochemical transistors

EDL - electric double-layer

EDLFET - electric double-layer field effect transistor

EGT - electrolyte gated transistors

EIS – electrochemical impedance spectroscopy

EDX - energy dispersive X-ray spectroscopy

FE – field-effect

FET – field effect transistor

FoM - figure of merit

FTIR - Fourier-transform infrared spectroscopy

GZO - gallium-doped zinc oxide

IC - integrated circuits

IGZO –indium gallium zinc oxide

IHP – inner Helmholtz plane

IS – impedance spectroscopy

ITO – indium tin oxide

IZO – indium zinc oxide

LED - light emitting device

MCC - microcrystalline cellulose

M/NFC – micro/nanofibrillated cellulose

MOSFET – metal-oxide-semiconductor field-effect transistor

MOCVD – metal-organic chemical vapour deposition

MWCNT - multiwalled carbon nanotubes

NBE - near band edge emission

NCC - nanocrystalline cellulose

NFC – nanofibrillated cellulose

NIR – near infrared

NMOS - n-channel metal oxide field effect transistor

NW - nanowire

OHP – outer Helmholtz plane

OLED - organic light-emitting diode

OTFTs - organic thin film transistors

PDMS - polydimethylsiloxane

PECVD – plasma enhanced chemical vapour deposition

PEN - polyethylene naphthalate

PET - polyethylene terephthalate

PI – polyimide

PL - photoluminescence

PMOS - p-channel metal oxide field effect transistor

poly-Si – poly-crystalline Si

PECVD - plasma enhanced chemical vapour deposition

PVD – physical vapour deposition

R-2-R - roll-to-roll manufacturing

rf – radio-frequency

RFID - Radio-Frequency Identification

RH - relative humidity

sccm – standard cubic centimetres per minute

SDS - sodium dodecyl sulphate

SEM – scanning electron microscopy

SPP - Surface Potential Profile

STA - simultaneous thermal analysis

SWCNT - single-walled carbon nanotubes

TCO – transparent conductive oxide

TFT – thin film transistor

TGA - thermogravimetric analysis

TSO – transparent semiconductive oxide

UBI - Beira Interior University

UV – ultra-violet

Vis. – visible

VTC – voltage transfer characteristics

XPS - X-ray Photoelectron Spectroscopy

XRD – x-ray diffraction

ZnO – zinc oxide

Symbols

A – optical absorption

$\vec{B}$ – magnetic field

B-M - Burstein-Moss effect

c – speed of light

C – capacitance per unit area

C_{dl} – double layer capacitance

C_{eff} – effective capacitance

C_{real} – real capacitance

CrI - crystallinity index

D – crystallite size

d_{hkl} - atomic inter-planar spacing

d₀₀₂ - lattice's interplanar distance

D_{H2} – H₂ dilution

D_{O2} – O₂ dilution

d_f – film thickness

d_s – sample thickness

E_a – thermal activation energy

E_C – conduction band

E_F – Fermi level

E_{opt} – optical bandgap

f – frequency

g_m – transconductance

h – Planck's constant (4.135×10^{-15} eV.s)

I – current

I_{DS} – drain-to-source current

I_{GS} – gate leakage current

I_{On} – on current

I_{Off} – off current

$I_{\text{On}}/I_{\text{Off}}$ - On/Off current ratio

L – channel length

n – free carrier concentration

N_t - trap density

q – elementary charge of a particle (1.6×10^{-19} C)

Q - charge carrier density

P – porosity

r – radius or radii

R – reflectance

R_H – Hall coefficient

R_{Load} – load resistance

R_{rms} – root-mean-square roughness

S – subthreshold swing

$^{\circ}\text{SR}$ - Schöpper-Riegler index

T – transmittance (%) | temperature ($^{\circ}\text{C}$, $^{\circ}\text{K}$)

V – voltage

V_{DS} – drain to source voltage

V_{FG} – potential established along the floating electrode

V_{GS} – potential established between the gate electrode and the source

V_{GS1} – primary gate voltage

V_{GS2} – secondary gate voltage

V_H – Hall voltage

V_{On} – turn-on voltage

V_{Th} – threshold gate voltage

W – channel width

Z – impedance

$Z' \equiv Z_{\text{real}}$ – real component of impedance

$Z'' \equiv Z_{\text{imag}}$ – imaginary component of impedance

α – absorption coefficient
 $\Delta V_{\text{hysteresis}}$ – FETs hysteresis
 ε - strain
 ε_0 - vacuum permittivity ($8.854 \times 10^{-12} \text{ F m}^{-1}$)
 η - d_f/d_s ratio,
 θ – Bragg angle
 2θ – angular position
 κ – dielectric constant
 λ – wavelength of electromagnetic wave
 λ_{pl} - plasma wavelength
 μ –mobility
 μ_{FE} –field effect mobility
 μ_{H} –Hall mobility
 μ_{Sat} –saturation mobility
 ν – frequency of electromagnetic wave
 ρ – electrical resistivity
 $\rho_{\text{cellulose}}$ - cellulose density (tabled value: 1.6 g cm^{-3})
 ρ_{sample} - apparent density of a cellulosic sample
 σ – electrical conductivity
 ϕ –work function
 χ - ratio of the film and substrate Young moduli
 ω - angular frequency
 ω_{p} - plasma frequency

Cellulose-based substrates for electronic devices

This chapter provides an overview and background regarding cellulose, paper, field-effect devices and paper-based field-effect transistors.

The contents of **Chapter 1** were adapted from the following publications:

E Fortunato, **D. Gaspar**, P. Duarte, L. Pereira, H. Águas, A. Vicente, F. Dourado, M. Gama, R. Martins, Chapter 11 “Optoelectronic Devices from Bacterial NanoCellulose”, in *Bacterial Nanocellulose - From Biotechnology to Bio-Economy*, 1st ed. Elsevier, 179-198, 2016 (DOI: 10.1017/CBO9781107415324.004)

A. T. Vicente, A. Araújo, **D. Gaspar**, L. Santos, A. C. Marques, M. J. Mendes, L. Pereira, E. Fortunato, and R. Martins, Chapter 3 “Optoelectronics and Bio Devices on Paper Powered by Solar Cells,” in *Nanostructured Solar Cells*, 1st ed. InTech, 33–65, 2017 (DOI: 10.5772/66695).

Cellulose-based substrates for electronic devices

Chapter 1. Cellulose-based substrates for electronic devices	5
1.1. Cellulose-based substrates	5
1.2. Cellulose	5
1.3. Paper and papermaking process	10
1.3.1. Sources: Raw materials	10
1.3.2. Pulping and papermaking processes	11
1.3.3. Paper classification	11
1.4. Micro/Nanofibrillated and Nanocrystalline cellulose	12
1.5. Bacterial Cellulose	15
1.6. Paper as a substrate for electronics and paper-based devices	16
1.6.1. Thermal and electrical properties	20
1.6.2. Field-effect transistors	21
1.7. References	31

Chapter 1. Cellulose-based substrates for electronic devices

1.1. Cellulose-based substrates

The interest in lightweight, flexible and low-cost electronic devices has increased in the recent past, pioneering novel applications. One of the major concerns is on the end-of-life and sustainability of devices and materials being used. Polyester-based polymers as polyethylene naphthalate (PEN) or polyethylene terephthalate (PET) stand out as the most common substrates used in large area and flexible electronics mainly due to their mechanical and thermal stability, surface's morphology (high smoothness), and also being good as an electrical insulator. Although the interesting properties offered by these petrol-based materials, it is clear that recyclable and more sustainable alternatives are necessary for devices aimed to be low-cost and disposable.

The use of paper or other cellulose-based substrates as a platform for eco-friendly electronics became a reality in the last years. The ubiquity of paper is unquestionable; this multifunctional material has been for a long time and still is widely used in a variety of applications in our daily life. Thus, thinking of it as part of “green” electronic devices in the future is a legitim ambition. Solid steps were taken during the last decade with the advent of a range of electronic or electrochemical devices manufactured directly onto paper substrates or from cellulose-based functional materials. Some examples are biosensors, energy storage and conversion devices, or even crucial electronic building blocks such as diodes or field-effect transistors, demonstrating that the paper electronics era is establishing its foundations [1]–[6].

1.2. Cellulose

Cellulose is the most abundant natural biopolymer and the elementary building block of paper. In 1838 Anselme Payen isolated it and discovered it is a linear polysaccharide with a repeating unity called cellobiose (Figure 1.1) with the molecular formula $[C_6H_{10}O_5]_n$ [7], [8]. Cellulose consists of a chain with thousands of β (1 $\rightarrow$ 4) linked D-glucose units that are covalently bonded through acetal functional groups. This means that the C₁ carbon atom¹ from one cellobiose is bonded to the C₄ carbon of the next unit with a 180° rotation in respect to each other (Figure 1.1) [7], [9]–[11].

¹ Carbon 1 or C₁ from each glucose units is commonly denominated as anomeric carbon and is the stereocenter of the acetal functional group.

Independently of the source, those chains tend to become in parallel assemblies, forming elementary fibrils which can be assembled in bundles with diameters of several nanometres via intermolecular hydrogen bonding between the hydroxyl groups [10], [11]. The ability to form hydrogen bonds confers to cellulose several important characteristics, such as the capability to create a hierarchical organisation with crystalline and amorphous regions, and also important mechanical and physical properties [11]–[13]. The structure of cellulose macromolecules and their hierarchical association in vegetable cell walls is schematically shown in Figure 1.1.

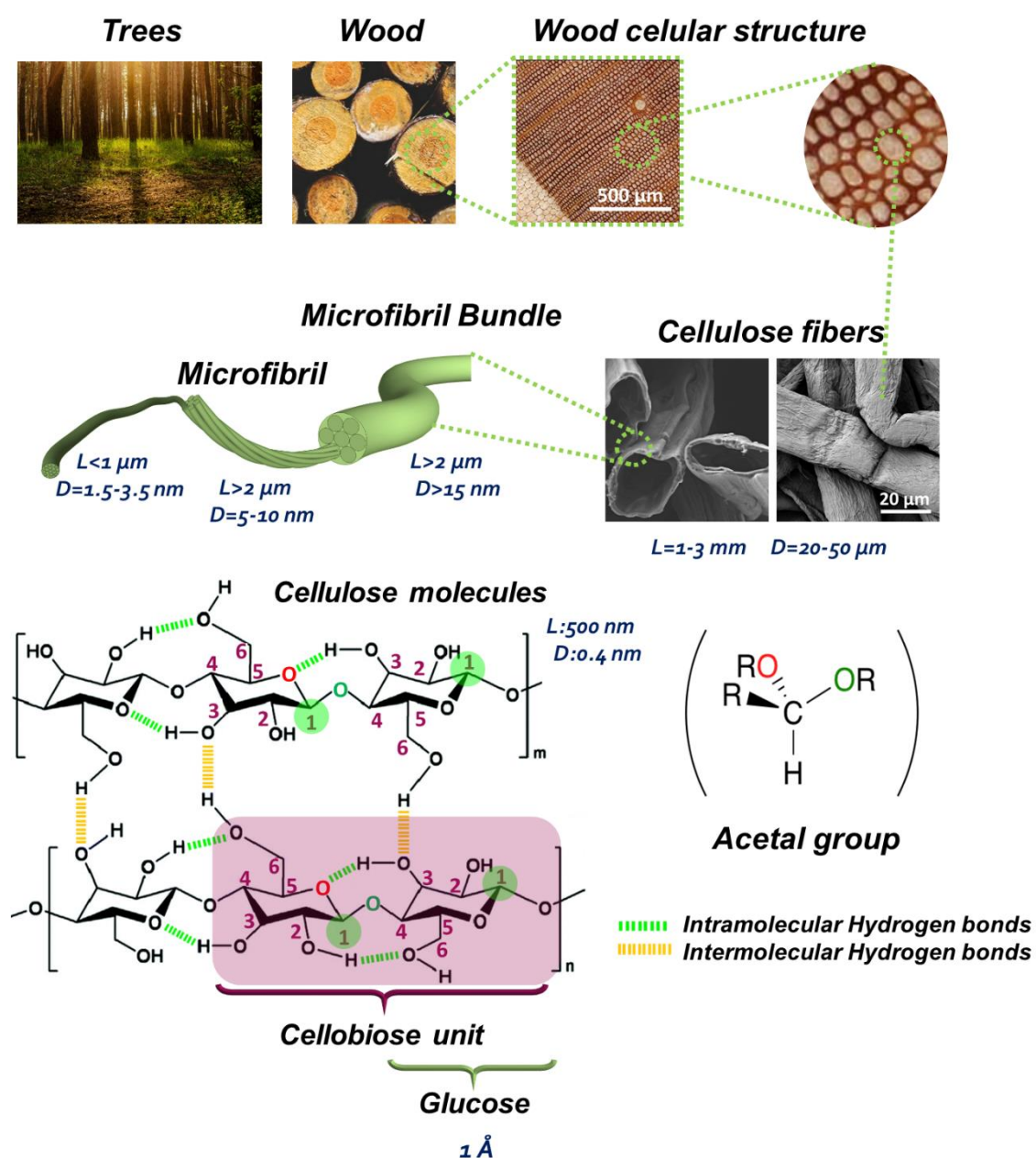


Figure 1.1 Schematic association of cellulose at the molecular level in the vegetable cell walls [10], [14]–[16].

In vegetal sources, cellulose is obtained mostly from the cell walls; in wood and plant fibres they are organised hierarchically as shown in Figure 1.2. In the middle lamella and primary cell-wall, the cellulose fibrils are short and thin, and its matrix is rich in hemicellulose, structural proteins, and pectin. The secondary cell wall is thicker than the primary one and is formed by three differently structured layers: an outer layer S1, a middle layer S2 and an inner layer S3 (Figure 1.2) [17]. All the fibrils in each layer run parallel to each other, but all the layers present different directions between them. Besides the higher amount of cellulose, relatively to the primary cell wall, the secondary wall also has hemicellulose reinforced with lignin, which surrounds the cellulose fibrils (Figure 1.2) [7], [18].

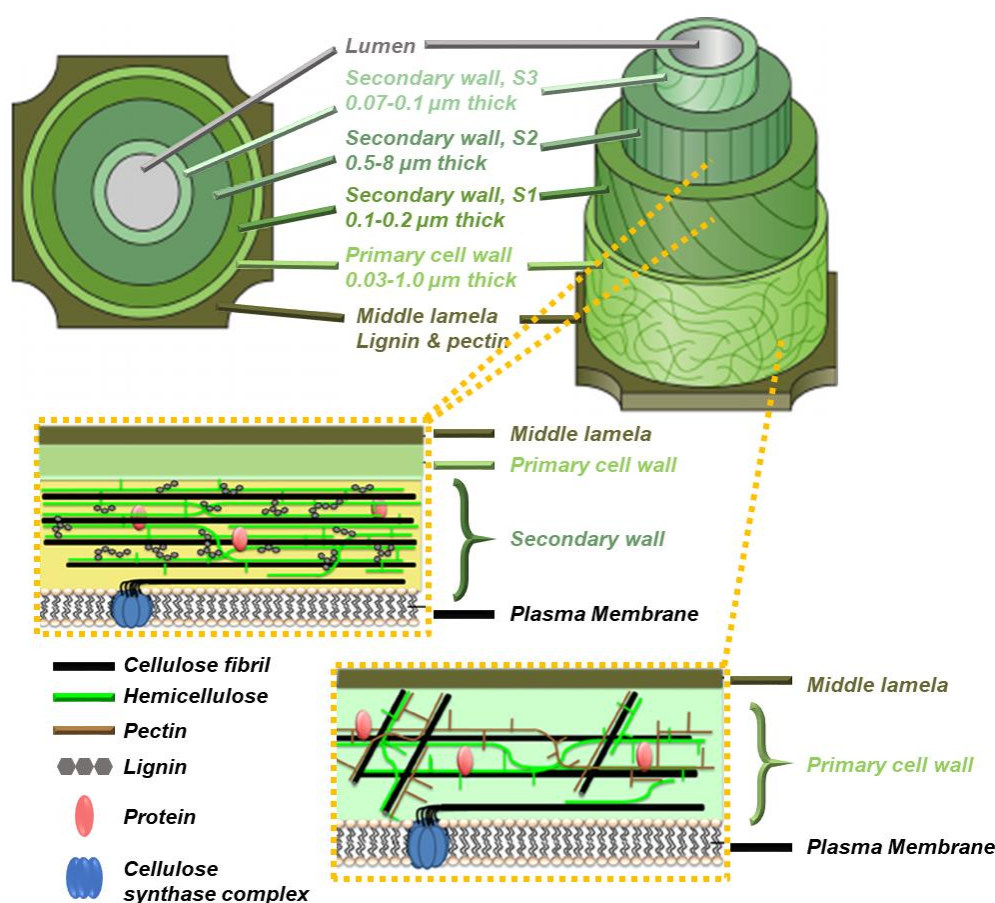


Figure 1.2 Scheme of the general structure of the cell wall of fibre, and respective layers (adapted from [17]–[19]).

As mentioned before, besides cellulose other lignocellulosic and non-cellulosic polysaccharides materials can be found in the cell walls structure, namely lignin, and hemicelluloses. Both materials are amorphous, and most of the time it is desirable to

eliminate them for the papermaking process, although both play an essential role in the cells' walls.

Hemicelluloses are heteropolymers - like xylose, arabinose mannose, galactose, glucose, among others - with low polymerisation degree combined in small non-crystalline chains which can be found in the primary and secondary cell wall and can correspond to 30% of the dry weight depending on the source [17], [19].

Lignin is a three-dimensional macromolecule and considered one of the most resistant materials in nature, which can be found in the cellulose voids in the primary, secondary cell wall, and middle lamella, similarly to hemicelluloses, and its content differs depending on the species. The lignin confers structure and stiffness to the fibre, and also works as a binder, being responsible for holding the fibres gathered in the wood or plants also preventing deterioration of the cellulose [17], [20].

Although the most conventional cellulose's source in nature are trees and some annual plants as cotton, flax or bamboo, it is possible to find alternative sources in other living beings as cellulose-producing bacteria, algae and fungus-like protists, or even marine animals as the tunicates (Figure 1.3) [8], [11], [21]. The source not only affects the fibril's length, crystallite size, but also the cellulose's crystallinity. Bacterial and algal cellulose can present a degree of crystallinity above 80%, while for the vegetal sources as flax or dissolved pulp the crystallinity rounds 50 to 60 %. Furthermore it is possible to reach up to 80% of crystalline fraction for nanowhiskers obtained from cotton [7], [22].

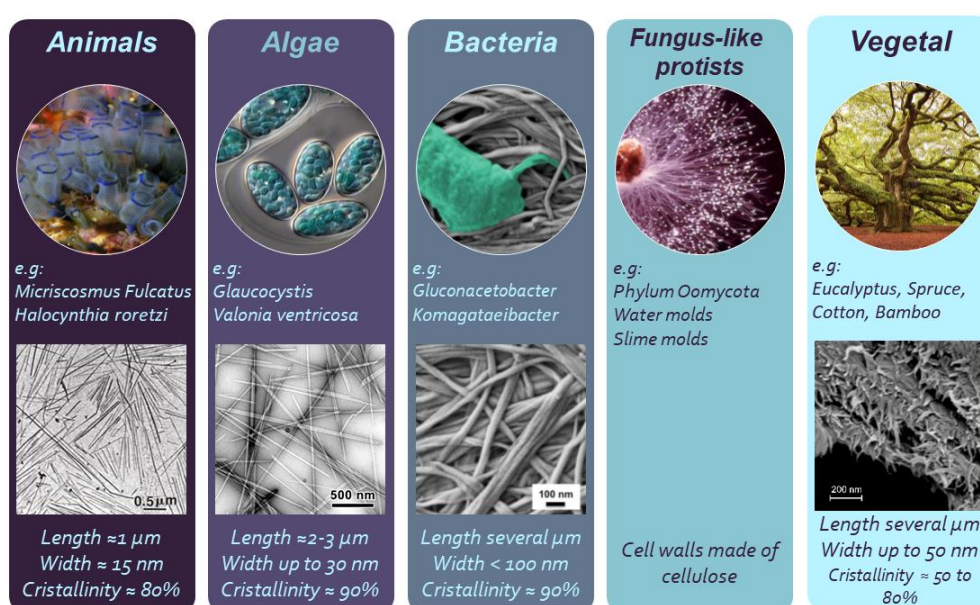


Figure 1.3 Different cellulose sources in Nature [14], [23]–[26].

Cellulose has four polymorphs: I, II, III, and IV (Figure 1.4). The native one or that found in nature is cellulose I. In its crystalline form the chains are parallelly packed via hydrogen bonding, where each can differ depending on the allomorph, I_α and I_β [12]. Both polymorphs can occur in the cellulosic materials, and the ratio of the two allomorphs is deeply related to the species. Cellulose I_α is mainly found in cell walls of algae and bacterial cellulose, while the second allomorph is related to vegetable resources such as wood, flax, cotton, and marine animals. The existence of crystalline domains can be assessed by X-ray diffraction, presenting characteristic peaks at $2\theta = 14.7^\circ$, 16.8° and 22.7° corresponding respectively to the $1\bar{1}0$, 110 and 200 crystallographic planes of monolithic cellulose type I.

The second polymorph, cellulose II (or regenerated cellulose), has an antiparallel chain packaging and is a result of the irreversible re-crystallisation or mercerisation with an aqueous alkali solution of the cellulose I [11]–[13]. Treatment with liquid ammonia of the celluloses I and II lead to the cellulose III_I and III_{II} , respectively. Finally, cellulose IV (IV_I and IV_{II}) derives from a heating treatment of cellulose III_I and III_{II} in glycerol [12].

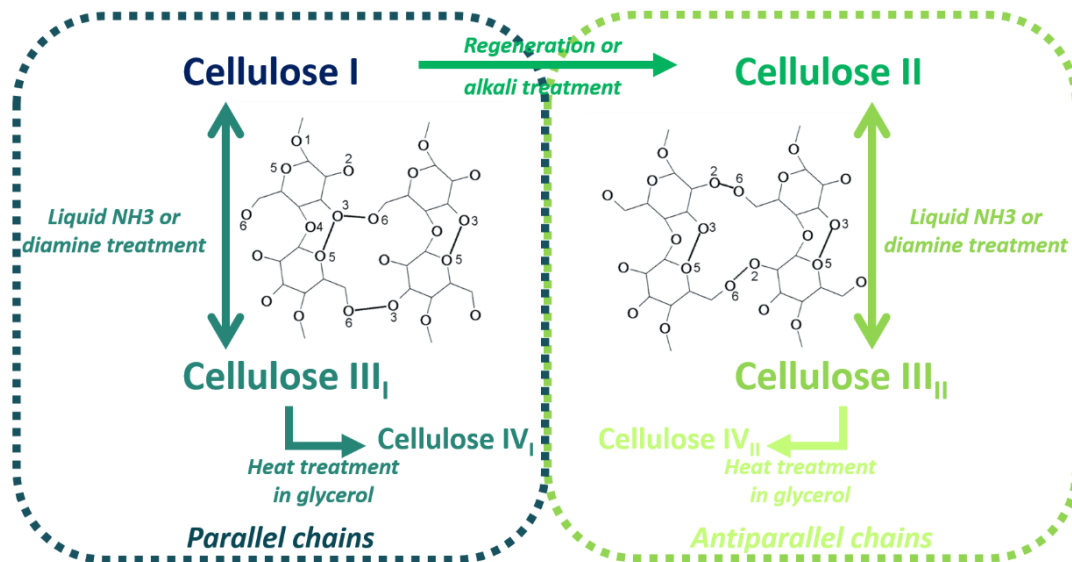


Figure 1.4 Cellulose polymorphs (adapted from [11]).

1.3. Paper and papermaking process

1.3.1. Sources: Raw materials

Paper as we know it consists of a matrix of moist pressed fibres, produced mainly from vegetable cellulosic fibres, which can be obtained from wood or other annual plants (e.g. flax, sisal, jute). The last ones are also used for special paper/board grades in some regions of the globe which is commonly defined as nonwood-paper [20].

For the paper used in our daily life for writing, printing or food packaging, for instance, the most common source are undoubtedly the trees; depending on the origin, the fibres can be classified as softwood – from gymnosperm trees, or hardwood – angiosperms trees [27]. The significant differences between those fibres are length, thickness, and chemical composition. Long ($> 2\text{-}3\text{ mm}$) and thicker walled fibres are characteristic of softwood species as pine, spruce, and white fir, while smaller fibres with $\approx 1\text{ mm}$ and thinner cell walls are typical in hardwood trees as oak, birch, and eucalyptus [27].

Those differences extend to the chemical composition of the fibres, tendentially hardwood fibres present higher cellulose/lower lignin grade, in comparison to softwood fibres, while the hemicellulose content is similar for both origins only varying the hemicellulose nature (Table 1.1) [19], [28].

Table 1.1. Approximate chemical composition of Softwoods and Hardwoods (adapted from [19], [28]).

	<i>Cellulose</i> (*%)	<i>Hemicellulose</i> (*%)	<i>Lignin</i> (*%)
Softwoods	39-44	15-27	27-32
Hardwoods	38-47	17-30	21-31
* % dry weight			

The use of softwood or hardwood fibres results in paper with distinct physical and mechanical properties. Long fibres, after beating, usually make dense and strong papers that can be used in liquid packaging boards, carton board and newsprint paper, whereas the short fibres, which are more flexible and easily collapsed, lead to smoother papers with good printability, thus they are widely used to produce tissues and printing paper [20], [27]. Despite the final use of the paper, the choice of softwood or hardwood fibres can also be related to the geographical location, for instance in Scandinavia, spruce is one of the most used sources, while in the south of Europe the eucalyptus is commonly used to obtain paper pulp [24].

1.3.2. Pulping and papermaking processes

Cellulose fibres from softwood or hardwood origin can be obtained by chemical and/or mechanical pulping processes [9], [30]. The mechanical and thermo-mechanical (woodchips pre-heated) processes act physically, tearing the fibres from each other by application of high shear forces, combined with temperature. The mechanical action leads to a consequent shortening of the fibres keeping the approximate amount of lignin and hemicelluloses present in the wood (20–30%), resulting in a pulp yield above 90 %. Papers formed with this type of pulp generally present low densities due to the highly porous matrix. Since the mechanical pulp results in higher lignin content the paper tends to become brittle over time and yellow with UV exposure [27], [30].

The chemical pulping process involves the “cooking” of raw materials. The fibres are separated by the removal of cross-linked lignin and hemicellulose, using temperature and chemicals. In the kraft (sulphate) process, hydroxide (OH^-) and sulphide (HS^-) are the active species in cooking. In sulphite processes, different proportions of sulphite (SO_3^{2-}) and bisulphite (HSO_3^-) are present, depending on cooking pH [20], [31]. The yield of both processes is substantially lower than the mechanical routes, leading to values between 40 to 50%. After cooking, the pulp fibres are submitted to several (3 to 5) bleaching stages in order to produce the bleached pulp.

To produce paper, one or more types of pulps are submitted to a beating process in order to increase fibre flexibility and collapsibility and are mixed with other components, such as fillers and functional additives in a diluted aqueous suspension. This suspension is afterwards subjected to a successive unit operation, mainly sheet forming (including water drainage), pressing and drying. In the drying process, hydrogen bonds between the cellulosic fibres are established, providing the natural resistance to the paper [9], [30]. The extent of beating, the type of pulps, the fillers and the additives are paper grade dependent.

1.3.3. Paper classification

The properties of the paper are deeply related to the fibre’s origin (hardwood or softwood), pulping process, refining extent, fillers, and calendaring; however the most conventional and simple classification adopted to define the paper is based on their weight or *grammage* [27], [30], [32]. For papermakers and the paper industry it can be roughly defined as *tissue* - soft and smooth paper with grammage in the range 15–25

g m^{-2} ; *fine* – grammage range from 50–100 g m^{-2} , e.g. office paper; *printing* – newsprint and magazine paper (40–45 g m^{-2}), and board/packaging – grammage from 100 up to 400 g m^{-2} [27]. Tobjörk *et al.*, suggested a more straightforward classification dividing the paper into three different categories [30], [32]:

- **Light paper:** *grammage* is in the range of 12–30 g m^{-2} , or thickness below 75 μm . In this category two highly transparent, lightweight, and smooth cellulose substrates can be included that are attracting much attention in the recent years: nanocrystalline cellulose (NCC) and bacteria-produced cellulose (BC), that will be described in Section 1.4 and Section 1.5, respectively.
- **Standard Paper:** includes a wide variety of paper whose basis weight is in the range of 80 to 120 g m^{-2} and 100 μm thick. Examples for this category are the office paper (80 to 120 g m^{-2}), the translucent parchment paper ($\sim 40 \text{ g m}^{-2}$), or even tracing paper ($\sim 90 \text{ g m}^{-2}$). Transparent, highly dense and thin papers produced using micro-nanofibrillated cellulose fibres can also be included in this category. Further details about the last will be presented in Section 1.4.
- **Cardboard or paperboard:** good mechanical resistance and *grammage* exceeding 200 g m^{-2} , or thickness above 300 μm .

1.4. Micro/Nanofibrillated and Nanocrystalline cellulose

The pulp fibres usually have a high aspect ratio, presenting fibres whose lengths can go up to 4 mm depending on the source, and a width of 20 to 60 μm for hardwood sources or in the range of 30 to 120 μm in the case of softwood [33]. Those fibres can be downsized using a top-down deconstruction to obtain different products depending on the used method and crystalline content. Acid hydrolysis processes lead to microcrystalline bundles and/or nanocellulose crystals (or whiskers), while mechanical ones (with or without enzymatic or chemical treatments) lead to cellulose micro and nanofibrils. (Figure 1.5) [12], [13], [34].

The terminology for the so-called micro and nanofibrillated cellulose (M/NFC) is not clearly established leading to some misunderstandings. Other designations, such as cellulose microfibrils and nanofibrils, fibrillated cellulose, nanofibrillar cellulose, microfibrillated cellulose nanofibers, among others, refer to refined cellulose microfibrils with monocrystalline and amorphous regions, which are composed of nanosized fibrils with 5 to 100 nm of width and few μm in length, leading to a high

aspect ratio (Figure 1.5) [12], [13]. The production of micro/nanofibrillated cellulose from pulp fibres can be done through mechanical disintegration where the fibre's structure is disrupted to release the micro and nanofibrils. The mechanical route consists of cutting the fibres into smaller parts passing the dilute pulp suspension through a refiner or a homogeniser several times. However, this route has some drawbacks such as the energy consumption and associated fibrillation limits. Thus, the mechanical shearing can be combined with chemical (mainly oxidation) and/or enzymatic (mainly enzymes with cellulolytic activity) pre-treatments (Figure 1.5) [11], [13], [30]. Prior chemical treatment with TEMPO-mediated oxidation, carboxymethylation or acid hydrolysis can decrease the fibre size in a first stage, leading to better fibrillation and their modification them. Oxidation treatments, such as TEMPO-mediated oxidation and carboxymethylation, change the cellulose molecules replacing the CH_2OH groups by carboxyl groups ($-\text{COOH}$) or adding carboxymethyl groups ($-\text{CH}_2-\text{COOH}$), helping the disintegration of the wood fibres into fibrils with smaller widths [12]. The acid hydrolysis decreases the molecular weight and leads to small crystallites with a low aspect ratio.

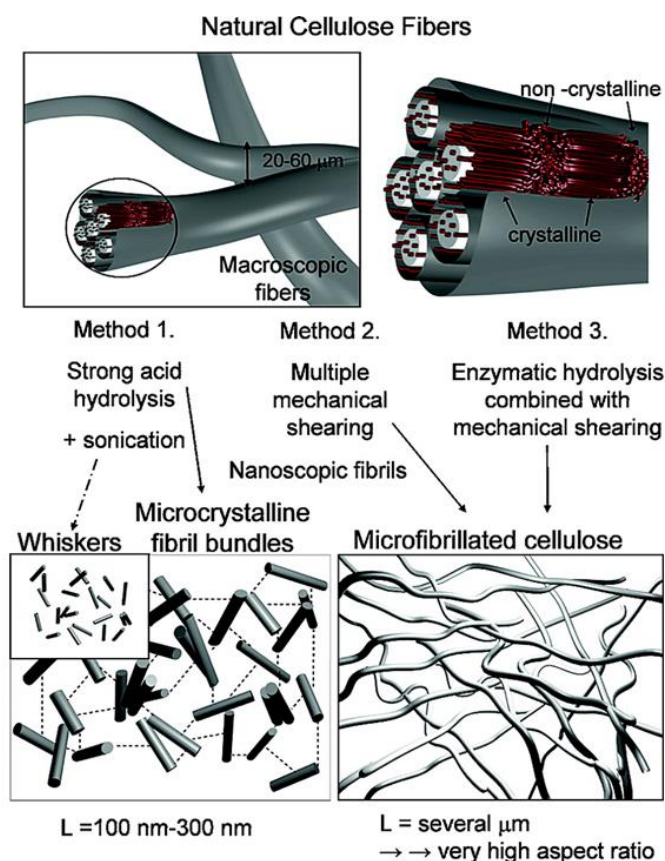


Figure 1.5 From macroscopic fibres to nanomaterials: Top-down approaches for the preparation of micro and nanoscale cellulosic materials [13].

During enzymatic hydrolysis with cellulases, enzymes are able to catalyse the hydrolysis of glucosidic bonds, shortening the polysaccharide chains and weakening the fibril surface [12], [14]. Finally, the pre-treated pulp is then mechanically sheared through the application of high pressures and shear forces, leading to micro or nano-refinement of the fibres depending on the pressure and mechanical treatment extent.

As mentioned before, the micro and nanofibrils consist of crystalline and amorphous regions; however, it is possible to down-size the cellulosic materials even more. Aggressive acid hydrolysis allows the removal of amorphous regions of the cellulose chains, leaving the crystalline regions intact in the form of cellulose I microcrystalline bundles, with lengths from 100 to 300 nm. This process involves several steps including more than one acid hydrolysis. The cellulose source is submitted to a first acid hydrolysis with HCl resulting in hydrolysed microcrystalline cellulose (MCC) particles that need to be neutralised with distilled water and washed through a filtration process with water and acetone. Those MCCs can be submitted to a second strong acid hydrolysis with H_2SO_4 resulting in a suspension that after successive washing and centrifugation steps, and further dialysis with ultrapure water, results in a nanocrystalline cellulose (NCC) suspension. The subsequent centrifugations of the suspension result in a gel-like substance that can be shear casted or evaporated producing a highly transparent, lightweight, and smooth membranes (Figure 1.6) [22]. An alternative route to obtain NCCs is through sonication processes which are able to downsize the bundles leading to particles (whiskers) with 50–60 nm in length and diameter around 5–10 nm [10], [11]. Several sources can be used to produce highly crystalline NCCs, however, cotton is one of the most used sources once it presents one of the highest amount of cellulose (90 wt.%) among vegetable sources, compared to 50 wt.% in wood or 80 wt.% in flax or hemp [10], [12], [22].

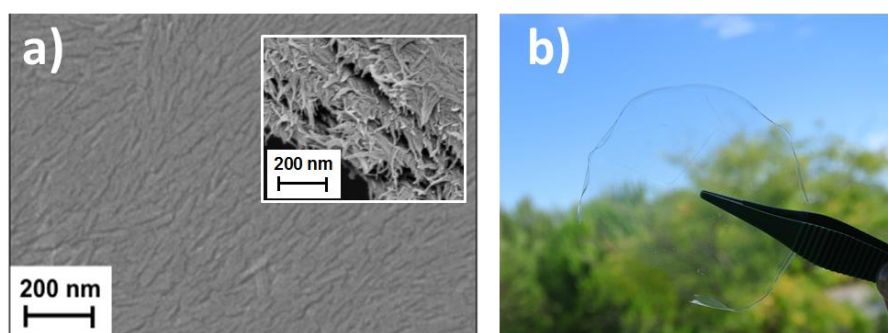


Figure 1.6 a) SEM micrograph of the surface morphology of nanocrystalline cellulose (NCC) membranes obtained from cotton and the corresponding cross section (inset), and b) photograph of the corresponding NCC membrane (adapted from [22]).

1.5. Bacterial Cellulose

In the previous sections, the approach to obtain smaller cellulose elements consisted in a top-down deconstruction; however, a bottom-up route can also be addressed by electrospinning of cellulose derivatives, ionic liquids and bacteria [25].

Bacterial cellulose (BC) has demonstrated to be a remarkably versatile biomaterial able to be used in a wide variety of applications, from an additive in the food industry to medical and cosmetic applications as wound dressings and facial masks, and even as an electronic material.

Bacterial cellulose is a bacteria-produced biopolymer composed of ultrafine nanofibers (< 100 nm wide). The major advantages of this material, compared to cellulose obtained from wood, lays in its crystallinity (cellulose I) and purity since it is free of lignin, hemicellulose and other components present in the vegetal sources [35]–[37]. One of the first descriptions of this material was made by Pasteur who defined it as “a sort of moist skin, swollen, gelatinous and slippery ...”, being only confirmed as cellulose latter in 1886 by Brown while working with *Bacterium aceti*, who identified the growth of gelatinous pellicle named “vinegar plant” with the chemically equivalent structure as plant cellulose [12], [25].

Bacterial (nano)cellulose is a primary metabolic product, resulting from the fermentation of low molecular weight sugars, being synthesised by several cellulose-producing bacteria such as *Komagataeibacter* genus (Figure 1.7a), *Agrobacterium tumefaciens*, and bacteria of the genera *Pseudomonas*, among others. This biomaterial is produced extracellularly since the bacteria excretes the cellulose through 100 pores placed in a linear row (Figure 1.7a), into an aqueous culture medium of low molecular weight sugars, directly as nanofibers, which form an entangled porous three-dimensional nanocellulose web-like network formed by inter-fibrillar hydrogen bonding (Figure 1.7a and c) [8], [10], [35], [38]. The grown pellicle is then harvested from the medium, sliced and dried (Figure 1.7b), which results in a porous nanolayered membrane with very thin layers packed one on top of the other (Figure 1.7d), resulting from the extrusion process along the parallel axis of the bacteria [8], [25].

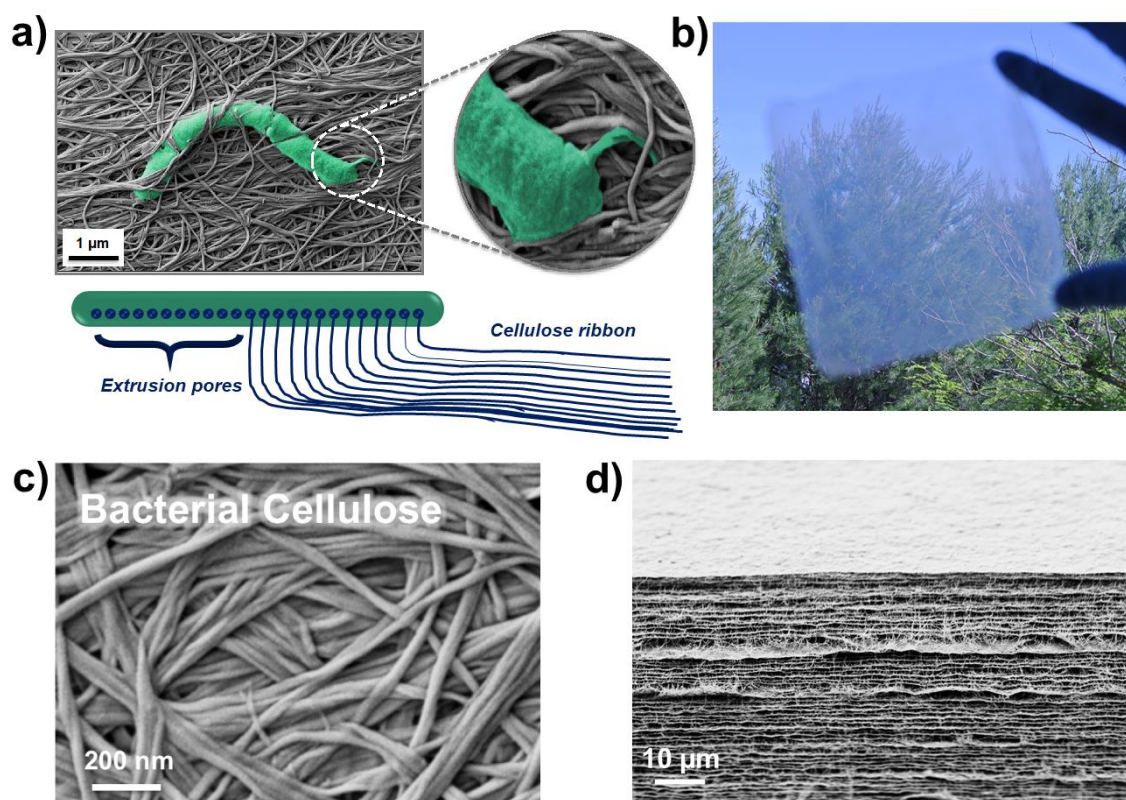


Figure 1.7 Bacterial Cellulose - a) *Komagataeibacter xylinus* micrographs and schematic representation from the extrusion mechanism; b) photograph from a dried membrane, c) SEM image from the membrane's surface, and d) corresponding cross section [39].

1.6. Paper as a substrate for electronics and paper-based devices

Electronic devices built on cellulose-based substrates have attracted considerable attention in the past decade, despite the broad spectrum of applications that had been already foreseen in the late '60s. Concepts of “paper electronics” appeared for the first time in the International Conference on Solid-State Devices, where T. Peter Brody from Westinghouse Electric Corp. showed tellurium-based transistors on paper [2], [40], [41]. The demonstrator consisted of arrays with one hundred transistors and was produced in vacuum through evaporation and patterned with metal masks or stencils. At that time T.P. Brody predicted an assortment of applications for this innovation, as circuits on data cards, manuals with printed working circuits, or even sensors for biological and medical use [30], [40]. Despite the enormous impact and interest aroused at that time, the paper transistors or even the possibility of having electronics in a throw-away material like paper, vanished.

The interest of paper as material for electronics came up again in the recent past driven, curiously, by the same motivations: disposable/recyclable cost-effective electronics, smart packaging or point-of-care diagnostics. This also happened due to the advent of nanotechnology and new processes. Paper is very attractive as a substrate for electronics due to its low price ($\approx 10^{-3}$ cent m⁻², more than one order of magnitude lower than polyethylene terephthalate – PET or polyimide – PI, the most common polymeric substrates in electronics), lightweight, flexibility and foldability, biodegradability and recyclability. The yearly production of paper is about 100 million tons, and its production technology is state of the art, where the process speed (roll-to-roll -R2R-manufacturing) can exceed 30 m s⁻¹ [9], [20], [22], [26].

Several attempts have been made recently to explore the potential of paper as a stratum for low-cost and flexible electronics, and several applications, using it either as a passive or active part of the device, have already been demonstrated by several research groups. Some examples are: capacitors and supercapacitors [42], microfluidic devices [43], [44], inorganic powder electroluminescence devices [45], light-emitting diodes [46] and electrochemical cells [47], in batteries as substrate [48], pencil-on-paper chemiresistors [49], piezoresistive and strain sensors [50]–[52], capacitive and piezoelectric touch pads [53]–[55] and Radio-Frequency Identification (RFID) tags, antennas and foldable printed circuit boards and displays [56], [57], PN junction diodes [58], [59], substrate for organic thin film transistors (OTFTs) [60], [61], carbon nanotubes and cellulose composite transistors [62], [63], oxide field-effect transistors (FETs) and complementary metal oxide semiconductor (CMOS) devices [64]–[66], ultra-flexible memories [67], [68] and flexible low-voltage electric double-layer thin film transistors (TFTs) [69], or even as substrate for organic photovoltaic devices [70] and a-Si:H based solar cells [71], [72].

From all the applications mentioned above, diodes and transistors stand out as key elements of most of the electronic circuits. The production of such device is quite straightforward using conventional and well-established integrated circuits (ICs) technology on rigid substrates like glass and silicon. However, it becomes much more challenging when making them on paper, mostly due to the unique substrate's properties, such as temperature limitations, patterning process and the surface's roughness.

Despite the issues pointed out, diodes, OTFTs, and FETs were successfully produced on paper, using it either as a physical support or as an active part, acting as a gate dielectric.

From the reported works, most of them refer to paper-based FETs using paper solely as physical substrate and not as part of the devices. Several workgroups reported Si-based devices on paper; in 2009 Härtling *et al.* presented silicon field-effect transistors on paper, fully printed by traditional screen printing and the devices' performance was stable and comparable to amorphous silicon thin film transistors [73]. On the other hand, Kim *et al.* presented a different method in which the silicon circuits were first produced using conventional ICs manufacturing techniques and then transferred to the flexible substrates [74].

Recently poly-Si transistors were produced at low temperatures using Si ink cyclopentasilane and excimer laser treatment, creating poly-Si at a maximum temperature of 150 °C. That group produced successfully n-channel metal oxide field-effect transistor (MOSFET) and p-channel MOSFET (NMOS and PMOS, respectively) devices with mobilities above 20 cm² V⁻¹ s⁻¹ [75]. Also in the same year, Kim and co-workers developed a technique that allows the production of ultrathin silicon circuits (NMOS, PMOS, and CMOS) with a high performance and a subsequent transfer of those devices to flexible substrates, whose surface was previously prepared with a polydimethylsiloxane (PDMS) coating [74].

Besides these examples, other devices with oxide-based semiconductors, protonic and electronic conductors used as dielectrics, such as chitosan and SiO₂-based solid electrolyte, and paper as substrate were reported. Some of the most recent works reported are summarised in Table 1.2.

Using paper as substrate provides flexibility, while the use of electrolytes as dielectric allows similar performance to that achieved in devices on glass with the advantage of having a low-voltage operation. The devices are mainly deposited on top of bare paper substrates, as office or photo paper; some of them were prepared on top of paper without any treatment [76], [77] and some groups showed work with passivation and smoother layers, as SiO₂ [69].

The fabrication of the devices needs to be compatible with the bottlenecks that paper presents. Nevertheless, the possibility of room temperature deposition of the semiconductors was demonstrated, allowing for devices with high $I_{\text{On}}/I_{\text{Off}}$, above

2.0×10^6 , and field-effect mobility, in the range of 9 to $47 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, as good as the ones produced on standard substrates and dielectrics [76]–[82].

Table 1.2. Summary of oxide-based transistors using paper as the substrate.

<i>Author</i>	<i>Year</i>	<i>Semiconductor</i>	<i>Dielectric</i>	<i>Techniques</i>	<i>I_{on}/I_{off}</i>	μ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	<i>Ref.</i>
<i>Sun et al.</i>	2009	SnO ₂ Sb	Microporous SiO ₂	PECVD ² , sputtering	2.0×10^5	47.3 (FE) ³	[76]
<i>Sun et al.</i>	2010	GIZO	Microporous SiO ₂	PECVD, sputtering	1.5×10^6	21 (FE)	[78]
<i>Lu et al.</i>	2011	ITO	Microporous SiO ₂	PECVD, sputtering	3.0×10^5	25.5 (FE)	[79]
<i>Jiang et al.</i>	2011	ITO	SiO ₂ -based solid electrolyte	PECVD, sputtering	8.0×10^5	22.4 (FE)	[83]
<i>Jiang et al.</i>	2012	ITO	SiO ₂ -based solid electrolyte	PECVD, sputtering	2.0×10^6	28.6 (FE)	[81]
<i>Dou et al.</i>	2013	ITO	Chitosan	PECVD, sputtering ⁴	4.0×10^6	9.3 (FE)	[69]
<i>Dou et al.</i>	2013	ITO	Chitosan	PECVD, sputtering, spinning	$\sim 10^4$	Not specified	[84]
<i>Wu et al.</i>	2014	IZO	Nanogranular SiO ₂	PECVD, sputtering	2.0×10^6	~ 14 (FE)	[82]
<i>Wu et al.</i>	2014	IZO	Chitosan	Sputtering, drop-casting	Not specified	Not specified	[85]
<i>Wu et al.</i>	2014	IZO	Phosphosilicate glass solid electrolyte	PECVD, sputtering	6.0×10^6	~ 13.4 (FE)	[77]

² Plasma-enhanced chemical vapor deposition³ Field-effect mobility⁴ Chitosan deposition technique not specified.

1.6.1. Thermal and electrical properties

Thermal endurance and electrical resistivity are highly relevant parameters to consider when choosing the substrate for electronics. Paper has unique properties as dimensional stability and low thermal expansion coefficient. Moreover, the onset thermal degradation of the cellulose begins around 180 °C, reaching a significant weight loss between 270 and 350 °C, making it suitable for low-temperature processes [8], [26]. On the other hand, paper is known as an electrical insulator and its use as a dielectric for capacitors and supercapacitors is widely reported. The dielectric constant (k) for pure dried cellulose varies typically between 6-8 presenting an electrical resistivity (ρ) around $10^{18} \Omega \text{ cm}$ (moist content $\approx 0 \%$), while for paper those values are lowered due to its' porous nature. The entangled porous fibres matrix contain air which has a $k \approx 1$ leading to a substantial decrease of the effective k to values in the range of 1.3 to 4 (at 1 MHz) [8], [30], [86].

The electrical resistivity of the paper is deeply related to several factors such as the moisture content, that is affected by the relative humidity (RH) of the surrounding atmosphere, the fibres' refining extent and orientation, and also used additives. In the early '80s, Josefowicz and Deslandes conducted a study where some of those parameters were tested, and a significant influence of the additives and atmospheric RH in the electrical resistivity of the paper was observed, mostly due to ionic nature of the additives commonly used during the papermaking process, as sodium chloride (NaCl). Later Oyj *et al.* showed that with the addition of NaCl content the bulk resistivity can be decreased one or two orders of magnitude (Figure 1.8a) [26], [87], [88]. Concerning the atmosphere's RH, the ρ of cotton can be reduced from 200 M Ω to 0.5 M Ω increasing the RH from 52% to 75%. In the case of paper, the decrease of ρ can reach nearly three orders of magnitude with a variation of the RH from 25% to 60% [85]. The susceptibility of ρ to atmospheric RH is not exclusive of the "bare" paper as kraft paper. Le Bras *et al.* observed that other cellulosic materials such as wood nanofibrillated cellulose and *Cladophora* cellulose (algae cellulose) are highly susceptible to the RH variation (Figure 1.8b) [8], [87]–[90].

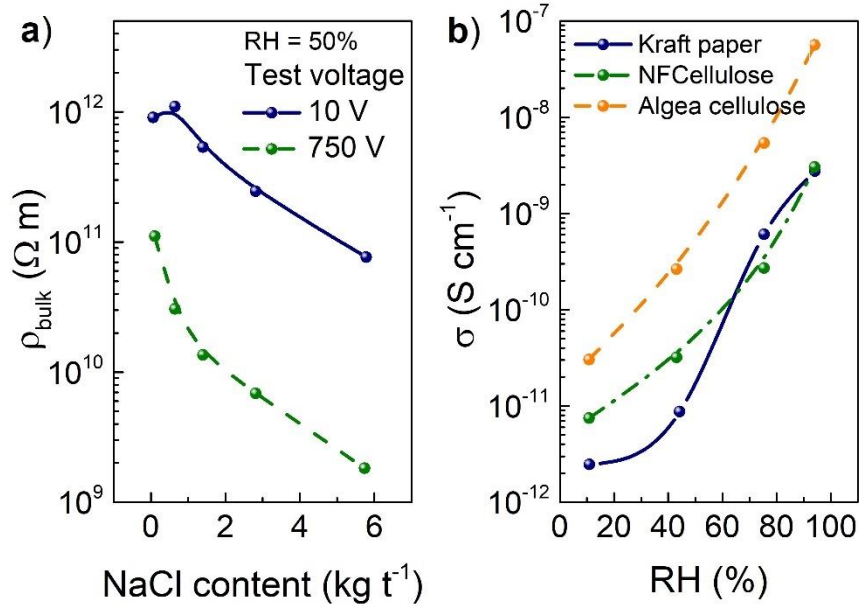


Figure 1.8 a) Bulk resistivity of paper (160 g m^{-2}) as a function of NaCl addition, with RH constant and tested voltages of 10 and 750 V, and b) Conductivity variation with the RH for kraft paper, wood nanofibrillated and algae cellulose (adapted from [88], [90]).

1.6.2. Field-effect transistors

Thin film transistors (TFTs) are commonly used when aiming for flexible electronic systems on low-cost substrates. TFTs are three-terminal field-effect devices where the current flows through the semiconductor, which is placed between drain and source electrodes and is modulated by the potential established between the gate electrode and the source (V_{GS}), similar to what happens in MOSFETs. The difference is that V_{GS} leads to the accumulation of free carriers in the dielectric/semiconductor interface instead of inversion [91]. Another difference between TFTs and MOSFETs lays in the employed substrate and semiconductor (Figure 1.9); whereas in TFTs the active thin film layers (semiconductor – oxide or amorphous/polycrystalline silicon, dielectric and contacts) are deposit onto an insulating substrate, typically glass or polymeric substrate, in MOSFETs the semiconductor is bulky and also acts as the substrate, as is the case of the silicon wafers [91], [92].

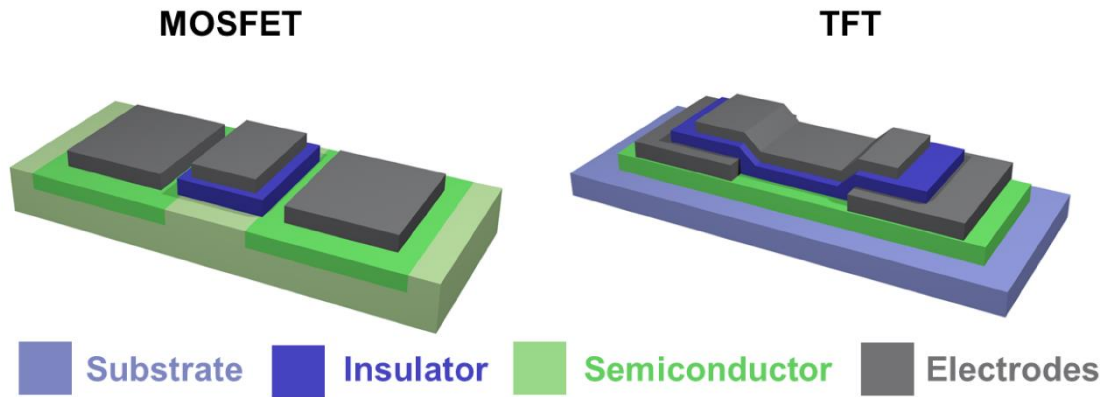


Figure 1.9 Schematic representation of a TFT and a MOSFET [93].

The use of thin films allows for the production of different configurations, depending on the position of the gate electrode and the distribution of the electrodes relative to the semiconductor (Figure 1.10). In the case where the drain/source and gate electrodes are on opposite or on the same side of the semiconductor, the structures are identified as staggered and coplanar, respectively. Moreover, depending on the positioning of the gate electrode those structures can be top or bottom gated [94].

Each one of these structures has benefits and drawbacks, and its' choice depends mostly on the materials used, processing techniques, post-processing temperatures or the number of lithographic/patterning steps involved. Regardless of the configuration, the working principle is the same for all the configurations. In chapter 2, more details on how to extract the typical electrical parameters of these devices will be covered.

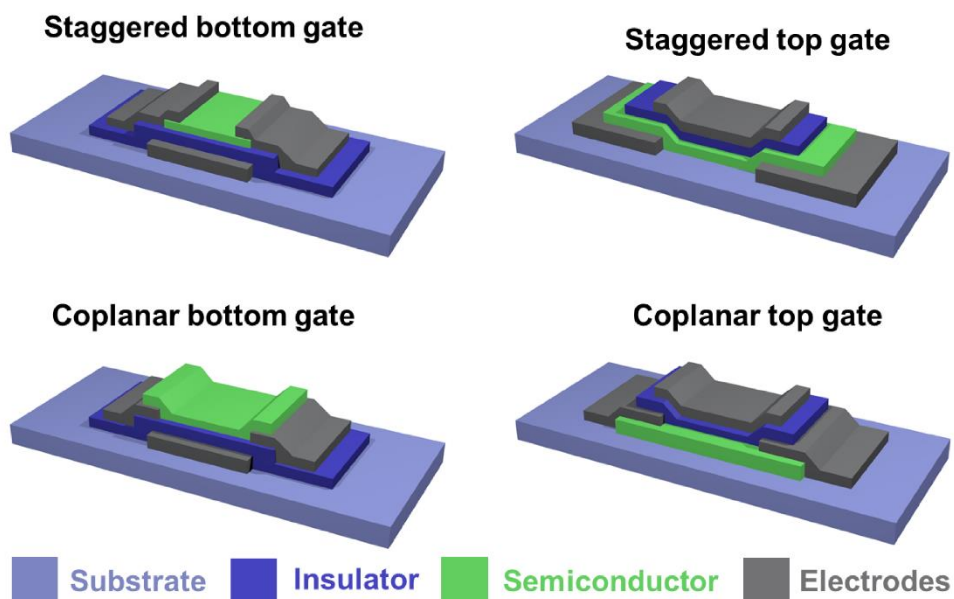


Figure 1.10 Conventional TFT structures depending on the positioning of layers.

The use of paper as a gate dielectric in FETs was reported for the first time in 2008 [64]. Those devices do not correspond to any of the conventional architectures presented above. They can not be considered as a regular staggered bottom gate TFT due to the thick character of the gate dielectric. The authors named it as “*interstrate*” structure since the paper is itself an active part of the devices and simultaneously the physical support for the remaining layers, as depicted in Figure 1.11. However, paper does not work as a conventional dielectric but like a solid electrolyte instead. Thus, the working principle of such paper FETs depends on the formation of two narrow electric double-layers at the semiconductor/paper and paper/gate electrode interfaces as will be explained in the next sub-section.

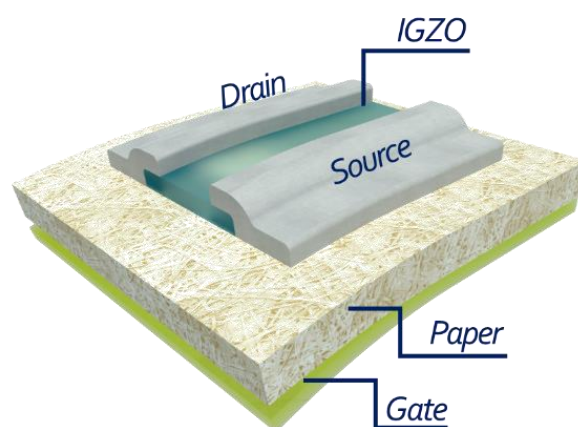


Figure 1.11 Schematic representation of staggered-bottom gate FETs using cellulose as a gate dielectric.

1.6.2.1. *Electric Double-Layer Transistors*

In the past 15 years, an enormous effort and fundamental research have been made regarding the study of semiconductors, as observed for instance with the transparent semiconducting oxides (TSOs) with a particular focus in amorphous oxide semiconductors (AOSs), mostly driven by the transparent electronics topic.

A new chapter begun in 2004 when Nomura and co-workers presented transparent flexible TFTs using amorphous oxide semiconductors based on the In-Ga-Zn-O system and produced at room-temperature with field-effect mobilities exceeding $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [95]. This breakthrough started an unprecedented revolution and a tremendous advance in materials science and electronics. Since 2004 nearly 5000 works⁵ were published

⁵ Figures from Google Scholar for the search with the keywords: "indium gallium zinc oxide" & "In-Ga-Zn-O" & "IGZO", for the years 2004-2018.

focusing on indium gallium zinc oxide (IGZO). Besides the AOS, nowadays there are several mature technologies able to be used in flexible TFTs, such as organic semiconductors, amorphous silicon (a-Si), or low-temperature polycrystalline silicon [96]. From these examples, the AOSs are by far the most suitable in paper-based electronics, once they combine several important aspects, briefly summarised in the following table.

Table 1.3. Comparison of some properties of mature semiconductor technologies.

	<i>AOSs</i>	<i>Organic</i>	<i>a-Si</i>	<i>LTPS</i>
<i>Electrical performance</i>	★	★	★	★ ★
<i>Complexity</i>	★	★	★	★
<i>Cost</i>	★	★	★	★
<i>Uniformity</i>	★	★	★	★
<i>Paper compatible</i>	★	★	★	★
Note: ★ is good/adequate/low; ★ is fair, and ★ is bad/high				

If on the one hand the semiconductor can be defined as the “*heart*” of the TFTs, on the other hand the dielectric can be identified as the “*brain*”, since it controls the semiconductor’s conductance. Ultimately, the devices’ performance will be led by the dielectric, and somehow those materials have been partially neglected. The dielectric determines the charge accumulation at the dielectric/semiconductor interface. Consequently, not only its bulk, but also interfacial quality or defects with the semiconductor, will determine the electrical performance, endurance and stability of the devices [91].

The common dielectrics in TFTs are silicon nitride (Si_3N_4), silicon dioxide (SiO_2), and nowadays also high k materials, such as tantalum pentoxide (Ta_2O_5), hafnium oxide (HfO_2), or zirconium oxide (ZrO_2). High gate capacitance is usually desired, to compensate the effect of interface defects and allow for low-voltage operation. Since charge carrier density (Q) accumulation will depend on the dielectric constant of the material, which can be achieved by using high k materials, which maintain the high capacitance even in relatively thicker insulating films. Another way to reach high gate capacitance is to reduce the dielectric thickness, verifying the capacitance expression: $C = \frac{\epsilon_0 \cdot k \cdot A}{t}$, where ϵ_0 is the vacuum permittivity, k is the dielectric constant, A and t are the area and thickness, respectively [92].

A conventional dielectric is polarised when an electric field is applied. The field is constant along the dielectric thickness with the corresponding voltage drop associated with charge accumulation at the electrodes (Figure 1.12a). On the other hand, the mechanism that allows using paper and cellulose-based substrates as a gate dielectric is different from conventional dielectrics. In this case, the modulation of the semiconductor conductance relies on the formation of two electric double-layers (EDL) comparable to what happens in EDL capacitors. Paper behaves as a solid-state electrolyte which is ionically conducting and electronically insulating, filled with mobile ionic species. Moreover, if an external electric field is applied, the ionic species can be slightly displaced and accumulated at the metal/paper interface (cations/protons), at the same time anions/electrons with equal densities will be induced at the opposite side, forming cation/anion interfacial coupling EDL (Figure 1.12b) [97], [98].

The interfacial coupling EDLs present thicknesses of ≈ 1 nm - sizes of the anions and cations - and can be defined as *nanometre-thick capacitors* reaching very high capacitances. In the review paper from 2013, Kim and co-workers estimated that the EDL capacitance is higher than $1 \mu\text{F cm}^{-2}$ using the Helmholtz equation, $C \approx \frac{\epsilon_0 k}{\lambda}$, where λ is the thickness of the double layer (assuming EDL thicknesses of ≈ 1 nm) and $k \approx 10$, each exceeds the Ta_2O_5 capacitance by at least 1 order of magnitude [97], [99]. This is very important, since the gate capacitance becomes basically insensible to the paper thickness.

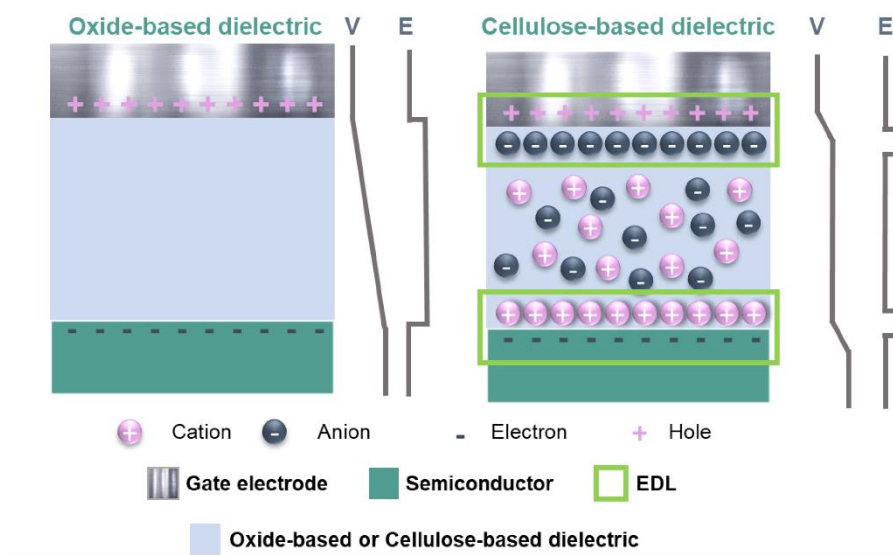


Figure 1.12 Schematic diagram of the device structure and respective charges modulation for a) oxide-based dielectric and b) EDL in cellulose-based dielectric.

According to the Stern model, each formed EDL consists of three regions, a thinner and a compact Helmholtz layer or inner Helmholtz plane (IHP) – closest to the interface, followed by an outer Helmholtz plane (OHP), and a diffuse layer (DL) (Figure 1.13) [100]. The inner and outer layers usually contain the adsorbed ions and the non-specifically adsorbed ions, respectively. The DL is dependent on the ionic concentration in the bulk and its' distance increases with an increase in ionic concentration [98], [99]. In cellulosic materials, the EDL formation is fundamentally dependent on the mobile free ions present in the paper matrix and sorbed water within the paper. The mechanism beneath this movement consists of proton transport by hopping along the hydrogen bond network of water molecules or hydroxyl groups [101], [102]. This mechanism is well reported for protonic conductors as chitosan, which has a molecular structure similar to cellulose. The transport mechanism in the paper is not properly reported but is expected to have a Grotthuss-like mechanism since it was observed that for vacuum conditions, where the water is partially desorbed from the paper, the EDL is not formed once the protons' hopping decreases or even ceases [26].

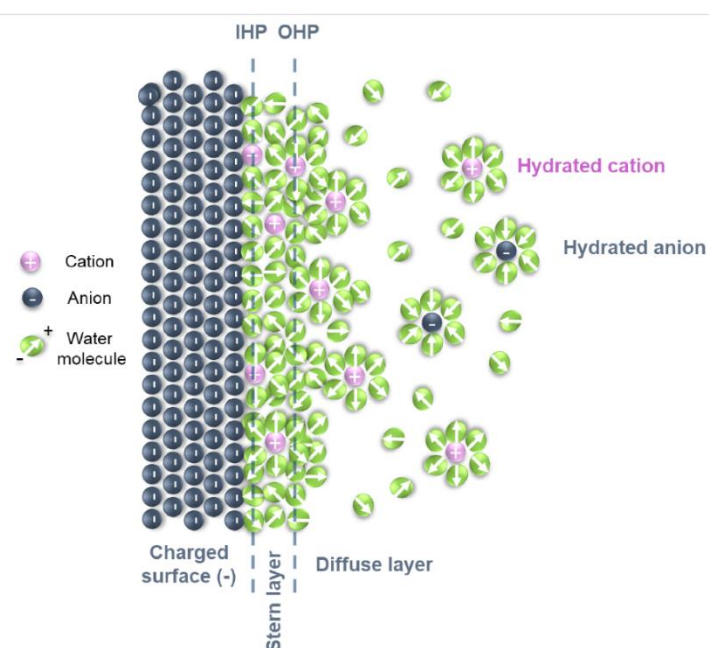


Figure 1.13 Stern model of the electrical double layer at a negatively charged surface.

EDL gated devices can operate in two modes depending on the permeability of the semiconductor to the ions. Permeable semiconductors (more typically organic ones) work in electrochemical mode and are known as electrochemical transistors (ECTs). In these devices, the applied V_{GS} leads to the migration of the ions to the electrolyte/semiconductor interface, but no EDL formation occurs in this region. Part of

the mobile ions can migrate into the semiconductor promoting its oxidation/reduction and consequently modulating its conductivity, whereas in the interface electrolyte/gate an EDL is formed (Figure 1.14a) [97]–[99].

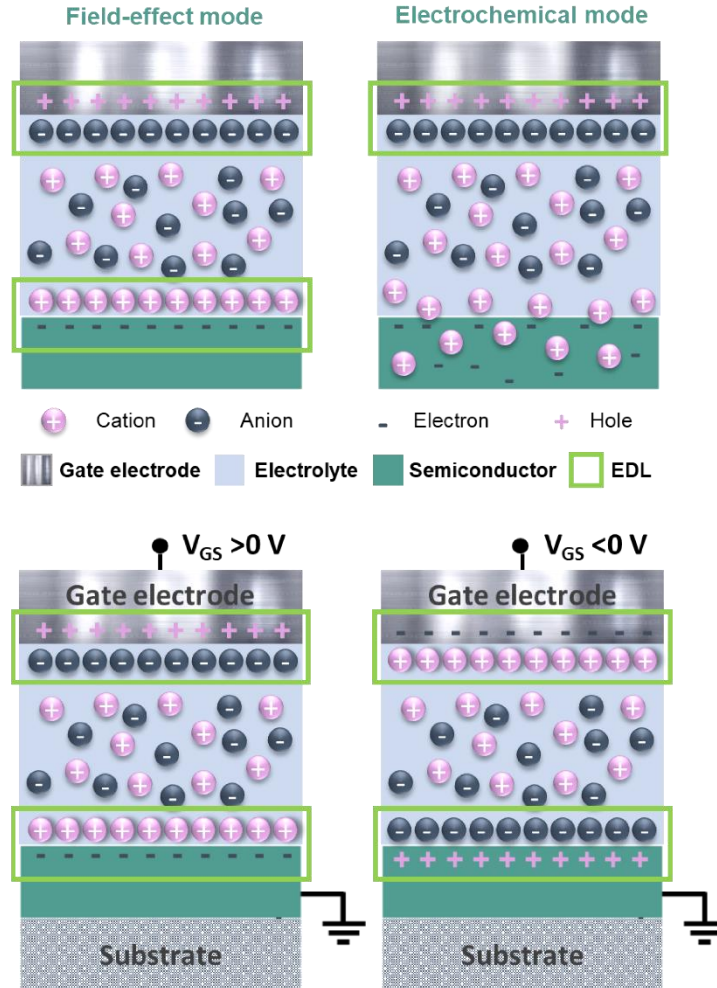


Figure 1.14 Cross section of an EDL gated devices working in a) electrochemical mode (ECTs), b) field-effect mode, and c) EDL behaviour under a negative and positive V_{GS} , respectively.

In the case of low V_{GS} or non-permeable semiconductors, the devices operate in the field-effect mode. With a negative or positive V_{GS} applied, ionic charges will be accumulated at both gate electrode/electrolyte and electrolyte/semiconductor interfaces forming two interfacial coupling EDLs (Figure 1.14b). As in FETs, the electric double-layer field-effect transistors (EDLFETs), the accumulation or depletion of the free carriers at the electrolyte/semiconductor interface is dependent on the V_{GS} (Figure 1.14c). Due to the high capacitance of the electrolytes, a small increase of V_{GS} promotes very high charge density accumulation in the channel, allowing for the device operation [97].

1.6.2.2. Cellulose-based field-effect transistors

N-channel oxide-based FETs using paper as gate dielectric were reported for the first time by Fortunato *et al.* [64]. In that work, hybrid FETs with a staggered-bottom gate structure were deposited on paper without surface modification. The devices were produced entirely at room temperature, patterned using shadow masks and exhibited $I_{\text{On}}/I_{\text{Off}}$ modulation ratio above 10^4 . This achievement was a breakthrough to further research, and since then research groups have made tremendous developments. Table 1.4 provides an overview of inorganic FETs developed using paper as a dielectric [64]. Later in 2008, the same group showed that these devices could operate as non-volatile memories once the injected charges stay trapped in the entangled fibre matrix [103], [104].

Lim's group presented devices with the same structure using amorphous InGaZnO_4 , but the performance of the devices was not better than those previously reported; the novelty presented by the authors consisted in the patterning of the semiconductor channel and electrodes with lithography and lift-off processes [105].

More recently, already in the frame of this PhD plan, the influence of the fibres in the devices' performance was reported. It was noticed that small fibrils (width in the nanoscale range) lead to papers with a smoother surface and a compact matrix. Moreover, devices produced with this paper showed higher $I_{\text{On}}/I_{\text{Off}}$ ratio and lower susceptibility to relative humidity changes since the small fibril can bond strongly to the water [3], [26], [106]. Besides the conventional paper, other cellulose-based substrates were tested bringing novelty to this work, like highly transparent cotton-based nanocrystalline cellulose (NCC). The use of free-standing NCC membranes as gate-dielectric was reported for the first time along this PhD work resulting in FETs with electrical performances similar to those obtained on regular paper. However, the high crystallinity of the cellulose films seems to improve the $I_{\text{On}}/I_{\text{Off}}$ modulation ratio (above 10^5) [22].

Finally, bacterial cellulose has been also considered as substrates for the implementation of electronic devices such as organic light-emitting diodes (OLEDs) [107]–[109]. More recently, and again in the frame of this PhD work, this special type of nanocellulose was implemented as dielectric in FETs capable of achieving an $I_{\text{On}}/I_{\text{Off}}$ modulation ratio above 10^4 [39].

Table 1.4. Summary of oxide-based transistors using cellulose substrates as a dielectric.

<i>Author</i>	<i>Year</i>	<i>Oxide</i>	<i>Paper</i>	<i>Techniques</i>	<i>I_{on}/I_{off}</i>	μ (cm ² V ⁻¹ s ⁻¹)	<i>Ref.</i>
Fortunato et al.	2008	IGZO	Cellulose-based paper (parchment paper)	Magnetron sputtering and e-beam	2.9×10 ⁴	34	[64]
Martins et al.	2008	IGZO	Cellulose-based paper with ionic resin matrix	Magnetron sputtering and e-beam	~ 1×10 ⁴	40	[103]
Martins et al.	2009	IGZO	Cellulose-based paper with ionic resin matrix	Magnetron sputtering and e-beam	3×10 ⁴	29	[104]
Lim et al.	2009	IGZO	Cellulose-based paper	Magnetron sputtering	1×10 ⁴	35	[105]
Gherendi et al.	2013	In ₂ O ₃	Not defined	Pulsed electron beam	6×10 ⁴	40000	[110]
Pereira et al.	2014	IGZO	Micro and nanofibrillated cellulose-based paper	Magnetron sputtering and e-beam	7.5×10 ⁴	16	[26]
Gaspar et al.	2014	IGZO	Nanocrystalline cellulose	Magnetron sputtering and e-beam	2×10 ⁵	7	[22]
Fortunato et al.	2016	IGZO	Bacterial cellulose	Magnetron sputtering and e-beam	4×10 ⁴	Not defined	[39]
Shao et al.	2017	IZO	nanofibrillated cellulose coated onto photo paper	Magnetron sputtering	10 ⁷	26 (FE)	[111]
Grey et al.	2018	IGZO	Chiral cellulose nanocrystal membrane	Magnetron sputtering	10 ⁷	9	[112]
Gaspar et al.	2018	IGZO	Cellulose-based paper (parchment paper)	Magnetron sputtering	10 ⁴	2-3	[113]

Concerning the paper FET architecture, in last decade several groups presented flexible hybrid dual-gate transistors on paper. These transistors present a particular configuration, where two gate electrodes are placed in the same plane of the source, drain, and semiconductor. Devices with this configuration are usually named as oxide-

based neuron transistor or synaptic transistors due to the possibility of inducing artificial synapse switching between high and low currents.

Some of the reported devices use chitosan gate dielectric since it is a good protonic conductor and presents a large specific capacitance EDL, allowing the devices' operation at low-voltages, similar to the ones produced with SiO₂-based solid electrolyte [69], [84], [85]. Nevertheless, just recently this architecture was tested using cellulose as a gate dielectric. In 2017, Shao *et al.* drop casted nanofibrillated cellulose onto photographic paper and patterned a multi-gate oxide-based homojunction using shadow masks; the produced devices show good electrical performances with $I_{\text{On}}/I_{\text{Off}}$ ratio of 10^7 and mobility $\approx 26 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [111]. No further works with this architecture using cellulose as dielectric were presented until now. During this PhD, a similar architecture was tested using commercial parchment paper. Those device architectures enable the control of the on-voltage of the devices and also the change from depletion to enhancement mode. Moreover, this specific characteristic allowed the implementation of simple logic gates, as AND and OR, universal logic gates (NAND and NOR), and also an inverter depending on the combination of the voltage level applied at each gate. This topic will be subject to further discussion in Chapter 6.

Although the focus of this work only emphasises the oxide thin film technology using magnetron sputtering, it is worth to mention that a few attempts to use paper in a more efficient and profitable way were made, using essentially carbon nanotubes and organic semiconductors [3], [114]. Composites with cellulose and carbon nanotubes (CNTs) were developed by Yun and co-workers [62] and later improved by Kim *et al.* [63]. Yun's group reported a flexible paper transistor made with regenerated cellulose and covalently bonded multiwalled carbon nanotubes (MWCNTs). The composite MWCNT paper works as an electron channel, allowing the transistor's operation using only the paper without the need of other conducting and insulating layers. The devices exhibited low field-effect mobility with average values between $[5.8\text{--}7.8] \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and an $I_{\text{On}}/I_{\text{Off}}$ ratio that is highly dependent on the concentration of MWCNTs [62]. In another study carried out by Kim *et al.*, a flexible paper transistor was described made with single-walled carbon nanotubes (SWCNTs) covalently bonded to a cellulose composite without requiring additional semiconducting layers. They found that the alignment of the SWCNTs influences the electrical characteristics of the device: The

mobility and $I_{\text{On}}/I_{\text{Off}}$ ratio are improved from 0.036 to 0.67 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and from 2.0 to 12.4, respectively, when fibre alignment is promoted through stretching [63].

The named examples are just a small sample of the work and research made in the past years using cellulose as a truly electronic material. Although it is not a recent technology, it is still in an early-stage compared to highly established technologies for instance Si or metal-oxides. The scientific community is highly driven around the paper electronics field, where it is exciting to witness the creation of the foundations of this *new(old)* technology and simultaneously searching for new and better approaches to improve it.

1.7. References

- [1] J. P. Rolland and D. a. Mourey, "Paper as a novel material platform for devices," *MRS Bull.*, vol. 38, no. 04, pp. 299–305, Apr. 2013.
- [2] A. J. Steckl, "Circuits on cellulose," *IEEE Spectr.*, vol. 50, no. 2, pp. 48–61, Feb. 2013.
- [3] S. Dai, Y. Chu, D. Liu, F. Cao, X. Wu, J. Zhou, B. Zhou, Y. Chen, and J. Huang, "Intrinsically ionic conductive cellulose nanopapers applied as all solid dielectrics for low voltage organic transistors," *Nat. Commun.*, vol. 9, no. 1, p. 2737, Dec. 2018.
- [4] Q. Zheng, H. Zhang, H. Mi, Z. Cai, Z. Ma, and S. Gong, "High-performance flexible piezoelectric nanogenerators consisting of porous cellulose nanofibril (CNF)/poly(dimethylsiloxane) (PDMS) aerogel films," *Nano Energy*, vol. 26, pp. 504–512, Aug. 2016.
- [5] D. Zhao, C. Chen, Q. Zhang, W. Chen, S. Liu, Q. Wang, Y. Liu, J. Li, and H. Yu, "High Performance, Flexible, Solid-State Supercapacitors Based on a Renewable and Biodegradable Mesoporous Cellulose Membrane," *Adv. Energy Mater.*, vol. 7, no. 18, p. 1700739, Sep. 2017.
- [6] C. Fischer, A. Fraiwan, and S. Choi, "A 3D paper-based enzymatic fuel cell for self-powered, low-cost glucose monitoring," *Biosens. Bioelectron.*, vol. 79, pp. 193–197, May 2016.
- [7] D. Klemm, B. Heublein, H. P. Fink, and A. Bohn, "Cellulose: Fascinating biopolymer and sustainable raw material," *Angew. Chemie - Int. Ed.*, vol. 44, no. 22, pp. 3358–3393, 2005.
- [8] J.-L. Wertz, O. Bédoué, and J. P. Mercier, *Cellulose Science and Technology*, 1st ed. Lausanne: EPFL Press, 2010.
- [9] S. K. Mahadeva, K. Walus, and B. Stoeber, "Paper as a Platform for Sensing Applications and Other Devices: A Review," *ACS Appl. Mater. Interfaces*, vol. 7, no. 16, pp. 8345–8362, Apr. 2015.
- [10] O. J. Rojas, Ed., *Cellulose Chemistry and Properties: Fibers, Nanocelluloses and Advanced Materials*. Springer International Publishing, 2016.
- [11] N. Lavoine, I. Desloges, A. Dufresne, and J. Bras, "Microfibrillated cellulose - Its barrier properties and applications in cellulosic materials: A review," *Carbohydr. Polym.*, vol. 90, no. 2, pp. 735–764, 2012.

- [12] A. Dufresne, *Nanocellulose: From Nature to High Performance Tailored Materials*, 1st ed. Berlin, Boston: De Gruyter, 2012.
- [13] M. Pääkkö, M. Ankerfors, H. Kosonen, A. Nykänen, S. Ahola, M. Österberg, J. Ruokolainen, J. Laine, P. T. Larsson, O. Ikkala, and T. Lindström, “Enzymatic Hydrolysis Combined with Mechanical Shearing and High-Pressure Homogenization for Nanoscale Cellulose Fibrils and Strong Gels,” *Biomacromolecules*, vol. 8, no. 6, pp. 1934–1941, Jun. 2007.
- [14] D. Trache, M. H. Hussin, M. K. M. Haafiz, and V. K. Thakur, “Recent progress in cellulose nanocrystals: sources and production,” *Nanoscale*, vol. 9, no. 5, pp. 1763–1786, 2017.
- [15] A. Isogai, T. Saito, and H. Fukuzumi, “TEMPO-oxidized cellulose nanofibers,” *Nanoscale*, vol. 3, no. 1, pp. 71–85, 2011.
- [16] J.-H. J. J. H. Kim, B. S. Shim, H. S. Kim, Y.-J. J. Lee, S.-K. K. Min, D. Jang, Z. Abas, and J.-H. J. J. H. Kim, “Review of nanocellulose for sustainable future materials,” *Int. J. Precis. Eng. Manuf. Technol.*, vol. 2, no. 2, pp. 197–213, Apr. 2015.
- [17] C. J. Biermann, *Handbook of Pulping and Papermaking*, 2nd ed. London: Academic Press, 1996.
- [18] Y. Nakano, M. Yamaguchi, H. Endo, N. A. Rejab, and M. Ohtani, “NAC-MYB-based transcriptional regulation of secondary cell wall biosynthesis in land plants,” *Front. Plant Sci.*, vol. 6, no. May, pp. 1–18, May 2015.
- [19] J. Rytioja, K. Hildén, J. Yuzon, A. Hatakka, R. P. de Vries, and M. R. Mäkelä, “Plant-Polysaccharide-Degrading Enzymes from Basidiomycetes,” *Microbiol. Mol. Biol. Rev.*, vol. 78, no. 4, pp. 614–649, 2014.
- [20] V. I. Popa, Ed., *Pulp Production and Processing: From Papermaking to High-Tech Products*, 1st ed. Shawbury, Shrewsbury, Shropshire: iSmithers Rapra Publishing, 2013.
- [21] V. K. Varshney and S. Naithani, “Cellulose Fibers: Bio- and Nano-Polymer Composites,” in *Cellulose Fibers: Bio- and Nano-Polymer Composites*, S. Kalia, B. S. Kaith, and I. Kaur, Eds. Berlin, Heidelberg: Springer Berlin Heidelberg, 2011, pp. 43–61.
- [22] D. Gaspar, S. N. Fernandes, A. G. de Oliveira, J. G. G. Fernandes, P. Grey, R. V. V. Pontes, L. Pereira, R. Martins, M. H. H. Godinho, and E. Fortunato, “Nanocrystalline cellulose applied simultaneously as the gate dielectric and the substrate in flexible field effect transistors,” *Nanotechnology*, vol. 25, no. 9, p. 094008, Mar. 2014.
- [23] M. A. S. A. Samir, F. Alloin, J.-Y. Sanchez, and A. Dufresne, “Nanocomposite polymer electrolytes based on poly(oxyethylene) and cellulose whiskers,” *Polímeros*, vol. 15, no. 2, pp. 109–113, Jun. 2005.
- [24] M. Kaushik, C. Fraschini, G. Chauve, J.-L. Putaux, and A. Moores, “Transmission Electron Microscopy for the Characterization of Cellulose Nanocrystals,” in *The Transmission Electron Microscope - Theory and Applications*, InTech, 2015.
- [25] M. Gama, F. Dourado, and S. Bielecki, *Bacterial Nanocellulose - From Biotechnology to Bio-Economy*, 1st ed., vol. 1. Elsevier, 2016.
- [26] L. Pereira, D. Gaspar, D. Guerin, A. Delattre, E. Fortunato, and R. Martins, “The influence of fibril composition and dimension on the performance of paper gated oxide transistors,” *Nanotechnology*, vol. 25, no. 9, p. 094007, Mar. 2014.
- [27] H. Theliander, *Pulping Chemistry and Technology Volume 2*, vol. 2. Berlin, New York: Walter de Gruyter, 2009.

- [28] R. J. Thomas, "Wood: Structure and Chemical Composition," in *ACS Symposium Series*, 1977, vol. 110, no. 9, pp. 1–23.
- [29] European Paper & Packaging Industries, "Pulping properties of hardwoods and softwood," 2017. [Online]. Available: <http://www.paperonline.org/paper-making/paper-production/pulping/pulping-properties-of-hardwoods-and-softwood>. [Accessed: 28-Dec-2017].
- [30] D. Tobjörk and R. Österbacka, "Paper electronics," *Adv. Mater.*, vol. 23, no. 17, pp. 1935–61, May 2011.
- [31] P. Bajpai, *Chemistry and Sustainability in Pulp and Paper Industry*. 2015.
- [32] A. T. Vicente, A. Araújo, D. Gaspar, L. Santos, A. C. Marques, M. J. Mendes, L. Pereira, E. Fortunato, and R. Martins, "Optoelectronics and Bio Devices on Paper Powered by Solar Cells," in *Nanostructured Solar Cells*, 1st ed., no. February, N. Das, Ed. InTech, 2017, pp. 33–65.
- [33] A. Bentur and S. Mindness, "Natural Fibres," in *Fibre Reinforced Cementitious Composites*, 1st ed., A. Bentur and S. Mindness, Eds. New York: Elsevier Applied Science, 1990, p. 472.
- [34] M. Toivakka, J. Peltonen, R. Österbacka, M. (Mihai) Irimia-Vladu, E. D. Glowacki, N. S. Sariciftci, and S. Bauer, "Paper Electronics," in *Green materials for electronics*, 1st ed., M. Irimia-Vladu, E. D. Glowacki, N. S. Sariciftci, and S. Bauer, Eds. Wiley-VCH Verlag GmbH & Co. KGaA, 2017, pp. 163–189.
- [35] M. Gama, P. Gatenholm, D. Klemm, and E. Al, *Bacterial NanoCellulose*. 2013.
- [36] T. Zhou, D. Chen, J. Jiu, T. T. Nge, T. Sugahara, S. Nagao, H. Koga, M. Nogi, K. Suganuma, X. Wang, X. Liu, P. Cheng, T. Wang, and D. Xiong, "Electrically conductive bacterial cellulose composite membranes produced by the incorporation of graphite nanoplatelets in pristine bacterial cellulose membranes," *Express Polym. Lett.*, vol. 7, no. 9, pp. 756–766, Jun. 2013.
- [37] T. Abitbol, A. Rivkin, Y. Cao, Y. Nevo, E. Abraham, T. Ben-Shalom, S. Lapidot, and O. Shoseyov, "Nanocellulose, a tiny fiber with huge applications," *Curr. Opin. Biotechnol.*, vol. 39, no. I, pp. 76–88, Jun. 2016.
- [38] M. Iguchi, S. Yamanaka, and A. Budhiono, "Bacterial cellulose - a masterpiece of nature's arts," *J. Mater. Sci.*, vol. 35, no. 2, pp. 261–270, 2000.
- [39] E. Fortunato, D. Gaspar, P. Duarte, L. Pereira, H. Águas, A. Vicente, F. Dourado, M. Gama, and R. Martins, "Optoelectronic Devices from Bacterial NanoCellulose," in *Bacterial Nanocellulose*, Elsevier, 2016, pp. 179–197.
- [40] T. P. Brody, "Paper transistors," *Radio Electron. Eng.*, vol. 36, no. 4, p. 240, 1968.
- [41] T. Liang, X. Zou, and A. D. Mazzeo, "A flexible future for paper-based electronics," in *Micro- and Nanotechnology Sensors, Systems, and Applications VIII*, 2016, vol. 9836, p. 98361D.
- [42] Y. Tanaka, N. Ishii, J. Okuma, and R. Hara, "Electric double-layer capacitor having a separator made from a cellulose fiber," US5963419 A, 1999.
- [43] E. Carrilho, A. W. Martinez, and G. M. Whitesides, "Understanding wax printing: a simple micropatterning process for paper-based microfluidics," *Anal. Chem.*, vol. 81, no. 16, pp. 7091–5, Aug. 2009.
- [44] M. N. Costa, B. Veigas, J. M. Jacob, D. S. Santos, J. Gomes, P. V Baptista, R. Martins, J. Inácio, and E. Fortunato, "A low cost, safe, disposable, rapid and self-sustainable paper-based platform for diagnostic testing: lab-on-paper," *Nanotechnology*, vol. 25, no. 9, p. 094006, Mar. 2014.
- [45] J.-Y. Y. Kim, S. H. Park, T. Jeong, M. J. Bae, S. Song, J. Lee, I. T. Han, D. Jung, and S. Yu, "Paper as a Substrate for Inorganic Powder Electroluminescence

- Devices,” *IEEE Trans. Electron Devices*, vol. 57, no. 6, pp. 1470–1474, 2010.
- [46] S. Purandare, E. F. Gomez, and A. J. Steckl, “High brightness phosphorescent organic light emitting diodes on transparent and flexible cellulose films,” *Nanotechnology*, vol. 25, no. 9, p. 094012, 2014.
- [47] A. Asadpoordarvish, A. Sandström, C. Larsen, R. Bollström, M. Toivakka, R. Österbacka, and L. Edman, “Light-Emitting Paper,” *Adv. Funct. Mater.*, vol. 25, no. 21, 2015.
- [48] Q. Cheng, Z. Song, T. Ma, B. B. Smith, R. Tang, H. Yu, H. Jiang, and C. K. Chan, “Folding paper-based lithium-ion batteries for higher areal energy densities,” *Nano Lett.*, vol. 13, no. 10, pp. 4969–4974, 2013.
- [49] C.-W. Lin, Z. Zhao, J. Kim, and J. Huang, “Pencil drawn strain gauges and chemiresistors on paper,” *Sci. Rep.*, vol. 4, p. 3812, 2014.
- [50] X. Liu, M. Mwangi, X. Li, M. O’Brien, and G. M. Whitesides, “Paper-based piezoresistive MEMS sensors,” *Lab Chip*, vol. 11, no. 13, p. 2189, 2011.
- [51] C. Yan, J. Wang, W. Kang, M. Cui, X. Wang, C. Y. Foo, K. J. Chee, and P. S. Lee, “Highly stretchable piezoresistive graphene-nanocellulose nanopaper for strain sensors,” *Adv. Mater.*, vol. 26, no. 13, pp. 2022–2027, 2014.
- [52] E. Lemaire, R. Moser, C. J. Borsa, and D. Briand, “Green paper-based piezoelectronics for sensors and actuators,” *Sensors Actuators A Phys.*, vol. 244, pp. 285–291, Jun. 2016.
- [53] A. D. Mazzeo, W. B. Kalb, L. Chan, M. G. Killian, J.-F. F. Bloch, B. a. Mazzeo, and G. M. Whitesides, “Paper-Based, Capacitive Touch Pads,” *Adv. Mater.*, vol. 24, no. 21, pp. 2850–2856, Jun. 2012.
- [54] R.-Z. Li, A. Hu, T. Zhang, and K. D. Oakes, “Direct Writing on Paper of Foldable Capacitive Touch Pads with Silver Nanowire Inks,” *ACS Appl. Mater. Interfaces*, vol. 6, no. 23, pp. 21721–21729, 2014.
- [55] X. Li, Y.-H. Wang, C. Zhao, and X. Liu, “Paper-Based Piezoelectric Touch Pads with Hydrothermally Grown Zinc Oxide Nanowires,” *ACS Appl. Mater. Interfaces*, vol. 6, no. 24, pp. 22004–22012, 2014.
- [56] T. Inui, H. Koga, M. Nogi, N. Komoda, and K. Suganuma, “A Miniaturized Flexible Antenna Printed on a High Dielectric Constant Nanopaper Composite,” *Adv. Mater.*, vol. 27, no. 6, pp. 1112–1116, 2015.
- [57] A. C. Siegel, S. T. Phillips, B. J. Wiley, and G. M. Whitesides, “Thin, lightweight, foldable thermochromic displays on paper,” *Lab Chip*, vol. 9, no. 19, pp. 2775–2781, 2009.
- [58] A. Manekkathodi, M.-Y. Y. Lu, C. W. Wang, and L.-J. J. Chen, “Direct growth of aligned zinc oxide nanorods on paper substrates for low-cost flexible electronics,” *Adv. Mater.*, vol. 22, no. 36, pp. 4059–4063, Sep. 2010.
- [59] W. Zhang, X. Zhang, C. Lu, Y. Wang, and Y. Deng, “Flexible and transparent paper-based ionic diode fabricated from oppositely charged microfibrillated cellulose,” *J. Phys. Chem. C*, vol. 116, no. 16, pp. 9227–9234, 2012.
- [60] Y.-H. Kim, D.-G. Moon, and J.-I. Han, “Organic TFT Array on a Paper Substrate,” *IEEE Electron Device Lett.*, vol. 25, no. 10, pp. 702–704, Oct. 2004.
- [61] Y. Fujisaki, H. Koga, Y. Nakajima, M. Nakata, H. Tsuji, T. Yamamoto, T. Kurita, M. Nogi, and N. Shimidzu, “Transparent nanopaper-based flexible organic thin-film transistor array,” *Adv. Funct. Mater.*, vol. 24, no. 12, pp. 1657–1663, 2014.
- [62] S. Yun, S.-D. Jang, G.-Y. Yun, J.-H. J. Kim, and J.-H. J. Kim, “Paper transistor made with covalently bonded multiwalled carbon nanotube and cellulose,” *Appl. Phys. Lett.*, vol. 95, no. 10, p. 104102, 2009.

- [63] J. H. Kim, S. Yun, H. U. Ko, and J. Kim, "A flexible paper transistor made with aligned single-walled carbon nanotube bonded cellulose composite," *Curr. Appl. Phys.*, vol. 13, no. 5, pp. 897–901, 2013.
- [64] E. Fortunato, N. Correia, P. Barquinha, L. Pereira, G. Goncalves, and R. Martins, "High-Performance Flexible Hybrid Field-Effect Transistors Based on Cellulose Fiber Paper," *IEEE Electron Device Lett.*, vol. 29, no. 9, pp. 988–990, Sep. 2008.
- [65] R. Martins, A. Nathan, R. Barros, L. Pereira, P. Barquinha, N. Correia, R. Costa, A. Ahnood, I. Ferreira, and E. Fortunato, "Complementary Metal Oxide Semiconductor Technology With and On Paper," *Adv. Mater.*, vol. 23, no. 39, pp. 4491–4496, Oct. 2011.
- [66] P. Grey, D. Gaspar, I. Cunha, R. Barras, J. T. Carvalho, J. R. Ribas, E. Fortunato, R. Martins, and L. Pereira, "Handwritten Oxide Electronics on Paper," *Adv. Mater. Technol.*, vol. 2, no. 6, p. 1700009, Jun. 2017.
- [67] K. Nagashima, H. Koga, U. Celano, F. Zhuge, M. Kanai, S. Rahong, G. Meng, Y. He, J. De Boeck, M. Jurczak, W. Vandervorst, T. Kitaoka, M. Nogi, and T. Yanagida, "Cellulose nanofiber paper as an ultra flexible nonvolatile memory.," *Sci. Rep.*, vol. 4, p. 5532, 2014.
- [68] J. Jang, Y. Song, K. Cho, Y. Kim, W. Lee, D. Yoo, S. Chung, and T. Lee, "Non-volatile aluminum oxide resistive memory devices on a wrapping paper substrate," *Flex. Print. Electron.*, vol. 1, no. 3, p. 034001, Sep. 2016.
- [69] W. Dou, L. Zhu, J. Jiang, and Q. Wan, "Flexible Dual-Gate Oxide TFTs Gated by Chitosan Film on Paper Substrates," *IEEE Electron Device Lett.*, vol. 34, no. 2, pp. 259–261, Feb. 2013.
- [70] L. Hu, G. Zheng, J. Yao, N. Liu, B. Weil, M. Eskilsson, E. Karabulut, Z. Ruan, S. Fan, J. T. Bloking, M. D. McGehee, L. Wågberg, and Y. Cui, "Transparent and conductive paper from nanocellulose fibers," *Energy Environ. Sci.*, vol. 6, no. 2, p. 513, 2013.
- [71] H. Águas, T. Mateus, A. Vicente, D. Gaspar, M. J. Mendes, W. A. Schmidt, L. Pereira, E. Fortunato, and R. Martins, "Thin Film Silicon Photovoltaic Cells on Paper for Flexible Indoor Applications," *Adv. Funct. Mater.*, vol. 25, no. 23, pp. 3592–3598, 2015.
- [72] A. Vicente, H. Águas, T. Mateus, A. Araújo, A. Lyubchyk, S. Siitonen, E. Fortunato, and R. Martins, "Solar cells for self-sustainable intelligent packaging," *J. Mater. Chem. A*, vol. 3, no. 25, pp. 13226–13236, 2015.
- [73] M. Härting, J. Zhang, D. R. Gamota, and D. T. Britton, "Fully printed silicon field effect transistors," *Appl. Phys. Lett.*, vol. 94, no. 19, pp. 1–4, 2009.
- [74] D.-H. Kim, Y.-S. Kim, J. Wu, Z. Liu, J. Song, H.-S. Kim, Y. Y. Huang, K.-C. Hwang, and J. A. Rogers, "Ultrathin Silicon Circuits With Strain-Isolation Layers and Mesh Layouts for High-Performance Electronics on Fabric, Vinyl, Leather, and Paper," *Adv. Mater.*, vol. 21, no. 36, pp. 3703–3707, Sep. 2009.
- [75] M. Trifunovic, T. Shimoda, and R. Ishihara, "Solution-processed polycrystalline silicon on paper," *Appl. Phys. Lett.*, vol. 106, no. 16, p. 163502, 2015.
- [76] J. Sun, Q. Wan, A. Lu, and J. Jiang, "Low-voltage electric-double-layer paper transistors gated by microporous SiO₂ processed at room temperature," *Appl. Phys. Lett.*, vol. 95, no. 22, p. 222108, 2009.
- [77] G. Wu, X. Wan, Y. Yang, and S. Jiang, "Lateral-coupling coplanar-gate oxide-based thin-film transistors on bare paper substrates," *J. Phys. D: Appl. Phys.*, vol. 49, no. 47, 2014.
- [78] J. Sun, J. Jiang, A. Lu, and Q. Wan, "One-volt oxide thin-film transistors on paper substrates gated by SiO₂-based solid electrolyte with controllable

- operation modes,” *IEEE Trans. Electron Devices*, vol. 57, no. 9, pp. 2258–2263, 2010.
- [79] A. Lu, M. Dai, J. Sun, J. Jiang, and Q. Wan, “Flexible Low-Voltage Electric-Double-Layer TFTs Self-Assembled on Paper Substrates,” *IEEE Electron Device Lett.*, vol. 32, no. 4, pp. 518–520, 2011.
- [80] J. Jiang, J. Sun, L. Zhu, G. Wu, and Q. Wan, “Dual in-plane-gate oxide-based thin-film transistors with tunable threshold voltage,” *Appl. Phys. Lett.*, vol. 99, no. 11, p. 113504, Sep. 2011.
- [81] J. Jiang, J. Sun, W. Dou, and Q. Wan, “Junctionless flexible oxide-based thin-film transistors on paper substrates,” *IEEE Electron Device Lett.*, vol. 33, no. 1, pp. 65–67, 2012.
- [82] G. Wu, C. Wan, J. Zhou, L. Zhu, and Q. Wan, “Low-voltage protonic/electronic hybrid indium zinc oxide synaptic transistors on paper substrates,” *Nanotechnology*, vol. 25, no. 9, p. 094001, 2014.
- [83] J. Jiang, J. Sun, W. Dou, B. Zhou, and Q. Wan, “In-plane-gate indium-tin-oxide thin-film transistors self-assembled on paper substrates,” *Appl. Phys. Lett.*, vol. 98, no. 11, p. 113507, Mar. 2011.
- [84] W. Dou, L. Qiang Zhu, J. Jiang, and Q. Wan, “Flexible protonic/electronic coupled neuron transistors self-assembled on paper substrates for logic applications,” *Appl. Phys. Lett.*, vol. 102, no. 9, p. 093509, 2013.
- [85] G. Wu, J. Zhang, X. Wan, Y. Yang, and S. Jiang, “Chitosan-based biopolysaccharide proton conductors for synaptic transistors on paper substrates,” *J. Mater. Chem. C*, pp. 6249–6255, 2014.
- [86] H. Zhu, W. Luo, P. N. Ciesielski, Z. Fang, J. Y. Zhu, G. Henriksson, M. E. Himmel, and L. Hu, “Wood-Derived Materials for Green Electronics, Biological Devices, and Energy Applications,” *Chem. Rev.*, vol. 116, no. 16, pp. 9305–9374, Aug. 2016.
- [87] J. Y. JOSEFOWICZ and Y. DESLANDES, “Electrical Conductivity of Paper: Measurement Methods and Charge Transport Mechanisms,” in *Colloids and Surfaces in Reprographic Technology*, Michael Hair and M. D. Crouche, Eds. AMERICAN CHEMICAL SOCIETY, 1982, pp. 493–530.
- [88] P. Sirviö, J. Sidoravicius, R. Maldzius, K. Backfolk, and E. Montrimas, “Effect of NaCl and Moisture Content on Electrical and Dielectric Properties of Paper,” *J. Imaging Sci. Technol.*, vol. 53, no. 2, p. 020501, 2009.
- [89] B. Veigas, J. M. Jacob, M. N. Costa, D. S. Santos, M. Viveiros, J. Inácio, R. Martins, P. Barquinha, E. Fortunato, and P. V. Baptista, “Gold on paper—paper platform for Au-nanoprobe TB detection,” *Lab on a Chip*, vol. 12, p. 4802, 2012.
- [90] D. Le Bras, M. Strømme, and A. Mihranyan, “Characterization of dielectric properties of nanocellulose from wood and algae for electrical insulator applications,” *J. Phys. Chem. B*, vol. 119, no. 18, pp. 5911–5917, 2015.
- [91] L. Pereira, “Produção e caracterização de silício policristalino e sua aplicação a TFTs,” Faculdade de Ciências e Tecnologia - Universidade Nova de Lisboa, 2008.
- [92] P. Barquinha, R. Martins, L. Pereira, and E. Fortunato, *Transparent Oxide Electronics: From Materials to Devices*, 1st ed. West Sussex: Wiley, 2012.
- [93] P. M. C. Barquinha, “Transparent Oxide Thin-Film Transistors: production, characterization and integration,” Universidade Nova de Lisboa, 2010.
- [94] A. Correia, P. Barquinha, and J. Goes, “Thin-Film Transistors,” in *A Second-Order $\Sigma\Delta$ ADC Using Sputtered IGZO TFTs*, 2016, pp. 5–16.
- [95] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, and H. Hosono, “Room-

- temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors,” *Nature*, vol. 432, no. 7016, pp. 488–492, Nov. 2004.
- [96] K. Myny, “The development of flexible integrated circuits based on thin-film transistors,” *Nat. Electron.*, vol. 1, no. 1, pp. 30–39, Jan. 2018.
- [97] S. H. Kim, K. Hong, W. Xie, K. H. Lee, S. Zhang, T. P. Lodge, and C. D. Frisbie, “Electrolyte-gated transistors for organic and printed electronics,” *Adv. Mater.*, vol. 25, no. 13, pp. 1822–1846, 2013.
- [98] H. Du, X. Lin, Z. Xu, and D. Chu, *Electric double-layer transistors: a review of recent progress*, vol. 50, no. 17. Springer US, 2015.
- [99] L. Santos, D. Nunes, T. Calmeiro, R. Branquinho, D. Salgueiro, P. Barquinha, L. Pereira, R. Martins, and E. Fortunato, “SI - Solvothermal Synthesis of Gallium–Indium-Zinc-Oxide Nanoparticles for Electrolyte-Gated Transistors,” *ACS Appl. Mater. Interfaces*, vol. 7, no. 1, pp. 638–646, Jan. 2015.
- [100] L. Herlogsson, X. Crispin, N. D. Robinson, M. Sandberg, O. J. Hagel, G. Gustafsson, and M. Berggren, “Low-voltage polymer field-effect transistors gated via a proton conductor,” *Adv. Mater.*, vol. 19, no. 1, pp. 97–101, 2007.
- [101] I. Smolarkiewicz, A. Rachocki, K. Pogorzelec-Glasser, R. Pankiewicz, P. Ławniczak, A. Łapiński, M. Jarek, and J. Tritt-Goc, “Proton-conducting microcrystalline cellulose doped with imidazole. Thermal and electrical properties,” *Electrochim. Acta*, vol. 155, pp. 38–44, 2015.
- [102] J. Zhang, J. Dai, L. Zhu, C. Chen, and Q. Wan, “Laterally Coupled IZO-Based Transistors on Free-Standing Proton Conducting Chitosan Membranes,” *IEEE Electron Device Lett.*, vol. 35, no. 8, pp. 838–840, Aug. 2014.
- [103] R. Martins, P. Barquinha, L. Pereira, N. Correia, G. Gonçalves, I. Ferreira, and E. Fortunato, “Write-erase and read paper memory transistor,” *Appl. Phys. Lett.*, vol. 93, no. 20, p. 203501, 2008.
- [104] R. Martins, P. Barquinha, L. Pereira, N. Correia, G. Gonçalves, I. Ferreira, and E. Fortunato, “Selective floating gate non-volatile paper memory transistor,” *Phys. status solidi - Rapid Res. Lett.*, vol. 310, no. 9, pp. 308–310, 2009.
- [105] W. Lim, E. a. Douglas, S.-H. Kim, D. P. Norton, S. J. Pearton, F. Ren, H. Shen, and W. H. Chang, “High mobility InGaZnO₄ thin-film transistors on paper,” *Appl. Phys. Lett.*, vol. 94, no. 7, p. 072103, 2009.
- [106] D. Gaspar, L. Pereira, A. Delattre, D. Guerin, E. Fortunato, and R. Martins, “Engineered cellulose fibers as dielectric for oxide field effect transistors,” *Phys. Status Solidi Curr. Top. Solid State Phys.*, vol. 12, no. 12, pp. 1421–1426, Dec. 2015.
- [107] S. Ummartyotin, J. Juntaro, M. Sain, and H. Manuspiya, “Development of transparent bacterial cellulose nanocomposite film as substrate for flexible organic light emitting diode (OLED) display,” *Ind. Crops Prod.*, vol. 35, no. 1, pp. 92–97, Jan. 2012.
- [108] C. Legnani, C. Vilani, V. L. Calil, H. S. Barud, W. G. Quirino, C. A. Achete, S. J. L. Ribeiro, and M. Cremona, “Bacterial cellulose membrane as flexible substrate for organic light emitting devices,” *Thin Solid Films*, 2008.
- [109] E. R. P. Pinto, H. S. Barud, R. R. Silva, M. Palmieri, W. L. Polito, V. L. Calil, M. Cremona, S. J. L. Ribeiro, and Y. Messaddeq, “Transparent composites prepared from bacterial cellulose and castor oil based polyurethane as substrates for flexible OLEDs,” *J. Mater. Chem. C*, vol. 3, no. 44, pp. 11581–11588, 2015.
- [110] F. Gherendi, M. Nistor, and N. B. Mandache, “In₂O₃ thin film paper transistors,” *IEEE/OSA J. Disp. Technol.*, vol. 9, no. 9, pp. 760–763, 2013.

- [111] F. Shao, P. Feng, C. Wan, X. Wan, Y. Yang, Y. Shi, and Q. Wan, "Multifunctional Logic Demonstrated in a Flexible Multigate Oxide-Based Electric-Double-Layer Transistor on Paper Substrate," *Adv. Electron. Mater.*, vol. 3, no. 3, p. 1600509, Mar. 2017.
- [112] P. Grey, S. N. Fernandes, D. Gaspar, E. Fortunato, R. Martins, M. H. Godinho, and L. Pereira, "Field-Effect Transistors on Photonic Cellulose Nanocrystal Solid Electrolyte for Circular Polarized Light Sensing," *Adv. Funct. Mater.*, vol. 1805279, p. 1805279, Oct. 2018.
- [113] D. Gaspar, J. Martins, P. Bahubalindrani, L. Pereira, E. Fortunato, and R. Martins, "Planar Dual-Gate Paper/Oxide Field Effect Transistors as Universal Logic Gates," *Adv. Electron. Mater.*, vol. 1800423, p. 1800423, Oct. 2018.
- [114] S. Dai, Y. Wang, J. Zhang, Y. Zhao, F. Xiao, D. Liu, T. Wang, and J. Huang, "Wood-Derived Nanopaper Dielectrics for Organic Synaptic Transistors," *ACS Appl. Mater. Interfaces*, p. acsami.8b15063, Nov. 2018.

Materials and devices: production and characterisation

The work performed during this dissertation involved the production and characterisation of thin films, cellulosic membranes and their combination in device applications. The fabrication of the devices was performed in the clean room facilities of CEMOP while characterisation was performed in the CENIMAT and CEMOP.

Materials and devices: production and characterisation

Chapter 2. Materials and devices: fabrication and characterisation	43
2.1. Preparation of the cellulose substrates	43
2.1.1. Papermaking process	43
2.1.2. Nanocellulose membranes	47
2.1.3. Nanocrystalline cellulose membranes	48
2.1.4. Bacterial Cellulose	49
2.2. Thin films deposition and device fabrication techniques	51
2.2.1. Thin film deposition	51
2.2.1.1. Magnetron sputtering	51
2.2.1.2. Electron-beam assisted thermal evaporation	52
2.2.2. Field effect transistors	53
2.3. Cellulose substrates and thin-film characterisation	55
2.3.1. Structural, morphological, and compositional characterisation	55
2.3.1.1. X-ray diffraction	55
2.3.1.2. Porosity	56
2.3.1.3. Atomic force microscopy	56
2.3.1.4. Scanning Electron Microscopy	58
2.3.1.5. X-ray Photoelectron Spectroscopy	59
2.3.2. Optical characterisation	60
2.3.2.1. UV-Visible-NIR transmittance spectroscopy	60
2.3.2.2. Fourier-transform infrared spectroscopy	61

2.3.3.	Electrical characterisation	62
2.3.3.1.	Hall Effect	62
2.3.3.2.	Electrochemical Impedance Spectroscopy	63
2.3.4.	Complementary characterisation techniques	64
2.3.4.1.	Simultaneous Thermal analysis	64
2.4.	Electrical characterisation of cellulose-based transistors	65
2.5.	References	67

Chapter 2. Materials and devices: fabrication and characterisation

This chapter summarises relevant techniques related to the production and characterisation of the cellulose-based membranes, thin films and devices produced during this PhD work. The cellulose-based samples were prepared in three different labs: in the Paper Engineering laboratories at Beira Interior University (UBI), at Centre Technique du Papier (CTP) and at Minho University in the Biological Engineering Department, while the thin-films and devices were fabricated cleanroom facilities of CEMOP, and the respective characterisation was performed in the CENIMAT and CEMOP laboratories.

Regarding the cellulose-based substrates produced at lab scale from the vegetal source, both isotropic and anisotropic sheet former were used. The bacterial cellulose was produced, harvested and dried in Minho University at the Biological Engineering Department and provided by Prof. Miguel Gama. In the section 2.1.4, the process is briefly explained; however, the production was exclusively made by Prof. Miguel Gama group.

Concerning thin film deposition techniques and devices production, the process chosen to deposit the oxide-based thin films was magnetron sputtering and electron-beam evaporation for the metal contact layers. The patterning of the thin-films was made during the deposition through a metallic shadow masks

The final part of this chapter covers briefly the techniques and processes involved in the characterisation of the cellulose-based substrates, thin-films and electrical characterisation of the devices.

2.1.Preparation of the cellulose substrates

2.1.1. Papermaking process

During this work, the paper used was produced at a lab scale. Thus, the hand-sheet formation has some significant differences from the regular production process used at the industrial level, namely on the fibres' alignment, mineral charges and functional additives. The laboratory sheets are mostly produced in a static sheet former leading to random orientation of the fibres, and its distribution tend to be uniform. Nevertheless, dynamic formers may be used to get closer to fibre orientation obtained in industrial paper machines. In the following paragraphs will be described the techniques and steps involved in the cellulose membranes' formation process.

Independently of the wood pulp fibres (softwood or hardwood) used to produce the papers, either CTP and UBI used commercial bleached Kraft pulp avoiding long and highly complex processes' which involves the lignin and hemicellulose removal through the Kraft method and bleaching process. For convenience in the end of the section can be found a table where is listed all the samples used during this work (Table 2.1 and Table 2.2).

The hand-sheets manufacture requires a prior preparation of the dried pulp. The slurry is obtained from commercial bleached Kraft dried pulp by disintegration, after soaking in water. The disintegrated fibres are then refined using a PFI mill, consisting in a housing container and a steel disc; the beating is made through the rotation of both parts in the same direction with different speed. The pulp suspension at 10% consistency is pressed against the wall of the housing and the number of revolutions is directly related to the beating index resulting in different refining grades. The beating process leads to the internal and external fibrillation of the cellulose fibres, the fibres tend to be delaminated and *hairier*, and to fines generation (Figure 2.1a).

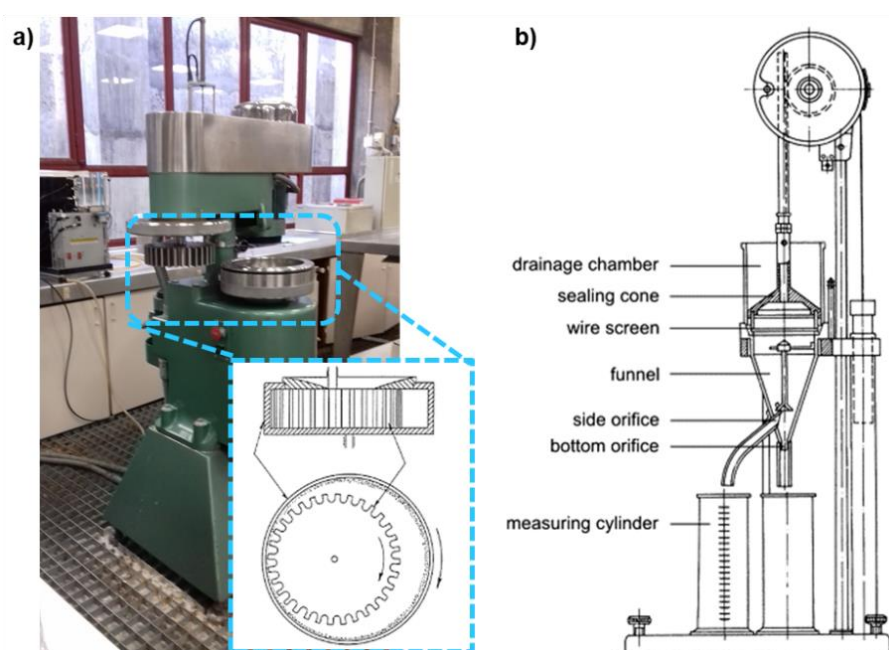


Figure 2.1 a) PFI mill in UBI and schematic representation of the working principle. b) Schopper–Riegler apparatus [3].

The refining grade can be assessed measuring the pulp freeness or drainability on a Schöpper-Riegler (°SR) apparatus according to the standard ISO 5267. This technique measures the refining effects based on the dewatering properties of the pulps and easiness which water drains from the pulp through a wire mesh (Figure 2.1b). High beating index

(°SR) stand for pulp highly refined and with substantial water retention. The lab papers produced for this work at UBI labs presented °SR in the range of 30 °SR for papers prepared with 1000 PFI revolutions, and 40-50 °SR for 2500 PFI; for the papers submitted to TEMPO-mediated oxidation, this value will increase [1], [2].

The manufacture of self-standing paper sheets lays mostly on the isotropic sheet formers, which can be manuals or semi-automatics. These formers consist of a hollow cylinder containing a metallic sieve at its bottom where the diluted pulp or pulp slurry with low concentration is poured (Figure 2.2a). The principle of this equipment consists of draining the water of the diluted pulp suspension through the wire screen where the fibres will be deposited without preferred orientation.

After filtration the wet sheet or the gel cake is peeled off from the mesh and stacked between two blotting papers and afterwards is deposited onto a stainless-steel drying plate, and pressed. These laboratory sheets attached to the drying plate are transferred to the drying frames and put in the conditioned atmosphere with 50% relative humidity and 23 °C, accordingly with ISO 187:1990, with a small pressure applied in the edge to prevent the shrinking of the sheets.

A dynamic hand-sheet former was used to obtain papers with preferentially oriented fibres. This equipment consists of a circular container covered with fabric and maintained in rotation at a certain speed (Figure 2.2b). Water is injected into the container and forms a water wall on the container by centrifugal action; afterwards, the pulp suspension is projected onto the water wall by a nozzle. The speed of the jet depends on the pump's flow and the section of the nozzle; the difference in speed between the jet and the wire confers the preferred orientation to the fibres that tend to align due to extensional forces that exist at the interface. Then the water is evacuated by centrifugal forces, and the pulp slurry is distributed uniformly on the fabric. The sheet formed thus is separated from the fabric and placed in between two blotting papers to absorb water and then pressed and dried in a drier equipped with a fabric; the wire side being in contact with the drier maintained at a temperature of 100°C for 15 minutes.

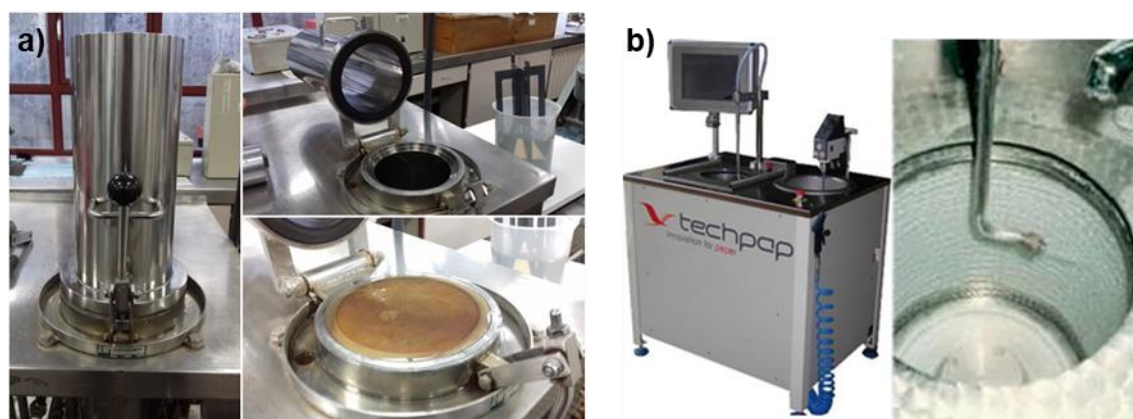


Figure 2.2 a) Hand sheet former at UBI facilities, and b) dynamic former.

Apart of the hand-sheet former used, the dried paper sheets can be submitted afterwards to the calendaring process during which the paper is compressed between two or more heated rolls leading to a smoother surface of paper by replication of the roll surface while the pressure effect reduces the bulk. This finishing process besides the smoothness improvement also leads to the densification of the paper and porosity reduction [2].

Besides using the hardwood and softwood pulps, several micro-nanofibrillated cellulose papers (M/NFC) were tested. These samples were produced at CTP facilities using as fibre source commercial pulp made from bleached mix hardwood kraft pulp. Similarly, to the process above described, the pulp was soaked, disintegrated and then refined. The resulting pulp is submitted to enzymatic treatment with endoglucanase and submitted to a homogenization process in a GEA homogeniser. In this process, the pulp slurry with low consistency passes through a thin slit with very high pressure, being this way subject to large shear forces; simultaneously a valve open and close at high frequency leading to a high shearing of the pulp. During this procedure, the suspensions tend to become more viscous and translucent with the increasing of the fibrillation. The number of homogenization passes is generally high in order to increase the fibrillation.

After this process, the resulting suspension can be diluted and used to produce free-standing sheets. In this particular case, the M/NFC papers were produced in a semi-automatic sheet former (Rapid-Khöten). The principle of this former is common to the isotropic former, and consequently, the fibres do not present favoured orientation. The diluted suspension is poured into the hollow cylinder containing a metallic sieve at its bottom, covered with a mixed cellulose ester (nitrocellulose, cellulose acetate) membrane with 0.65 μm pore size and then filtrated. After this step, the wet sheet is peeled off from the membrane and stacked

between two cover papers and two carrier boards and placed in a sheet dryer at 93 °C and vacuum for 10 minutes.

The hand-sheets preparation parameters (source, refining grade, fibres' orientation, calendaring, TEMPO-mediated oxidation) were varied to study their influence on electrical properties of the paper and the performance of the devices with these engineered papers.

2.1.2. Nanocellulose membranes

The nanofibrillated cellulose membranes were made with NFC gels obtained at the UBI and CTP (France) facilities.

The approach to obtain it can involve different type of mechanical processes, chemical or enzymatic pre-treatments, or a combination of them. The NFC from the CTP was obtained from bleached birch kraft pulp (BBKP) and was received in the form of a gel (Figure 2.3a) with a solid content of 2%. No further details about the production process were disclosed by the producers. Commercial bleached sulphite eucalypt pulp (BSEP) was used to produce NFC from UBI. The BSEP was successively submitted to a pre-treatment with TEMPO-mediated oxidation and mechanical treatment, through a two-step homogenization in a high-pressure homogeniser: the first passage with 500 bar, followed by a second one at 1000 bar [4], resulting in a gel with a solid content of $\approx 1\%$ (Figure 2.3a). The gel consistency observed for both samples is due to long entangled fibres usually with diameters of 5 to 30 nm and length that can reach values above 1 μm , which can result in length/diameter aspect ratio between 100 to 150 [5], [6].

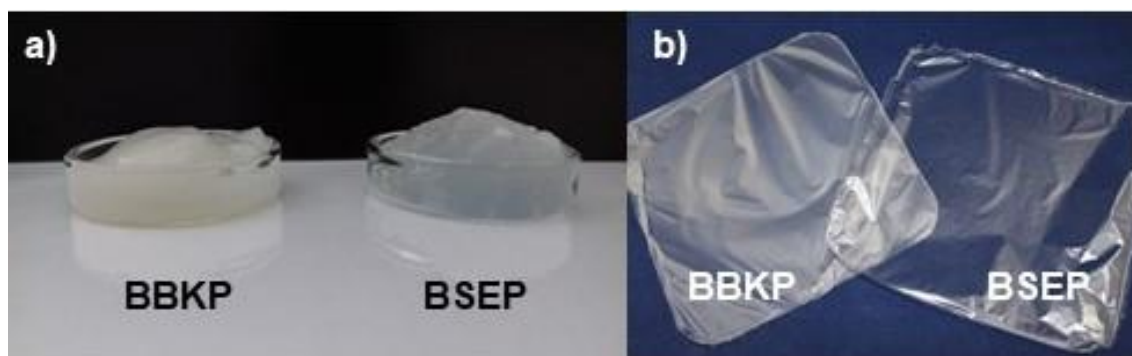


Figure 2.3 a) BBKP and BSEP NFC gel produced at CTP and UBI, respectively. b) NFC dried membranes produced by casting evaporation.

To produce the free-standing membranes, the gels were dispersed in deionised water and stirred to obtain a good dispensability of the NFC. Then the dispersion was poured to Petri dishes and let to dry at controlled room temperature and relative humidity. After the complete evaporation of the water, the membranes were peeled-off from the containers and used to produce the devices (Figure 2.3b).

For the case of the alkali-doped membranes, the dried membranes had an extra step, where they were soaked in a 0.5 M alkaline solution (LiOH, NaOH, KOH) for an hour, then washed in deionised water and rinsed.

2.1.3. Nanocrystalline cellulose membranes

The free-standing cotton-based nanocrystalline cellulose (NCC) were prepared through acid hydrolysis of amorphous cellulose using as raw cotton. The Soft Materials group from the Materials Science Department made the extraction of the cotton-based NCC and preparation of the membranes

The process to obtain the NCC involves several steps. Firstly, the cotton, used as raw material, was submitted to acid hydrolysis with HCl obtaining hydrolysed microcrystalline cellulose (MCC) particles that were neutralised with distilled water and washed through a filtration process with water and acetone. The MCC is then submitted to strong acid hydrolysis with H_2SO_4 leading to a suspension that after successive washing and centrifugation processes, and further dialysis with ultrapure water, results in an NCC suspension. The subsequent centrifugations of this suspension results in a gel-like substance [7]. More details about the process can be found elsewhere [7]–[10].

With the prepared NCC gel, it was possible to produce free-standing transparent membranes prepared by two different methods: solvent casting-evaporation further designated only as evaporation and sheared casting. The evaporated films were dried under ambient conditions in polystyrene Petri dishes, resulting in films with a thickness of approximately 30 to 55 μm , while the shear-casted were made by moving a calibrated Gardner knife at 1.25 mm s^{-1} speed over a polystyrene sheet and were allowed to dry at room temperature. These films were 35-55 μm thick.

2.1.4. Bacterial Cellulose

The bacterial cellulose membranes were produced at Minho University by Prof. Miguel Gama's group from the Biological Engineering Department. Those membranes were gently provided and tailored for this work.

In the following paragraphs the production of those cellulose membranes will be briefly explained and no main details as the shape of a bioreactor, surface area, and medium volume, will be discussed once it's production was the done at Minho University under the supervision of Prof. Miguel Gama's group whose work is widely known and reported [11], [12].

As mentioned in Chapter 1, the bacterial cellulose is a bacteria-produced biopolymer, and several bacterial species can be used as producers. The membranes used for this work resulted from the harvesting of cellulose produced by *Komagataeibacter xylinus* (in the literature can be often referred as *Gluconacetobacter xylinum*^{*}) bacteria grown in a culture medium optimised for higher biopolymer yields [13].

The BC fermentation requires several ingredients to be carried out; needs a carbon source, a nitrogen source, phosphorus, additives and air. This medium provides all those needs since in its composition is possible to find molasses and corn steep liquor (inexpensive industry by-products which are rich in nutrients), ethanol, ammonium sulphate, sodium hydrogen phosphate and citric acid.

The growing was made in static culture conditions for a few weeks within a temperature-controlled environment, keeping the temperature constant at 30 °C and the pH in the range of 4.5 to 5.5.

In Figure 2.4 are presented several bioreactors used for fermentation of the bacterial cellulose, using the medium previously explained. The blue arrows indicate the BC slab grown.

After some time of fermentation, the BC slab is harvested and extensively washed at room temperature to remove bacteria and residual culture medium. The BC membranes were first purified through alkaline treatment with a 0.1 M NaOH solution for 4 days, sliced to a thickness of 4 mm, washed again with NaOH and rinsed with distilled water until reaching the pH of the distilled water, meaning that all of the alkaline solution have been removed. In the frame of this work was aimed highly pure BC and with different pH.

^{*} *Komagataeibacter xylinus* is the updated name of the *Gluconacetobacter xylinum*.



Figure 2.4 Bacterial cellulose fermentation in several bioreactors. The BC slab is identified with the blue arrows.

The highly pure membranes were obtained making additional washing steps: with a solution of 2% Divosan (a concentrated mixture of surfactants and alkaline additives with bleaching properties) and distilled water until neutral pH; with a solution of 5% sodium dodecyl sulphate (SDS) to remove rests of bacterial capsules, and distilled water until removal of this solution; acidic solution of 0.01M HCl to solubilize phosphate and calcium salts, and ultra-pure water until complete removal of the solution. In some of those wet membranes, the pH was adjusted with NaOH.

Table 2.1 Paper-like substrates used during this work, and respective details.

Pulp/paper	Source	Supplier	Acronym
Samples used in Chapter 4			
Bleached softwood kraft pulp	Spruce (softwood)	CTP	BSKP
Bleached hardwood kraft pulp	Eucalypt (hardwood)	UBI	BHKP
Commercial standard paper	Unknown	RENOVA	CSP
Micro-nanofibrillated cellulose pulp/paper	Mix of bleached hardwood kraft pulp	CTP	M/NFC
Bleached eucalypt kraft pulp	Eucalypt (hardwood)	UBI	BEKP

Table 2.2 Nanocellulose samples used during this work, and respective details.

Pulp/paper	Source	Supplier	Acronym
Samples used in Chapter 5			
Bleached birch kraft pulp	Birch (hardwood)	CTP	BBKP and NFC-BBKP
Bleached sulphite eucalypt pulp	Eucalypt (hardwood)	UBI	BSEP and NFC-BSEP
Nanocrystalline cellulose	Cotton	FCT-UNL	NCC
	Unknown	CelluForce	
Bacterial Cellulose	<i>Komagataeibacter xylinus</i>	Minho University	BC

2.2. Thin films deposition and device fabrication techniques

2.2.1. Thin film deposition

The rf magnetron sputtering was the reference technique used to produce the transistors along this PhD work, namely to deposit the oxide semiconductor and the gate electrode layer. E-beam evaporation was employed to deposit the source and drain electrodes of the transistors. Both techniques will be briefly described in the following sub-sections.

2.2.1.1. Magnetron sputtering

The magnetron sputtering is a well-established physical vapour deposition (PVD) technique used in a wide range of applications. As main advantages can be pointed the possibility to work at room temperature without intentional heating of the substrate, the deposition a broad range of materials with or without a reactive sputtering atmosphere with composition and stoichiometry control.

The technique consists of the bombardment of a target with ions resulting from the ionisation of a noble gas, usually argon (Ar) due to its high ionic radius (high impact section) and relatively low price. The ionised species are accelerated gaining so high energy that by transference of momentum remove atoms or atomic aggregates from the target.

The target, which can be metallic or ceramic, is the cathode and is connected to an external source of excitation (as a radio frequency generator) while the vacuum chamber (including the substrate) is grounded. Due to the low pressure in the deposition chamber, the sputtered

species are not in thermodynamic equilibrium and tend to deposit on the chamber' wall and in the substrate (Figure 2.5).

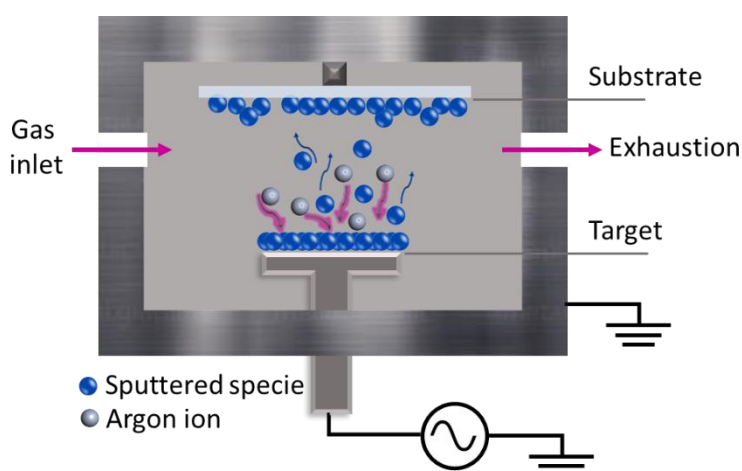


Figure 2.5 Schematic representation of a magnetron sputtering deposition system.

For excitation frequencies above 50 kHz, the (heavier) ions are no longer able to follow the electric field, creating a self-bias voltage in order to maintain the electronic balance. In order to increase the erosion efficiency, and consequently the deposition, the plasma can be confined by the effect of magnetic fields, using magnets (magnetron). Thus, it is created a higher density of ionised species which results in higher sputtering and growth rates.

Rf magnetron sputtering was used to deposit the semiconductor and the gate electrode on the paper-based FETs. During this work, that depositions were done in three different AJA ATC systems equipped with a load-lock chamber and rf generator (13.56 MHz). The base pressure before the deposition was around 5×10^{-5} Pa and the depositions were made without intentional heating, using commercial ceramic targets.

2.2.1.2. *Electron-beam assisted thermal evaporation*

This technique is based on the heat produced by electronic bombardment in the material to be deposited, which is melted and evaporated from a source, condensing them onto a substrate.

The electron beam is generated in an incandescent filament by thermo-ionic emission. The electrons are then accelerated by an electric field (with a voltage in the order of kilovolts) towards the crucible containing the material, whose walls are cooled by water to prevent

contaminations. In addition, to prevent contamination by impurities that may originate from it the filament is placed below the level of the crucible, while the emitted electrons are deflected by the magnetic field (Figure 2.6).

Since the electron beam can be focused, it is possible to have localised heating, allowing the control of evaporation rate and enabling the deposition of materials with a high melting point, as molybdenum or platinum.

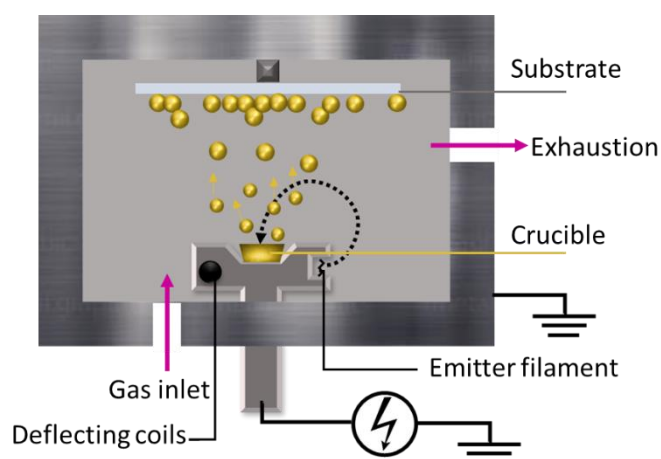


Figure 2.6 Representation of electron-beam assisted thermal evaporation system.

Electron beam assisted thermal evaporation was used to deposit the source and drain electrodes in the paper-based FETs and was carried out in a system designed and built at CEMOP/UNINOVA and installed in the cleanroom facilities. The deposition of the electrodes was made at room temperature with a base pressure around 5×10^{-4} Pa. The current applied in the filament was adjusted according to the metal and the desired deposition rate.

2.2.2. Field effect transistors

The structure of the cellulose-based FET is similar to a regular FET with staggered bottom gate structure. However, for the particular case where the cellulose is an active layer and the physical support of the device, the FET is produced in both faces of the paper.

The fabrication of these devices follows the same principle that a conventional TFT, requiring the patterning and deposition of several layers. The production of the cellulose-

gated FET produced in this work followed this sequence: oxide-based semiconductor; source and drain metal electrodes; oxide-based gate electrode.

The semiconductor, source and drain electrodes are patterned using metallic shadow masks, while the gate electrode could be patterned or not. The deposition steps sequence is depicted in Figure 2.7.

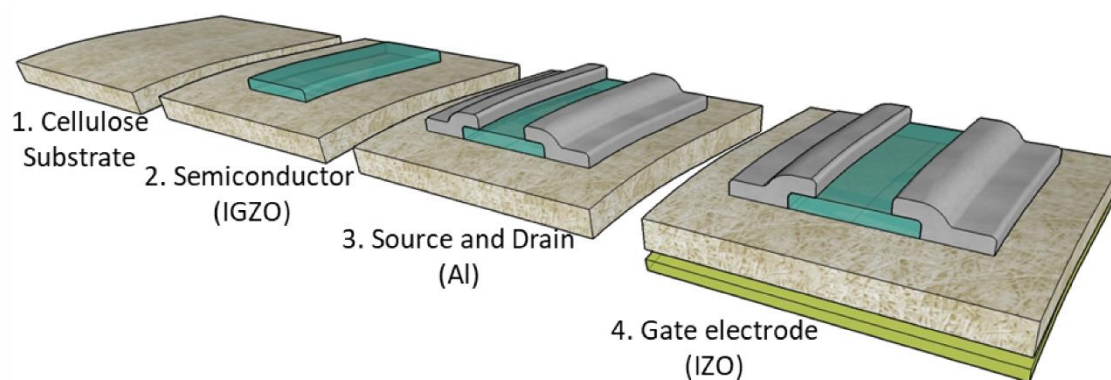


Figure 2.7 Schematic representation of cellulose-based FET deposition steps sequence.

The devices are based in oxide-based thin films produced by rf sputtering. The semiconductor consists in the ternary In-Ga-Zn oxide system, and the gate electrode is based in the In-Zn oxide system. Those films were produced using as reference the previous work developed in the group related to transparent oxide thin films produced at room temperature [14], [15]. The metal source and drain electrodes were deposited by e-beam evaporation. Details on each layer are given in Table 2.3.

Table 2.3. Production details of the cellulose-based FETs layers.

<i>Layer</i>	<i>Materials</i>	<i>Deposition technique</i>	<i>Thickness</i>
Semiconductor	IGZO $\text{In}_2\text{O}_3\text{--Ga}_2\text{O}_3\text{--ZnO}$ 1:2:2 mol%	r.f. magnetron sputtering without intentional heating	15 – 40 nm
Source and drain electrodes	Aluminium	E-beam at room temperature	100 nm
Gate electrode	IZO $\text{In}_2\text{O}_3\text{--ZnO}$ 5:2 mol%	r.f. magnetron sputtering without intentional heating	200 nm

2.3. Cellulose substrates and thin-film characterisation

During this PhD, several techniques were used in order to obtain information and better understating of the structure, morphology and composition cellulose membranes produced and thin films used in the transistors and logic circuits. Concerning specifically the optical and electrical properties of the oxide thin films, it was used UV-Visible-NIR transmittance spectroscopy and Hall effect, while for the electrical and electrochemical characterisation of the cellulose membranes were done by impedance spectroscopy.

2.3.1. Structural, morphological, and compositional characterisation

2.3.1.1. *X-ray diffraction*

X-ray diffraction (XRD) is a non-destructive technique commonly used in materials science to obtain information on the structure of a material, being possible to identify whether amorphous or crystalline phases. Furthermore, in polycrystalline materials, it is possible to determine the phase composition, grain size and preferred orientations.

When an X-ray beam strikes a material, occurs the oscillation of the atomic orbital of the irradiated atoms and the photons of the incident beam may be absorbed or scattered by the atoms. If the atoms are organised periodically, forming planes, constructive and destructive interferences may occur, resulting in a diffracted beam in a direction dependent on the structure and atoms of the material being analysed.

For incident radiation at an angle (θ) constructive interference occurs in multiples (n_i) of the wavelength (λ) being correlated with the different atomic planes with a spacing (d_{hkl}). This phenomenon is described by Bragg's law (Figure 2.8a):

$$n_i \cdot \lambda = d_{hkl} \cdot \sin \theta \quad \text{Equation 2.1}$$

Varying the incident angle θ , also known as Bragg's angle, and monitoring the intensity of the diffracted angle, it is possible to trace a diffractogram of the material that is being analysed where the constructive interferences appear as peaks which relative position is related to the different crystallographic planes.

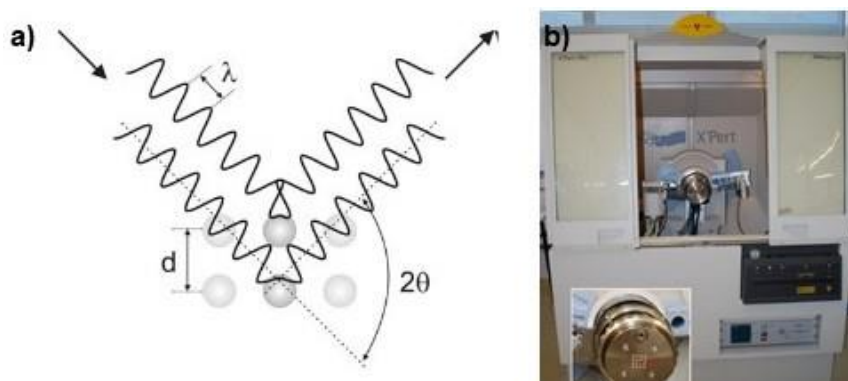


Figure 2.8 (a) Representation of a constructive interference according to Bragg's Law. b) Panalytical X'Pert Pro diffractometer at CENIMAT/CEMOP facilities.

During this work, XRD was used to characterise the structure of the cellulose substrates and oxide thin films. The characterisation was made at CENIMAT with PANalytical X'Pert PRO equipment with Cu K α radiation ($\lambda=1.540598$ Å), using a Bragg-Brentano θ - 2θ configuration (Figure 2.8b). The range of 2θ varied accordingly to the sample's nature.

2.3.1.2. Porosity

The porosity (P) of the cellulose substrates was estimated according to the following:

$$P(\%) = \left(1 - \frac{\rho_{\text{sample}}}{\rho_{\text{cellulose}}}\right) \times 100 \quad \text{Equation 2.2}$$

Where $\rho_{\text{cellulose}}$ is the density of cellulose with a tabled value of 1.6 g cm^{-3} , and ρ_{sample} is the apparent density of the sample (g cm^{-3}) [16].

2.3.1.3. Atomic force microscopy

Atomic force microscopy (AFM) is a high-resolution three-dimensional imaging technique. The AFM consists of several components as detectors, a laser, a photodetector (usually a photodiode), various piezoelectric actuators and a cantilever where, at one end, the probe is located. The image is built by a three-dimensional scan of the surface made by a nanometric probe. During the analysis, the probe is monitored using a detection system which consists of a laser focused on the cantilever and the light reflected by the probe to the sensitive photodiode.

During the scanning process, the cantilever will move according to the surface's topography, where a change of topography results in a change of the positioning of the

probe. For small distances between the probe and the sample, the cantilever is deflected due to the van der Waals forces (attraction/repulsion) established between the probe and the surface. This deflection results in a change in the direction of the laser beam reflected by the cantilever. This deflection is monitored in a photodetector, and the variation is transduced to voltage, allowing to build the map of the surface.

The AFM scan can be made using three modes:

- Contact Mode - is the most common data acquisition method. The probe is in contact with the sample, and the cantilever deflects in the opposite direction away from the sample. This mode is often used for electrical characterisation of the samples.
- Non-contact mode – the cantilever oscillates near the surface without entering contact with it operating with attractive van der Waals forces.
- Tapping mode – this mode combines both modes described operating with repulsive and attractive forces. In the repulsion regime, the probe intermittently touches the sample, making its recognition. However, the forces involved are sufficiently high to ensure the probe detachment when it touches the sample.

The AFM analysis was performed using an Asylum Research MFP-3D Stand Alone AFM system in CENIMAT. This technique was used to characterise the oxide thin films used as a gate electrode, the semiconductor, and also the nanofibrillated cellulose used as gate dielectric. Measurements were performed in tapping (alternate contact) mode in air, using commercially available silicon AFM probes (Olympus AC160TS; $k=26\text{ N m}^{-1}$; $f_0=300\text{ kHz}$) and the resulting images were plane fitted.



Figure 2.9 Asylum MFP3D atomic force microscope system existent in CENIMAT.

2.3.1.4. *Scanning Electron Microscopy*

Scanning Electron Microscopy (SEM) is a powerful technique, which allows for high-resolution images of the surface of a sample. The information obtained from the morphology of the sample depends on the way how they are examined.

To get an image by SEM, a highly energetic electron beam is focused at the surface of the sample. The interaction with the surface can result in the absorption by the sample, reflection of primary (backscattered) electrons, emission of secondary electrons and emission of electromagnetic radiation.

To obtain a three-dimensional appearance of the sample's surface, the images are often acquired through the analysis of the secondary electrons, which are emitted by the sample after the incidence of the primary electron beam.

Further information can be assessed with the use of different detectors. The analysis of the backscattered electrons provides information about the chemical composition of the sample since the contrast of the image is related to the different atomic numbers of elements present in the region being analysed.

The SEM images of samples produced in this work were performed using an SEM-FIB Cross-Beam Auriga system equipped with energy dispersive X-ray spectroscopy (EDX) measurements, from Carl Zeiss (Figure 2.10), and a Hitachi TM 3030Plus equipped with a secondary electrons detector existent in CENIMAT.



Figure 2.10 SEM-FIB Cross-Beam Auriga system existent in CENIMAT facilities.

2.3.1.5. *X-ray Photoelectron Spectroscopy*

X-ray Photoelectron Spectroscopy (XPS) is a surface analysis tool for chemical and electronic characterisation of materials. In this technique, a material is irradiated in vacuum with a monochromatic X-ray beam. This radiation has enough energy to excite the electrons of a material through the photoelectric [17].

The emitted electrons are filtered regarding their kinetic energy and detected, counted by the detector. The uniqueness of each element results in a singular spectrum, while the combination of several elements into a material approximately results in a combined spectrum from all the elements present [18].

The photoexcited electrons have assigned kinetic energy, which is dependent on their binding energy. For instance, electrons whose kinetic energy is low are bonded closely to the nucleus; thus their binding energy is high. The information obtained from the binding energies and its shift relatively to the tabled values allow inferring the chemical states and oxidation states of the material being analysed [19].

The XPS analysis was made in an Axis Supra spectrometer by Kratos Analytical equipped with monochromatic Al K α radiation, existing in the CEMOP facilities. The X-ray power was 225 W and the analyser was operated at a pass energy of 160 eV for the survey scan and at 5 eV for the detailed spectra.



Figure 2.11 XPS Axis Supra by Kratos Analytical system existent in CEMOP facilities.

2.3.2. Optical characterisation

2.3.2.1. *UV-Visible-NIR transmittance spectroscopy*

The interaction of photons with a TCO depends on the bandgap of the material. When the photons have higher energy than the bandgap they are absorbed, whereas those having an energy lower than plasma energy may be absorbed or reflected. Between these two energy limits (bandgap and plasma) the photons are mostly transmitted.

With this technique, it is possible to determine important optical parameters particularly relevant for transparent materials, such as the transmittance (T), reflectance (R), plasma frequency, the absorption coefficient (α), and the optical band gap.

The optical transmittance (T) as a function of the wavelength (λ) can be obtained using a spectrophotometer. The optical band gap was obtained using the Tauc law, accordingly to the following equation:

$$\alpha h\nu = A(h\nu - E_{op})^m \quad \text{Equation 2.3}$$

Where α is the absorption coefficient, $h\nu$ the energy, A is a constant, E_{op} the optical band gap and m is related to the type optical transitions, being equal to 2, 2/3, 1/2 or 1/3 depending if the transition is allowed direct, forbidden direct, allowed indirect or forbidden indirect, respectively [14], [20]. For the ZnO-based, and In₂O₃-based systems it is assumed that the transition is direct. Therefore, the bandgap determined for the TCOs and IGZO films during this work assumed $m=2$ [14], [15].

The optical transmittance of the thin films and some of the cellulose substrates was performed in a double beam Shimadzu UV-3101 spectrophotometer system existing in CEMOP, by varying λ between 250 and 2500 nm. This technique was mainly used to obtain the optical band gap energy of rf sputtered thin films, and also to assess their average visible transmittance (AVT).

2.3.2.2. *Fourier-transform infrared spectroscopy*

The Fourier-transform infrared spectroscopy (FTIR) is a vibrational spectroscopy is a technique, where it is possible to analyse the absorption of radiation by the vibrational excitation of molecular bonds. This characteristic enables the identification of species and molecular groups present in a material if the optical bandgap is higher than the infrared range.

This light is split into two components, one will be reflected in a mirror with a fixed position, and a mobile mirror will reflect the second one. After passing an interferometer, the two formed beams are recombined (the fixed optical beam and the second one whose optical path was modified) and a transmittance/reflectance spectrum is obtained through the constructive and destructive interference. After the beam passes the samples, the interference spectrum is then analysed by a detector. The light sensed by the detector is subjected to a Fourier transform to obtain the absorbance as a function of the wavenumber [21]. For each different molecular group is assigned a frequency, and in some cases, the same molecular group can have more than one frequency allocated due to the different vibrational (stretching or bending and respective variations) modes allowed. When the frequency of incident energy coincides with the frequency of a molecular group present, the radiation is absorbed. The FTIR technique is a powerful method to analyse different types of materials. In the present case has particular relevance to evaluating the differences between the cellulose samples, for instance, the variation of water content in the paper or its carboxylation.

In this work, the spectra were acquired between 4000 and 650 cm^{-1} with a 4 cm^{-1} step using an attenuated total reflectance (ATR) sampling accessory (Smart iTR) equipped with a single-bounce diamond crystal on a Thermo Nicolet 6700 Spectrometer.



Figure 2.12 Thermo Nicolet 6700 Spectrometer equipment used during this work.

2.3.3. Electrical characterisation

2.3.3.1. Hall Effect

The Hall effect was discovered in 1879 by Edwin Hall, who subjected an electrically conductive material to a magnetic field perpendicular to the direction of the electric current applied. This technique relies on the Lorentz force, which depends on the electrical and magnetic field. When a semiconductor material is submitted to the action of a magnetic field ($\vec{B}$) perpendicular to the current that flow passing through it, the free carriers are deflected to one side of the sample creating an electric field. This allows to determine the voltage generated at the terminals, the Hall voltage (V_H) and the majority carriers are electrons or holes.

The intrinsic parameters of the films such as the type majority of the carriers present in the material, the electrical resistivity (ρ), carrier concentration (n) and mobility (μ) can be directly extracted from the V_H as the following [15]:

- Hall voltage

$$V_H = \frac{\vec{B}I}{qnd_s} \quad \text{Equation 2.4}$$

Where I is the constant current passing through the electrodes, q is electron charge (1.61×10^{-19} C), n the carriers' concentration, and d_s is the thickness of the thin film.

- Hall coefficient (R_H)

$$R_H = \frac{V_H d_s}{\vec{B}I} \quad \text{Equation 2.5}$$

Where the sign of R_H indicates whether if the semiconductor is n-type or p-type if the sign is negative or positive respectively. For the case where the thickness of the films is known the resistivity is immediately determined.

- Carrier concentration or density (n)

$$n = \frac{1}{qR_H d_s} \quad \text{Equation 2.6}$$

- Mobility (μ)

$$\mu = \frac{R_H}{\rho} \quad \text{Equation 2.7}$$

The van der Pauw configuration is often used performed the Hall effect measurement and was the geometry adopted for the characterisation of the oxide thin films produced during this work. In this configuration, a current is applied to the terminals 1 and 2, while a magnetic field is applied, and the voltage measured at terminals 3 and 4 (Figure 2.13a).

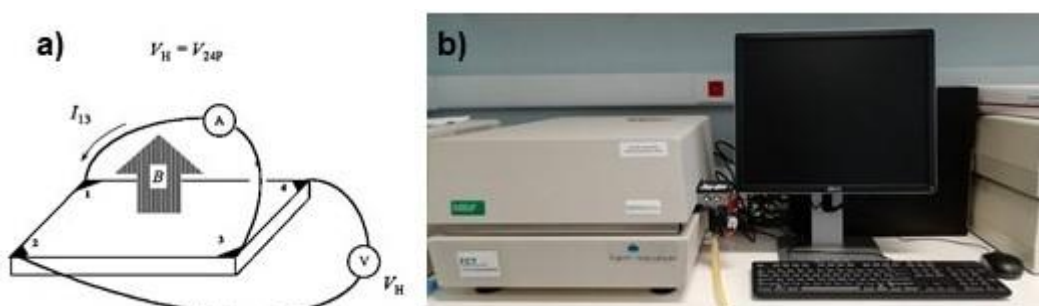


Figure 2.13 a) Van der Pauw geometry used for the Hall effect measures. b) Biorad 5500PC Hall effect system installed in the CEMOP.

During this work was used a Biorad 5500PC Hall effect system installed in the CEMOP laboratories (Figure 2.13b). Three to five measurement cycles were performed per sample with a constant field of 0.5 T and at room temperature. To study the mechanisms of conduction of TCOs, some films were measured in temperature, ranging from 100 to 350 K.

2.3.3.2. *Electrochemical Impedance Spectroscopy*

Electrochemical Impedance Spectroscopy (EIS) is a useful method to characterise the electrical properties of materials. Its versatility allows investigating the dynamics of charge in the bulk or interfacial regions of solid or liquid material, regardless of the ionic or electronic character. Thus, it is possible to characterise semiconductor and even insulating materials.

In EIS is applied an ac voltage to the sample while the phase shift and amplitude, or real and imaginary parts of the resulting current, are measured. Besides this information, it is possible to make potentiostatic impedance spectroscopy measurements. These measurements were used to determine the capacitance of the cellulosic membranes developed and verify the behaviour as a function of frequency. The same analysis allows the comprehension of the phase shift and how to relate it with the sample response for the different frequencies.

Due to the ionic character of the cellulose membranes, electrochemical doping of semiconductor may occur when measuring the electrical characteristics of the transistors, changing the mode how the transistor operates. The occurrence of electrochemical reactions in the interface of the cellulose/semiconductor can be investigated by cyclic voltammetry, where the appearance of faradaic currents is evaluated in a specific voltage range.

The electrochemical cells for the determination of the capacitance are slightly different. For the potentiostatic impedance spectroscopy, the cellulose was metalised in each side and placed between two gold electrodes (Figure 2.14a). In the case of these electrochemical analysis, a cell emulating the transistor was produced using the same materials and thicknesses existing in the final device (Figure 2.14b).

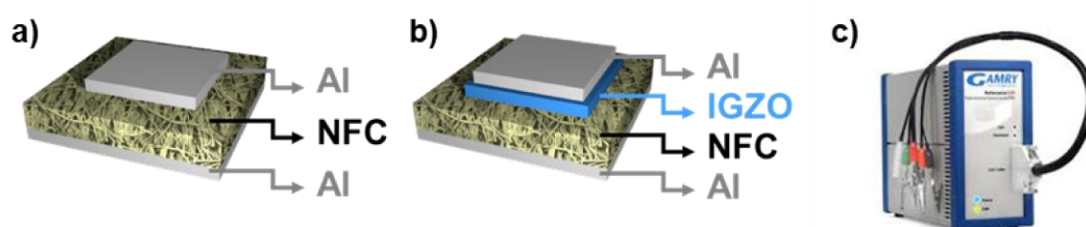


Figure 2.14 Electrochemical cell produced for the a) potentiostatic, and b) electrochemical impedance spectroscopy. c) Potentiostat 600TM Gamry Instruments used for impedance measurements of the cellulose samples.

Impedance measurements were performed using a Gamry Reference 600 Potentiostat/Galvanostat/ZRA with built-in electronics for electrochemical impedance measurements. This equipment has a frequency range of 10 μHz to 1 MHz, a current range of 0.6 A to 60 pA and a measurement voltage range of -8 V to 8 V. Cable connections include an earth lead, reference electrode, counter-electrode and working electrode.

2.3.4. Complementary characterisation techniques

2.3.4.1. Simultaneous Thermal analysis

During this work, the Simultaneous Thermal analysis (STA) was used as a complementary technique to infer the thermal stability of the cellulose membranes. The STA refers to the simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) measurements of a sample in the same instrument. Due to this characteristic, it is possible to collect the data of the TGA and DSC simultaneously ensuring the identical conditions. The TGA the mass variation is monitored as a function of temperature

according to a controlled temperature program. The DSC measures the change of the difference in the heat flow rate to the sample and a reference material. With this technique, it is possible to determine the changes in the enthalpy of the samples, specific heat and the temperature at which these occur.

The cellulose substrates were characterised in a simultaneous thermal analyser (TGA-DSC - STA 449 F3 Jupiter) from Netzsch, existing in the CENIMAT laboratories.

2.4. Electrical characterisation of cellulose-based transistors

In a transistor it is possible to define two working modes: enhancement and depletion mode. In the first case there is no channel formed between the source and drain if the gate voltage (V_{GS}) is zero and, ideally, there is no current flowing in the device (off-state). On the other hand, in a transistor operating in depletion mode the channel is partially formed and current flows between source and drain (I_{DS}), when there is no gate voltage applied. When considering this, in a n-type transistor (channel “formed” by free electrons) as typically happens for oxide semiconductors, the threshold gate voltage (V_{Th}) will be positive for enhancement mode devices while depletion mode ones will have negative V_{Th} .

In a MOSFET, when the drain to source voltage (V_{DS}) is smaller than $V_{GS} - V_{Th}$, the I_{DS} varies linearly with the V_{DS} – linear regime, as described in the following equation:

$$I_{DS} \approx \frac{W}{L} \cdot \mu_{FE} \cdot C \cdot (V_{GS} - V_{Th}) \cdot V_{DS} \quad \text{Equation 2.8}$$

where W is the channel width, and L is the channel length, μ_{FE} is the field-effect mobility, and C is the gate capacitance per unit area.

When $V_{DS} \geq V_{GS} - V_{Th}$ the I_{DS} become independent of the V_{DS} applied, reaching a saturation regime, being described as:

$$I_{DS} \approx \frac{W}{2L} \cdot \mu_{Sat} \cdot C \cdot (V_{GS} - V_{Th})^2 \quad \text{Equation 2.9}$$

Where μ_{sat} it is the saturation mobility.

The static characterisation of field-effect transistors (FETs) consists typically in the acquisition of the transfer and output characteristics of the FETs, allowing to obtain both quantitative and qualitative information about the devices. The transfer characteristics are obtained by monitoring I_{DS} for a given V_{DS} , as function V_{GS} . On the other hand, the output

characteristics are obtained measuring the current flowing through the device as a function of V_{DS} for several V_{GS} .

As described in Chapter 1, a thin film transistor (TFT) and, consequently the cellulose-based FETs, have some differences when comparing with a MOSFET. One of the most relevant ones is that in MOSFETs the channel is formed by inversion of the semiconductor while in the TFTs it is formed by accumulation of carriers at the dielectric/semiconductor interface. Although Equation 2.8 and Equation 2.9 are still valid, it is normally reported an additional parameter – V_{on} , as being the V_{GS} value at which the I_{DS} starts to increase from its minimal value (I_{off}), being determined from semi-log plot of the transfer characteristics. Electrical parameters such as the On/Off current ratio ($I_{on/off}$), On voltage (V_{on}), sub-threshold operating range (S), and field effect mobility (μ_{FE}) or saturation (μ_{sat}) can also be extracted from the transfer characteristics. The output characteristics allow to determine if the current of the device reached a saturation plateau or even evaluate the quality of the source and drain electrodes.

The typical parameters that reveal the quality of devices can be determined using the following equations [14], [23]:

- Sub-threshold operating range (S)

$$S = \left(\frac{\partial \log I_{DS}}{\partial V_{GS}} \Big|_{\max} \right)^{-1} \quad \text{Equation 2.10}$$

- Field effect mobility (μ_{FE}) for low V_{DS} :

$$\mu_{Fe} = \left(\frac{\partial I_{DS}}{\partial V_{GS}} \right) \frac{L}{W.C.V_{DS}} \quad \text{Equation 2.11}$$

- Saturation mobility (μ_{Sat}):

$$\mu_{Sat} = \left(\frac{\partial \sqrt{I_{DS}}}{\partial V_{GS}} \right)^2 \frac{2L}{W.C} \quad \text{Equation 2.12}$$

Where V_{GS} is the voltage applied at the gate, and W and L correspond to the width and length of the channel, respectively. In paper FETs, the capacitance (C) is the value determined by EIS corresponding to the electric double layer (EDL) capacitance of the paper at the lowest frequency measured to assure the accuracy of the calculated mobility values.

Along this work, the transfer and the output curves were measured at atmospheric pressure with a relative humidity of 40% to 50%, on an Agilent 4155C analyser, coupled to a Cascade M150 microprocessor, installed in a dark box to avoid the influence of ambient light on measurements (Figure 2.15a). The gate voltage (V_{GS}) and the drain voltage (V_{DS}) were tuned accordingly to the type of cellulose substrate used. For the measurement made under vacuum was used a microprobe station from Janis Research Company connected to an Agilent 4155C semiconductor parameter analyser (Figure 2.15b).

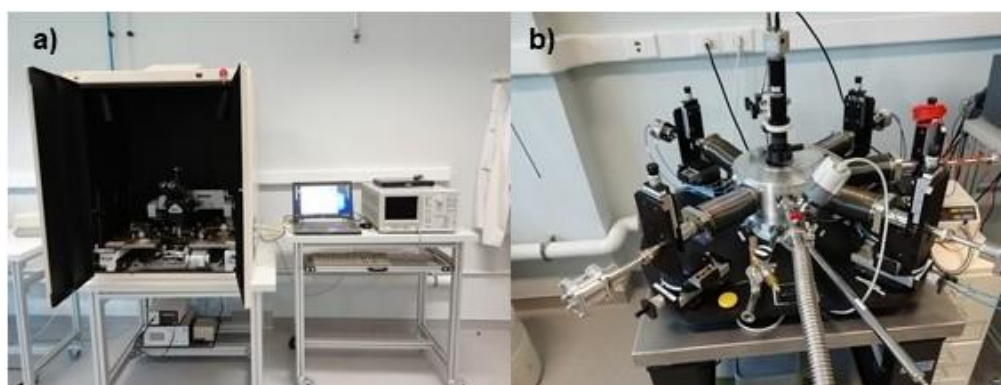


Figure 2.15 a) Agilent 4155C analyser coupled to a Cascade M150 microprocessor (dark box), and b) microprobe station from Janis Research Company.

2.5. References

- [1] V. I. Popa, Ed., *Pulp Production and Processing: From Papermaking to High-Tech Products*, 1st ed. Shawbury, Shrewsbury, Shropshire: iSmithers Rapra Publishing, 2013.
- [2] L. Pereira, D. Gaspar, D. Guerin, A. Delattre, E. Fortunato, and R. Martins, “The influence of fibril composition and dimension on the performance of paper gated oxide transistors,” *Nanotechnology*, vol. 25, no. 9, p. 094007, Mar. 2014.
- [3] D. Dienes, S. Kemény, A. Egyházi, and K. Réczey, “Improving the capability of the Schopper–Riegler freeness measurement,” *Measurement*, vol. 38, no. 3, pp. 194–203, Oct. 2005.
- [4] “Atas do I Simpósio 2016 - Materiais Fibrosos e Tecnologias Ambientais FibEnTech - Universidade da Beira Interior 28 - 29 de janeiro de 2016, Covilhã – Portugal,” 2016, p. 118.
- [5] T. Abitbol, A. Rivkin, Y. Cao, Y. Nevo, E. Abraham, T. Ben-Shalom, S. Lapidot, and O. Shoseyov, “Nanocellulose, a tiny fiber with huge applications,” *Curr. Opin. Biotechnol.*, vol. 39, no. I, pp. 76–88, Jun. 2016.
- [6] A. Barhoum, P. Samyn, T. Öhlund, and A. Dufresne, “Review of recent research on flexible multifunctional nanopapers,” *Nanoscale*, vol. 9, no. 40, pp. 15181–15205,

- 2017.
- [7] D. Gaspar, S. N. Fernandes, A. G. de Oliveira, J. G. G. Fernandes, P. Grey, R. V. V. Pontes, L. Pereira, R. Martins, M. H. H. Godinho, and E. Fortunato, “Nanocrystalline cellulose applied simultaneously as the gate dielectric and the substrate in flexible field effect transistors,” *Nanotechnology*, vol. 25, no. 9, p. 094008, Mar. 2014.
 - [8] J. F. Revol, H. Bradford, J. Giasson, R. H. Marchessault, and D. G. Gray, “Helicoidal self-ordering of cellulose microfibrils in aqueous suspension,” *Int. J. Biol. Macromol.*, 1992.
 - [9] E. D. Cranston and D. G. Gray, “Morphological and Optical Characterization of Polyelectrolyte Multilayers Incorporating Nanocrystalline Cellulose,” *Biomacromolecules*, vol. 7, no. 9, pp. 2522–2530, Sep. 2006.
 - [10] S. N. Fernandes, P. L. Almeida, N. Monge, L. E. Aguirre, D. Reis, C. L. P. de Oliveira, A. M. F. Neto, P. Pieranski, and M. H. Godinho, “Mind the Microgap in Iridescent Cellulose Nanocrystal Films,” *Adv. Mater.*, 2017.
 - [11] M. Gama, P. Gatenholm, D. Klemm, and E. Al, *Bacterial NanoCellulose*. 2013.
 - [12] M. Gama, F. Dourado, and S. Bielecki, *Bacterial Nanocellulose - From Biotechnology to Bio-Economy*, 1st ed., vol. 1. Elsevier, 2016.
 - [13] A. C. Rodrigues, A. I. Fontão, A. Coelho, M. Leal, F. A. G. Soares da Silva, Y. Wan, F. Dourado, and M. Gama, “Response surface statistical optimization of bacterial nanocellulose fermentation in static culture using a low-cost medium,” *N. Biotechnol.*, 2019.
 - [14] P. M. C. Barquinha, “Transparent Oxide Thin-Film Transistors: production, characterization and integration,” Universidade Nova de Lisboa, 2010.
 - [15] G. P. Gonçalves, “Filmes finos de óxido de índio e zinco e sua aplicação em díodos orgânicos emissores de luz,” Universidade Nova de Lisboa, 2011.
 - [16] V. L. D. Costa, A. P. Costa, M. E. Amaral, C. Oliveira, M. Gama, F. Dourado, and R. M. Simões, “Effect of hot calendering on physical properties and water vapor transfer resistance of bacterial cellulose films,” *J. Mater. Sci.*, vol. 51, no. 21, pp. 9562–9572, Nov. 2016.
 - [17] A. Einstein, “Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt,” *Ann. Phys.*, 1905.
 - [18] John F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy A Reference Book of Standard Spectra for Identification and Interpretation of Xps Data*, 2nd ed. Minnesota: Physical Electronics, Inc., 1995.
 - [19] J. Deuermeier, “Origins of limited electrical performance of polycrystalline Cu₂O thin-film transistors,” Universidade NOVA de Lisboa, 2017.
 - [20] J. Tauc, R. Grigorovici, and A. Vancu, “Optical Properties and Electronic Structure of Amorphous Germanium,” *Phys. Status Solidi*, vol. 15, no. 2, pp. 627–637, 1966.
 - [21] H. Águas, “Dispositivos de Estrutura Metal/Isolante/Semicondutor - MIS: Aplicação a Sensores de Posição de Silício Amorfo,” Universidade Nova de Lisboa, 2005.
 - [22] P. Barquinha, R. Martins, L. Pereira, and E. Fortunato, *Transparent Oxide Electronics: From Materials to Devices*, 1st ed. West Sussex: Wiley, 2012.
 - [23] L. Pereira, “Produção e caracterização de silício policristalino e sua aplicação a TFTs,” Universidade Nova de Lisboa, 2008.

Functional oxide thin films

The research work summarised in this dissertation involved the production and characterisation of functional inorganic thin films for application on paper FETs. The deposition of such films was made by PVD in the clean room facilities of CEMOP and characterisation was performed in the CENIMAT and CEMOP laboratories.

Part of the contents of **Chapter 3** was adapted from the publication:

D. Gaspar, L. Pereira, K. Gehrke, B. Galler, E. Fortunato, R. Martins, “High mobility hydrogenated zinc oxide thin films”, *Sol. Energy Mater. Sol. Cells.*, vol 163, 2017.

Functional oxide thin films

Chapter 3. Functional oxide thin films	73
3.1. Transparent conductive and semiconductor oxides	73
3.2. Hydrogenated TCOs	76
3.2.1. Hydrogenated Zinc Oxide TCOs	78
3.2.1.1. Structure and morphology	79
3.2.1.2. Electrical and optical properties	82
3.2.1.3. Chemical state and composition	87
3.2.2. Aluminium-doped zinc oxide and gallium-doped zinc oxide thin films	89
3.2.2.1. Electrical and optical properties	90
3.2.2.2. Al and Ga co-doped ZnO thin films	92
3.2.3. Hydrogenated Indium Zinc Oxide TCOs	95
3.2.3.1. Structure and morphology	96
3.2.3.2. Electrical and optical properties	97
3.2.3.3. Electrical properties of IZO:H on different substrates	100
3.2.3.4. Chemical state and composition	101
3.3. Semiconductor oxide thin films	104
3.3.1. IGZO system	104
3.3.1.1. Optical and electrical properties	105
3.3.1.2. IGZO-based FETs	107
3.4. References	109

Chapter 3. Functional oxide thin films

This chapter presents the work on the optimisation of inorganic functional thin films, namely transparent conductive oxides and oxide active semiconductors. Due to the notorious differences between the conventional substrates and cellulose based ones, the deposition conditions and thickness had to be optimised tuned in order to turn these films suitable for application in the cellulose-based FETs.

While deposition of oxides semiconductors is a well-established technology in CENIMAT/I3N and CEMOP/UNINOVA, there was a lack of knowledge on the non-consensual role of hydrogen incorporation in conductive oxide thin films as a way to improve the electro-optical properties of zinc oxide and indium oxide thin films. This was the focus on this PhD work with encouraging results in obtaining transparent conductive oxides (TCOs) with excellent properties when deposited without any intentional heating, exploring the physical vapour deposition (PVD), namely magnetron sputtering technique, and the role of hydrogen to improving overall electronic performances of the TCOs grown, as required for application in cellulose substrates.

3.1. Transparent conductive and semiconductor oxides

The idea of transparent electronics arose for the first time in the late '30s of the 20th century when a transparent display appeared in the science fiction film "*Things to come*" based on the H. G. Wells's book edited in 1933 and entitled *The Shape of Things to Come*. Nearly one century later, the *utopia* became a *reality*, and transparent electronics is currently one of the most emerging and promising technologies enabling an unprecedented development of new products with innovative materials or reinventing and challenging well-established technologies. The used materials for this end have performances, reproducibilities and reliabilities that are getting closer to that enabled by silicon technology, but with a unique leverage: transparency [1].

The first transparent materials, which would become the stepping stone of transparent electronics, were reported in 1907 by K. W. Baedeker. He observed a change in the optical properties of thin films of cadmium when exposed to an oxidising atmosphere as a result of the formation of transparent and conductive films of cadmium oxide (n-type) – the first reported transparent conductive oxide [2]–[4].

TCOs are a class of materials with unique optical and electrical characteristics, exhibiting simultaneously high transmittance in the visible range and high electrical conductivity, comparable to the metals. These characteristics can only be achieved in materials with a high energy gap (> 3.1 eV) to avoid the absorption of visible light in combination with significant free carrier concentrations ($\approx 10^{19} - 10^{20} \text{ cm}^{-3}$) and mobilities superior to $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These characteristics are enabled by the possibility of adjusting the position of the Fermi level, as a result of the processing conditions, which can be located either near the conduction band or within it if completely degenerated, thus enabling a large number of carriers and facilitating electrical conduction [5]–[7].

This class of materials gained the interest of the scientific community and has been the object of intense research for many decades, leading to the development of new and better processing techniques. Materials such as indium oxide (In_2O_3), tin oxide (SnO_2), zinc oxide (ZnO), and cadmium oxide (CdO) are commonly used as the primary material for TCOs and can be tailored when combined with each other or doped with elements in order to improve their electrical and optical properties. Table 3.1 shows some examples of the most common binary, ternary and multicomponent oxides [2], [4]–[6].

Table 3.1 TCOs materials and some dopants (adapted from [2], [5])

<i>TCO</i>	<i>Doping materials</i>
ZnO	Al, Ga, B, In, Y, Sc, F, V, S, Ge, Ti, Zr, Hf, CdO
In₂O₃	Sn, Ge, Mo, F, Ti, Zr, Mo, Hf, Nb, Ta, W, Te
SnO₂	Sb, F, As, Nb, Ta, In ₂ O ₃
CdO	In, Sn
<i>Multicomponent oxides</i>	
ZnO- In₂O₃	$\text{Zn}_2\text{In}_2\text{O}_5$, $\text{Zn}_3\text{In}_2\text{O}_6$
Zn- In₂O₃- SnO₂	$\text{Zn}_2\text{In}_2\text{O}_5\text{-In}_4\text{Sn}_3\text{O}_{12}$

The versatility of these materials can be easily identified, through the application as transparent electrodes in a wide range of applications such as electrochromic windows or solar cells, anti-corrosion and anti-static coatings, gas sensors, among others [8]. However, the high concentration of free carriers and high electrical conductivity required for “passive” applications is a limitation when aiming for active layers in TFTs. Thus, it is necessary to shape the properties of the materials through the control of doped and embedded impurities and the annihilation of defects, leading to a high electrical

conductivity (σ), without compromising the optical properties, enabling the production of a new class of materials – oxide semiconductors [7], [8].

As briefly referred in Chapter 1, in the past 15 years, the scientific community witnessed significant evolutions in this field, especially for the amorphous oxide semiconductors (AOSs), leading to low-temperature processed materials with high optical transmittance, low surface roughness and reduced internal stress [9].

The idea of transparent AOSs was presented in 1996 by Hosono and his team which reported studies based on Ag-Sb-O, Cd-Pb-O and Cd-Ge-O systems. In the proposed model AOSs must contain two or more post-transition metal cations with an electron configuration $(n-1)d^{10}s^0$ ($n \geq 4$), where zinc, indium and gallium are included [2], [7].

The figure shows a periodic table with columns labeled by electronic configuration: ns^1 , ns^2 , d^1 , d^2 , d^3 , d^4 , d^5 , d^6 , d^7 , d^8 , d^9 , d^{10} , np^1 , np^2 , np^3 , np^4 , np^5 , np^6 . The d -block is labeled $d \text{ block shell} = (n-1)$ and the f -block is labeled $f \text{ block shell} = (n-2)$. Elements with the configuration $(n-1)d^{10}s^0$ are highlighted in pink: Zn, Ga, In, Tl, Sn, Pb, Bi, Po, At, Rn, and the Lanthanide/Actinide series. The Lanthanide Series (La to Lu) and Actinide Series (Ac to Lr) are shown at the bottom.

Figure 3.1 Periodic table where the elements whose electronic configuration is $(n-1)d^{10}s^0$ are highlighted.

The AOSs exhibit a different electronic conduction from conventional covalent semiconductors where the conduction is made fundamentally by hybridised anisotropic orbitals sp^3 . The mobility of charge carriers is affected by the unbalanced bonds and the distorted structure that originate localised states in the energy gap [2]. On the other hand, for the amorphous ionic semiconductors – where the AOSs are included - the conduction band is composed of isotropic ns molecular orbitals of the metallic cations. The overlap of these orbitals is supposed to occur in metallic cations with $n > 4$ thus facilitating the electron transport and enabling carrier mobilities in AOSs films not that different from those

observed in the polycrystalline form (Figure 3.2) [2], [5]. The inexistence of grain boundaries contributes to the high mobility values observed in these films ($> 10 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$), that can be obtained over large areas [2], [7], [8]. Currently, multicomponent systems such as $\text{In}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-ZnO}$, $\text{In}_2\text{O}_3\text{-ZnO}$ and ZnO-SnO_2 are the most promising options for TFTs and electronic circuits.

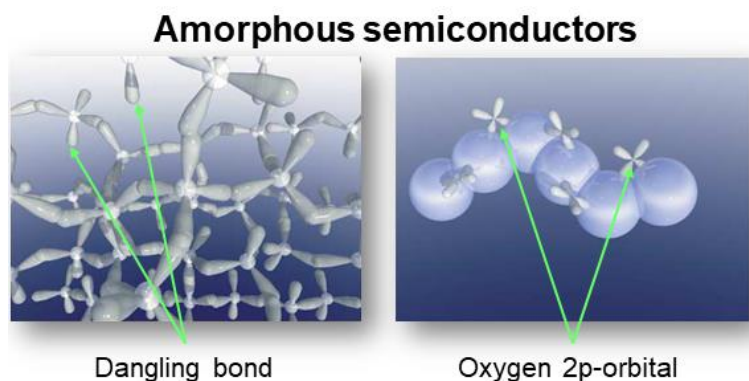


Figure 3.2 Schematic representation of the conduction band for the covalent amorphous (on the left) and ionic semiconductors (on the right), respectively [8].

3.2. Hydrogenated TCOs

Indium-based TCOs, such as indium zinc oxide (IZO) and indium tin oxide (ITO), usually gather the best combination of excellent optical and electrical properties. Although being considered as reference, indium is pointed out as a critical raw material in Europe. Thus, many efforts have been made to optimise TCOs without criticality issues and lower environmental impact. In the following section, the work developed during this PhD on In-based and In-free TCOs will be presented, with a particular focus on the effect of hydrogen addition to the sputtering atmosphere. The goal was to develop a transparent electrode with suited properties to be used as the gate in the developed paper FETs.

Indium-based oxides and Zinc oxide (ZnO) have been in the focus of research for many decades due to their multi-functionality opening ways for their use in a plethora of applications, that go from transparent conductive electrodes, channel layers in thin film transistors (TFTs), light emitting devices (LEDs), laser diode or chemical and gas sensors [3], [10]–[14]. The interest in ZnO is mainly due to the easiness of optical and electrical properties tuning by using doping elements from group-III (e.g. In, Ga, Al), which occupy substitutional Zn positions in the lattice, increasing the free carrier concentration and

optical band gap [15]. Undoped ZnO may also present native defects that affect its electrical and optical properties such as oxygen vacancies (V_O), zinc vacancies (V_{Zn}), zinc interstitial atoms (Zn_i) and antisites, or even residual hydrogen. [16]–[18]

The effect of hydrogen is a controversial topic since it is defined as an amphoteric impurity in most of the semiconductors and typically counteracts the dominant effect that determines the electrical conductivity of the material: it acts as an acceptor (H^-), and as a donor (H^+) in n-type and p-type materials, respectively [19], [20]. However, in the recent past many works were focused on using ZnO or (SnO_2) and it was shown that the introduction of H_2 in the films leads to improvements of optical and electrical properties, such as high near-infrared transparency and high mobility. This suggests a non-amphoteric character of the H_2 in those oxides, that is not consensual among the scientific community. Some theoretical studies suggest that H_2 has a non-amphoteric behaviour, compensating native defects, enabling electrically active defects and consequently enhancing n-type conductivity [17], [21].

The amphoteric or non-amphoteric behaviour of the hydrogen in the semiconductors seems to be related to the position of the hydrogen $\epsilon(+/-)$ level relative to the bandgap of the semiconductor [21], [22]. For most of the semiconductors, the $\epsilon(+/-)$ lies within the bandgap as happens for aluminium nitride (AlN) or gallium nitride (GaN) (Figure 3.3), where it can never act as a source of free carriers [21]. However, for materials where the $\epsilon(+/-)$ level is close or above the conduction band minimum – as is the case for ZnO, it is expected that hydrogen behaves as a shallow donor [22]. For the cases where the $\epsilon(+/-)$ is placed near or within the valence band, as germanium (Ge) or gallium antimonide (GaSb), the hydrogen should act as shallow acceptor, enhancing thus the p-type conductivity [22].

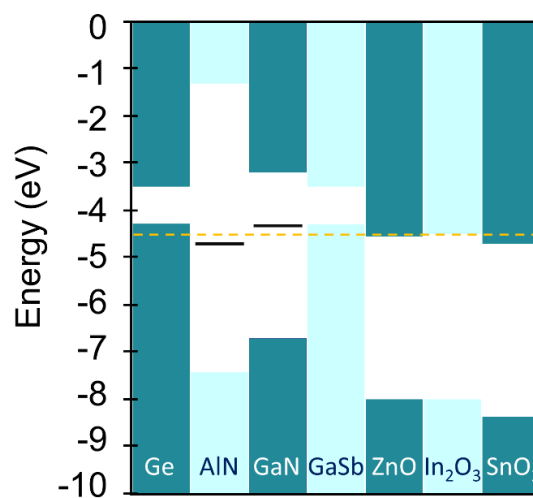


Figure 3.3 Universal alignment of hydrogen level in semiconductors (adapted from [21]).

In the 1950s, Thomas *et al.* reported an increase in the electrical conductivity of a ZnO crystal, after hydrogen diffusion [23]. Since then several papers were published reporting on the improvement of the electrical properties of the ZnO through different techniques, such as post-deposition ionic implantation, H₂ plasma treatment or in-situ, through metal organic chemical vapour deposition [23], [24]. Despite the many reports dealing with the improvement of the electrical conductivity with hydrogen incorporation, the mechanism behind it is not clearly understood. Several explanations have been reported such as the shallow donor behaviour acting as positively charged states; passivation of native defects (oxygen vacancies - V_O filling); occupation of interstitial sites connected to multicentre bonds; or promoting the relaxation of the ZnO lattice [10], [17], [25]–[30].

3.2.1. Hydrogenated Zinc Oxide TCOs

The depositions of the zinc oxide thin films were carried out at room temperature by radio frequency magnetron sputtering at 13.56 MHz from a 3 inches ZnO ceramic commercial target (purity>99.99%). A set of films was produced under different H₂ dilutions (D_{H2}), aiming to determine the influence on the electro-optical properties and how this is related to the structure and the chemical state of the hydrogen incorporated in the oxide matrix.

The hydrogen (99.9999% purity) was incorporated by mixing it with argon (Ar+H₂) during the films' growth, where the H₂ dilution (D_{H2}=H₂ flow / (Ar+H₂) flow) was changed from 0% to 2%. The hydrogenated thin films were prepared without any intentional substrate heating or post-deposition treatment. The deposition conditions of hydrogenated ZnO thin films are listed in Table 3.2.

Table 3.2 Experimental parameters used for the production of ZnO thin films by rf. sputtering.

<i>D_{H2}</i> (%)	<i>H₂ flow</i> (sccm)	<i>Ar flow</i> (sccm)	<i>Base</i> <i>pressure</i> (Pa)	<i>Working</i> <i>pressure (Pa)</i>	<i>Power</i> <i>density</i> (W cm ⁻²)	<i>Target/substrate</i> <i>distance (cm)</i>
0	0	100	7×10 ⁻⁵	0.4	4.4	15
0.5	0.5	99.5				
1	1	99				
1.5	1.5	98.5				
2	2	98				
<i>D_{H2}</i> = <i>H₂ flow</i> / (<i>Ar</i> + <i>H₂</i>) <i>flow</i>						

3.2.1.1. Structure and morphology

The addition of hydrogen during the sputtering deposition reduced the growth rate of the ZnO films from 10.5 to 5-6 nm/min (Figure 3.4). This effect can be partially explained by the smaller ionic radius of the hydrogen comparatively to the argon, which reduces the impact section. This means that the increase of the hydrogen in the sputtering gas leads to the reduction of the sputtering yield due to the reduction of the Ar^+ ion density in the plasma and so on cathode bombardment, as predicted by Bogaerts et al. [31].

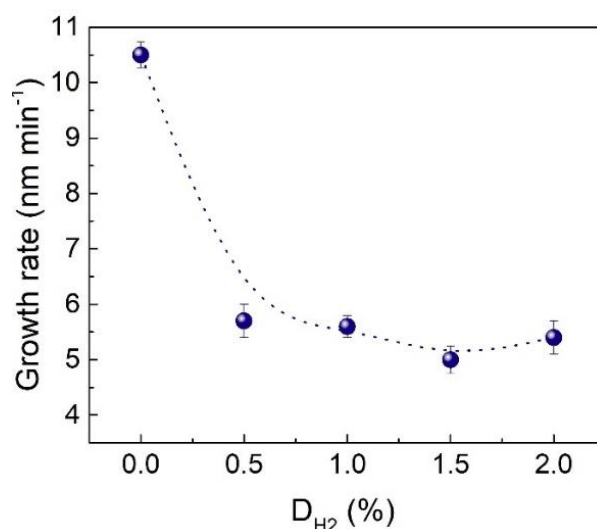


Figure 3.4 ZnO thin film growth rate variation as a function of H_2 dilution ratio (D_{H_2}).

The same effect was experimentally observed also for the sputtering deposition of other materials as reported by Saikia et al. during the deposition of TiO_2 thin films [32], or even in other ZnO-based thin films as aluminium-doped ZnO or gallium-doped ZnO, as will be discussed later in section 3.2.2.

Nevertheless, the poisoning of the target's surface must also be considered. Metal hydrates may be formed due to the presence of hydrogen, which leads to changes in the potential of the plasma, reducing the deposition yield. Finally, the possibility of re-sputtering (etching) of the grown film should also not be neglected. This process is promoted by hydrogen atoms that eliminate preferentially weak bonds and small agglomerates, which on the other hand improves the films' crystallinity [33].

The ZnO and ZnO:H films deposited with different D_{H_2} are polycrystalline. In the XRD diffractograms sharp peaks in the angular position (2θ) around $34.2 - 34.3^\circ$ are easily identified (Figure 3.5a), which can be related to the (002) planes of ZnO hexagonal *wurtzite* structure (ICDD n° 98-009-0505). The introduction of H_2 causes a shift towards lower

angles, suggesting an increase of the lattice's interplanar distance (d_{002}). (Figure 3.5b, and c). Van de Walle and Chen *et al.* associated this with the relaxation of residual tensile strain in the lattice [10], [11], [24]. In addition, the enhancement of (002) peaks with an increase of D_{H_2} means that the films become texturised along the [001] direction (c-axis) of the ZnO hexagonal structure, thus minimising the surface energy [24], [34]. It has been reported that preferential orientation is less favoured when depositing sub-stoichiometric ZnO, as it is the case of the films presented here deposited only with Ar. [35] This also confirms that hydrogen has a similar effect to that of oxygen in determining a preferential growth direction in ZnO thin films.

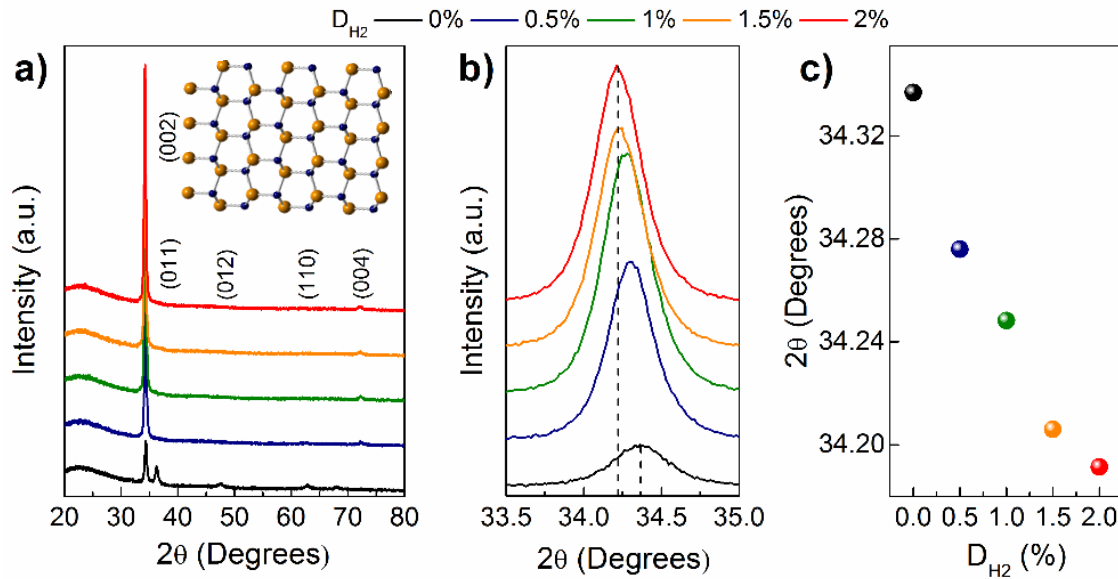


Figure 3.5 a) XRD diffraction patterns of ZnO thin films deposited with different H_2 dilution ratios (D_{H_2}). The patterns show the preferential growth along [001] directions for the highest D_{H_2} ; in the inset the top view of the ZnO crystal for [001] direction is depicted (orange and blue atoms represent O and Zn, respectively). b) and c) detailed view of the (002) reflex shift towards lower 2θ values as D_{H_2} increases.

The size of crystallites (D) was determined using the Debye-Scherrer equation:

$$D = \frac{0.9\lambda}{FWHM \cos\theta} \quad \text{Equation 3.1}$$

where λ represents the wavelength of X-ray ($Cu_{\alpha}=1.54 \text{ \AA}$), $FWHM$ the width at half height ($FWHM$ - Full Width at Half Maximum) and θ the diffraction angle. The increase $FWHM$ for D_{H_2} between 1 and 2%, suggests a decrease in the crystallite dimension, in agreement with previous studies [36], [37]. The average size, estimated by the Debye-Scherrer equation, is around 20 and 24-25 nm for the ZnO and ZnO:H films (Figure 3.6), respectively, which is also in line with other reports [33], [38].

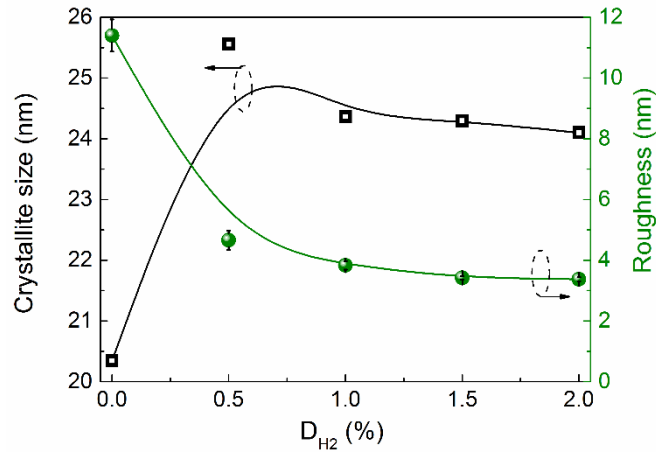


Figure 3.6 Dependence of the crystallite size, and RMS roughness determined by AFM on the H_2 dilution (D_{H_2}) ratio used. (The lines are guide for the eyes.)

In Figure 3.7 SEM micrographs of the films deposited under $D_{H_2}=0\%$ and 1.5% are presented. When no H_2 is added to the sputtering atmosphere, the films present a rough surface (RMS=11.4 nm estimated by AFM) with large agglomerates that are supposed to be formed by small grains, as suggested by the average crystallite size determined from the XRD data (Figure 3.6). When H_2 is added, the surface becomes more homogeneous and smoother with no evidence of agglomerates, while the RMS roughness decreases down to 3.4 nm for $D_{H_2}=2\%$. This behaviour can be connected to the decrease in the growth rate and re-sputtering of the growing films.

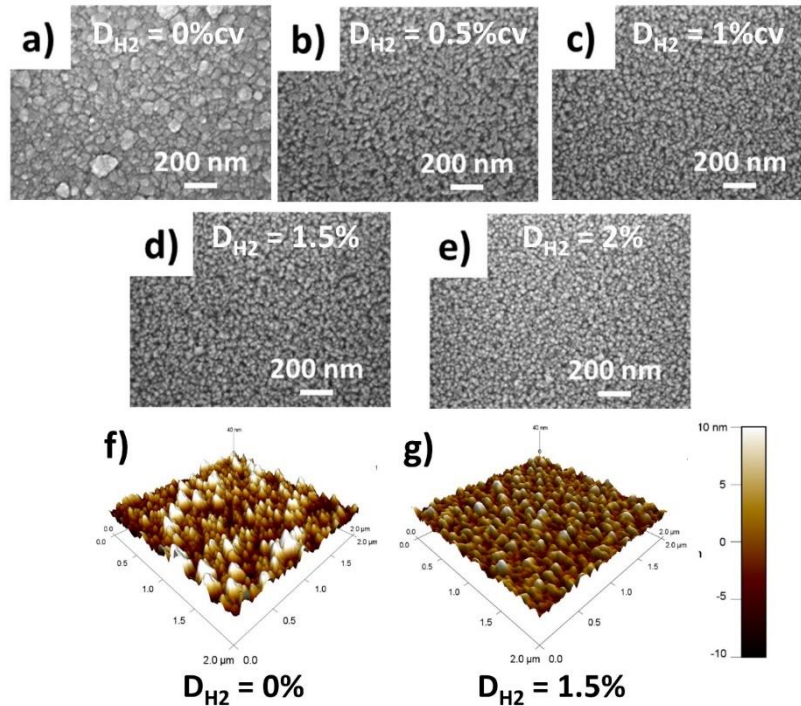


Figure 3.7 SEM micrographs obtained for ZnO thin films for different D_{H_2} tested: a) 0%, b) 0.5%, c) 1%, d) 1.5% and e) 2%, and AFM images D_{H_2} of f) 0 % and g) 1.5 %.

3.2.1.2. Electrical and optical properties

The ZnO and ZnO:H films present n-type conductivity while the electrical resistivity (ρ) decreases significantly as H_2 is added to the sputtering atmosphere (Figure 3.8). The increment of D_{H_2} from 0 to 1.5% results in a substantial improvement of the Hall mobility (μ_H) from 6 to a maximum of $47.1 \text{ cm}^2/\text{Vs}$, while the carrier concentration (n) also increases reaching a value of $4.4 \times 10^{19} \text{ cm}^{-3}$, resulting in a ρ of $3 \times 10^{-3} \Omega \text{ cm}$.

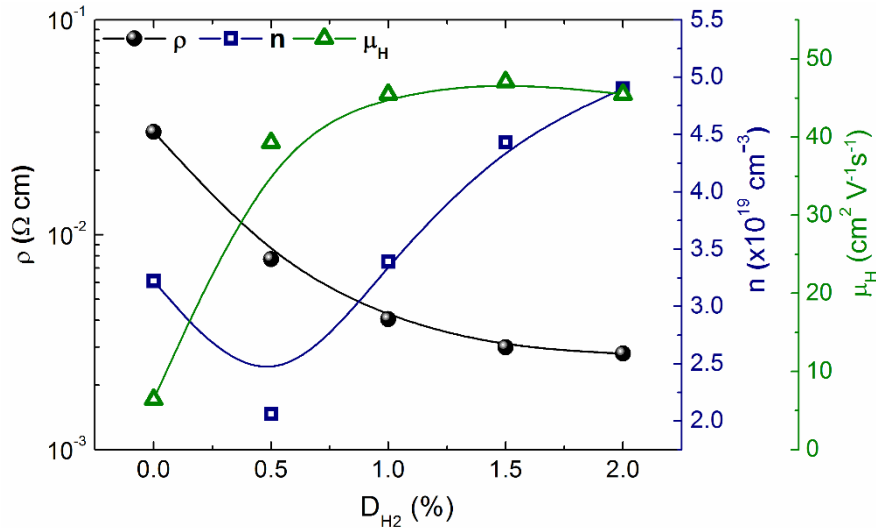


Figure 3.8 Variation of resistivity (ρ) carrier concentration (n), and electron mobility (μ_H) for the ZnO films deposited with different H_2 dilution ratios (D_{H_2}).

(The lines are guides for the eyes.)

The ZnO films sputtered in an Ar atmosphere are sub-stoichiometric, and the carrier concentration is controlled by V_O . However, when H_2 is intentionally added to the sputtering atmosphere, these defects start to be compensated, which results in improvement of the transparency and a decrease in the number of free electrons generated by V_O , while the μ_H increases consistently with the increase observed in the crystallite sizes. It is expected that the formation of other donor like defects, such as Zn_i , will dominate at higher H_2 content and so the carrier concentration will then increase.

A further increase in D_{H_2} (above 1.5%) leads to an even higher n but μ_H slightly decays, with no major variation on ρ . Several explanations can be found in the literature for the improvement of both ρ and μ_H , such as donor effect either by the creation of interstitial hydrogen (anti-bonding O sites, bond-centred sites O-Zn, in the grain boundary with bond-like O-H) or V_O filling ($V_O + H^+ \rightarrow H_O^+$). This leads to ZnO reduction with hydrogen atoms

and/or hydride ions or a combination of oxygen vacancies with hydrogen creating V_O -H complexes. [10], [11], [18], [26], [36], [37], [39], [40].

In addition to the improvements in the electrical properties, the optical transmittance of ZnO thin films is also largely enhanced with H_2 . The hydrogenated films show an average transmittance in the visible range (AVT) around 90%, well above the one measured for films deposited without H_2 (AVT $\sim 60\%$) (Figure 3.9a). This can be compared to the effect of oxygen addition to the sputtering atmosphere. When ZnO thin films are deposited with $Ar+O_2$ ($D_{O_2} < 1\%$) and $Ar+O_2+H_2$ ($D_{O_2} < 1\%$ and $D_{H_2}=1.5\%$) the films have improved transparency (AVT above 80%) as expected when reducing the V_O density and getting close to the stoichiometry. However, it is important to highlight that O_2 by itself does neither result in any improvement in transmittance nor in the electrical properties (lower μ and slightly higher ρ) when compared to the ZnO films deposited with $Ar+H_2$.

This allows to conclude that H_2 compensates V_O in ZnO thin films, improving transparency and causing strain relaxation caused by oxygen deficiency in the lattice.

When the D_{H_2} increases from 0.5 to 2% a blue shift in the absorption edge was observed (depicted in the inset of Figure 3.9a), as result of the increase in E_{op} from 3.31 to 3.39 eV. This behaviour is consistent with the Burstein-Moss (B-M) effect confirmed by the approximately linear relation of the optical band gap vs $n^{2/3}$ shown in Figure 3.9b).

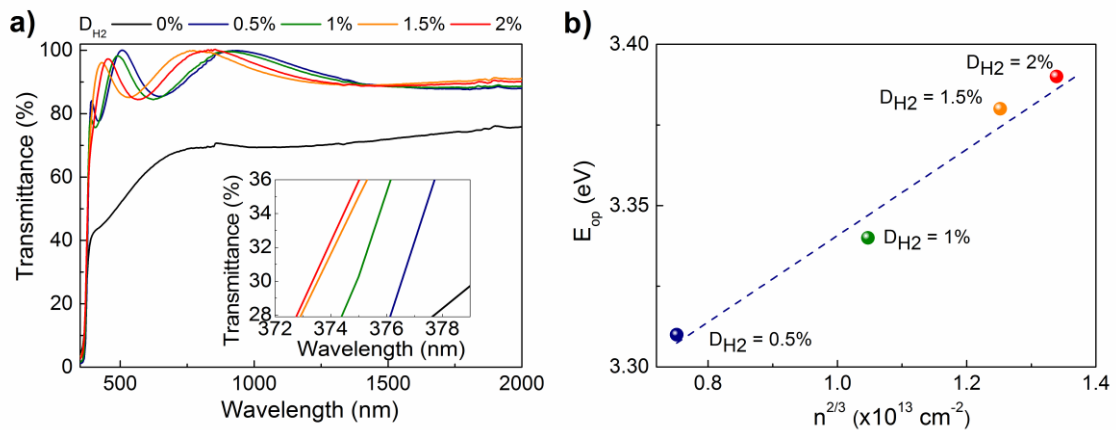


Figure 3.9 Optical characterisation of ZnO films processed at different H_2 dilution ratios (D_{H_2}): a) Optical transmittance spectra. The inset shows the blue-shift of the absorption edge with D_{H_2} , b) Linear relation of E_{op} vs $n^{2/3}$, corroborating the B-M effect (The line is a guide for the eyes.).

The best compromise between the aimed electrical and optical properties (low resistivity and high AVT) is given by the figure of merit (FoM) [41], [42]. Different definitions can

be found in the literature but in this work, the one established by Haacke was used, which is defined through the equation:

$$FoM = \frac{AVT^{10}}{R_{sh}} \quad \text{Equation 3.2}$$

where AVT is the average transmittance in the visible range, and R_{sh} is the sheet resistance [41].

Changing D_{H_2} from 0% to 1% leads to a drastic increase in FoM (Figure 3.10), due to the variations observed both in the AVT and ρ . Above this value, and for the range of D_{H_2} used, no significant variation was observed with the highest FoM being obtained for a D_{H_2} of 1.5%. Although the remarkable improvement of the FoM with hydrogen addition, the values are smaller than for standard TCO's such as ITO or FTO but close to aluminium-doped zinc oxide (AZO), and gallium-doped zinc oxide (GZO) [4].

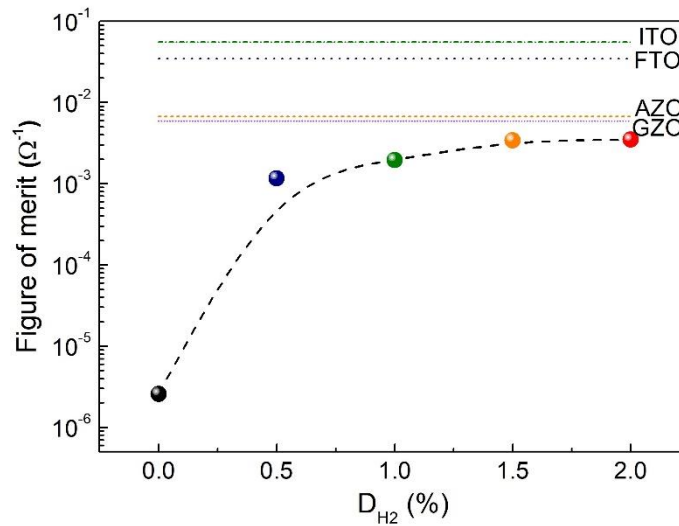


Figure 3.10 Dependence of the figure of merit (FoM) on the H_2 dilution (D_{H_2}). FoM of ITO, FTO, AZO, and GZO are also indicated in the graph using a dashed line only as a guide for the eyes.

The mobility in the TCOs depends on several scattering mechanisms, such as neutral and ionised impurities, grain boundaries, dislocations and thermal lattice vibrations [1], [5], [43]. These mechanisms can be distinguished by looking at the dependency of the electrical properties of the films as a function of the temperature (T). In Figure 3.11a the μ_H and n between 373 K and 173 K for films deposited with $D_{H_2}=0$ and 1.5 % are presented. The data for the ZnO:H films exhibit a typical behaviour of degenerated semiconductors, whereas the μ_H for the film produced without H_2 is thermally activated.

For lower carrier concentrations ($n < 10^{18} \text{ cm}^{-3}$) the dominant mechanism is expected to be grain boundary scattering, while for highly degenerated films ($n > 10^{19} \text{ cm}^{-3}$) the n and μ_H tend to be independent of T and ionised impurity scattering becomes dominant [43], [44]. Once that both samples have a n in the range of 10^{19} cm^{-3} they can be considered essentially as a degenerated semiconductor.

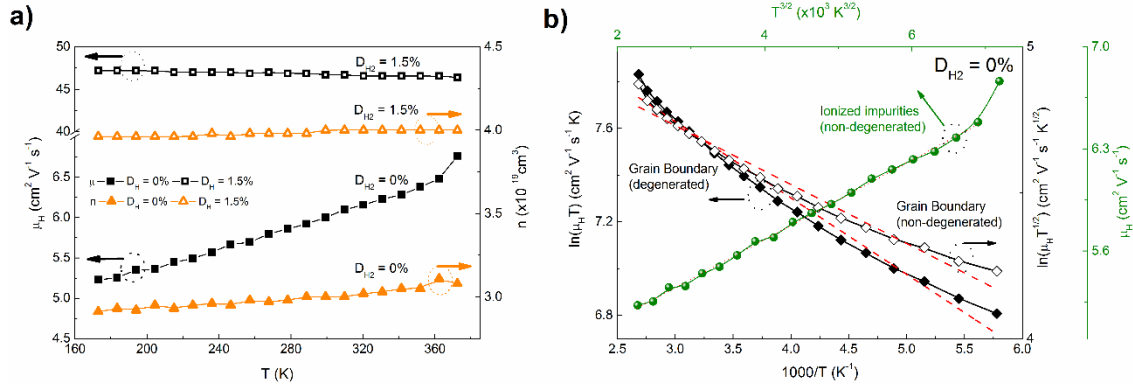


Figure 3.11 Temperature dependence of the electrical properties for the ZnO films prepared with D_{H_2} of 0 and 1.5 %: a) Temperature dependence for both μ_H and n ; b) Relation between μ_H and T for $D_{H_2} = 0\%$ using the grain boundary (degenerated and non-degenerated) and ionised impurities (non-degenerated) scattering models.

For the hydrogenated film, the independence of n from T denounces the degeneration of the film, while non-variation of the μ_H corresponds to a typical ionised impurity scattering mechanism, which dominates at RT. Nevertheless, for these hydrogenated films, the thermal lattice vibration scattering starts to be relevant at high T , as revealed by the slight decrease observed for μ_H [43]. On the other hand, the n and μ_H slightly increase with T for the film deposited without H_2 , which suggests the presence of a thermally activated conduction mechanism, for which the grain boundary scattering greatly contributes. However, none of the models (degenerated and non-degenerated) fits precisely the experimental data obtained (Figure 3.11b), leading so to the conclusion that the grain boundary scattering occurs in parallel with another scattering mechanism. This is indeed understandable since within this range of T the kT product is lower than the typical potential barriers existing at the grain boundaries and therefore it is expected that the carrier transport through the grain boundaries will be mainly dominated by tunnelling [45].

For the ZnO thin films deposited without H_2 , the ionised impurities for non-degenerated semiconductors model fits quite well in the μ_H variation with T , showing an approximately linear dependence with $T^{3/2}$ (see Figure 3.11b). It is therefore assumed that trapped carriers

exist in films deposited without H_2 , which are *detrapped* with the increase of T , contributing so to the increase of both n and μ_H , similarly to what happens in other materials where the degeneracy is not completed, and all donor levels are not entirely ionised. These trapped carriers are considered to have an origin at grain boundary trap states. Indeed, Ellmer *et al.* have determined that the trap density (N_t) is in the range of 10^{13} cm^{-2} for ZnO thin films prepared by sputtering [46].

Despite scattering at the grain boundaries not being the dominant transport mechanism, it limits the mobility in films with small grain sizes, as happens for the films presented here, where trapped charge carriers, according to Seto's model developed for polycrystalline semiconductors, create larger depletion regions [47]. This means that when H_2 is added during the sputtering deposition, it contributes to the reduction of the trap density in the films.

Despite the defect compensation made by the hydrogen in the ZnO observed in the UV-Visible-NIR transmittance plots, further details about the kind of annihilated defects can be extracted through photoluminescence (PL). The PL in ZnO is widely reported, and the mechanisms behind these emissions are often related to defects and electronic transitions, as summarised in Figure 3.12.

The violet emission is due to zinc-related defects, such as zinc vacancies (V_{Zn}), zinc interstitials (Zn_i), or electron transitions between ionised zinc interstitials (Zn_i^+). On the other hand, green, and yellow emission are mostly associated to deep level transitions and oxygen and zinc defects, such as V_{Zn} once more, oxygen anti-sites or V_O [40], [48], [49]. Finally, the UV emission is related to near band edge emission (NBE), band-to-band transitions, and a radiative recombination of free excitons.

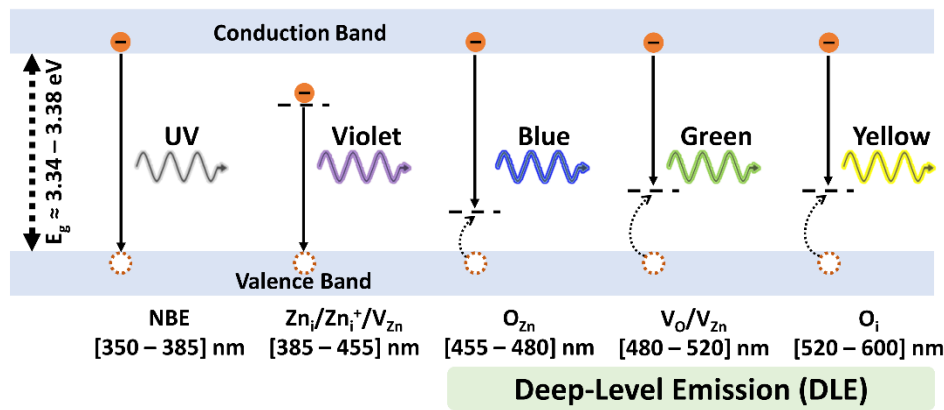


Figure 3.12 Schematic band diagram of the possible electronic transitions responsible for the different emissions in ZnO films.

The PL spectra obtained for ZnO and ZnO:H thin films only revealed a violet-UV emission band centred at 381 nm that is undoubtedly enhanced by the addition of H₂ during deposition ($D_{H_2}=1.5\%$) (Figure 3.13). Similarly to the findings in this work, Sekiguchi *et al.* and Cai *et al.*, reported ZnO luminescence modifications through H₂ plasma, observing an enhancement of UV excitonic emission [37], [48], [49]. The intensity enhancement of the UV emission observed in this work for the ZnO:H is attributed to the crystalline quality improvement of the film, and partial passivation of radiative defects or hydrogen filling up of competitive recombination centres, such as V_O and other carrier trapping centres [37], [50], [51].

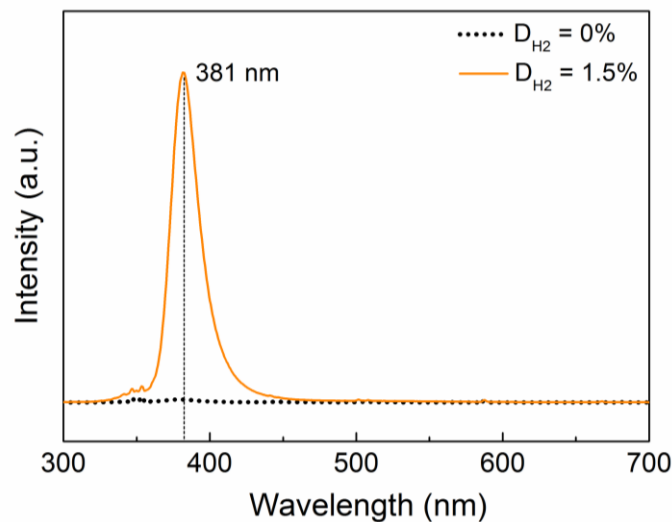


Figure 3.13 Room temperature PL spectra ZnO films deposited without H₂ (dotted line) and with $D_{H_2}=1.5\%$ (solid line).

3.2.1.3. Chemical state and composition

The knowledge of the chemical state and composition of the ZnO-based thin films allows for a better understanding of the electrical properties. Thus, the films were analysed using X-ray photoelectron spectroscopy (XPS) to get some further insights on how hydrogen behaves in the ZnO lattice.

At a first glance, the analysis of the Zn 2p peaks (Figure 3.14a) is not conclusive, giving no hints about the presence of hydrogen. The Zn 2p peak can be split into the Zn 2p_{3/2} peak ($\approx 1021 - 1022$ eV) and Zn 2p_{1/2} peak ($\approx 1044 - 1045$ eV) [33]. In the case of the hydrogenated films ($D_{H_2}=1.5\%$) both Zn 2p peaks have a small deviation towards lower energy values. The Zn 2p_{3/2} peak is shifted from 1021.4 to 1021.2 eV, while the Zn 2p_{1/2} is shifted by 0.1 eV (Figure 3.14a). The variation in the binding energies cannot be considered

as an evident demonstration that Zn is being reduced. Even so, the data suggest that hydrogen is not preferentially bonded to Zn since it is expected that Zn-H bond formation would result in a shift of the Zn 2p peaks towards higher binding energies [33], [34].

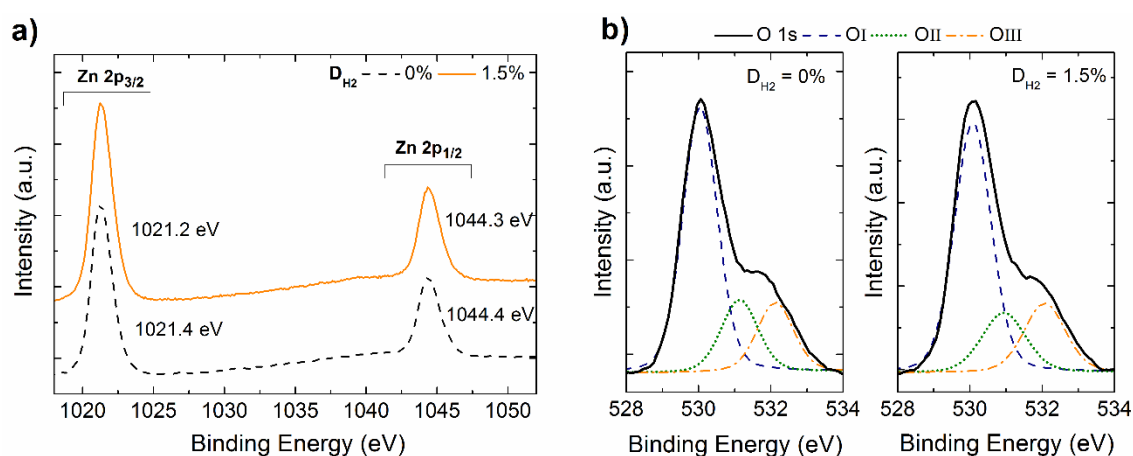


Figure 3.14 XPS spectra for films processed without (dashed line) and with H_2 dilution ($D_{H_2}=1.5\%$, full line): a) ZnO and ZnO:H Zn 2p XPS spectra; b) O 1s Peak from ZnO and ZnO:H.

The O 1s band (Figure 3.14b) can be helpful, and its careful analysis can be used to further understand the hydrogen incorporation into ZnO. This band can be developed into three sub-peaks: OI, OII and OIII. The first is related to O^{2-} ions of metal-O bonds and since it is centred at 530.1 eV for both films, it confirms that the formation or annihilation of Zn-O bonds with hydrogen incorporation does not occur [33]. The OII peak is centred at 531.2 eV and is associated with O^{2-} ions in oxygen-deficient regions within the ZnO lattice. For the films produced with $D_{H_2}=1.5\%$ this peak shifts toward lower binding energies (530.9 eV) and the sub-peak area decreases from 18.5% to 17.7%, indicating a reduction of V_O density [33], [52], [53]. Finally, the higher binding energy component sub-peak relates to oxygen chemisorbed and weakly bonded at the films' surface such as that existing in carbonates ($-CO_3$), hydroxyl groups ($-OH$) or even adsorbed O_2 can be associated. The data collected for these films does not show any significant shift (532.2 and 532.1 eV for ZnO and ZnO:H, respectively) when H_2 is added during the ZnO deposition. However, the increase of the sub-peak area observed for these films (19.4% instead the 17.4% determined for the films deposited with Ar), indicates an increase of the quantity of the absorbed hydroxyl group, as well as other negatively charged oxygen species [34], [53].

3.2.2. Aluminium-doped zinc oxide and gallium-doped zinc oxide thin films

The study on the hydrogenated ZnO thin films provided relevant insights into the role of the hydrogen, which was used for further improvement of the most commonly used indium-free TCOs in the CEMOP-CENIMAT working group. In the following section studies on aluminium-doped zinc oxide, and gallium-doped zinc oxide will be presented.

Aluminium and gallium are by far the most common dopant elements in ZnO, allowing the enhancement of the electric properties through the generation of free carriers via Al^{3+} and Ga^{3+} ions which substitute the Zn^{2+} without a negative impact on the optical and structural properties as long as the dopant concentration is kept low. A substitution of a Zn^{2+} ion (Figure 3.15) can occur easily once the radius of Al^{3+} (0.54 Å) and Ga^{3+} (0.62 Å) are smaller than the Zn^{2+} (0.74 Å), without a severe distortion of the ZnO's structure, since the metal ion-oxygen length lays in the same order of magnitude Al-O (0.181 nm) < Ga-O (0.192 nm) < Zn-O (0.197 nm) [54]–[56].

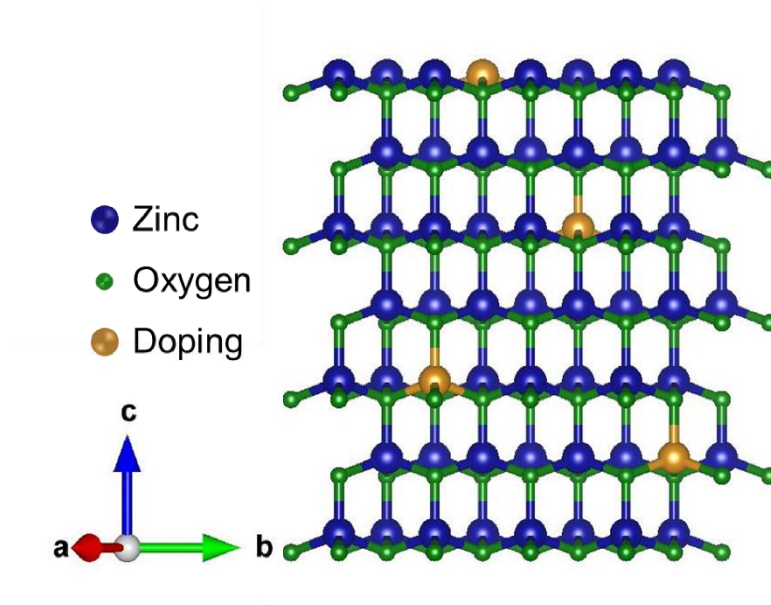


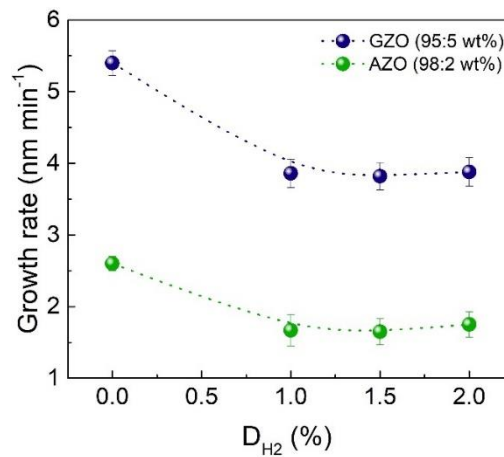
Figure 3.15 Doped zinc oxide structure, the substitutional position of the doping atoms is represented by the golden atoms.

In this work, the AZO and GZO thin films were deposited by radio frequency magnetron sputtering, using $\text{ZnO}:\text{Al}_2\text{O}_3$ - 98:2 wt% and $\text{ZnO}:\text{Ga}_2\text{O}_3$ -95:5 wt% targets, and D_{H_2} =0, 1, 1.5, and 2 %. The experimental details of the doped-ZnO thin films are listed in Table 3.3.

Table 3.3 Experimental parameters used for the sputtered doped-ZnO thin films.

D_{H_2} (%)	Base pressure (Pa)	Working pressure (Pa)	Power density (W cm ⁻²)	Target/substrate distance (cm)
0	7×10 ⁻⁵	0.2	≈3.3	15
1				
1.5				
2				
$D_{H_2} = H_2 \text{ flow} / (Ar+H_2) \text{ flow}$				

In Figure 3.16, it is possible to observe that a similar trend occurs to what happens for undoped ZnO: the growth rate of the GZO and AZO decreases with the introduction of hydrogen, being nearly 50% of that obtained when using only Ar. Therefore, it is acceptable to assume that the reasons pointed out before for ZnO thin films are also valid for doped ones.

Figure 3.16 AZO and GZO growth rate variation as a function of H₂ dilution ratio (D_{H_2}).

3.2.2.1. Electrical and optical properties

In Figure 3.17 the electrical properties of the AZO and GZO thin films are plotted. The addition of the hydrogen during sputtering promotes a significant decrease of the resistivity and improvement of the mobility. A D_{H_2} of 1.5% reveals to be the best condition for both AZO and GZO films, being much more evident for the first.

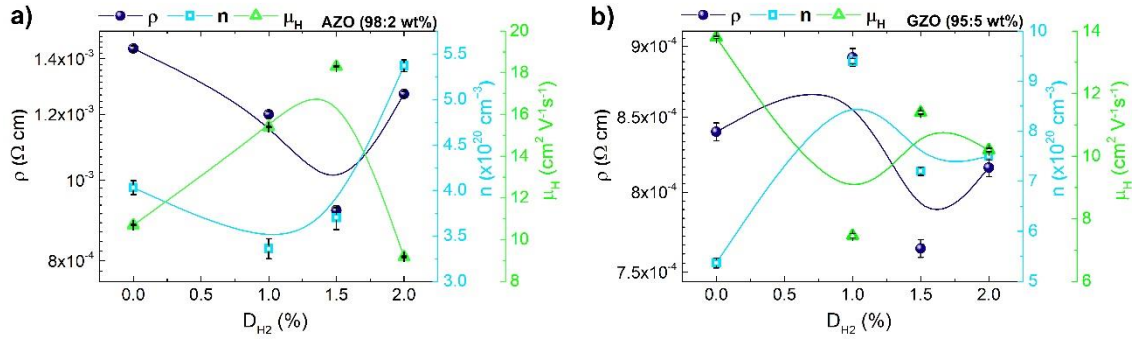


Figure 3.17 Electrical properties variation - resistivity (ρ) carrier concentration (n), and electron mobility (μ_H) - for the a) AZO films, and b) GZO deposited with different H_2 dilution ratios (D_{H_2}). (The lines are a guides for the eyes.)

For the AZO, the n value initially decreases similarly to what was observed for ZnO thin films, suggesting that hydrogen passivates defects such as V_O . This results in a reduction of the number of free electrons generated by those defects although improving the AVT from 76 to 84 % (Figure 3.18a). For $D_{H_2}=1.5\%$ the number of the carriers increase up to $3.7 \times 10^{20} \text{ cm}^{-3}$, μ_H is improved from ≈ 10 to a maximum of $18.3 \text{ cm}^2/\text{Vs}$, while ρ decreases to $9.2 \times 10^{-4} \Omega \text{ cm}$, which can be attributed to the activation of other donor like defects (different from V_O) responsible for the generation of free electrons. Further increase in D_{H_2} , results in a reduction of the μ_H (due to scattering) and ρ due to free carrier scattering.

In the case of the GZO films, the effect on the electrical properties is less evident, since n is already high when hydrogen is absent in the sputtering atmosphere. Thus μ_H is affected by scattering and ρ is almost unaffected ($\sim 8 \times 10^{-4} \Omega \text{ cm}$) (Figure 3.17b). Nevertheless, the films deposited with hydrogen in their composition show an increase of nearly 15% comparatively to the ones sputtered only with Ar, reaching an AVT of 85% (Figure 3.18b). In both materials a blue-shift of the absorption edge with D_{H_2} is observed (Figure 3.18c and d) and a consequent increase of E_{op} according to the expected B-M effect. In the non-hydrogenated films, the calculated E_{op} is 3.76 and 3.72 eV for the AZO and GZO, respectively, reaching in both cases 3.86 eV for a $D_{H_2}=2\%$.

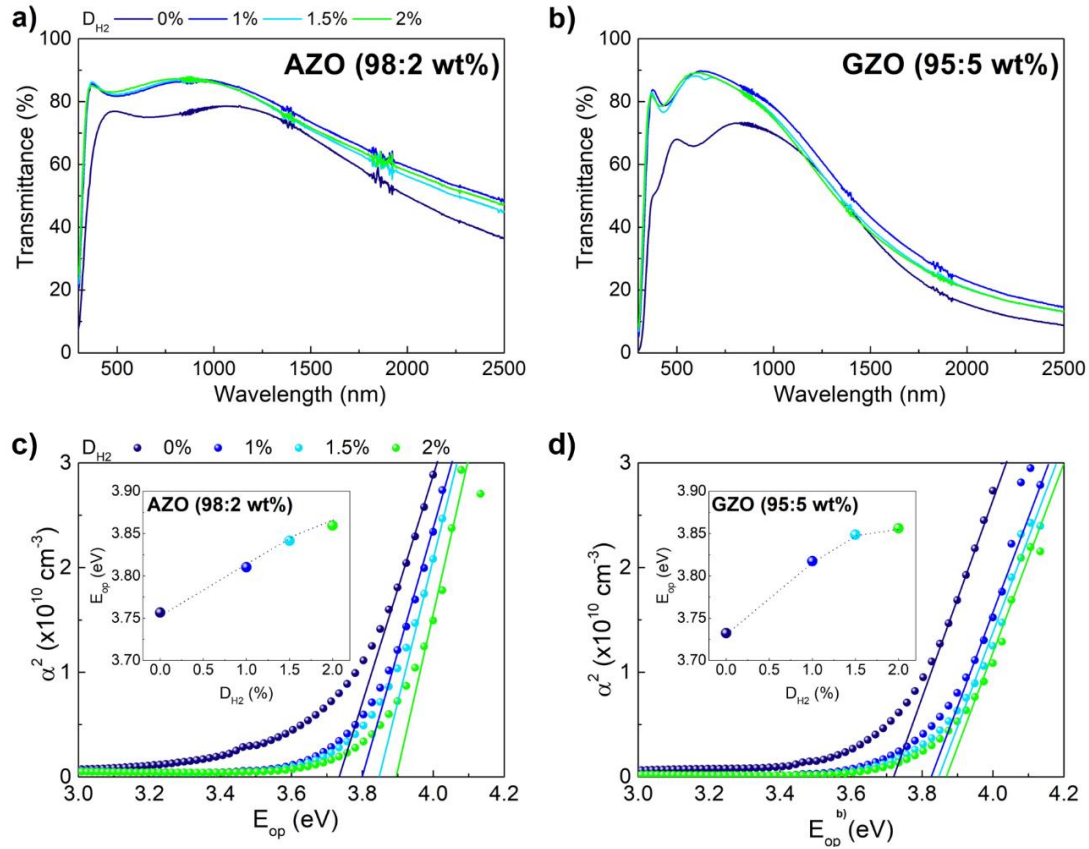


Figure 3.18 Influence of the H₂ dilution ratios (D_{H_2}) on the optical properties of the AZO and GZO films. Optical transmittance spectra of a) AZO, and b) GZO thin films. Plot c) and d) represents α^2 as a function of E_{op} , for the AZO and GZO, respectively. In the insets E_{op} as a function of D_{H_2} are plotted. (The lines are guides for the eyes.)

3.2.2.2. Al and Ga co-doped ZnO thin films

It was seen in previous sections that for either AZO and GZO thin films, the best combination of the electrical and optical properties was achieved for a $D_{H_2}=1.5\%$. Thus, it was decided to use the same conditions for the deposition of Al and Ga co-doped ZnO, denominated as AGZO.

In Table 3.4 the electrical and optical properties of the individual AZO and GZO films are summarised. The influence of the sputtering power density in doped-ZnO films is well reported, and the obtained results match the literature [57]–[59]. However, in the range used here it did not much affect any of the electrical or optical properties. Yet, it is possible to see that larger power densities lead to a reduction in ρ since larger grains, due to the high energy of the sputtered species, are expected [60]. Moreover, the increase of the power density promotes a higher ionisation rate of the donors, responsible for the enhancement of free carriers [57].

Table 3.4 Properties of the AZO and GZO thin films for different sputtering power densities.

<i>Material</i>	<i>Power density</i> ($W\ cm^{-2}$)	ρ ($\Omega\ cm$)	μ_H ($cm^2\ V^{-1}\ s^{-1}$)	n ($\times 10^{20}\ cm^{-3}$)	E_{op} (eV)	AVT (%)
AZO	≈ 3.3 (reference)	9.2×10^{-4}	18.3	3.7	3.86	84
	≈ 4.4	9.9×10^{-4}	10.6	5.9	3.86	87
	≈ 5.5	7.9×10^{-4}	13.4	5.9	3.85	86
GZO	≈ 2.2	1.1×10^{-3}	9.2	6.7	3.83	87
	≈ 2.7	7.1×10^{-4}	10.6	8.3	3.85	87
	≈ 3.3 (reference)	7.6×10^{-4}	11.4	7.2	3.86	85
$D_{H_2} = 1.5\%$; Working pressure = 0.2 Pa; Target/substrate distance = 15 cm						

Based on the conditions listed in Table 3.4, three different AGZO films were deposited by co-sputtering. For this the growth rate of the individual AZO and GZO are considered, targeting Ga content larger than Al (Ga >> Al), Ga content slightly higher than Al (Ga > Al), and Al content higher than Ga (Al > Ga) (Table 3.5).

Table 3.5 Electrical and optical properties of the AGZO thin films processed at room temperature.

<i>Power density</i> ($W\ cm^{-2}$)		ρ ($\Omega\ cm$)	μ_H ($cm^2\ V^{-1}\ s^{-1}$)	n ($\times 10^{20}\ cm^{-3}$)	E_{op} (eV)	AVT (%)
AZO	GZO					
≈ 3.3	≈ 3.3	8.1×10^{-4}	12	6.4	3.83	85
≈ 5.5	≈ 3.3	7.3×10^{-4}	13.2	6.5	3.83	87
≈ 5.5	≈ 2.2	5.6×10^{-4}	16	6.9	3.84	86
$D_{H_2} = 1.5\%$; Working pressure = 0.2 Pa; Target/substrate distance = 15 cm						

A clear improvement of the electrical properties is observed as the power density in the AZO target becomes much higher than in the GZO one. This suggest that for a condition where the Al content in ZnO is higher than Ga, a higher efficiency is achieved, leading to a decrease of the resistivity down to $5.6 \times 10^{-4}\ \Omega\ cm$, for a n of $6.9 \times 10^{20}\ cm^{-3}$.

The improvement observed in the electrical properties does however not compromise the optical characteristics of the AGZO films (Table 3.5 and Figure 3.19a).

The AZO and GZO films individually have a FoM lower than standard TCO's as ITO or FTO (Figure 3.19b) (data collected from reference values [4]). However, the AGZO produced with a larger amount of Al, which shows a similar AVT (AVT_{AGZO} = [85-87] %) compared to the AZO and GZO and a low sheet resistance, results in improved FoM (Figure 3.19b) and thus values closer to the ones reported for ITO and FTO.

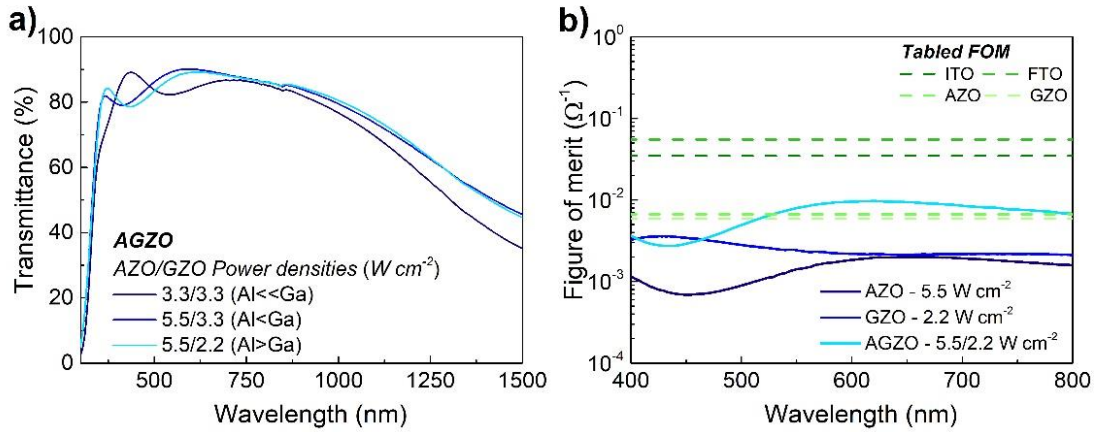


Figure 3.19 a) Optical transmittance spectra of AGZO films processed with different power densities; b) Figure of merit (FoM) of the sputtered AZO, GZO and AGZO films in the visible range (solid lines). Reference values of the FoM for ITO, FTO, AZO, and GZO are also indicated in the graph using the dashed line [4].

The XRD patterns (Figure 3.20a) for the AZO (5.5 W cm^{-2}), GZO (2.2 W cm^{-2}), and AGZO ($5.5/2.2 \text{ W cm}^{-2}$) show that the films crystallise in the hexagonal *wurtzite* structure (ICDD n° 98-001-7921 and ICDD n° 98-008-1280). The sharp peaks at angular position (2θ) near 34.2° - 34.3° (Figure 3.20b) evidences that they are highly textured along the c-axis perpendicular to the substrate, thus minimising the crystal surface free energy.

The FWHM of the AZO (5.5 W cm^{-2}), and GZO (2.2 W cm^{-2}) are higher than the value obtained for the AGZO ($5.5/2.2 \text{ W cm}^{-2}$), meaning that the crystallinity is improved when compared with individual AZO and GZO. Moreover, it also demonstrates that the ZnO lattice is not severely distorted with the simultaneous incorporation of Ga^{3+} and Al^{3+} [54].

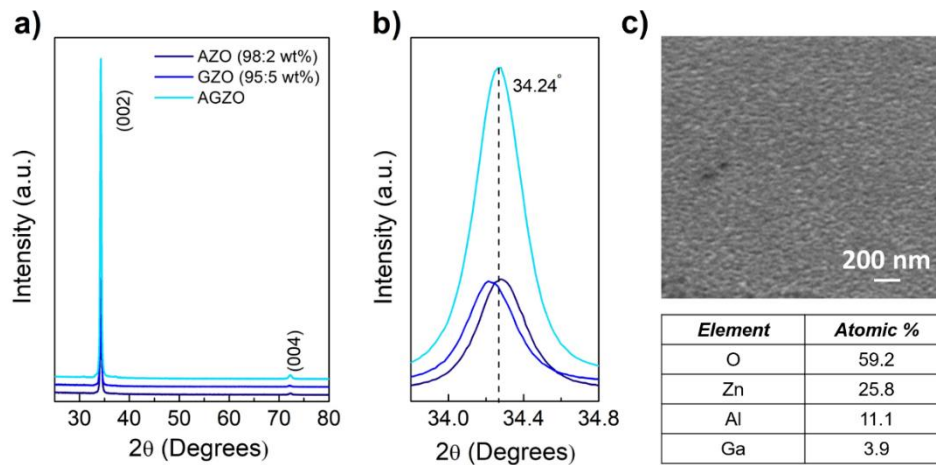


Figure 3.20 a) XRD diffraction patterns of AZO (5.5 W cm^{-2}), GZO (2.2 W cm^{-2}) and AGZO ($5.5/2.2 \text{ W cm}^{-2}$) thin films deposited with $\text{D}_{\text{H}_2}=1.5 \%$, b) and detailed view of the (002) reflex peak. c) SEM micrograph of the AGZO ($5.5/2.2 \text{ W cm}^{-2}$) film and respective elementary identification (table).

The SEM micrograph of the AGZO ($5.5/2.2 \text{ W cm}^{-2}$) (Figure 3.20c), shows a smooth and homogeneous surface, with resemblances of the hydronated ZnO films discussed in the previous section. The EDX of the film shows that the atomic % of Al is nearly three times higher than the Ga atomic % confirming the higher incorporation as expected from the difference in the power density applied at each target.

3.2.3. Hydrogenated Indium Zinc Oxide TCOs

The previous section contains the results obtained on the optimisation of the ZnO-based TCOs produced during this PhD work, namely on understanding the role of hydrogen. Nevertheless, the FoM is still not as good as that obtained for ITO. It is known that indium-based TCOs normally present an interesting combination of electro-optical properties, that result from a high carrier mobility [3]. Considering this, in the following section a study and results on the optimisation of another indium-based TCO – IZO, namely the hydrogen incorporation in the electro-optical properties, focusing on its application as a transparent gate electrode in the cellulose-based field effect transistors [61].

Considering the alignment of hydrogen levels for the different semiconductors shown in Figure 3.3, it is possible to realise that it is likely to act as a non-amphoteric impurity in In_2O_3 or indium-based TCOs. In the recent past a lot of works have reinforced this assumption, demonstrating that hydrogen incorporation (e.g. during the sputtering process or even in post-deposition treatments) leads to the improvement of mobility and near-infrared transparency of In_2O_3 [62], [63].

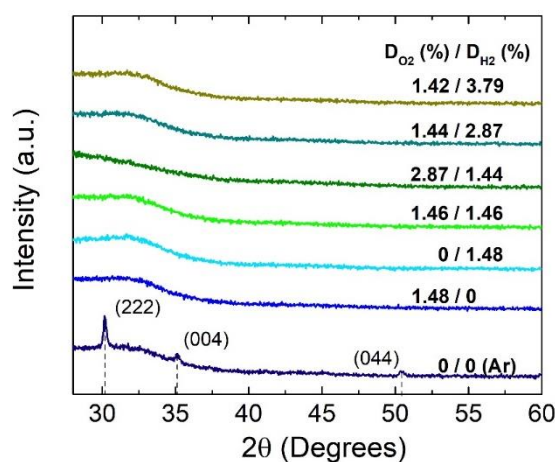
During this PhD the interest was on the influence of hydrogen in amorphous In_2O_3 -ZnO (IZO) thin films deposited by rf reactive magnetron sputtering at room temperature, which provide excellent electro-optical properties, even when deposited at room temperature, in contrast to what happened for polycrystalline In_2O_3 based TCOs. The set of hydrogenated IZO (IZO:H) thin films were prepared using a commercial target with a composition of In_2O_3 :ZnO 89.3:10.7 wt.%, using Ar, O_2 and H_2 in the sputtering gas mixture. The experimental conditions of the RT sputtered IZO:H are listed in Table 3.6.

Table 3.6 Deposition conditions of IZO thin films by rf reactive magnetron sputtering.

D_{O_2} (%)	D_{H_2} (%)	O_2 flow (sccm)	H_2 flow (sccm)	Ar flow (sccm)	Working pressure (Pa)	Power density (W cm ⁻²)
0	0	0	0			
1.48	0	0.3	0			
0	1.48	0	0.3			
1.46	1.46	0.3	0.3	20	0.3	2.2
2.87	1.44	0.6	0.3			
1.44	2.87	0.3	0.6			
1.42	3.79	0.3	0.8			
$D_{O_2}=O_2$ flow / (Ar+H ₂ +O ₂) flow				$D_{H_2}=H_2$ flow / (Ar+H ₂ +O ₂) flow		

3.2.3.1. Structure and morphology

IZO is often reported in the literature as an amorphous TCO, where crystallisation can be induced through annealing treatments or when deposited above 300°C [2], [64]. The diffractograms of the hydrogenated IZO films reveal an amorphous structure, regardless of the reactive sputtering conditions used. For the films sputtered in inert conditions (D_{O_2} and D_{H_2} equal to 0%) it is possible to find three small peaks, suggesting a crystalline arrangement in the film. The films exhibit a more intense peak for $2\theta \approx 30.16^\circ$, which is consistent with the (222) plane of the In_2O_3 cubic structure (*bixbyite*) with a corresponding crystallite size of 35.3 nm (determined by Scherrer formula). A second peak with a lower intensity near 35.10° corresponds to the plane (004), while the plane (044) appears for $2\theta \approx 50.41^\circ$ (ICDD n° 98-008-9095).

Figure 3.21 Diffractograms of the sputtered IZO:H films prepared with different D_{O_2} and D_{H_2} .

The films deposited only with Ar, present a smooth uniform surface (rms roughness of 1.2 nm) formed by small grains, most likely of In_2O_3 (crystalline phase identified by XRD) with an approximate size of 20 to 25 nm (Figure 3.22a and b). When either O_2 or H_2 (or both) are added to the sputtering gas mixture, the films become amorphous.

The surface is again smooth and homogenous but with some randomly dispersed agglomerates which contribute to an increase in roughness, (rms between 2.4 and 3.6 nm).

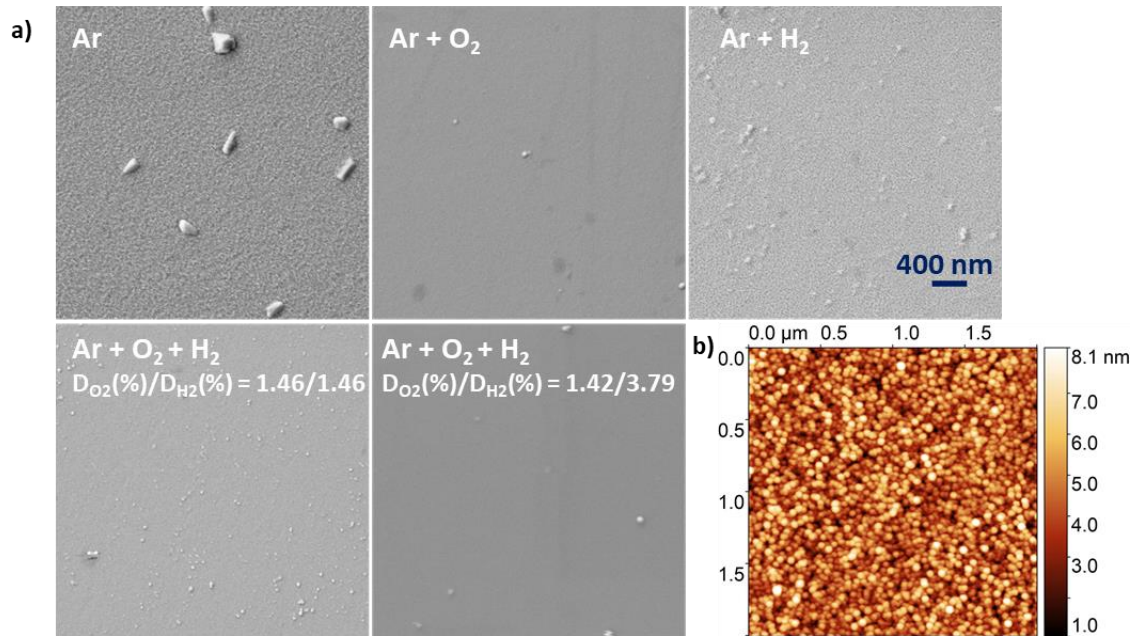


Figure 3.22 a) SEM micrographs of the IZO thin films produced under different sputtering atmospheres (Ar and five different reactive atmospheres), and b) AFM image of the Ar sputtered IZO film.

3.2.3.2. Electrical and optical properties

According to the deposition parameters, the mobility of the films can be very high combined with excellent optical properties. The spectrum of the properties achieved is mostly due to the oxygen dilution during the sputtering process. Despite the undeniable relevance, the aim of this work was the study of the hydrogen and its combination with O_2 in the thin films.

The study of the electro-optical properties was focused on three sputtering conditions: only with Ar, $\text{Ar}+\text{O}_2$, and $\text{Ar}+\text{H}_2$. The $\text{IZO}:\text{H}$ thin films present, as expected, an n-type conductivity and the introduction of a small amount of oxygen ($\text{D}_{\text{O}_2} \approx 1.5\%$) leads to a substantial decrease of the resistivity from 1.11×10^{-3} to $6.69 \times 10^{-4} \Omega \text{ cm}$, where μ_{H} increases nearly four times reaching $\approx 51 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Figure 3.23a and b). Nevertheless, the n is lower when O_2 is present (Figure 3.23c). That is attributed to the annihilation of V_{O} that are

one of the origins of free electrons ($O^{2-}=1/2O_{2g} + 2e$) [5]. The V_O compensation is corroborated by the improvement of optical transmittance of the oxygenated films, that have an AVT $\approx$ 80% whereas for the Ar this value is only 23% (Figure 3.24a).

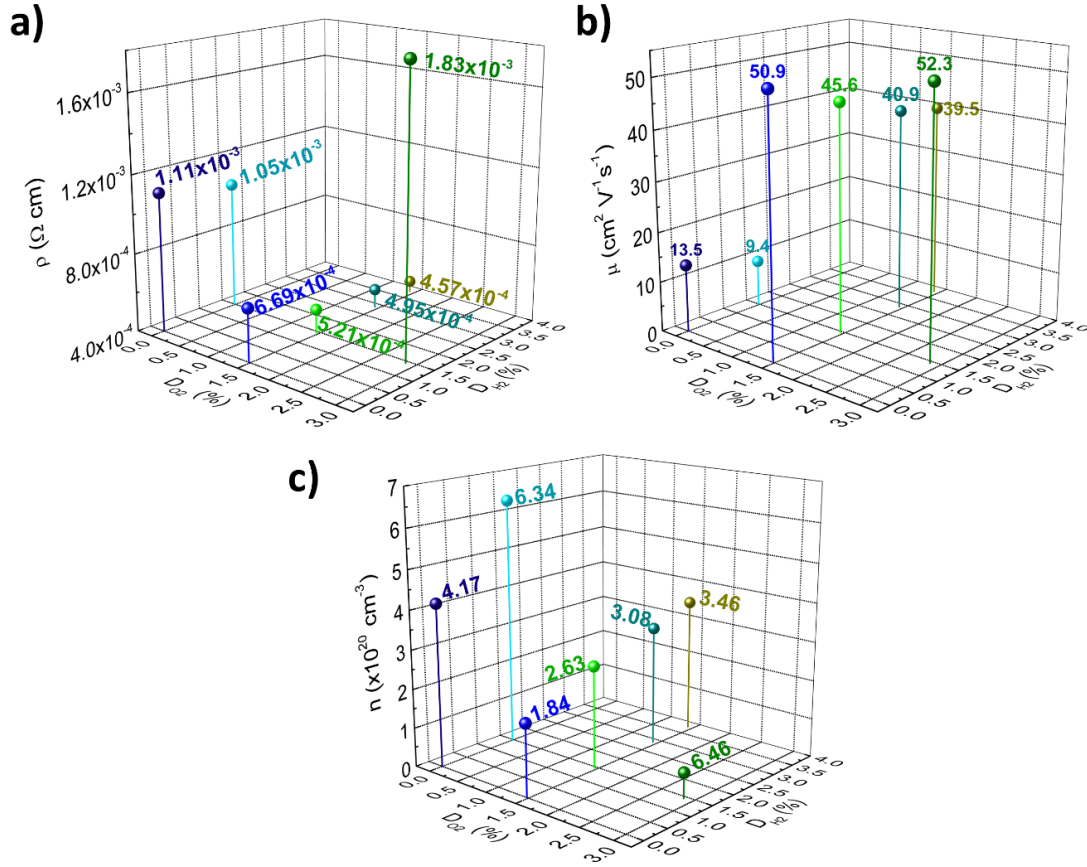


Figure 3.23 Influence of the deposition conditions on the IZO:H thin films' electrical parameters: a) resistivity, b) mobility, and c) carrier concentration.

As mentioned before, in theory, the interaction of the hydrogen with the In_2O_3 would enhance the conductivity since the positioning of hydrogen $\epsilon(+/-)$ is above the conduction band minimum, being expected to behave as a shallow donor [22]. As a first approach, the same assumption can be made for IZO:H thin films. In fact, the films deposited with Ar+H₂ show a slightly lower resistivity ($1.05 \times 10^{-3} \Omega \text{ cm}$ vs $1.11 \times 10^{-3} \Omega \text{ cm}$) and a larger carrier concentration ($n = 6.34 \times 10^{20} \text{ cm}^{-3}$ vs $4.17 \times 10^{20} \text{ cm}^{-3}$) than the films produced only with Ar (Figure 3.23 a and c).

In contrast to what happens for ZnO, the introduction of H₂ to the sputtering atmosphere of IZO does not improve the AVT ($\approx 20 - 23\%$) (Figure 3.24a), indicating that hydrogen itself does not passivate the V_O in the IZO films. However, a substantial increase in the free electron density exposes the shallow donor role of the hydrogen in the IZO, as previously

suggested. Another detail worthwhile to mention is the lowest μ measured for the conditions tested (Figure 3.23b); this is deeply related with the existence of many V_O which act as additional scattering centres for free charge carriers.

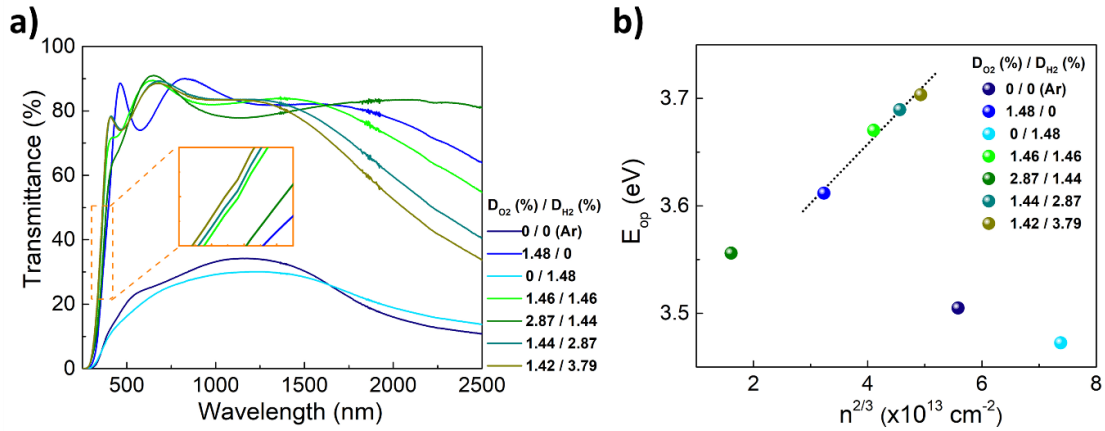


Figure 3.24 a) Optical transmittance of the IZO:H films, and b) E_{op} as a function of the $n^{2/3}$, according to the Burstein-Moss effect. (The lines are guide for the eyes.)

The individual influence of O_2 and H_2 in the sputtering atmosphere allow to comprehend two distinct characteristics: i) oxygen is responsible for the compensation of V_O generated during the sputtering process, and ii) hydrogen does not compensate (all) the V_O in the IZO, acting as a shallow donor and enhancing the electrical conductivity.

The combination of both oxygen and hydrogen during the sputtering process is inadequately explored neither reported. Considering the assumptions mentioned above, several combinations of $D_{O_2}+D_{H_2}$ were tested. For a $D_{O_2} \approx 1.5\%$, the introduction of H_2 leads to improvement of the optical and electrical properties. The variation of D_{H_2} from 0% to a maximum of 3.79%, results in a monotonic reduction of ρ from $6.69 \times 10^{-4} \Omega \text{ cm}$ down to a minimum of $4.57 \times 10^{-4} \Omega \text{ cm}$ (Figure 3.23a). As expected, n is sensitive to the D_{H_2} , reaching nearly twice the value measured in the films deposited with $D_{O_2} \approx 1.5\%$ and $D_{H_2} = 0\%$ (Figure 3.23c).

The AVT for this set of films is almost insensitive to different D_{H_2} ($AVT_{O_2} \approx 80\%$ and $AVT_{O_2+H_2} \approx 83\%$). Nevertheless, in the near infrared region it is possible to see a progressive decrease of the transmittance with D_{H_2} related to an increase in free charge carriers. According to the Drude's theory for free electrons in metals and classical interaction with electromagnetic radiation, a transition from transparent to reflective occurs at the plasma frequency (ω_p) or plasma wavelength (λ_{pl}) [4], [5]. Due to degeneration of the IZO (and from most of the TCOs) the Drude's theory can be applied, being possible to relate its

optical transmittance with electrical properties, such as n , through the relation $\lambda_{pl} \propto n^{-1/2}$. Thus, it is possible to corroborate the decrease of the NIR transmittance with the increase of n and subsequently in the shift of λ_{pl} to lower wavelengths (Figure 3.24a).

In the near UV region, a blue-shift of the absorption edge from 269 to 254 nm occurs with the addition of D_{H_2} , resulting in an increase of the E_{op} from 3.61 to 3.70 eV. This suggests the existence of a Burstein-Moss effect (inset of Figure 3.24a), which is confirmed by the approximately linear relation of the optical band gap vs $n^{2/3}$ of the films produced with fixed $D_{O_2} \approx 1.5\%$ and $1.46\% \leq D_{H_2} \leq 3.79\%$, shown in Figure 3.24b (dashed line).

3.2.3.3. Electrical properties of IZO:H on different substrates

Since the films are intended to be used on cellulose membranes it was required to verify the electrical properties of the IZO:H on this kind of substrates. Thus, IZO:H thin films were deposited on glass, nanofibrillated cellulose (NFC), sodium-doped nanofibrillated cellulose (NFC:Na), and commercial standard paper (CSP) in the same run. Although the characteristics of these cellulose-based substrates will be addressed in more detail in Chapter 4 and 5 it is important to highlight right now some differences in order to better understand the results obtained for the IZO:H. The NFC and NFC:Na consist in thin and compact membranes formed by nanocellulose fibres (nanoscale) with an RMS roughness in the order of 40-60 nm, while the CSP is thicker ($\approx 75 \mu m$), porous and formed by microscale fibres with high surface roughness ($\approx 5 \mu m$). This justifies why the electrical properties of IZO:H deposited on NFC and NFC:Na membranes are remarkably similar to those obtained on glass (Figure 3.25).

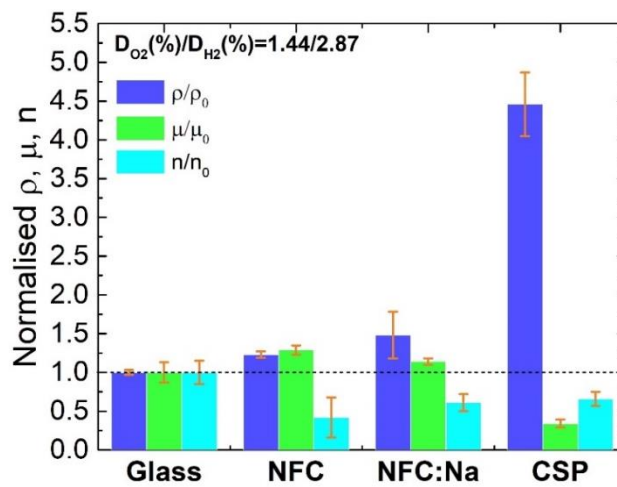


Figure 3.25 Normalised electrical parameters of IZO:H deposited on glass, nanofibrillated cellulose (NFC), sodium-doped NFC (NFC:Na) and commercial standard paper (CSP) with $D_{O_2}/D_{H_2} = 1.44\%/2.87\%$.

In both cases there is a reduction on the free carriers' concentration, assumed to result from passivation of oxygen vacancies, that is balanced by the increase in the mobility since it is in a regime controlled by ionised impurity scattering.

On the other hand, the rough surface of the CSP lead to inferior electrical properties of the IZO:H films. Despite a good step coverage of the fibres, the significative difference between the microscale roughness and the IZO:H layer (thickness < 200 nm) affects the continuity of the film, although it is still possible to have percolation. Consequently, both carrier concentration and mobility decreases to about 25% and 70%, respectively, of the values measured on glass, resulting in an increase in the resistivity to values in the range of $10^{-3} \Omega \text{ cm}$, Nevertheless these values still allow the use of IZO:H used as gate electrodes in FETs on CSP substrates.

3.2.3.4. *Chemical state and composition*

The XPS is a powerful and useful tool to evaluate modifications of the chemical state and composition of the IZO thin films with the incorporation of O_2 and H_2 during the deposition. The Zn $2p_{3/2}$ peak in IZO films is properly reported elsewhere [33]. In this case, its position (Zn $2p_{3/2} \approx 1022 \text{ eV}$) is insensitive to the used D_{H_2} , allowing to conclude that no significant modifications on the chemical state of the Zn occur (Figure 3.26a). Moreover, regardless of the sputtering atmosphere, the full width at half maximum of the Zn $2p_{3/2}$ peak is nearly the same (FWHM $\approx 1.84 \text{ eV}$) suggesting that the formation of different species do not occur. Since this peak does not move towards lower binding energies, it is possible to conclude that in the samples, deposited with Ar and $\text{Ar}+\text{H}_2$ (those with low AVT), no metallic Zn formation occurs (also confirmed in XRD). Similarly, to what happens with the Zn 2p peak, no significant changes are observed for the In $3d_{5/2}$ peak; this particular peak corresponds to the bonding of In^{3+} and O [65], [66]. Thus, it is also possible to assume that H_2 does neither modify the In-O bonding nor induces the formation of new species with lower valence, as the In^{2+} or In^0 [67], in the IZO:H films (Figure 3.26b).

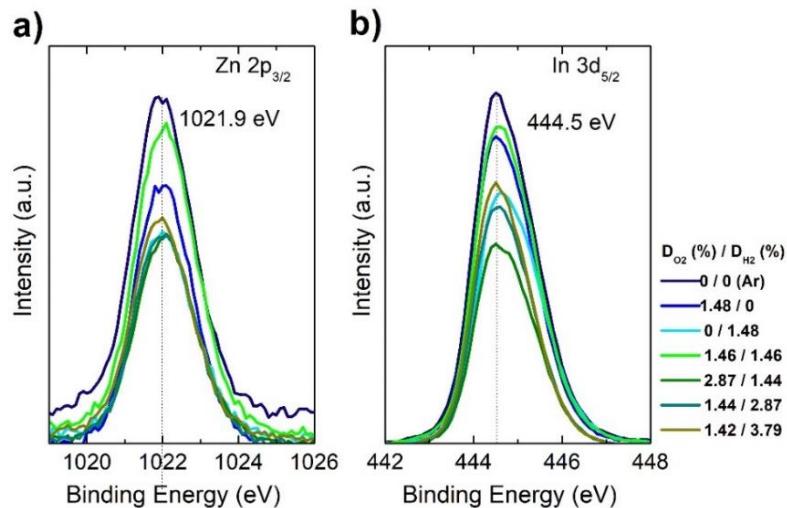


Figure 3.26 XPS spectra for IZO:H films processed without and with different H_2 dilution: a) $Zn\ 2p_{3/2}$, and b) $In\ 3d_{5/2}$ XPS spectra.

The O 1s band can be used to disclose how the O_2 and the H_2 interact with the IZO matrix. As previously mentioned, (section 3.2.1.3), the O 1s is typically developed into three sub-peaks: O_I , O_{II} and O_{III} . In the IZO the first is related to O^{2-} ions of metal-O bonds, on other words, it is related to the fully coordinated oxygen. For all the films this peak is centred at 530.1 eV, nevertheless the differences in the sub-peak areas exposed differences in the oxygen coordination depending on the sputtering condition (Figure 3.27). The films produced only with Ar and $Ar+H_2$ have lower sub-peak areas ($\approx 58\%$ and $\approx 55\%$, respectively), and consequently are the ones with lower oxygen coordination, a fact that can be easily understood due to the absence of oxygen during deposition (Figure 3.27a and c). On the other hand, the condition with $Ar+O_2$ leads to films where the oxygen coordination is higher (Figure 3.27b), which is slightly reduced in the films produced simultaneously with O_2 and H_2 . Based on previously reported works, hydrogen incorporation in IZO should result in an abrupt decrease of the area related with O_{II} , which is associated with O^{2-} ions in oxygen-deficient regions. However, it is not possible to establish a parallelism between IZO and other TCOs where ZnO is the base of the lattice. For instance, in pure ZnO or for ZTO (atomic ratio 1:1) a significant reduction of V_O density is observed when hydrogen is introduced during the deposition [68], [69].

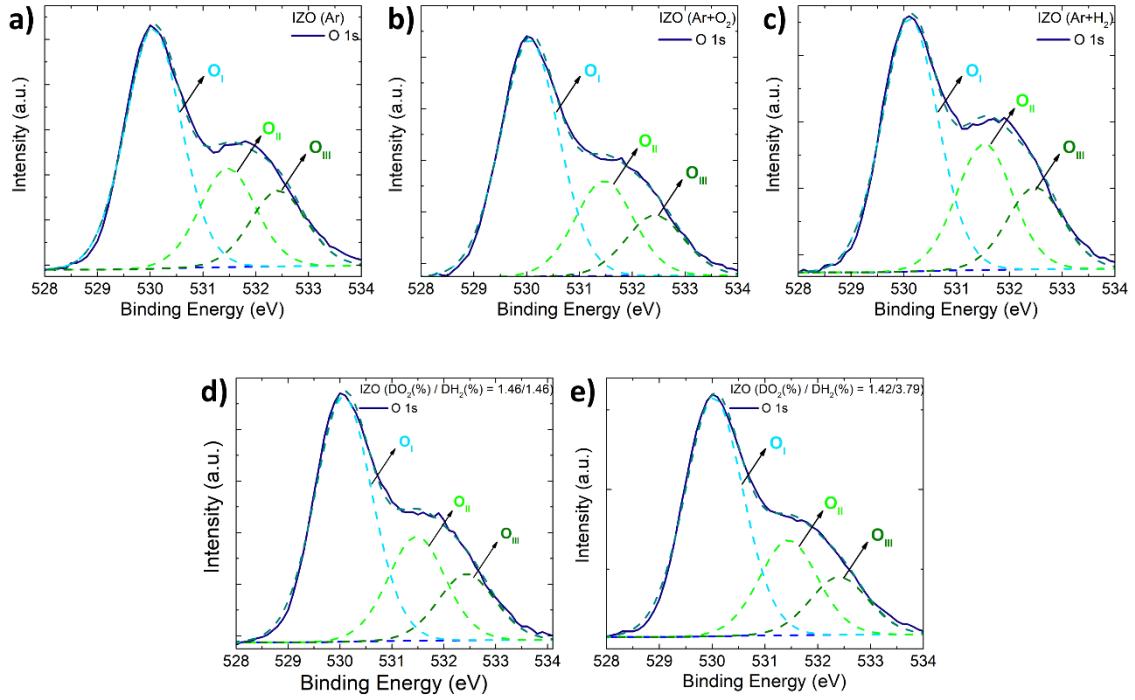


Figure 3.27 XPS spectra of O 1s peak for IZO produced under atmosphere of a) Ar, b) Ar + O₂, c) Ar + H₂, d) and e) Ar + O₂ + H₂, with D_{O2}(%)/D_{H2}(%) = 1.46/1.46 and 1.42/3.79, respectively.

Modifications on the ratio of the sub-peak area O_{II}/O_I for each film can be indicative for the relative V_O [70], [71]. In this study the ratio O_{II}/O_I slightly decrease from 42.5% to 39.8% when D_{H2} changes from 1.46% to 3.79%, with a fixed D_{O2} ≈ 1.5% (Figure 3.27d and e). Based on this, it is expected that V_O, assumed as a source of free carriers, decreases with the introduction of H₂. Using the same line of thought, it is possible to relate the decrease in the V_O density with the optical properties of the films. For instance, the addition of O₂ into the sputtering atmosphere leads to transparent films, which is often reported as a sign of compensation of oxygen deficiency, resulting from the sputtering deposition. This agrees well with the information obtained from the O 1s peak since it has been found that the ratio O_{II}/O_I for the Ar films is ≈42%, whereas for the Ar+O₂ is ≈40%, which agrees with what was stated in section 3.2.3.2.

A final consideration should be made regarding the films produced with the Ar+H₂ mixture. Under this condition, the O_{II} area is the largest, which can be explained by a lack of oxygen during the deposition, inducing the formation of V_O and sub-stoichiometric species, as discussed above.

At higher binding energies it is possible to find information related to weakly bonded oxygen, including absorbed O₂, H₂O, or -CO₃. Although the difference is not high, films

prepared with Ar, and the Ar+H₂ mixture present the largest sub-peak area (18.3% and 17.8%, respectively), which is indicative for the largest amount of other negatively charged oxygen species on the IZO surface (Figure 3.27a and c).

3.3.Semiconductor oxide thin films

3.3.1. IGZO system

IGZO deposited by rf sputtering is a well-established technology at CENIMAT/I3N for both rigid and flexible substrates, such as glass, silicon, PEN, PET and polyimide. The holistic study made by P. Barquinha provides a high-level overview on the influence of compositional and processing conditions on the properties of amorphous IGZO [1]. This was used as a reference for the implementation of IGZO FET on cellulose membranes.

Due to the difference between conventional substrates and cellulose-based ones, here the focus was on defining the best deposition conditions and optimal thickness of the IGZO layer in order to get the best performance in the cellulose-based FETs. Structure and morphology.

During this PhD a commercial target of the ternary multicomponent system with the composition In₂O₃–Ga₂O₃–ZnO 1:2:2 mol% (IGZO 1:2:2) was used. The films were deposited by radio-frequency magnetron sputtering, at room temperature, in an AJA ORION system. The influence of the oxygen dilution ($D_{O_2} = O_2 \text{ flow} / (Ar+O_2) \text{ flow}$) was studied, varying it from 0 to 3 sccm, which corresponds to D_{O_2} of 0, 6.8, 12.5, and 17.6%, in order to reach the best electrical performance for FETs.

IGZO is vastly reported in the literature as amorphous up to 500 °C [1], [72]. Thus, it is not surprising that the films produced for this study have an amorphous structure, (Figure 3.28a) even after a post-deposition annealing step at 150 °C. The amorphous character of the IGZO films leads to a highly smooth surface with some embedded agglomerates (Figure 3.28b), resulting in an RMS roughness of 2.12 nm (on glass) measured by AFM (Figure 3.28c). This is always lower than the roughness of the different cellulose membranes used in this PhD work, meaning it will be not a limitation factor on optimal coverage of such substrates.

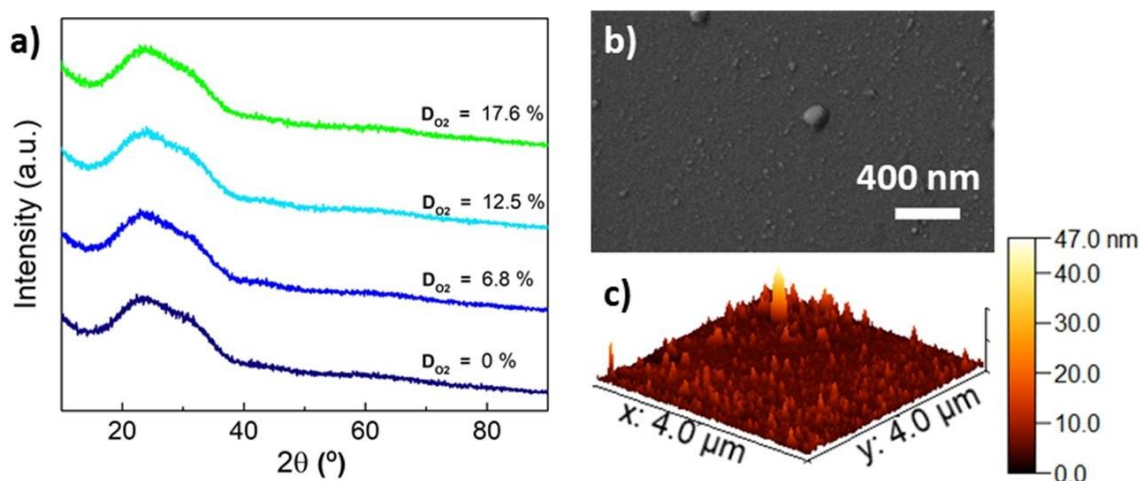


Figure 3.28 a) XRD diffractograms of the sputtered IGZO 1:2:2 for the different D_{O_2} tested. b) Micrograph and c) AFM 3D topography of the IGZO 1:2:2 produced with $D_{O_2}=17.6\%$.

3.3.1.1. Optical and electrical properties

The variation of the O_2 content in the sputtering atmosphere mixture does not affect the optical properties of the IGZO. The films present high transmittance in the entire visible range, which is basically unaffected by the different oxygen amounts used during the deposition (Figure 3.29a). However, in the Tauc plots (α^2-E) it is possible to verify that the optical bandgap increases monotonically with D_{O_2} , changing from 3.68 eV for a pure Ar sputtering atmosphere up to 3.79 eV for the films produced with $D_{O_2}=17.6\%$ (Figure 3.29a). The widening of E_{op} can be related to two factors: on the one hand, the addition of oxygen will compensate oxygen deficiency defects resulting in a higher E_{op} . On the other hand, the different reactive atmospheres lead to films with a different atomic concentration ratio of Zn, Ga and In. The atomic concentration of those elements in the films slightly increases with D_{O_2} (Figure 3.29b). A larger concentration of Ga and In, leads to the broadening of E_{op} since Ga_2O_3 (4.16 eV) and In_2O_3 (3.5-3.7 eV) have larger E_{op} , which is the characteristic reflected in the optical bandgap of the deposited IGZO films [1], [5], [7].

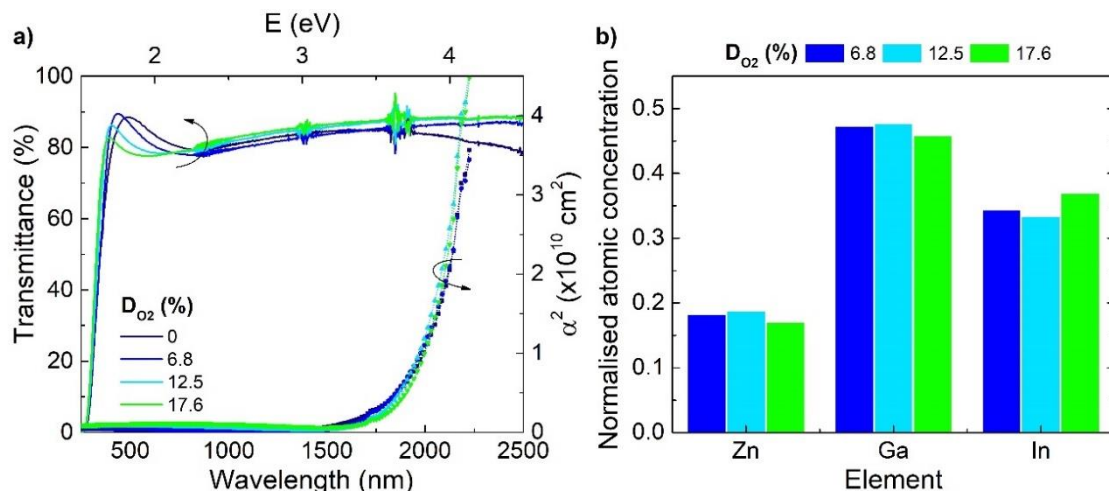


Figure 3.29 a) Optical characterisation (optical transmittance and α^2 -E plots) of the IGZO thin films produced with different O₂ dilutions. b) Normalised atomic concentration of zinc, gallium and indium (excluding oxygen) in the IGZO thin films produced with different reactive atmospheres.

The dependence of the dark conductivity of IGZO as a function of the temperature was measured by depositing two aluminium electrodes with a width of 2330 μm and a separation of 210 μm . This allowed the evaluation of the thermal activation energy (E_a), that can be understood as the energy required for the carriers to overcome the potential barrier, in this case, the energy difference between the Fermi level and the conduction band of the semiconductor [73]. This is relevant for the selection of the most suitable deposition conditions to be implemented in transistors on cellulose membranes.

The conductivity of the films deposited in pure Ar atmosphere show no temperature dependency, being around $4 \times 10^2 \text{ S cm}^{-1}$ and suggesting a relatively high free carrier density. However, for the thin films deposited with oxygen, it is possible to verify a linear increase of the logarithm of the conductivity as a function of the reciprocal temperature, indicating the presence of a thermally activated conduction mechanism typical of a semiconductor material (E_a : 0.29 – 0.33 eV) (Figure 3.30). In the IGZO thin films it is expected that the primary source of free electrons is from oxygen vacancies (V_{O}^{2+}). The addition of oxygen during the deposition will compensate/fill those defects, and consequently, the electrical conductivity will be affected.

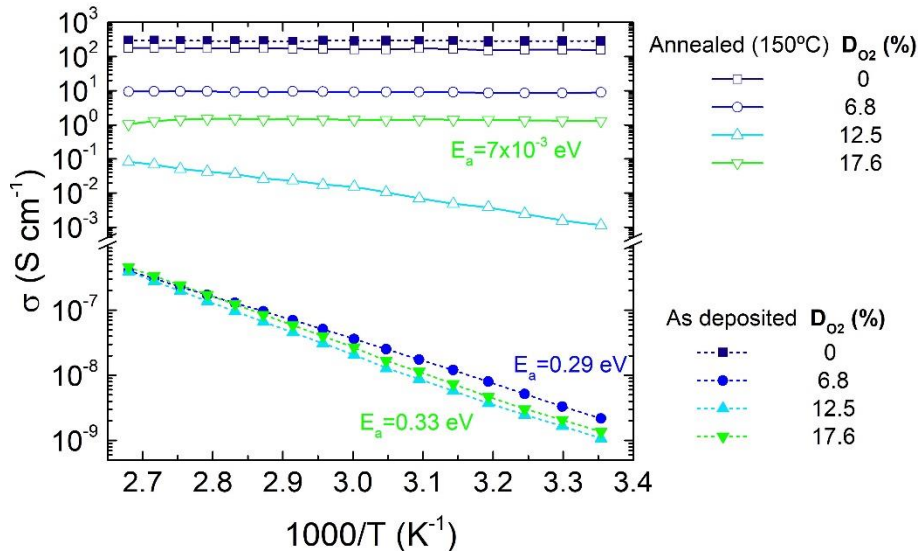


Figure 3.30 Arrhenius plot of electrical conductivity dependence as a function of the temperature, used to determine the thermal activation energy the IGZO thin films for the different D_{O_2} .

The thermal dependency of the conductivity in IGZO films deposited with oxygen is partially lost after annealing at 150 °C in air, while the films also become more conductive, which is more notorious for the lowest D_{O_2} used. The films deposited with D_{O_2} =12.5% still show thermal activation (E_a =0.23 eV) and a conductivity at room temperature of around 10^{-3} S cm $^{-1}$. However, the conductivity of IGZO films sputtered with the highest amount of oxygen (D_{O_2} =17.6%) show no thermal activation after annealing. The EDX analysis reveals an explanation for this behaviour, since the normalized atomic content of Zn/Ga/In is modified (Figure 3.29b). The films become In richer, which leads to an increase of free carriers and electrical conductivity after annealing, when compared with the ones deposited with D_{O_2} =12.5%. This means that the Fermi level in these films is getting closer to the conduction band edge or on the percolation limit [74].

3.3.1.2. IGZO-based FETs

The oxygen dilution has a tremendous influence on the electrical properties of the IGZO thin films. It is known that even the base pressure defined for the deposition of the semiconductor layer will have a great impact on the electrical performance of the FETs due to the presence of residual oxygen [1], [7]. To check this, FETs were produced by depositing ≈ 15 nm thick IGZO layers on nanofibrillated-cellulose membranes (that will have further discussion in Chapter 5) without any intentional substrate heating. The deposition pressure and power density on the target were 0.3 Pa and 4.9 W cm $^{-2}$, respectively, using a base pressure of 7×10^{-5} Pa. The IGZO was patterned by using metallic

shadow masks during the deposition. After the aluminium source and drain contacts deposition and patterning (also using shadow masks), the devices were annealed at 150 °C.

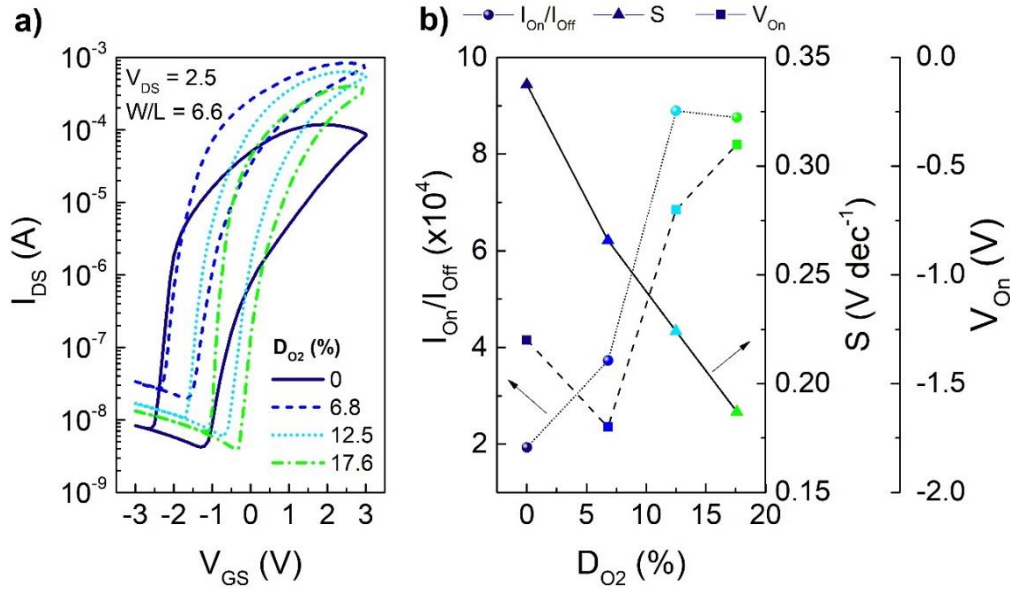


Figure 3.31 Effect of the D_{O_2} on the transfer characteristics of the IGZO FETs on paper annealed at 150 °C: a) I_{DS} - V_{GS} transfer characteristic, and b) I_{ON}/I_{OFF} , S , and V_{ON} .

Observing the transfer characteristics (Figure 3.31a) of the devices, it is possible to see that the turn-on voltage (V_{ON}) is shifted towards positive values with an increase of D_{O_2} . The conductivity in IGZO thin films deposited with more oxygen is lower, and still thermally activated, justifying the higher V_{ON} . On the other hand, the subthreshold slope decreases with D_{O_2} , meaning a less defective semiconductor layer and better interface with the cellulose membrane. This is attributed to the reduction of shallow donor defects (V_O^{2+}) densities, which is in line with what was discussed previously. Regardless of the D_{O_2} used the hysteresis (≈ 1 V) of the devices is nearly the same, while the FETs with an IGZO deposited only with Ar have the largest hysteresis. This effect should be related with non-passivated dominant donor-like traps that may exist in the interface semiconductor/dielectric [75]. With the introduction of O_2 in the sputtering gas, the traps will be (fully or partially) passivated, and thus the hysteresis will be mostly ruled by the nature of the dielectric.

The FETs produced with a reactive atmosphere had a better current modulation (higher I_{ON}/I_{OFF}) in the FETs (Figure 3.31b). As V_{GS} increases, the accumulated charges will firstly compensate some defects, as unfilled traps (both at the interface and in the semiconductor) and bringing it to the conduction band, which will be more effective when the trap density is reduced. This also has a positive effect on the saturation mobility.

The FETs with an IGZO deposited only with Ar, present the worst electrical performance with the lowest current modulation and highest S , which is attributed to the defect density. Although the high conductivity, it is still possible to modulate their conductance when used as a channel in the FETs. It is worth to remind that the thickness of the IGZO is very small and that the channel layer is partially depleted due to surface effects. Consequently, it is still possible to compensate this depletion along the IGZO through the V_{GS} and thus modulate the current that flows in the devices. Considering all these factors, the IGZO deposition condition with the highest D_{O_2} was chosen as the reference for the devices that will be presented in the following chapters.

3.4. References

- [1] P. M. C. Barquinha, “Transparent Oxide Thin-Film Transistors: production, characterization and integration,” Universidade Nova de Lisboa, 2010.
- [2] D. Ginley, H. Hosono, and D. C. Paine, Eds., *Handbook of Transparent Conductors*, 1st ed. New York, NY: Springer New York, 2010.
- [3] E. Fortunato, D. Ginley, H. Hosono, and D. C. Paine, “Transparent Conducting Oxides for Photovoltaics,” *MRS Bull.*, vol. 32, no. March, pp. 242–247, 2007.
- [4] H. L. Hartnagel, A. L. Dawar, A. K. Jain, and C. Jagadish, Eds., *Semiconducting Transparent Thin Films*, 1st ed. London: CRC Press, 1995.
- [5] G. P. Gonçalves, “Filmes finos de óxido de índio e zinco e sua aplicação em díodos orgânicos emissores de luz,” Universidade Nova de Lisboa, 2011.
- [6] A. Facchetti and T. Marks, Eds., *Transparent Electronics: From Synthesis to Applications*, 1st ed. West Sussex: John Wiley & Sons Ltd, 2010.
- [7] P. Barquinha, R. Martins, L. Pereira, and E. Fortunato, *Transparent Oxide Electronics*. Wiley, 2012.
- [8] J. F. Wager, D. A. Keszler, and R. E. Presley, Eds., *Transparent Electronics*, 1st ed. Springer US, 2008.
- [9] E. Fortunato, P. Barquinha, and R. Martins, “Oxide semiconductor thin-film transistors: a review of recent advances,” *Adv. Mater.*, vol. 24, no. 22, pp. 2945–86, Jun. 2012.
- [10] C. G. Van de Walle, “Hydrogen as a Cause of Doping in Zinc Oxide,” *Phys. Rev. Lett.*, vol. 85, no. 5, pp. 1012–1015, Jul. 2000.
- [11] L.-Y. Chen, W.-H. Chen, J.-J. Wang, F. C.-N. Hong, and Y.-K. Su, “Hydrogen-doped high conductivity ZnO films deposited by radio-frequency magnetron sputtering,” *Appl. Phys. Lett.*, vol. 85, no. 23, p. 5628, 2004.
- [12] S. J. Pearton, D. P. Norton, M. P. Ivill, A. F. Hebard, J. M. Zavada, W. M. Chen, and I. A. Buyanova, “ZnO doped with transition metal ions,” *IEEE Trans. Electron Devices*, vol. 54, no. 5, pp. 1040–1048, 2007.
- [13] E. Fortunato, A. Gonçalves, A. Pimentel, P. Barquinha, G. Gonçalves, L. Pereira, I. Ferreira, and R. Martins, “Zinc oxide, a multifunctional material: From material to device applications,” *Appl. Phys. A Mater. Sci. Process.*, vol. 96, no. 1, pp. 197–205, Jan. 2009.
- [14] A. Pimentel, E. Fortunato, A. Gonçalves, A. Marques, H. Águas, L. Pereira, I.

- Ferreira, and R. Martins, "Polycrystalline intrinsic zinc oxide to be used in transparent electronic devices," *Thin Solid Films*, vol. 487, no. 1–2, pp. 212–215, 2005.
- [15] A. Lyubchyk, A. Vicente, B. Soule, P. U. Alves, T. Mateus, M. J. Mendes, H. Águas, E. Fortunato, and R. Martins, "Mapping the Electrical Properties of ZnO-Based Transparent Conductive Oxides Grown at Room Temperature and Improved by Controlled Postdeposition Annealing," *Adv. Electron. Mater.*, vol. 2, no. 1, p. 1500287, Jan. 2016.
- [16] D. Norton, Y. Heo, M. Ivill, and K. Ip, "ZnO: growth, doping & processing," *Mater. today*, vol. 7, no. 6, pp. 34–40, 2004.
- [17] A. Janotti and C. G. Van de Walle, "Fundamentals of zinc oxide as a semiconductor," *Reports Prog. Phys.*, vol. 72, no. 12, p. 126501, Dec. 2009.
- [18] A. Janotti, J. B. Varley, J. L. Lyons, C. G. Van De Walle, Y. Yang, J. W. Choi, and Y. Cui, *Functional Metal Oxide Nanostructures*, 1st ed., vol. 149. New York, NY: Springer New York, 2012.
- [19] C. W. Litton, T. C. Collins, and D. C. Reynolds, Eds., *Zinc Oxide Materials for Electronic and Optoelectronic Device Applications*, 1st ed., vol. 37, no. 3. West Sussex: John Wiley and Sons Ltd, 2011.
- [20] E. V Monakhov, a Y. Kuznetsov, and B. G. Svensson, "Zinc oxide: bulk growth, role of hydrogen and Schottky diodes," *J. Phys. D. Appl. Phys.*, vol. 42, no. 15, p. 153001, 2009.
- [21] C. G. Van De Walle, "Universal alignment of hydrogen levels in semiconductors and insulators," in *Physica B: Condensed Matter*, 2006.
- [22] C. G. Van De Walle, "Universal alignment of hydrogen levels in semiconductors and insulators," *Phys. B Condens. Matter*, vol. 376–377, no. 1, pp. 1–6, 2006.
- [23] D. G. Thomas and J. J. Lander, "Hydrogen as a Donor in Zinc Oxide," *J. Chem. Phys.*, vol. 25, no. 6, p. 1136, 1956.
- [24] B. L. Zhu, J. Wang, S. J. Zhu, J. Wu, R. Wu, D. W. Zeng, and C. S. Xie, "Influence of hydrogen introduction on structure and properties of ZnO thin films," *Thin Solid Films*, vol. 519, no. 11, pp. 3809–3815, Mar. 2011.
- [25] S. Y. Myong, K. S. Lim, and S. Y. M. Å, "Alternate deposition and hydrogen doping technique for ZnO thin films," *J. Cryst. Growth*, vol. 293, no. 2, pp. 253–257, Aug. 2006.
- [26] C. F. Windisch, G. J. Exarhos, C. Yao, and L.-Q. Wang, "Raman study of the influence of hydrogen on defects in ZnO," *J. Appl. Phys.*, vol. 101, no. 12, p. 123711, 2007.
- [27] L. Zhao, G. Shao, S. Song, X. Qin, S. Han, Q. Song, S. Xiujuan, and S. Han, "Development on transparent conductive ZnO thin films doped with various impurity elements," *Rare Met.*, vol. 30, no. 2, pp. 175–182, Mar. 2011.
- [28] F. Ruske, V. Sittinger, W. Werner, B. Szyszka, K. U. van Osten, K. Dietrich, and R. Rix, "Hydrogen doping of DC sputtered ZnO:Al films from novel target material," *Surf. Coatings Technol.*, vol. 200, no. 1–4 SPEC. ISS., pp. 236–240, 2005.
- [29] A. Bikowski and K. Ellmer, "Electrical transport in hydrogen-aluminium Co-doped ZnO and Zn_{1-x}Mg_xO films: Relation to film structure and composition," *J. Appl. Phys.*, vol. 113, no. 5, p. 053710, 2013.
- [30] C.-L. Yeh, S.-Z. Tseng, W.-T. Lin, C.-C. Kuo, and S.-H. Chen, "Thermal Stability of Hydrogen-Doped Zinc-Oxide Thin-Films," *Electrochem. Solid-State Lett.*, vol. 15, no. 1, p. H14, 2012.
- [31] A. Bogaerts, "Hydrogen addition to an argon glow discharge: a numerical simulation," *J. Anal. At. Spectrom.*, vol. 17, no. 8, pp. 768–779, 2002.

- [32] P. Saikia, B. K. Saikia, and H. Bhuyan, "Study on the effect of hydrogen addition on the variation of plasma parameters of argon-oxygen magnetron glow discharge for synthesis of TiO₂ films," *AIP Adv.*, vol. 6, no. 4, 2016.
- [33] F.-H. Wang, H.-P. Chang, C.-C. Tseng, and C.-C. Huang, "Effects of H₂ plasma treatment on properties of ZnO:Al thin films prepared by RF magnetron sputtering," *Surf. Coatings Technol.*, vol. 205, no. 23–24, pp. 5269–5277, Sep. 2011.
- [34] Y.-S. Kang, H.-Y. Kim, and J.-Y. Lee, "Effects of Hydrogen on the Structural and Electro-optical Properties of Zinc Oxide Thin Films," *J. Electrochem. Soc.*, vol. 147, no. 12, p. 4625, 2000.
- [35] S. Kunj and K. Sreenivas, "Residual stress and defect content in magnetron sputtered ZnO films grown on unheated glass substrates," *Curr. Appl. Phys.*, vol. 16, no. 7, pp. 748–756, 2016.
- [36] Y. R. Park, J. Kim, and Y. S. Kim, "Effect of hydrogen doping in ZnO thin films by pulsed DC magnetron sputtering," *Appl. Surf. Sci.*, vol. 255, no. 22, pp. 9010–9014, Aug. 2009.
- [37] P. F. Cai, J. B. You, X. W. Zhang, J. J. Dong, X. L. Yang, Z. G. Yin, and N. F. Chen, "Enhancement of conductivity and transmittance of ZnO films by post hydrogen plasma treatment," *J. Appl. Phys.*, vol. 105, no. 8, p. 083713, 2009.
- [38] N. H. Kim and H. W. Kim, "Room temperature growth of zinc oxide films on Si substrates by the RF magnetron sputtering," *Mater. Lett.*, vol. 58, no. 6, pp. 938–943, Feb. 2004.
- [39] K. Kinoshita, T. Okutani, H. Tanaka, T. Hinoki, H. Agura, K. Yazawa, K. Ohmi, and S. Kishida, "Flexible and transparent ReRAM with GZO memory layer and GZO-electrodes on large PEN sheet," *Solid. State. Electron.*, vol. 58, no. 1, pp. 48–53, Apr. 2011.
- [40] S. Y. Myong and K. S. Lim, "Alternate deposition and hydrogen doping technique for ZnO thin films," *J. Cryst. Growth*, vol. 293, no. 2, pp. 253–257, Aug. 2006.
- [41] G. Haacke, "New figure of merit for transparent conductors," *J. Appl. Phys.*, vol. 47, no. 9, p. 4086, 1976.
- [42] P. Nunes, E. Fortunato, P. Tonello, F. Braz Fernandes, P. Vilarinho, and R. Martins, "Effect of different dopant elements on the properties of ZnO thin films," *Vacuum*, vol. 64, no. 3–4, pp. 281–285, Jan. 2002.
- [43] D. H. Zhang and H. L. Ma, "Scattering mechanisms of charge carriers in transparent conducting oxide films," *Appl. Phys. A Mater. Sci. Process.*, vol. 62, no. 5, pp. 487–492, 1996.
- [44] K. Ellmer and R. Mientus, "Carrier transport in polycrystalline transparent conductive oxides: A comparative study of zinc oxide and indium oxide," *Thin Solid Films*, vol. 516, no. 14, pp. 4620–4627, May 2008.
- [45] R. Martins, P. Barquinha, L. Pereira, I. Ferreira, and E. Fortunato, "Role of order and disorder in covalent semiconductors and ionic oxides used to produce thin film transistors," *Appl. Phys. A*, vol. 89, no. 1, pp. 37–42, Jun. 2007.
- [46] K. Ellmer and R. Mientus, "Carrier transport in polycrystalline ITO and ZnO:Al II: The influence of grain barriers and boundaries," *Thin Solid Films*, vol. 516, no. 17, pp. 5829–5835, 2008.
- [47] J. Y. W. Seto, "The electrical properties of polycrystalline silicon films," *J. Appl. Phys.*, vol. 46, no. 12, pp. 5247–5254, 1975.
- [48] M. D. McCluskey and S. J. Jokela, "Defects in ZnO," *J. Appl. Phys.*, vol. 106, no. 7, pp. 1–13, 2009.
- [49] T. Sekiguchi, N. Ohashi, and Y. Terada, "Effect of Hydrogenation on ZnO Luminescence," *Jpn. J. Appl. Phys.*, vol. 36, no. Part 2, No. 3A, pp. L289–L291,

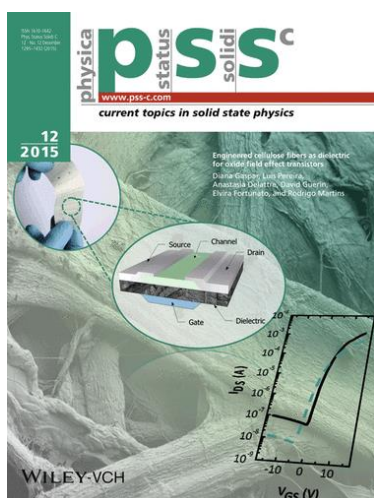
- Mar. 1997.
- [50] A. Dev, R. Niepelt, J. P. Richters, C. Ronning, and T. Voss, “Stable enhancement of near-band-edge emission of ZnO nanowires by hydrogen incorporation,” *Nanotechnology*, vol. 21, no. 6, p. 065709, Feb. 2010.
 - [51] K. Navin and R. Kurchania, “Structural, morphological and optical studies of ripple-structured ZnO thin films,” *Appl. Phys. A*, vol. 121, no. 3, pp. 1155–1161, 2015.
 - [52] B.-Y. Oh, M.-C. Jeong, D.-S. Kim, W. Lee, and J.-M. Myoung, “Post-annealing of Al-doped ZnO films in hydrogen atmosphere,” *J. Cryst. Growth*, vol. 281, pp. 475–480, 2005.
 - [53] Y. Jung, W. Yang, C. Y. Koo, K. Song, and J. Moon, “High performance and high stability low temperature aqueous solution-derived Li–Zr co-doped ZnO thin film transistors,” *J. Mater. Chem.*, vol. 22, no. 12, p. 5390, 2012.
 - [54] J. Kang, H. W. Kim, and C. Lee, “Electrical Resistivity and Transmittance Properties of Al-and Ga-codoped ZnO Thin Films,” *J. Korean Phys. Soc.*, vol. 56, no. 2, pp. 576–579, 2010.
 - [55] D. Sun, C. Tan, X. Tian, and Y. Huang, “Comparative study on ZnO monolayer doped with Al, Ga and in atoms as transparent electrodes,” *Materials (Basel)*, vol. 10, no. 7, 2017.
 - [56] C.-C. Chen and H.-C. Wu, “Electronic Structure and Optical Property Analysis of Al/Ga-Codoped ZnO through First-Principles Calculations,” *Materials (Basel)*, vol. 9, no. 3, p. 164, 2016.
 - [57] D. Song, “Effects of rf power on surface-morphological, structural and electrical properties of aluminium-doped zinc oxide films by magnetron sputtering,” *Appl. Surf. Sci.*, vol. 254, no. 13, pp. 4171–4178, 2008.
 - [58] J. K. Kim, S. J. Yun, J. M. Lee, and J. Wook Lim, “Effect of rf-power density on the resistivity of Ga-doped ZnO film deposited by rf-magnetron sputter deposition technique,” *Curr. Appl. Phys.*, vol. 10, no. SUPPL. 3, pp. S451–S454, 2010.
 - [59] S. Y. Kuo, K. C. Liu, F. I. Lai, J. F. Yang, W. C. Chen, M. Y. Hsieh, H. I. Lin, and W. T. Lin, “Effects of RF power on the structural, optical and electrical properties of Al-doped zinc oxide films,” *Microelectron. Reliab.*, vol. 50, no. 5, pp. 730–733, 2010.
 - [60] M. M. Aliyu, M. A. Islam, Q. Huda, S. Rahman, and N. Amin, “Influence of RF Power in the Growth of Aluminium Zinc Oxide (AZO) Thin Films by RF Sputtering,” *Adv. Mater. Res.*, vol. 925, pp. 295–299, 2014.
 - [61] E. Fortunato, N. Correia, P. Barquinha, L. Pereira, G. Goncalves, and R. Martins, “High-Performance Flexible Hybrid Field-Effect Transistors Based on Cellulose Fiber Paper,” *IEEE Electron Device Lett.*, vol. 29, no. 9, pp. 988–990, Sep. 2008.
 - [62] T. Koida, H. Fujiwara, and M. Kondo, “Hydrogen-doped In₂O₃ as high-mobility transparent conductive oxide,” *Japanese J. Appl. Physics, Part 2 Lett.*, vol. 46, no. 25–28, 2007.
 - [63] T. Koida, H. Sai, and M. Kondo, “Application of hydrogen-doped In₂O₃ transparent conductive oxide to thin-film microcrystalline Si solar cells,” *Thin Solid Films*, vol. 518, no. 11, pp. 2930–2933, Mar. 2010.
 - [64] G. Gonçalves, P. Barquinha, L. Raniero, R. Martins, and E. Fortunato, “Crystallization of amorphous indium zinc oxide thin films produced by radio-frequency magnetron sputtering,” *Thin Solid Films*, vol. 516, no. 7, pp. 1374–1376, Feb. 2008.
 - [65] Y. R. Denny, H. C. Shin, S. Seo, S. K. Oh, H. J. Kang, D. Tahir, S. Heo, J. G. Chung, J. C. Lee, and S. Tougaard, “Electronic and optical properties of hafnium indium zinc oxide thin film by XPS and REELS,” *J. Electron Spectros. Relat. Phenomena*,

- vol. 185, no. 1–2, pp. 18–22, 2012.
- [66] J. L. White and A. B. Bocarsly, “Enhanced Carbon Dioxide Reduction Activity on Indium-Based Nanoparticles,” *J. Electrochem. Soc.*, vol. 163, no. 6, pp. H410–H416, Mar. 2016.
- [67] G. Korotcenkov, V. Brinzari, S. H. Han, and B. K. Cho, “Gas-sensing properties of In₂O₃ films modified with gold nanoparticles,” *Mater. Chem. Phys.*, vol. 175, pp. 188–199, Jun. 2016.
- [68] D. Gaspar, L. Pereira, K. Gehrke, B. Galler, E. Fortunato, and R. Martins, “High mobility hydrogenated zinc oxide thin films,” *Sol. Energy Mater. Sol. Cells*, vol. 163, 2017.
- [69] C. Fernandes, A. Santa, Â. Santos, P. Bahubalindrani, J. Deuermeier, R. Martins, E. Fortunato, and P. Barquinha, “A Sustainable Approach to Flexible Electronics with Zinc-Tin Oxide Thin-Film Transistors,” *Adv. Electron. Mater.*, vol. 4, no. 7, pp. 1–10, 2018.
- [70] D. Das and P. Mondal, “Photoluminescence phenomena prevailing in c-axis oriented intrinsic ZnO thin films prepared by RF magnetron sputtering,” *RSC Adv.*, vol. 4, no. 67, p. 35735, Jul. 2014.
- [71] L. Yue, H. Pu, H. Li, S. Pang, and Q. Zhang, “Dip-coated Al-In-Zn-O thin-film transistor with poly-methylmethacrylate gate dielectric,” *J. Phys. D. Appl. Phys.*, vol. 46, no. 44, pp. 1–6, 2013.
- [72] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, and H. Hosono, “Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors,” *Nature*, vol. 432, no. 7016, pp. 488–492, Nov. 2004.
- [73] L. Pereira, “Produção e caracterização de silício policristalino e sua aplicação a TFTs,” Faculdade de Ciências e Tecnologia - Universidade Nova de Lisboa, 2008.
- [74] S. Lee, K. Ghaffarzadeh, A. Nathan, J. Robertson, S. Jeon, C. Kim, I.-H. Song, and U.-I. Chung, “Trap-limited and percolation conduction mechanisms in amorphous oxide semiconductor thin film transistors,” *Appl. Phys. Lett.*, vol. 98, no. 20, p. 203508, May 2011.
- [75] L. X. Qian and P. T. Lai, “Fluorinated InGaZnO Thin-Film Transistor With HfLaO Gate Dielectric,” *IEEE Electron Device Lett.*, vol. 35, no. 3, pp. 363–365, Mar. 2014.

Transistors on paper-like substrates

This chapter presents the most relevant results concerning the development of optimised cellulose-based dielectrics. The paper hand-sheets were produced by CTP (France) (gently provided by Dr David Guerin) and UBI paper making laboratories, while the FETs and paper samples were produced and characterised at CENIMAT and CEMOP facilities.

Part of the contents of **Chapter 4** was adapted from the publications:



L. Pereira, **D. Gaspar**, D. Guerin, A. Delattre, E. Fortunato, and R. Martins, “The influence of fibril composition and dimension on the performance of paper gated oxide transistors,” *Nanotechnology*, vol. 25, no. 9, p. 94007, 2014.

D. Gaspar, L. Pereira, A. Delattre, D. Guerin, E. Fortunato, and R. Martins, “Engineered cellulose fibres as dielectric for oxide field effect transistors,” *Phys. Status Solidi Curr. Top. Solid State Phys.*, vol. 12, no. 12, pp. 1421–1426, 2015.

A. T. Vicente, A. Araújo, **D. Gaspar**, L. Santos, A. C. Marques, M. J. Mendes, L. Pereira, E. Fortunato, and R. Martins, Chapter 3 “Optoelectronics and Bio Devices on Paper Powered by Solar Cells,” in *Nanostructured Solar Cells*, 1st ed. InTech, 33–65, 2017.

Transistors on paper-like substrates

Chapter 4. Transistors on paper-like substrates	119
4.1. Substrates from commercial kraft pulp	119
4.2. Influence of the pulp	120
4.3. Fibres' dimension	125
4.3.1. Influence of the water content on the paper's characteristics	125
4.3.2. Paper/semiconductor interface	128
4.3.3. Influence of the water content in the FETs performance	129
4.3.4. I_{ON}/I_{OFF} ratio dependence with frequency	132
4.3.5. Mechanical Stability	134
4.3.5.1. Bending tests	134
4.3.6. Electrical stability over time	136
4.4. Physical modification of bleached softwood kraft pulp (BSKP) papers	138
4.4.1. Refining and porosity/density influence	138
4.4.2. FETs on BSKP papers	141
4.4.2.1. Influence of the fibres' orientation	144
4.5. Chemical modification	145
4.5.1. Addition of extra ionic species to the micro-nanofibrillated cellulose	146
4.5.1.1. M/NFC papers: morphology, structure, and electrical characterisation	146
4.5.1.2. M/NFC papers as a gate dielectric in field-effect transistors	148
4.5.1.3. FETs stability over time	150
4.5.2. Papers produced with TEMPO-mediated oxidised pulps	151
4.5.2.1. TEMPO-mediated oxidised papers	152
4.5.2.2. Influence of the oxidation level in the FETs' performance	153
4.6. References	156

Chapter 4. Transistors on paper-like substrates

The categorisation of the paper or cellulose-based substrates according to their basis weight (BW) was already introduced in Chapter 1. The samples studied in this chapter are based on commercial kraft pulp, which due to its grammage can be defined as standard (basis weight between 30 and 80 g m⁻²). Moreover, micro-nanofibrillated and bacterial cellulose membranes, that will be presented in Chapter 5, are categorised as light paper due to its low grammage.

The following sections present an overview of a holistic characterisation performed on wood-pulp based samples. In this sequence, the results achieved for FETs produced on some of these cellulose substrates will be presented and discussed, explaining how their morphological properties and modifications affect the electrical performance of the devices. The assessment of the morphology of cellulose substrates was made by scanning electron microscopy (SEM), allowing simultaneously to evaluate fibre dimensions while cross-section images were useful to evaluate thickness and porosity. Other techniques such as X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermogravimetric analysis measurements (TGA), Fourier Transform Infrared (FTIR) spectroscopy, provided information regarding the paper structure and constituents. The study of the electrical properties of cellulose-based substrates was made essentially by impedance spectroscopy.

4.1.Substrates from commercial kraft pulp

The fibres used to produce samples from commercial kraft pulp were obtained using a pilot refiner equipped with steel discs, allowing to tailor the fibre dimension and prepare pulps that resulted in samples with a basis weight between 30 and ≈ 80 g m⁻².

The focus in this section is on the influence of the fibre's source, beating index, density/porosity, fibre orientation, chemical modification as the addition of extra ionic species, oxidation level and protonation. Table 4.1 summarises the paper-like substrates used along this chapter.

Table 4.1 Paper-like substrates used during this work, and respective details.

Pulp/paper	Source	Supplier	Acronym
Bleached softwood kraft pulp	Spruce (softwood)	CTP	BSKP
Bleached hardwood kraft pulp	Eucalypt (hardwood)	UBI	BHKP
Commercial standard paper	Unknown	RENOVA	CSP
Micro-nanofibrillated cellulose pulp/paper	Mix of bleached hardwood kraft pulp	CTP	M/NFC
Bleached eucalypt kraft pulp	Eucalypt (hardwood)	UBI	BEKP

4.2. Influence of the pulp

In this sub-section papers prepared with bleached softwood kraft pulp (BSKP), using Spruce (*Picea abies*) as the source, Eucalypt (*Eucalyptus globulus*) bleached hardwood kraft pulp (BHKP), and a commercial standard paper (CSP) are studied. The CSP was added to this study since this paper was appointed as the initial reference to this PhD work due to its availability and well-established production technology. The CSP consists of a commercial parchment with a basis weight of 38 g m^{-2} , produced by the Portuguese company RENOVA. Not many details are disclosed about the production process of the CSP, but the thin fibres observed by SEM (Figure 4.1a) might suggest a hardwood source or a mix of some bleached softwood and hardwood kraft pulp, which is commonly used in the paper industry.

Regarding the hand-sheets produced in the lab, the softwood (spruce) and hardwood (eucalyptus) pulps were refined to reach a beating index (drainage index) of 27°SR . The samples were then formed without inducing a preferred orientation of the fibres, having a porosity of 52% and 39%, respectively, while the commercial paper presents even higher porosities reaching 69% (Table 4.2). Regardless of the source, the paper samples prepared with beaten pulp are constituted by large fibres with non-uniform dimensions that can reach lengths above $500 \text{ }\mu\text{m}$, resulting in a rough surface formed by entangled cellulose fibres. On the other hand, the length of the softwood fibres can be up to 4 times higher than in the hardwood, reaching values $\approx 35 \text{ }\mu\text{m}$ (Figure 4.1b and c). It should be noticed that the dimensions where presented (Chapter 4 and 5) corresponds to the fibres in formed paper, and thus are merely indicative. The length value here determined by SEM is underestimated relatively to the real ones that could only be assessed by the analysis of the individual fibres.

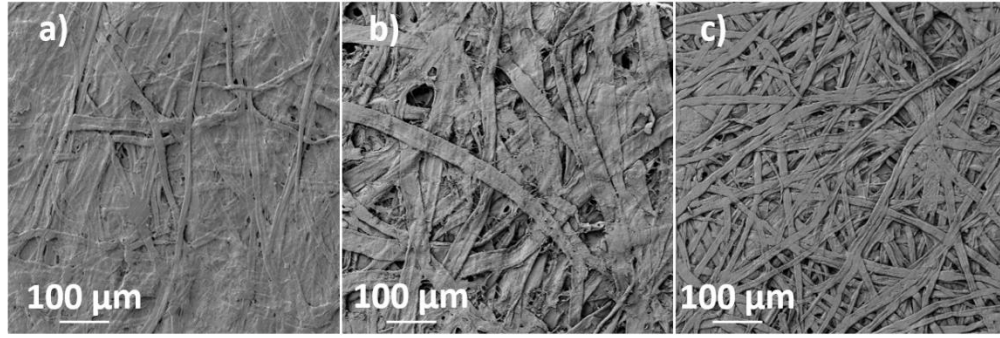


Figure 4.1 SEM micrographs of samples of a) commercial paper, b) lab prepared softwood pulp substrates and c) lab prepared hardwood pulp substrates.

Table 4.2 Characteristics of the paper samples produced with different sources.

<i>Properties</i>	<i>CSP</i>	<i>Softwood</i>	<i>Hardwood</i>
<i>Source</i>	Unknown	Spruce	Eucalyptus
<i>Thickness, μm</i>	75	59	64
<i>Basis weight, g m⁻²</i>	38	46	62
<i>Apparent density, g cm⁻³</i>	0.51	0.77	0.98
<i>Porosity, %</i>	68	52	39

The crystallinity index (CrI) or crystalline fraction of the samples, can be estimated by X-ray diffraction using the empiric method proposed by Segal *et al.* [1]:

$$CrI = \frac{I_{(002)} - I_{(am)}}{I_{(002)}} \times 100 \quad \text{Equation 4.1}$$

where $I_{(002)}$ is the overall intensity of the lattice plane (002) diffraction taken for $2\theta=22^\circ$, and $I_{(am)}$ is the intensity of the amorphous phase diffraction for a 2θ angle in the range of 18° [2], [3]. The crystallinity index estimated through this method is useful only for a qualitative comparison between samples since accurate values are difficult to be determined. The XRD analyses from the CSP, softwood and hardwood paper samples reveal the common $(1\bar{1}0)$, (110) and (002) crystallographic planes at $2\theta=14.9^\circ$, 16.3° and 22.7° , respectively, associated to semi-crystalline cellulose I, while all samples have a similar crystalline fraction (from 78 to 80%). In the CSP reference, an additional small peak around 28° is visible that can be associated with the presence of calcium carbonate (CaCO_3). Such pigments and fillers are often added to improve the optical properties during the industrial papermaking process. CaCO_3 is commonly found in paper since the printing quality is improved and the paper becomes brighter and opaquer at a minimum cost.

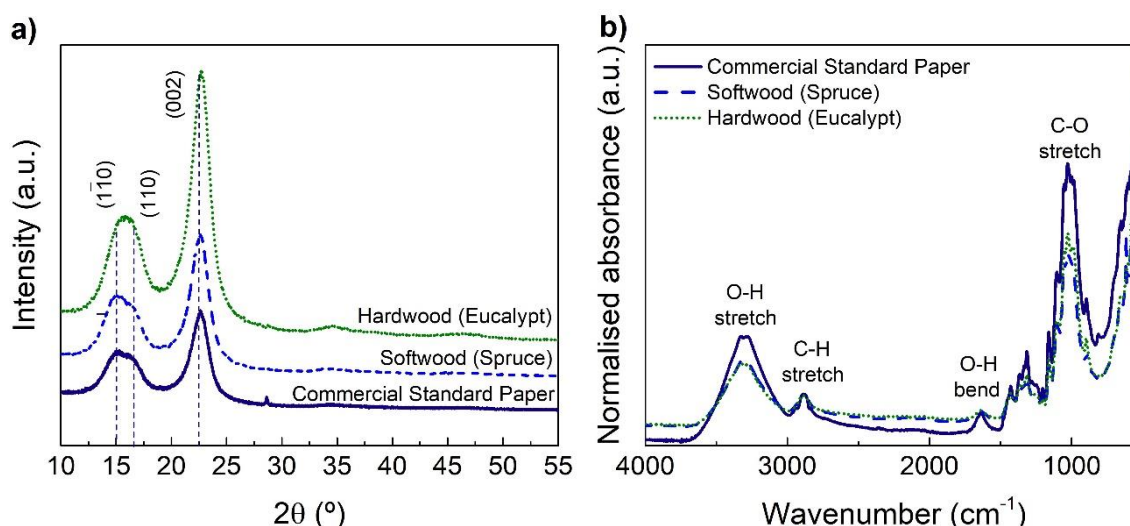


Figure 4.2 a) XRD diffractograms of samples produced with different pulp sources and b) ATR-FTIR spectra of the different paper samples (normalised to the intensity of the band at 2900 cm^{-1}).

The ATR-FTIR spectra in Figure 4.2b reveal the characteristic absorption bands of cellulose, such as the hydrogen-bonded OH stretching at $3600\text{--}3000\text{ cm}^{-1}$, the C-H stretching at 2900 cm^{-1} and a peak at 1060 cm^{-1} assigned to C-O stretching. Also, a characteristic fingerprint region from $1800\text{--}600\text{ cm}^{-1}$ related to hemicelluloses and lignin is observed [4], [5].

The presence of water in the samples can be determined by analysing different bands that can give clues about its sorption and how it is bonded. The band at approximately 700 cm^{-1} is assigned to the out-of-plane vibrations of O-H groups [6] or to rotational vibrations of the whole H_2O molecule [7], whereas the one at 1635 cm^{-1} is associated to the OH bending of adsorbed water [8]. In the case of spruce and eucalyptus pulp samples it is not possible to differentiate the water content or how it is bonded to the fibres through the analysis of the bands at 1635 cm^{-1} and $3600\text{--}3000\text{ cm}^{-1}$. These bands are often used to infer how water sorbs at the fibres surface, since it can result from strongly bound water by hydrogen bonds to the OH groups and more loosely bound water indirectly bonded to the OH groups via another water molecule [9], [10]. On the other hand, the CSP present a broad and more intense band at $3600\text{--}3000\text{ cm}^{-1}$, which means that the water is preferentially sorbed (either strongly or weakly) by hydroxyl groups at the fibres' surface, in the form of freezing bond water. Moreover the sharp band at 1635 cm^{-1} suggests that this paper owns a larger amount of adsorbed water [11]. Despite, hardwood pulps typically have a higher content of hemicelluloses, which are highly hydrophilic. The similarities observed in the FTIR spectra can be explained by the fact that both, hardwood and softwood fibres were submitted to a

kraft pulping process, where a selective dissolution of carbohydrates and lignin occurs, while most of the hemicellulose is degraded into monomeric and oligomeric sugars or sugar acids [12], [13].

The thermal stability of the cellulosic substrates is well reported; it is known that it is a suitable material for low-temperature processes once the thermal degradation of the cellulose begins around 180°C, reaching a noteworthy weight loss around 270°C [9], [14]. The study of the thermal properties is not among the main objectives of this work since most of the processes used for devices production do not involve intentional substrate heating. Nevertheless, one of the final steps is an annealing process carried on at 150°C and this motivated the analysis of the thermal degradation of the used cellulose substrates.

The thermogravimetry and differential scanning calorimetry (TGA-DSC) analysis of these three paper samples show similar results regardless of the used fibre sources (Figure 4.3). An initial weight loss (< 10%), at temperatures close to 100°C related to desorption of free water from the cellulose fibres was observed for all the samples. This is more evident in the CSP and hardwood sample where the water desorption begins immediately with the heating, confirming the presence of a higher amount of weakly bound water. The thermal degradation of cellulose, starts around 270°C for all paper samples and proceeds up to around 350°C, accordingly to the depolymerization and the formation and evaporation of monosaccharide derivatives and levoglucosan, resulting in a weight loss in the range of 70 to 80% regardless of the pulp source [9], [15], [16].

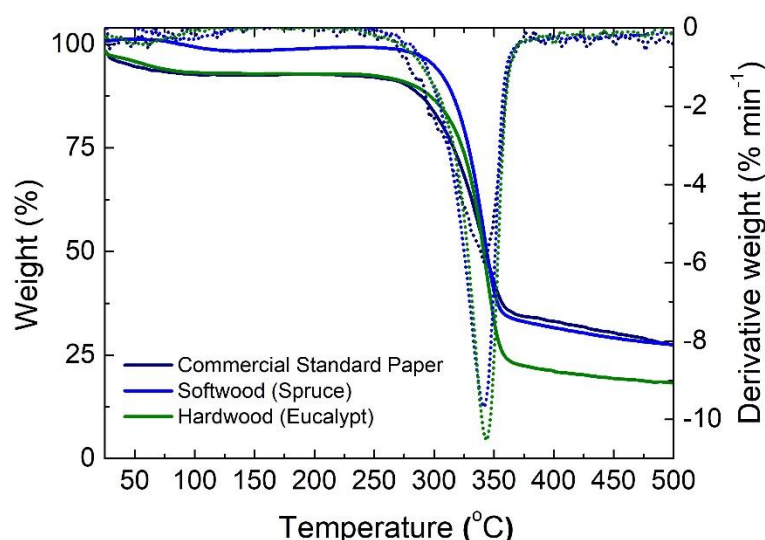


Figure 4.3 Thermogravimetry analysis (TGA and DTA) of the different paper samples.

The electrical characterisation of the papers was carried out through electrochemical impedance spectroscopy (EIS) using a metal-paper-metal capacitor structure (inset of Figure 4.4). The capacitance as a function of the frequency ($C_{\text{real}}-f$) was evaluated between 10 mHz and 1 MHz (Figure 4.4).

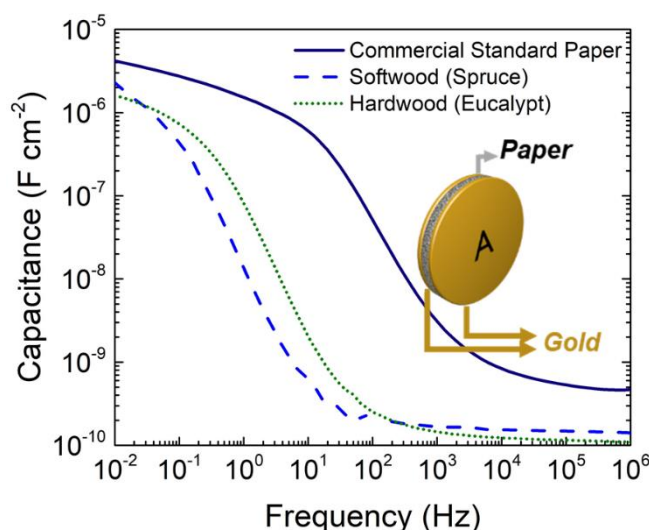


Figure 4.4 Capacitance variation with frequency ($C_{\text{real}}-f$) of the three paper samples analysed. The inset shows the structure of the capacitors produced for the EIS measurements.

The capacitance measurements allow to distinguish different polarisation mechanisms: at high frequencies, dipolar relaxation occurs, for intermediate frequencies, ionic relaxation dominates, while for low frequencies, electrode interface-related relaxation starts to occur. The steady increase in the capacitance observed at low frequencies is associated to electrode polarisation that results from the interaction of the charged electrode surface with the free charges existing in the paper, identical to what occurs in electric double-layer (EDL) capacitors [17]. These EDLs are formed in a narrow region at the electrode surface (<10 nm, depending on electrolyte properties), resulting in a large capacitance that has been explored to decrease the operation voltage of organic electrolyte gated transistors (EGT) [18]–[20] but also on oxide-based ones [21], [22]. This means that high capacitances can be obtained at low frequencies when paper is used as dielectric regardless of its thickness. Despite the lower protonic conduction in paper substrates, it is supposed that the formation of the EDL occurs similar to other protonic conductors, such as chitosan [23]–[25]. This can be explained through the Grotthius-type conduction mechanism, where under the influence of an electric field, proton hopping occurs through the hydrogen bonds [26], [27]. The capacitance values at 0.01 Hz for CSP, softwood and hardwood are 4.2, 2.3 and 1.6 $\mu\text{F cm}^{-2}$, respectively. It is expected that for hardwood sources ionised water is firmly

bonded, reducing the ionic mobility, and thus affecting the formation of the EDL at the paper/electrode interface.

4.3.Fibres' dimension

4.3.1. Influence of the water content on the paper's characteristics

As seen in the previous section, the use of paper as a dielectric relies on the formation of the EDL at the interfaces of the paper/gate electrode and paper/semiconductor. The mechanism which enables the ionic displacement and accumulation onto these interfaces is directly related to the water within the paper matrix. Thus, it is of high relevance to understand how the capacitance changes under vacuum.

This was studied in three paper samples with different characteristics; the CSP, a BSKP (long and wide fibre paper produced from a softwood source with drainage index=48°SR) and a micro-nanofibrillated cellulose paper (M/NFC paper) produced with a mix of BHKP. The morphology and fibre dimensions of these samples are represented in Figure 4.5 while some properties are listed in Table 4.3.

Table 4.3 Characteristics of the tested paper samples.

<i>Properties</i>	<i>CSP</i>	<i>BSKP</i>	<i>M/NFC</i>
<i>Source</i>	Unknown	Softwood	Hardwood
<i>Pulp</i>	Unknown	Spruce	Mix Species
<i>Thickness</i>	75	60	43
<i>Fibre average length/ width, μm</i>	>500/~10	>1000/~20	>10/<0.1
<i>Basis weight, g m^{-2}</i>	38	58	52
<i>Apparent density, g cm^{-3}</i>	0.51	0.96	1.21
<i>Porosity, %</i>	68	40	24

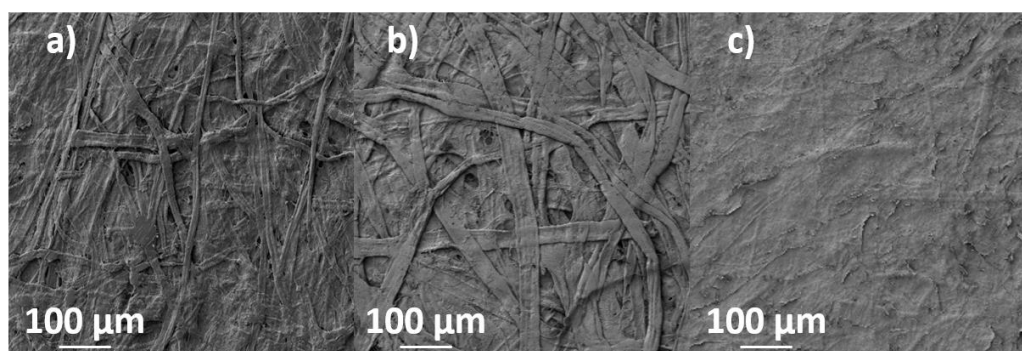


Figure 4.5 SEM micrographs of a) commercial standard paper (CSP), b) bleached softwood kraft paper (BSKP), and c) micro-nanofibrillated cellulose paper (M/NFC).

The capacitance variation with frequency (C-f) for the paper samples is shown in Figure 4.6a. The values at 0.01 Hz for CSP and BSKP are 4.2 and 3.9 $\mu\text{F cm}^{-2}$, respectively, while for M/NFC it reaches only 0.53 $\mu\text{F cm}^{-2}$. This difference can be due to the ionised water which is more strongly bound on M/NFCs, reducing the ionic mobility, affecting so the formation of the EDL at the paper surface. The capacitance for M/NFC paper follows an increasing tendency at 0.01 mHz that suggests the existence of another relaxation related to the contribution of strongly bound water.

The relation between the water content and EDL formation can be assessed by partially removing it. When measuring the capacitance under vacuum an abrupt decrease in the capacitance values at low frequencies after 15 minutes in a vacuum was observed, which means a reduction by 3 to 4 orders of magnitude for CSP and BSKP (open symbols in Figure 4.6a), confirming that the water sorption is directly related to the EDL formation in the paper.

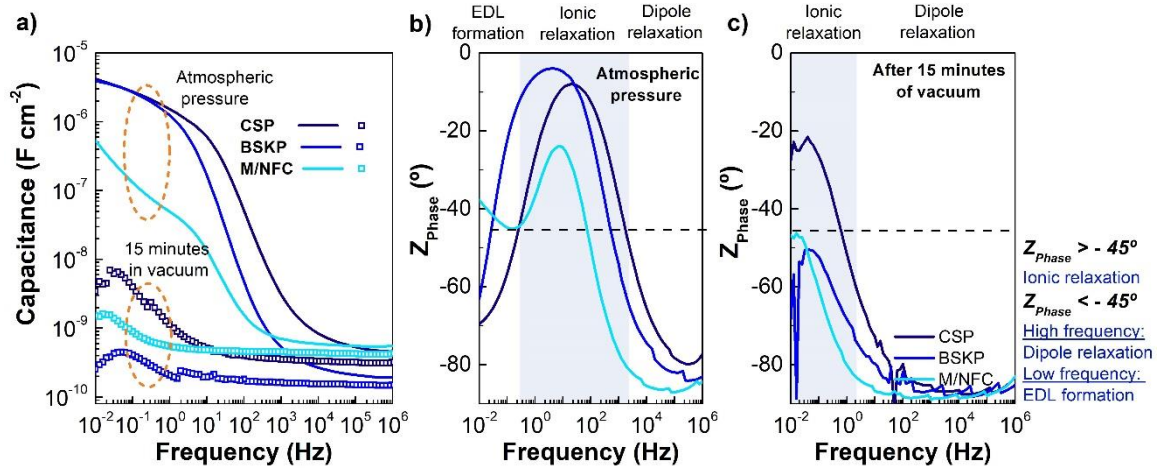


Figure 4.6 Electrochemical Impedance Spectroscopy: a) Capacitance variation with frequency (C-f) of the set of paper samples used. (Solid lines represent the capacitance measured at atmospheric pressure, while the open symbols represent the capacitance measured under vacuum after pumping for 15 minutes), b) Phase angle as a function of the frequency, at atmospheric pressure, and c) after under vacuum after pumping for 15 minutes.

The phase angle vs. frequency plots also reveal three domains (Figure 4.6b). At high frequencies, the phase angle between current and voltage is lower than -45° related to the dipole relaxation and is mostly justified due to the lack of time for a substantial dipole creation [10]. For intermediate frequencies all the samples exhibit values above -45° , indicating a resistive response resulting from ionic relaxation. Finally, for lower frequencies, there is a change from a purely resistive to a capacitive response ($Z_{\text{phase}} < -45^\circ$),

which is characterised by a high capacitance as a result of the EDL formation. In the samples measured under vacuum conditions (Figure 4.6c), the transition from resistive to capacitive behaviour at low frequencies does not occur for the CSP, and consequently, the EDL is not formed. On the other hand, the BSKP and M/NFC retain a capacitive response associated to the dipole relaxation.

Looking carefully at the FTIR spectra of the papers (solid line in the plots depicted in Figure 4.7a, b, and c), it is possible to confirm the presence of sorbed water, which is the primary source of the protons (H^+) and hydroxyls (OH^-), resulting from water dissociation at the fibres' surface and responsible for the high capacitance values obtained at low frequencies. FTIR data shows a more intense broad absorption band at 3600-3000 cm^{-1} for CSP and BSKP samples that suggests a high amount of weakly bonded water in these papers. For instance, thermogravimetric analysis (Figure 4.7d) shows an accentuated weight loss for CSP sample due to water desorption, that begins immediately after starting to heat the sample, confirming so the presence of weakly bonded water.

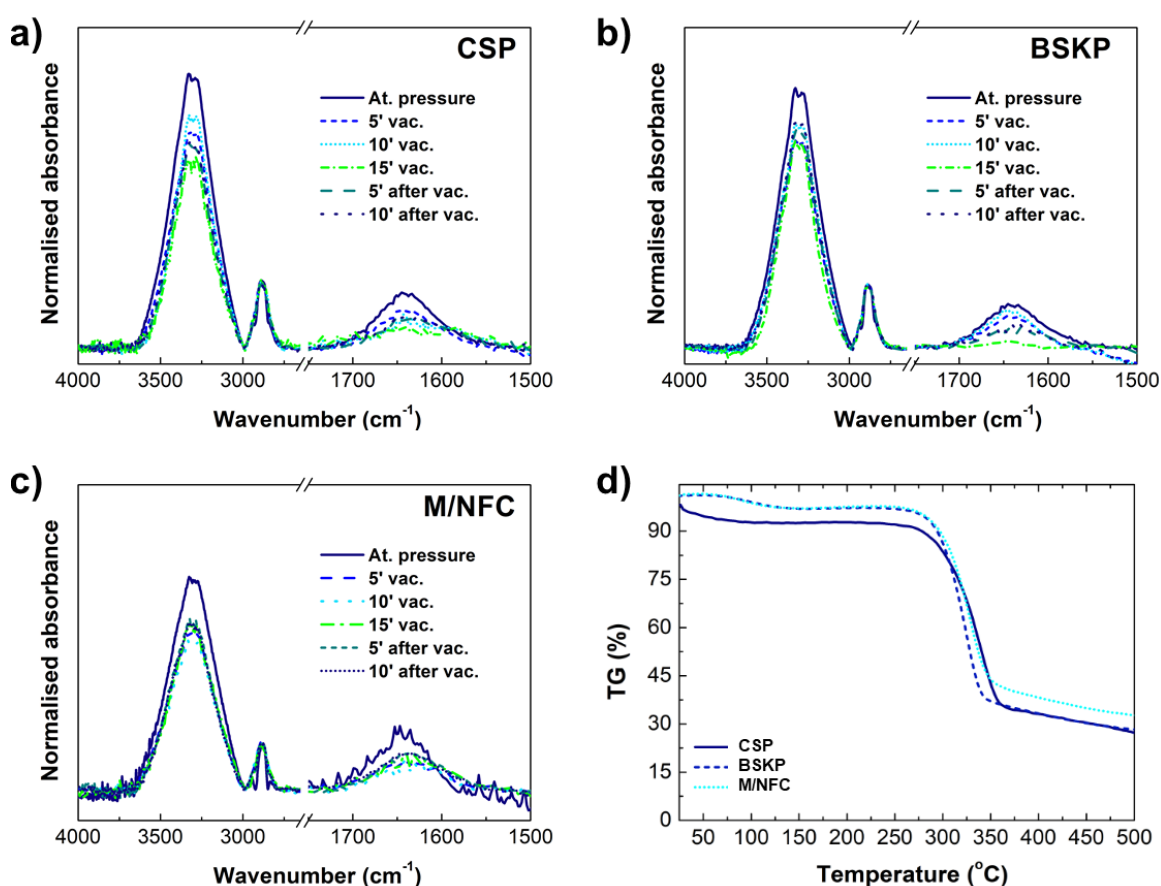


Figure 4.7 ATR-FTIR spectra of the bands at 3600-3000 cm^{-1} and 1635 cm^{-1} for a) CSP, b) BSKP, and c) M/NFC. The water content variation under vacuum and after recovery was analysed by the changes in the intensity of these bands. d) Thermal analysis of the three different paper samples.

Similarly, to what was done for the capacitance, the susceptibility of the samples to abrupt variations in the relative humidity was assessed by keeping the samples in vacuum for different time intervals and collecting the FTIR spectra immediately after removing them from the vacuum chamber. A reduction of the intensity of the $3600\text{-}3000\text{ cm}^{-1}$ broadband and that at 1635 cm^{-1} after some minutes in vacuum was noticed, indicating that the adsorbed water content is decreasing over time.

Despite the elapsed time between taking the sample from the vacuum chamber and performing the FTIR measurements (that may lead to a partial recovery of the water content) it is clear that the relative variation of the band at 1635 cm^{-1} in M/NFC paper is lower than the variation observed for the CSP and the BSKP samples. The more porous structure combined with a more heterogeneous surface, and/or weakly bound water at the fibres' surface explain why the reduction is more accentuated in those two paper samples than for M/NFC papers.

Analogously to the behaviour observed after keeping the samples in vacuum, the recovery of the water content is also faster for CSP and the BSKP samples. This fact can be credited to the more compact structure of the M/NFC paper that affects the capacity of water diffusion into the porous network and to the higher density of OH bonds between the small fibrils in M/NFC that slows down the sorption/desorption rate.

4.3.2. Paper/semiconductor interface

The roughness of the paper samples is a challenge when aiming for their as substrates for reliable electronic devices. In the SEM/FIB cross section of the paper/IGZO interface (Figure 4.8), it is possible to verify that a satisfactory step coverage of the fibres' topography is obtained, even when using a PVD process such as sputtering. Thus, one can conclude that the inherent roughness of the fibre-based samples is not a limiting factor for the sputtered oxide layers. Indeed, the use of oxide semiconductors provides here a unique advantage since they are highly stable in contact with cellulose even without any special passivation layers, which is not always the case for the organic counterparts (which degrade) or silicon thin films (which may oxidise).

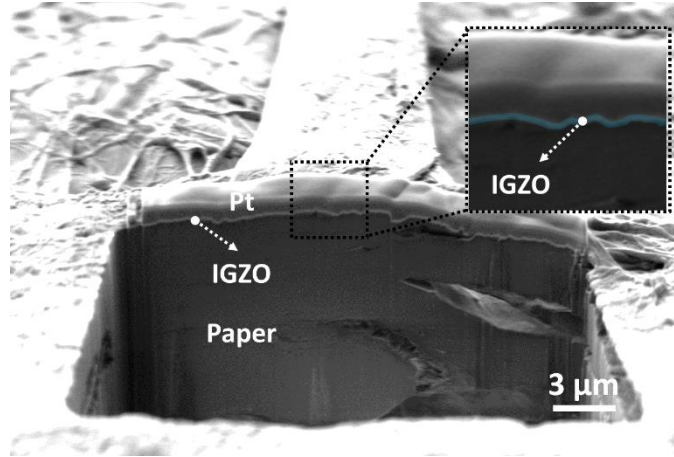


Figure 4.8 SEM of a cross-section of the paper/IGZO surface. The inset shows an artificial colouration of the IGZO for better visualisation, showing a perfect fibre coverage provided by the sputtered layer.

Besides the excellent conformability of the oxides to rough surfaces, these materials are not susceptible to atomic migration into the paper. In fact, this was verified in a CSP sample covered with a thick conductive layer of IZO (approximate thickness ≈ 200 nm). The EDX of the cross-section confirmed that there is no zinc nor indium migration into the paper substrate whatsoever, revealing the stability of the deposited oxide composition [28].

4.3.3. Influence of the water content in the FETs performance

As discussed in previous sections, the use of cellulose-based substrates as dielectrics depends on the formation of the EDL, which is deeply related to the existing water within the matrix. More information about the role of the water was studied by producing FETs with the configuration represented in Figure 4.9. The paper-gated FETs uses the paper samples as the gate dielectric, which acts simultaneously as the substrate. On one of the sides a very thin layer of IGZO followed by metallic electrodes (source and drain) are deposited and both are patterned through the use of a shadow mask. The IZO gate electrode is deposited on the other side of the paper sample. All the details regarding the materials and steps involved in the production of such devices can be found in Chapter 2 and 3.

The IGZO-based FETs, using paper as gate dielectric were characterised at room temperature and atmospheric pressure, with temperatures in the range of 23 to 25 °C and normal room relative humidity between 40% and 50%. The transfer characteristics (I_{DS} - V_{GS}) of these devices are presented in Figure 4.9, and the respective electrical parameters are listed in Table 4.4.

Although different fibres are used in each sample, the FETs have similar I_{On}/I_{Off} ratio, despite the highest I_{Off} value verified for the CSP sample. The plot of the gate leakage currents (I_{GS}) shows that it determines the I_{Off} in these devices. The I_{GS} is related with the resistivity of the paper samples, which was estimated to be 49 M Ω cm for the CSP, whereas for the BSKP and M/NFC values of 43 and 1.4 G Ω cm are reached, respectively.

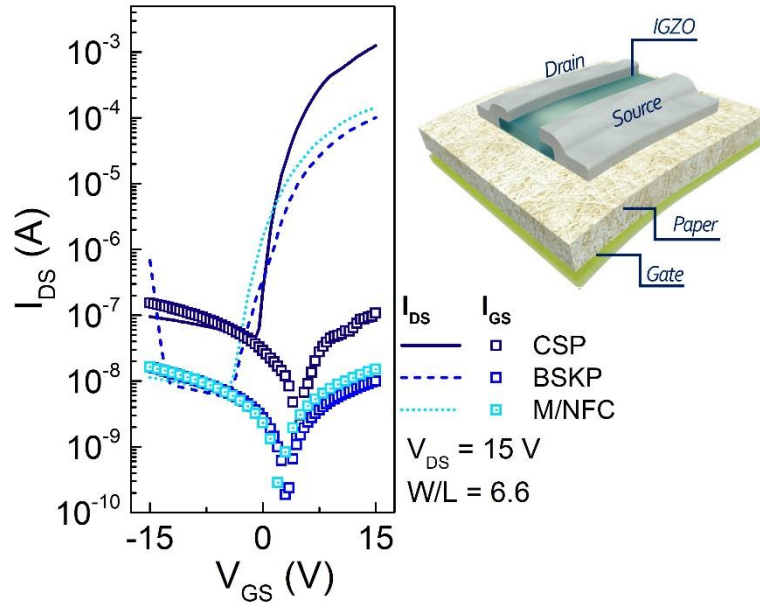


Figure 4.9 Transfer characteristics (I_{DS} - V_{GS}) for the IGZO-based paper FETs on the tested paper samples, and schematic representation of the devices.

Table 4.4 Summary of the electrical parameters of the IGZO-based paper FETs.

Properties	CSP	BSKP	M/NFC
μ_{sat} ($cm^2 V^{-1} s^{-1}$)	2.3	0.14	0.94
V_{on} (V)	-2.5	-5.5	-4.7
I_{On}/I_{Off}	2.5×10^4	1.7×10^4	2.2×10^4
S (V dec^{-1})	0.89	2.1	1.6
C_{real} at 10 mHz ($\mu F cm^{-2}$)	1.7	1.8	0.24

The type and dimension of the fibres become critical when testing the devices under extreme conditions. In Figure 4.10 the transfer characteristics of the FETs measured at atmospheric pressure and under vacuum for different times are plotted. The pressure in the vacuum chamber after 5 minutes was around 0.2 Pa, reaching 0.04 Pa after pumping for 1 hour.

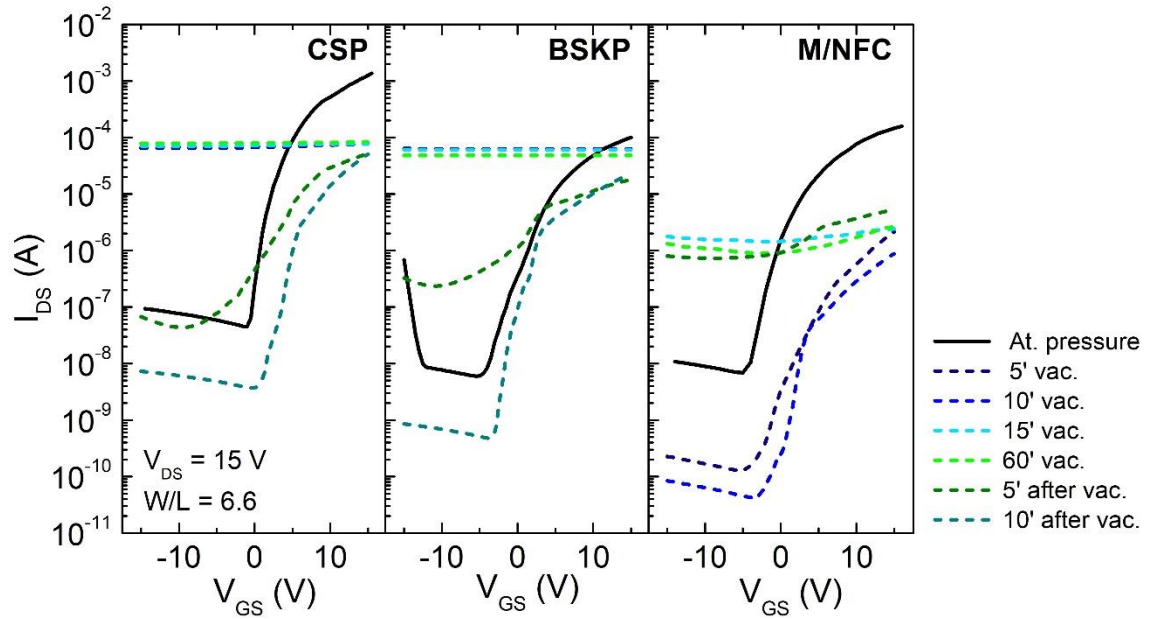


Figure 4.10 I_{DS} - V_{GS} transfer characteristics of the paper gated IGZO FETs ($V_{DS}=15$ V) measured initially at atmospheric pressure (solid line), under vacuum after different times and after recovery at atmospheric pressure.

The transfer curves confirm that longer fibres, as the ones present in CSP and BSKP paper, are more susceptible to the variation of the humidity (and thus water content) than samples produced with shorter fibres as the M/NFC. In the first two papers, the current modulation of the FETs ceases in less than 5 minutes in vacuum, as a result of the water desorption. On the other hand, for M/NFC it is still possible to modulate the current even after 10 minutes in vacuum. Only after 15 minutes in vacuum V_{GS} no longer modulates I_{DS} ; the exact moment when this occurs was not determined since a measurement was taken every 5 minutes.

The transistor characteristics are recovered after venting the vacuum chamber. Similarly, to what happened when pumping the test chamber, the response recovery is faster for the CSP and BKSP samples than for M/NFC ones. After only 5 minutes at atmospheric pressure the CSP exhibits an I_{ON}/I_{OFF} ratio around 3 orders of magnitude, while the current modulation for the M/NFC paper is still below 10.

The I_{GS} (Figure 4.11) is also affected by the pressure inside the test chamber since it is directly related to the water content in the paper samples. The I_{GS} taken at atmospheric pressure and under vacuum resembles the trend observed for the I_{DS} - V_{GS} transfer characteristics shown in Figure 4.10. It is also possible to verify that the I_{GS} decreases faster

in papers with longer fibres, while for the fibrillated papers the water desorption/sorption process occurs slower.

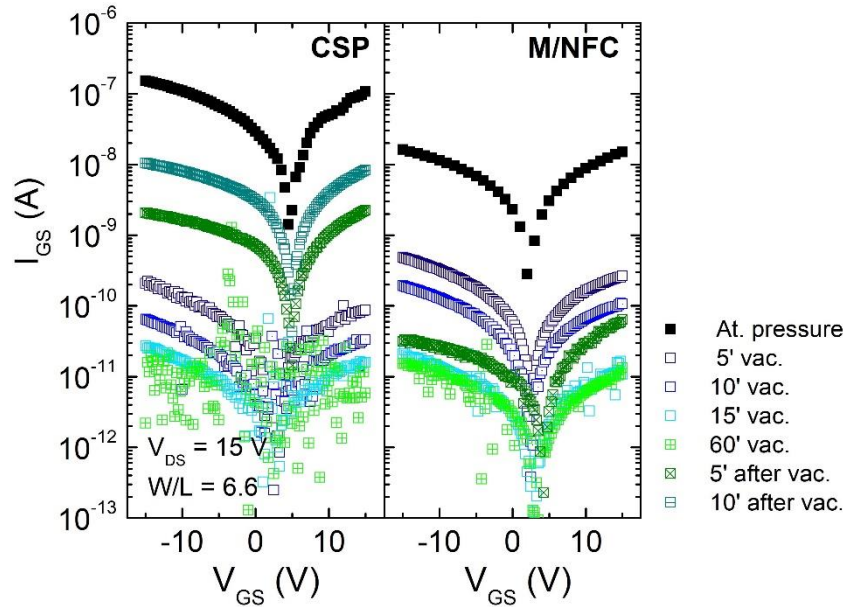


Figure 4.11 Gate leakage current (I_{GS}) variation under vacuum conditions and after recovery at atmospheric pressure.

The behaviour observed for each paper is fully aligned with the results discussed in subsection 4.3.1. The porous matrices formed by the longer fibres present in the CSP and BSKP bonds water that is easily removed under vacuum and rapidly recovered when the paper is brought back to atmospheric pressure. For compact structures (M/NFC) the desorption/sorption rate is slower explaining the differences observed in the FETs operation in vacuum and during the recovery at atmospheric pressure.

4.3.4. I_{ON}/I_{OFF} ratio dependence with frequency

Besides the static characterisation, the dynamic response of the FET devices can also be measured with frequency by applying a square wave as gate voltage, and by monitoring the I_{DS} as a function of time. The I_{ON}/I_{OFF} ratio of the FETs produced on the three papers was recorded as a function of the switching frequency (from 10 mHz up to 10 kHz), using a square wave input signal applied to the gate (V_{GS} between -20 V to 20 V), keeping a constant V_{DS} ($V_{DS}=15$ V) (Figure 4.12).

The different switching frequencies tested allowed to determine the highest frequency at which the devices can operate at; i.e. the frequency where it is no longer possible to distinguish between On and Off regimes (I_{ON}/I_{OFF} equals 1). Once again, the paper samples with longer fibres behave differently from fibrillated ones. In the paper with longer fibres

a difference between the two states is still possible to distinguish up to 10 Hz, while for the M/NFC based FETs the current modulation stops between 1 and 10 Hz (Figure 4.12).

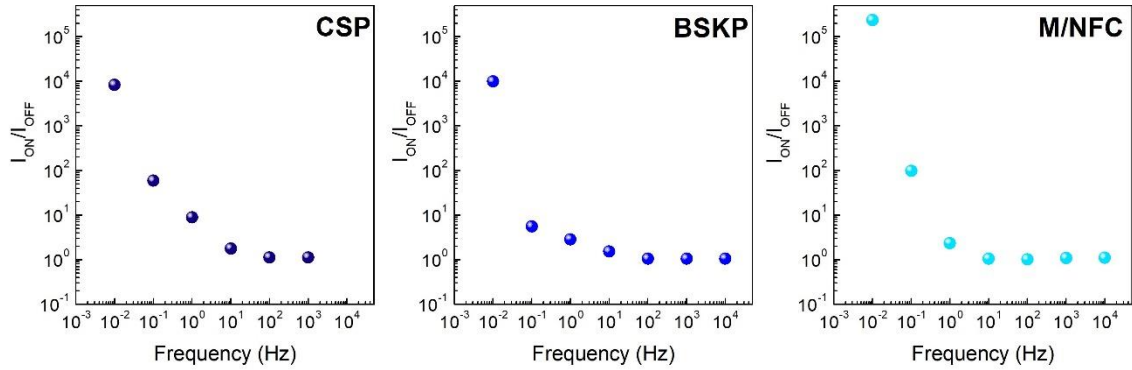


Figure 4.12 I_{ON}/I_{OFF} ratio as a function of the applied frequency to the gate of the paper-based FETs ($V_{DS}=15$ V).

The switching time of the devices is obtained from the variation of the I_{DS} , measuring the time elapsed to go from 10 to 90% of the total current variation. In Figure 4.13 the switching times for the FETs produced on CSP, BSKP, and M/NFC papers when measured at 10 mHz are plotted. It is possible to verify a distinct response time between the On and Off state for this frequency. The devices take nearly 40 seconds to reach their maximum I_{DS} , while the switching off is usually faster (CSP, BSKP papers) (Table 4.5). Both the lower threshold frequency and larger response type for devices on M/NFC paper samples might be related with the fact that the capacitive regime is not fully achieved (Figure 4.6b)

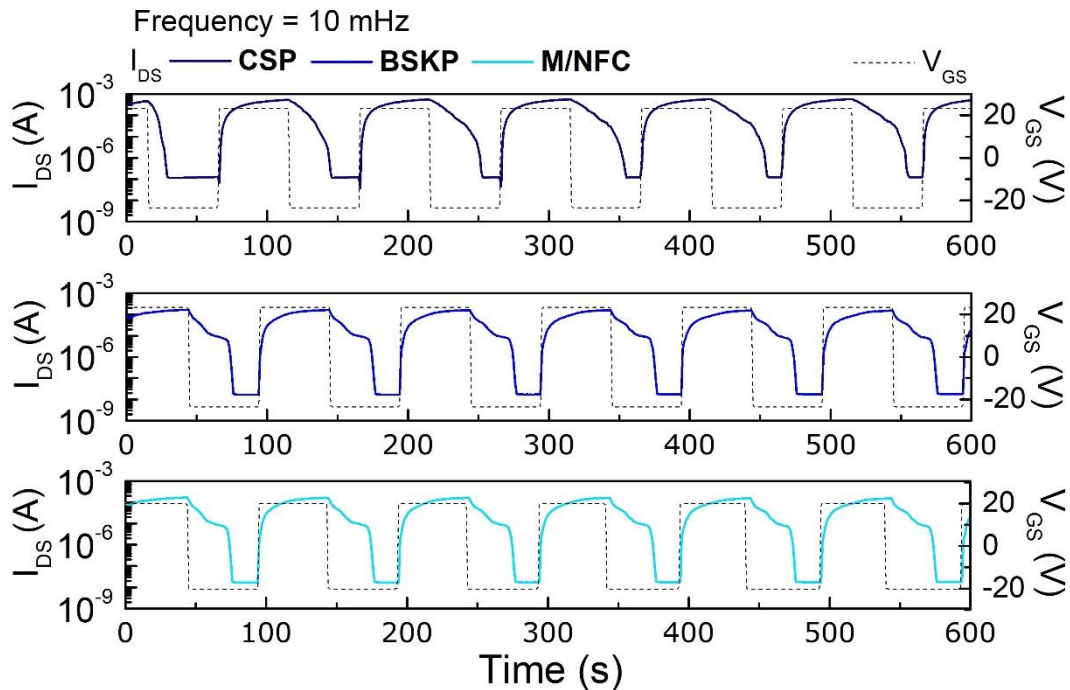


Figure 4.13 I_{DS} variation under a square wave of 10 mHz and an amplitude of 40 V (from -20 to 20V). ($V_{DS}=15$ V)

Table 4.5 Dynamic parameters obtained at 10 mHz for paper-based FETs.

	<i>CSP</i>	<i>BSKP</i>	<i>M/NFC</i>
<i>I_{on}/I_{off}</i> =1 Frequency (Hz)	>10	>10	1-10
Switching time @ 10 mHz (On) (s)	44	38	39
Switching time @ 10 mHz (Off) (s)	22	20	42

The limitation for a high frequency operation in paper gated FETs is ultimately related to the intrinsic ionic character of the paper, but also to its resistance and the interfacial capacitance. The ionic displacement/migration towards paper/metal or paper/semiconductor interfaces and the consequent establishment of EDLs will rule the response of these devices. Thus, the operation in the range of kHz is challenging. The phase angle as a function of the frequency, shown in Figure 4.6b, can be useful to predict the threshold frequency in these FETs. The transition from a resistive response of the paper (phase > -45°), to a capacitive response and EDL formation (phase < -45°) usually occurs for frequencies between 1 and 0.1 Hz. Therefore, a clear distinction between the On and Off state for much higher frequencies was not expected, as was confirmed by the results in Figure 4.12.

4.3.5. Mechanical Stability

One of the most exciting properties that paper owns is its bendability and flexibility. However, ensure proper operation of the devices under bending strain can be challenging mostly due to the brittle nature of the oxide and metallic thin films used.

4.3.5.1. Bending tests

The mechanical stability of the FETs produced on paper was evaluated by measuring their electrical characteristics under bending with outward radius curvatures of 45, 25, 15 and 5 mm, along the axis running through the channel, parallel to source and drain electrodes (Figure 4.14a, and schematic representation in the inset of Figure 4.14b). Despite having tested all the devices with the same curvature, the strain on the semiconductor layer can vary depending on the substrate thickness and also, in less extend, on its own thickness. The strain (ϵ) in the film deposited on a flexible substrate bent with an inner radius (r) can be determined through the equation [29]:

$$\epsilon = \frac{(d_f + d_s)}{2r} \frac{(1 + 2\eta + \chi\eta^2)}{(1 + \eta)(1 + \chi\eta)} \quad \text{Equation 4.2}$$

Where d_f and d_s represent the film and substrate thicknesses, respectively, η is the d_f/d_s ratio, and χ is the ratio of the film and substrate Young moduli (E_f/E_s).

Considering that the IGZO thickness of the devices is in the range of 30 to 45 nm, and χ is around 10^3 , which compensates the difference between the Young modulus of the paper and the oxide thin films, then ε can be simplified to:

$$\varepsilon \approx \frac{(d_f + d_s)}{2r} \quad \text{Equation 4.3}$$

The relative variation of the electrical parameters of the devices, namely μ_{Sat} (μ/μ_0), $I_{\text{On}}/I_{\text{Off}}$ ratio (I/I_0), and S (S/S_0), for a different tensile strains, is plotted in Figure 4.14b to d. The parameters that seem to be more susceptible are μ_{Sat} and $I_{\text{On}}/I_{\text{Off}}$ ratio, while S does not change significantly even for a small bending radius. For papers with longer fibres, such as the CSP, an increase of μ_{Sat} with ε up to 0.25% was observed, starting then to decrease when $\varepsilon=0.75\%$ (corresponding to a bending radius of 15 mm). The device on CSP paper recovers its initial characteristics when measured again on flat conditions after bending (open symbols).

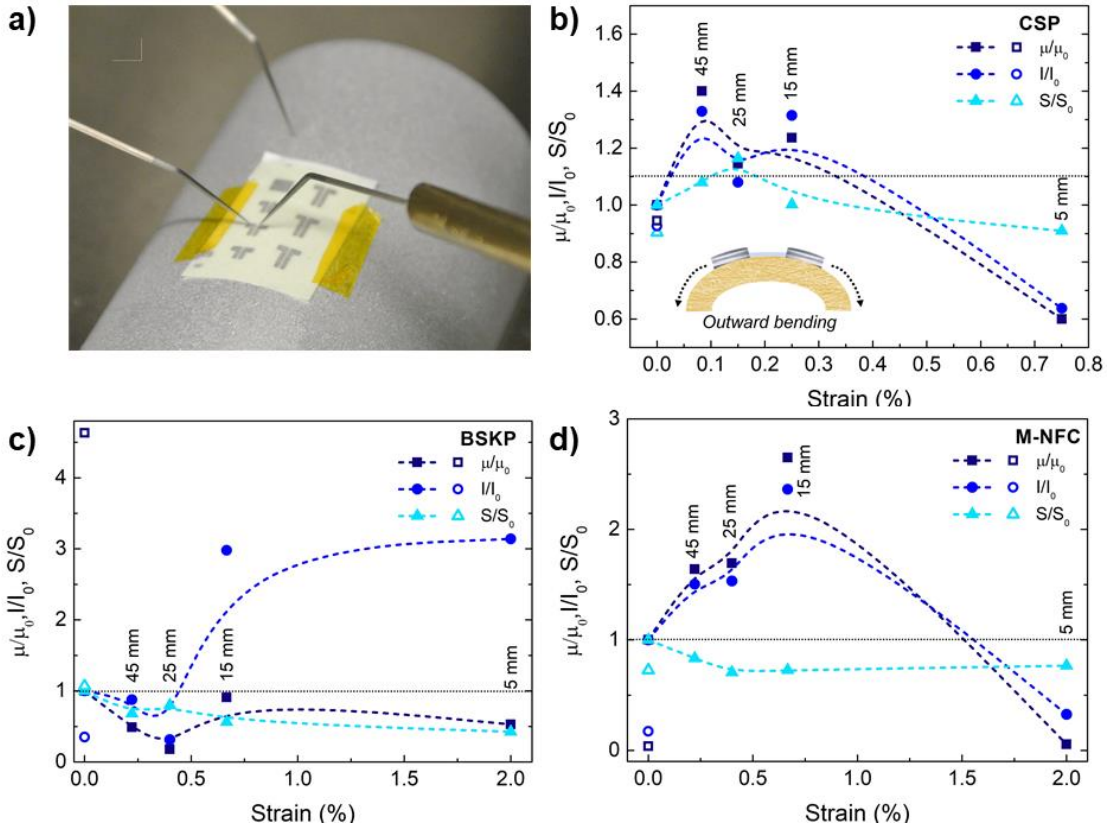


Figure 4.14 Bending test of the paper-based FETs: a) photograph of the devices under test, and normalized electrical characteristics of the devices' values (μ_{Sat} - μ/μ_0 , $I_{\text{On}}/I_{\text{Off}}$ ratio - I/I_0 , and S - S/S_0) on b) CSP (The inset shows schematic representation of the bending test), c) BSKP and d) M/NFC papers determined under tensile bending strain (solid symbols) and flat position after the bending (open symbols).

In the BSKP papers μ_{sat} , and S change under bending, although the increasing of ε does not result in any significant variation of those parameters. On the other hand, the $I_{\text{On}}/I_{\text{Off}}$ ratio increases reaching a maximum for $\varepsilon=2\%$, which is related to the consecutive decrease of I_{Off} . Finally, μ_{SAT} and the $I_{\text{On}}/I_{\text{Off}}$ ratio of the devices produced on the M/NFC paper reach a maximum for $\varepsilon\approx 0.7\%$, decreasing for higher ε . This variation results from the decrease in the source-drain current that also negatively affects the $I_{\text{On}}/I_{\text{Off}}$ ratio.

It is assumed that the differences observed are essentially related to the different fibre types and sizes of the paper substrates. The channel of the FETs on CSP and BSKP is formed on top of large entangled fibres that exist between the source and drain. Under bending conditions, these large fibres are able to rearrange and accommodate the strain, without damaging significantly the oxide layer on top, while M/NFC paper is more brittle than the others and the devices suffer from some irreversible local damage that reduces the On current of the FETs, which also justifies why the initial characteristics are not recovered when returning back to flat conditions.

4.3.6. Electrical stability over time

The electrical stability over time is a concern regardless whether the devices are of organic, inorganic or hybrid nature. Despite “paper electronics” being normally thought of as “disposable electronics” it is intended that the devices preserve proper operation and good electrical performance after some time, without requiring any specific encapsulation or storage conditions.

The non-encapsulated devices analysed in this section were characterised after storing them for four years. They were kept in sample boxes at room temperature and without any particular care on the control of the relative humidity. The aged devices were then characterised in similar conditions (as already described in section 4.3.3), including the use of the same characterisation system.

The overall electrical properties of the FETs degrade with the ageing process (Figure 4.15). The most significant loss is observed for the current modulation, that decreases about one order of magnitude in the case of the larger fibres (CSP and BSKP) (Table 4.8). In the M/NFC papers, the degradation is not as accentuated since the ratio remains above four orders of magnitude, despite a reduction in I_{On} , while S does not change significantly. This proves that the engineered papers allow a better electrical stability of the devices.

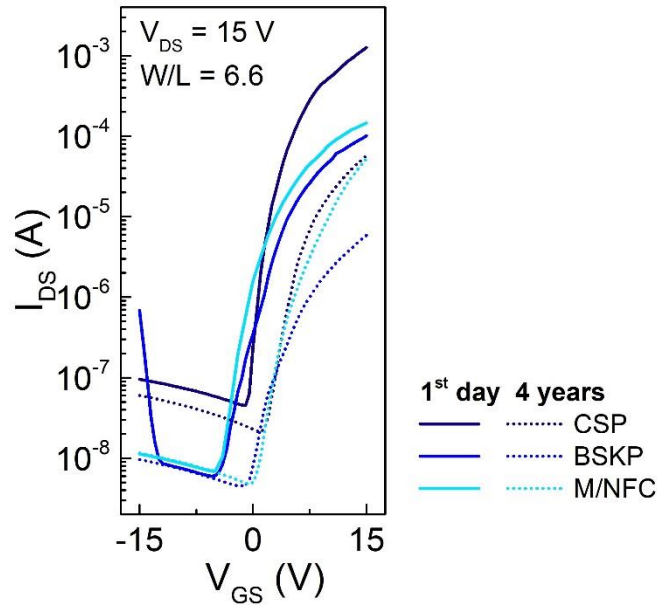


Figure 4.15 Transfer characteristics (I_{DS} - V_{GS}) of the fresh and four years aged FETs.

The noticeable shift of V_{On} towards higher V_{GS} is common to all the devices, affecting also the reached I_{On} for the same maximum applied gate voltage. The reason for this can be related with interface defects or to the adsorption of ambient O_2 onto the IGZO channel, since the devices are not passivated and were kept in air [30]. Depending on the application, the encapsulation/passivation of the devices, with either organic or inorganic materials or even with cellulose based materials, can be an interesting approach to improve the electrical stability of the IGZO-FETs [30]–[34].

Table 4.6 Variation of the electrical parameters of the aged non-encapsulated IGZO-based paper FETs.

<i>Properties</i>		<i>CSP</i>	<i>BSKP</i>	<i>M/NFC</i>
I_{on}/I_{off}	Day 1	2.5×10^4	1.7×10^4	4.9×10^4
	After 4 years	2.7×10^3	1.3×10^3	1.1×10^4
V_{on} (V)	Day 1	-2.5	-5.5	-4.7
	After 4 years	1	-2	-0.5
S ($V \text{ dec}^{-1}$)	Day 1	0.89	2.1	1.6
	After 4 years	1.7	2.1	1.7

4.4. Physical modification of bleached softwood kraft pulp (BSKP) papers

Along the process of paper production, physical modifications and tailoring can be performed at several stages. During stock preparation, the pulp can be further refined to create fines (which in jargon is usually referred to as beaten pulp) and increase fibre flexibility. Additionally, during hand-sheet formation, parameters such as preferential fibre orientation and the basis weight can be tuned. The final step, after the drying of the paper, adjusts the porosity/density through calendaring methods.

In this section an overview of the influence of these different modifications will be presented and how they correlate with morphological and electrical properties of papers used to produce the FETs.

4.4.1. Refining and porosity/density influence

A batch of eight different papers was produced to understand the effect of several treatments that pulp and paper are usually submitted to during the papermaking process. BSKP with two beating indexes (27 and 48°SR) were prepared, which were then used to prepare papers with randomly orientated fibres.

Papers prepared with both types of pulp present similar morphologies, where it is possible to identify a matrix formed by entangled long fibres with an average length/width of $>1000/\sim 20\text{ }\mu\text{m}$. The most evident difference is the porosity where voids between the fibres are easily identified for the paper produced with less refined pulp, while for highly beaten pulp the voids dimensions seem to be attenuated. This fact can be partially related with the fibres' modification, since higher magnification in the SEM micrographs shows the appearance of fines for a higher beating index (Figure 4.16a).

The refining leads to extra fibrillation of the cellulose, resulting in *hairier* fibres (external fibrils and fines) as depicted in the SEM micrographs. This plays an important role in the bonding between fibres and consequently in the porosity of the paper, which was reduced from 52% to 50%. The beating process does not induce changes in the structure of the cellulose, as suggested by XRD analysis. Both paper samples present the characteristic peaks for (1 $\bar{1}$ 0), (110) and (002) crystallographic planes related to cellulose I (Figure 4.16b), while the crystalline fraction is maintained ($\text{CrI} \approx 78\%$) for both beating indexes.

The same pulps were used to produced papers with two different grammages (40 and 50 g m⁻²) and preferential orientation of the fibres using a dynamic hand-sheet former. As

expected, the crystalline structure and CrI of the fibres are not affected. On the other hand, the papers produced in a dynamic hand-sheet former show an entangled and packet matrix. Moreover, the preferential orientation combined with high external fibrillation results in a lower porosity that is even more evident in the case of the highest basis weight.

The calendaring results in a densification of the paper and the porosity consequently decreases without any modification of the crystalline fraction of the paper, which is kept at $\approx 78\%$. In this process, the paper is compressed between two (or more) heated rolls, leading to subsequent smoothening of the surface (Figure 4.16a), while the pressure reduces the thickness. For samples produced with oriented fibres and high basis weight, it is possible to decrease the porosity in 7% when compared with those that were not calendared.

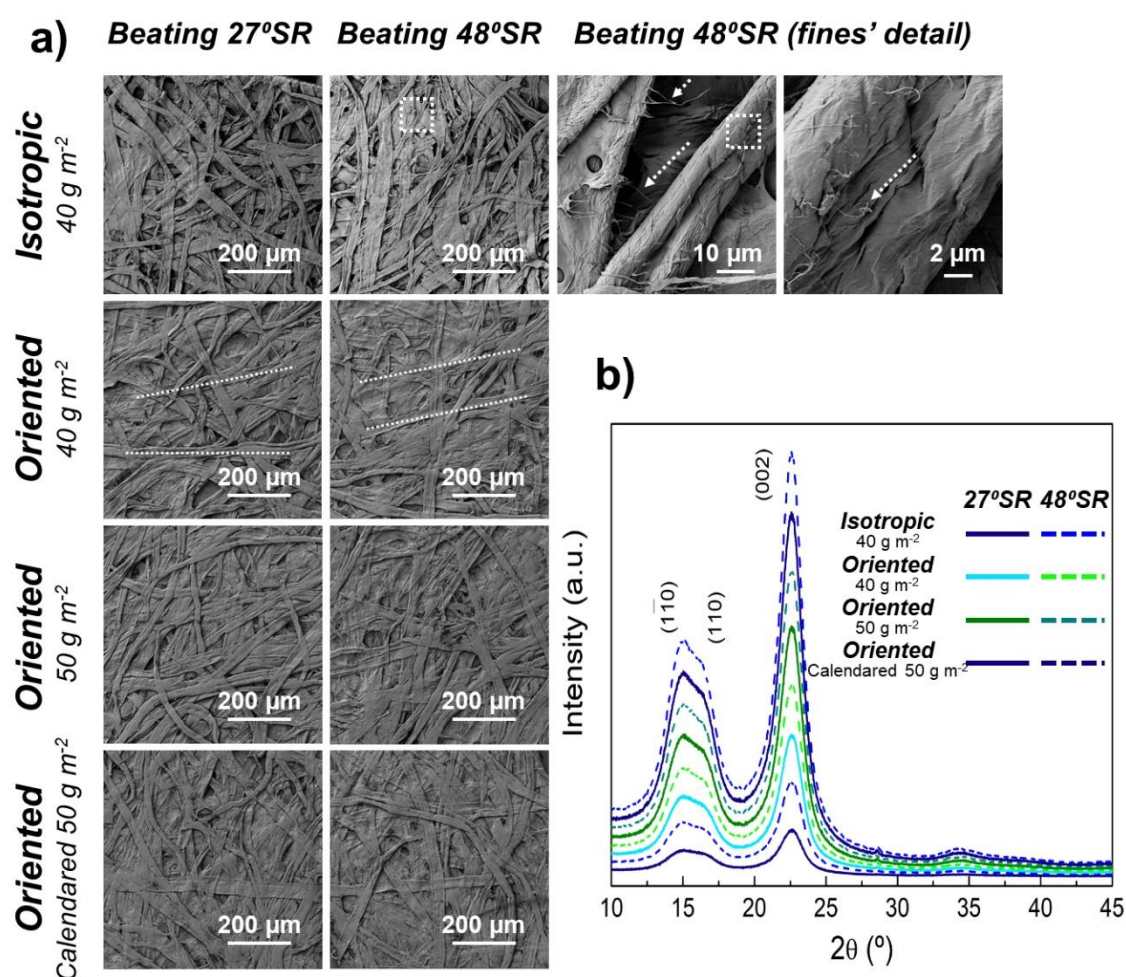


Figure 4.16 a) SEM micrographs for the produced BSKP papers, and b) corresponding diffractograms.

The results presented before demonstrate that a combination of high beating index and calendaring results in a continuous decrease of the porosity and a simultaneous increase of the density without modifying the crystalline structure nor inducing the formation of other

polymorphisms of the cellulose. It is important to mention that regardless of the beating index, the porosity decreases when preferential orientation of the fibres is induced. It is possible to further decrease it in papers with higher basis weight. Table 4.7 summarises the variation of the apparent density and porosity of the paper samples produced, according to the physical modifications tested.

Table 4.7 Characteristics of the tested paper samples.

<i>Sample</i>	<i>Beating 27°SR</i>		<i>Beating 48°SR</i>	
	<i>Apparent density, g cm⁻³</i>	<i>Porosity, %</i>	<i>Apparent density, g cm⁻³</i>	<i>Porosity, %</i>
<i>Isotropic, 40 g m⁻²</i>	0.77	52	0.80	50
<i>Oriented, 40 g m⁻²</i>	0.83	48	0.87	46
<i>Oriented, 50 g m⁻²</i>	0.92	42	0.91	43
<i>Oriented and calendared, 50 g m⁻²</i>	0.97	39	0.96	40

The impedance spectroscopy results in section 4.3.1 show that the capacitance in paper substrates may reach values in the range of $\mu\text{F cm}^{-2}$ at low frequencies (Figure 4.17a) as a result of EDL formation at the paper/electrode's interfaces. When analysing the samples modified by the physical processes described in this section it is possible to verify that the isotropic set presents similar capacitance values at 0.01 Hz (2.3 and 2.4 $\mu\text{F cm}^{-2}$), whereas papers with oriented fibres the values vary between 3.3 and 8.1 $\mu\text{F cm}^{-2}$, regardless of the beating index. The higher capacitance values for the oriented papers cannot be directly related to the amount of water bonded to the fibres since the FTIR data does not suggest considerable differences. Thus, one explanation may be the compacter matrix since it will facilitate migration of mobile ions (such as mobile protons) towards the paper/electrode's interfaces as a response to the applied external bias.

Impedance spectroscopy allows also to determine the bulk resistance of the paper samples. In the Cole-Cole plot (Figure 4.17b) the real part of the impedance corresponds to the bulk resistance of the material when the imaginary part is equal to zero. The data evidences a clear influence of fibre orientation on the resistance of the tested paper samples (Figure 4.17b). In the following paragraphs, only the results for the higher beating index (48°SR) will be discussed since similar results were observed for the papers with 27°SR.

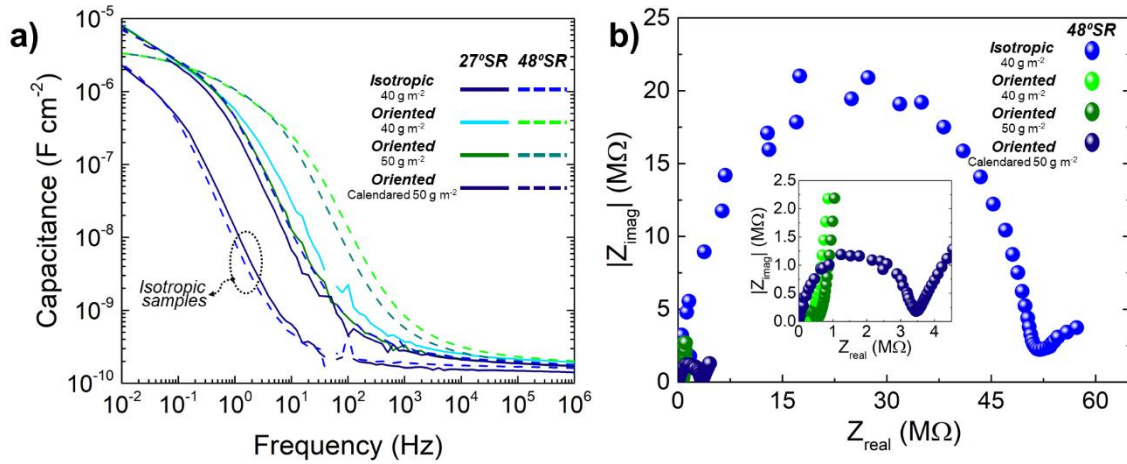


Figure 4.17 a) Capacitance as a function of the frequency for the papers produced with a beating index of 27°SR and 48°SR (solid and dashed lines, respectively), and b) Cole-Cole plots for the papers produced from pulp with 48°SR

For the papers with 48°SR, it is possible to observe an abrupt reduction of the resistance value of roughly two orders of magnitude from 52 $M\Omega$ to 0.33 $M\Omega$ just by giving a preferred orientation to the fibres. Such large variation represents a decrease of ρ from $\approx 16\ G\Omega\ cm$ to $\approx 0.1\ G\Omega\ cm$, respectively. Due to the large ρ values it is not possible to separate accurately the ionic contribution, not even by modelling the EIS data with an equivalent circuit model. Nevertheless, it is expected that a more compact structure of the paper matrix works better as a percolation path for ionic species. On the other hand, the difference in ρ for a given basis weight of 40 and 50 $g\ m^{-2}$ is neglectable for both cases (from ≈ 0.10 to $\approx 0.15\ G\Omega\ cm$).

4.4.2. FETs on BSKP papers

The study of the papers' characteristics can be indicative of its suitability as a gate dielectric in field-effect transistors. In Figure 4.18 the transfer characteristics (I_{DS} – V_{GS}) of the paper gated IGZO FETs at $V_{DS}=15\ V$ (saturation regime) are presented, while the extracted electrical parameters are listed in Table 4.8. The gate capacitance extracted from the C–f measurements at 0.01 Hz, according to the EDL formation, and discussed in the previous section was used to determine the saturation mobility (μ_{sat}) for the produced devices using these papers as a gate dielectric.

In the overall analysis, it is verified that paper with higher beating index leads to better electrical properties, i.e. higher I_{On}/I_{Off} ratio (values between 3×10^3 and $\approx 1 \times 10^4$) and μ_{sat} ,

lower subthreshold slope (S). The highest μ_{sat} ($\approx 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is obtained for the more refined oriented papers with a basis weight of 40 and 50 g m^{-2} , although the value of the capacitance for these papers is lower than for the other oriented papers. The observed increase of the $I_{\text{On}}/I_{\text{Off}}$ ratio and μ_{sat} can be explained due to the decrease in porosity as a result of enhanced bonding between the fibres promoted by the fines. Although there is no suitable explanation for the lower value of μ_{sat} for the calendared papers, it should not be neglected that the resistivity of the papers is higher than for the remaining oriented papers. Also, a more compact matrix may partially limit the amount of water adsorbed and thus compromise a better performance of the devices. The existence of preferential orientation of the fibres can also facilitate the formation of a conductive path for the electrons on the IGZO film between source and drain. The planarization of the surface through calendaring can partially destroy the “bus line” effect produced by the rough fibres. In sub-section 4.4.2.1, the role of the fibres’ orientation will be discussed.

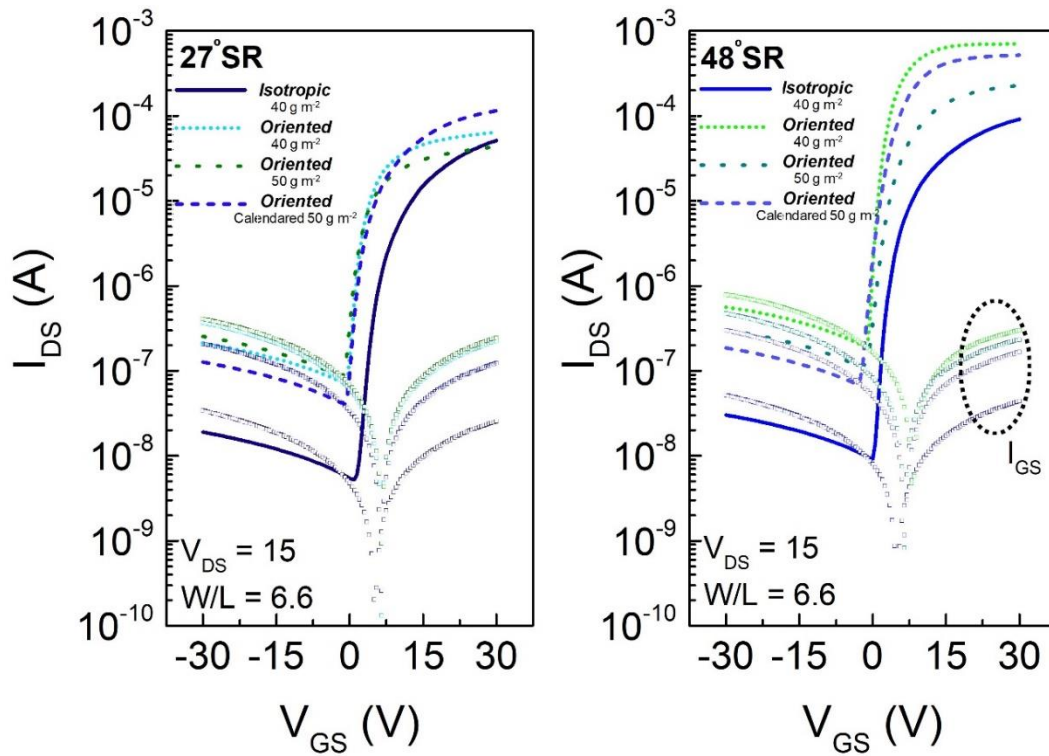


Figure 4.18 $I_{\text{DS}}-V_{\text{GS}}$ transfer curves ($V_{\text{DS}}=15 \text{ V}$) for the FETs produced on the BSKP papers with 27°SR (on the left), and 48°SR (on the right).

The smoother surface and denser matrix in the 48°SR calendared paper leads to an increase of the $I_{\text{On}}/I_{\text{Off}}$ ratio (even if lower than the ratio obtained for the isotropic paper), which is deeply related to the decrease of gate leakage current. In these paper-gated devices, the I_{Off} is ruled by the I_{GS} , resulting in lower I_{Off} values (almost one order of magnitude) for the

isotropic papers (Figure 4.18a), explaining the decrease in the I_{On}/I_{Off} ratio. The I_{GS} values are in line with the resistivity of the BSKP papers as determined by impedance spectroscopy (Figure 4.17b), since the papers with lower resistivity result in FETs with higher I_{Off} . Since there is no addition of extra ionic species during the paper production, it is possible to state that the refining and preferential orientation of the fibres facilitate ion percolation within the matrix (which can be enhanced by the bonded water), as previously mentioned.

Table 4.8 Comparison of the electrical properties of IGZO based FETs for the different BSKP papers tested as a gate dielectric. For the oriented papers, the preferential orientation of the fibres was placed along the width.

	<i>Isotropic</i> (40 g m ⁻²)		<i>Oriented</i> (40 g m ⁻²)		<i>Oriented</i> (50 g m ⁻²)		<i>Oriented</i> <i>Calendared</i> (50 g m ⁻²)	
<i>Properties</i>	<i>27°SR</i>	<i>48°SR</i>	<i>27°SR</i>	<i>48°SR</i>	<i>27°SR</i>	<i>48°SR</i>	<i>27°SR</i>	<i>48°SR</i>
μ_{sat} (cm ² V ⁻¹ s ⁻¹)	0.01	0.03	0.01	0.95	0.01	0.30	0.01	0.17
V_{on} (V)	0.5	0	-0.5	-1.5	-1	-2	-1	-3
I_{on}/I_{off}	9.7×10 ³	9.9×10 ³	9.0×10 ²	4.01×10 ³	5.1×10 ²	3.32×10 ³	2.8×10 ³	7.73×10 ³
S (V dec ⁻¹)	1.52	1.24	1.40	1.05	1.66	1.09	1.43	1.63
C_{real} at 10 mHz (μF cm ⁻²)	2.29	2.41	8.20	3.35	7.89	3.33	8.09	7.00
<i>Thickness</i> (μm)	59	59	57	56	62	63	61	60

The typical output characteristic (V_{DS} - I_{DS}) for the IGZO FETs on the calendared papers with 27°SR and 48°SR are shown in Figure 4.19a and b, respectively. In both devices current saturation for a V_{DS} =15 V in the output characteristics is possible to verify, meaning that the semiconductor is depleted under the drain electrode (pinch off). Similar behaviour was observed for the other papers (data not shown). There is no significant current crowding for low V_{DS} which is indicative for the quality of the S/D contacts. Despite satisfactory contact quality it is expected that device performance is partially affected by the source and drain contact resistance due to the rough surface (in the best-case scenario the RMS roughness of the paper is 5.8 μm).

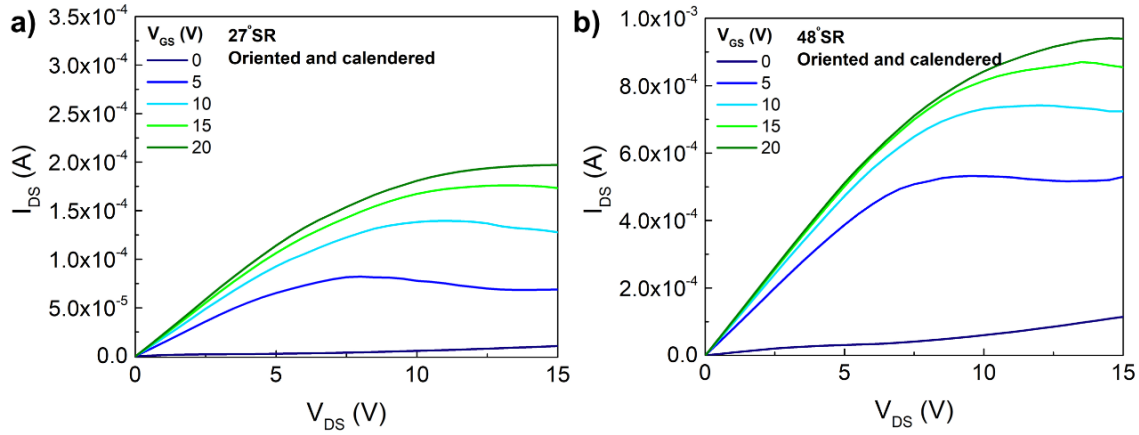


Figure 4.19 Output curves for the IGZO-FET on calendared orientated paper with a) 27°SR, and b) 48°SR, respectively.

4.4.2.1. Influence of the fibres' orientation

This section focusses on the influence of the orientation of the fibres in relation to the FETs channel (Figure 4.20). The electrical characteristics of devices produced on paper samples with the fibres oriented along the width of the channel were already presented in the previous section. Here, the ones produced on samples with the fibres oriented along the length of the channel will be discussed.

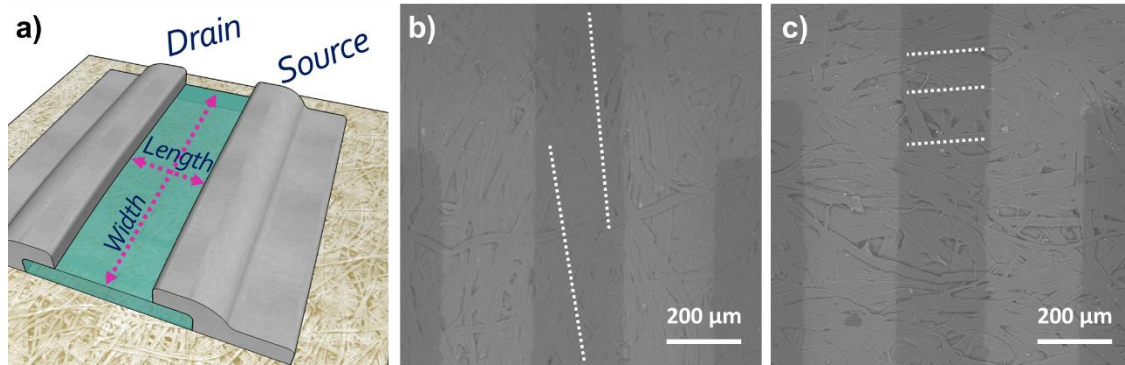


Figure 4.20 Preferential orientation of the fibres in respect to the FETs channel: a) schematic representation, b) width-oriented fibres, and c) length-oriented fibres. The dashed lines in b) and c) aim to highlight the fibres' orientation along the channel.

The orientation of the fibres according to the width or length of the channel seems to influence mostly the I_{On}/I_{Off} ratio and μ_{sat} . The FETs produced with the length-oriented fibres present higher μ_{sat} and I_{On}/I_{Off} ratios than the ones with the fibres oriented along the channel width. A maximum of $1.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is reached for μ_{sat} , which represents an increase of 8% compared to the μ_{sat} determined for the width-oriented FETs (Table 4.9).

Table 4.9 Comparison of the electrical properties of IGZO based FETs for BSKP papers with 48°SR with preferential fibre orientation parallel and perpendicular to the channel.

<i>Properties</i>	<i>Oriented (40 g m⁻²)</i>		<i>Oriented (50 g m⁻²)</i>		<i>Oriented Calendared (50 g m⁻²)</i>	
	<i>Width oriented</i>	<i>Length oriented</i>	<i>Width oriented</i>	<i>Length oriented</i>	<i>Width oriented</i>	<i>Length oriented</i>
μ_{sat} (cm ² V ⁻¹ s ⁻¹)	0.95	1.03	0.30	0.84	0.17	0.28
V_{on} (V)	-1.5	-2	-2	-4	-3	-4
$I_{\text{on}}/I_{\text{off}}$	4.01×10 ³	1.23×10 ⁴	3.32×10 ³	4.27×10 ³	7.73×10 ³	8.23×10 ³
S (V dec ⁻¹)	1.05	1.63	1.09	1.22	1.63	1.27
$C_{\text{real at}}$ 10 mHz (μF cm ⁻²)	3.35	3.35	3.33	3.33	7.00	7.00
<i>Thickness</i> (μm)	56	56	63	63	60	60

The use of artificially created bus lines in the transistor's channel to enhance the electrical properties of amorphous IGZO TFTs is documented [35]. It was verified that using Ag nanowires (NW) arrays it is possible to tune the mobility of the devices playing with the nanowire orientation and the current flow. In such devices, the field effect mobility varies from ≈ 27 to $114 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, for a 90° and 10° orientation between the NW and the current flow. This case has obvious differences to the one that is discussed here, namely the conductive nature of the Ag NW.

Despite the insulating character of the paper and the intricate rough surface, the alignment of the fibres with the current flow direction can actually works like “bus lines”, allowing a more straightforward path between the S/D electrodes, justifying the enhanced $I_{\text{on}}/I_{\text{off}}$ ratio and μ_{sat} [36], which is not verified when the fibre is perpendicularly oriented to the current flow of the deposited IGZO.

4.5. Chemical modification

The use of chemical treatments in the fibres aims essentially for surface chemistry modification. For instance, treatments as oxidation of the cellulose mediated with 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) is often used as pre-treatment to fibrillate the fibres more easily and obtain micro or nanocellulose since it weakens the bonds between the cellulose molecules [37].

In this section the influence of TEMPO-mediated oxidation on bleached eucalyptus kraft pulp¹ and the addition of ionic species to the pulp by the regulation of pH on micro-nanofibrillated cellulose² will be presented. This process changes the surface chemistry of the fibres/fibrils and an evaluation on how it affects the electrical properties of the paper and consequently the produced devices will be given.

4.5.1. Addition of extra ionic species to the micro-nanofibrillated cellulose

4.5.1.1. *M/NFC papers: morphology, structure, and electrical characterisation*

The easiest approach to modify the physiochemistry and surface chemistry of the pulp is through the addition of ionic species. Three different types of paper samples were produced from the pristine BHKP submitted to mechanical and enzymatic pre-treatment. The first type was an untreated paper whose pH was kept at a fixed value of 7. The other two were obtained from pulp with the addition of HCl to decrease the initial pH from 7 to 5.5, and the addition of NaOH to increase the pH up to 8.5.

Figure 4.21 shows that all the M/NFC paper samples have a smooth (RMS Roughness ≈ 2.6 to $3.0\ \mu\text{m}$, determined by 3D profilometry) and a homogenous surface formed by randomly orientated fibrils. For the three cases, it is possible to distinguish larger fibres (length higher than $100\ \mu\text{m}$) embedded in a matrix constituted by smaller ones. The small dimension of the fibrils led to highly compact paper structures with porosity $\approx 20\%$, with an apparent density between 1.21 and $1.24\ \text{g cm}^{-3}$, and thicknesses between 40 and $44\ \mu\text{m}$.

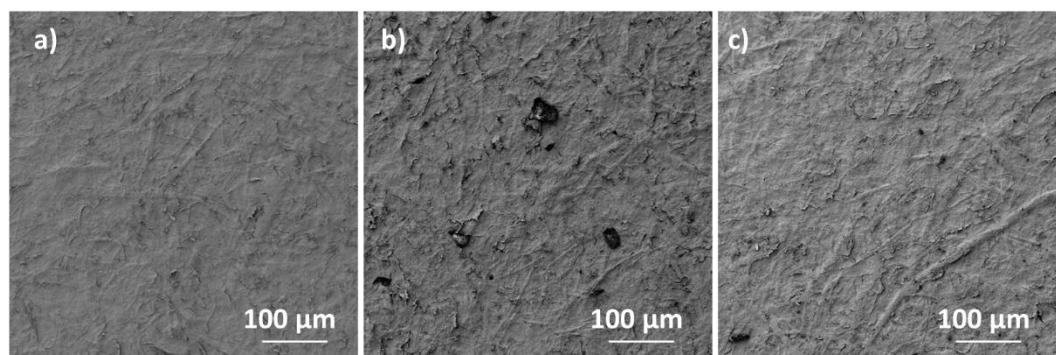


Figure 4.21 SEM micrographs of the M/NFC papers produced with: a) pristine fibres, b) alkaline pulp (pH=8.5 adjusted with NaOH addition), and c) acid pulp (pH=5.5 adjusted with HCl addition).

¹ Papers produced at UBI paper laboratories.

²Papers produced at CTP facilities.

The XRD diffractograms of these papers are similar (Figure 4.22), being possible to identify for all the samples the peaks corresponding to the characteristic monolithic cellulose ($1\bar{1}0$), (110) and (002) crystallographic planes [5]. Beside those crystalline planes, several other diffraction peaks are found that are assumed to be related with the presence of fillers. The peak found at $2\theta \approx 28^\circ$ can be assigned to the CaCO_3 and kalsilite (KAlSiO_4) while a second peak at $2\theta = 18.9^\circ$ can also be ascribed to kalsilite.

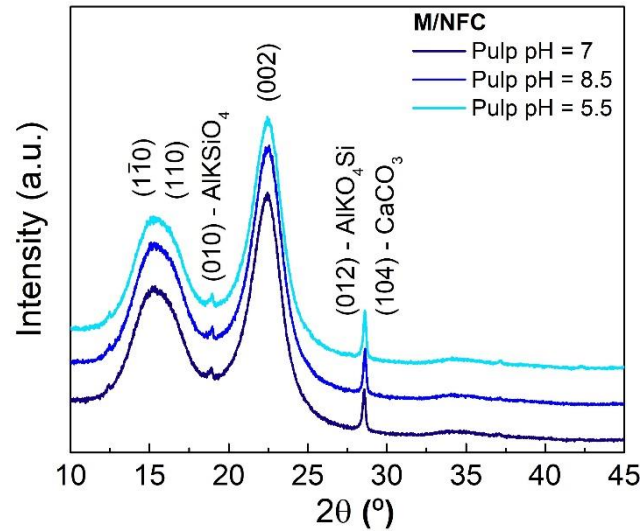


Figure 4.22 XRD diffractograms for the prepared M/NFC papers.

The performed treatment to the pulp does not affect the crystallinity of the cellulose, which is around 71% for all the tested M/NFC papers. These samples have the lowest CrI among all the prepared paper samples along this work. Since these M/NFC fibres were produced with a mixed hardwood pulp, the content of hemicellulose is higher than in the case of softwood. The hemicelluloses are usually amorphous which contributes to the lowering of the crystallinity index of these papers. Also, the mechanical refining and enzymatic treatment of the pulp reduces the size of fibres gradually and opens the cell wall structure. The small fibril dimensions result in high surface area meaning the ratio between disordered surface chains over internal ones is higher than in larger fibres, which leads to the reduction of the CrI [9].

Similarly, to what was discussed in the previous sections, the EDL formation for low frequencies is observed for all the M/NFC papers. However, the increasing tendency for $f=0.01$ mHz, suggests the existence of another relaxation related to the contribution of strongly bound water (Figure 4.23). The capacitance values for these papers are 0.53, 0.25, and $0.11 \mu\text{F cm}^{-2}$, for pH=7, 8.5, and 5.5, respectively.

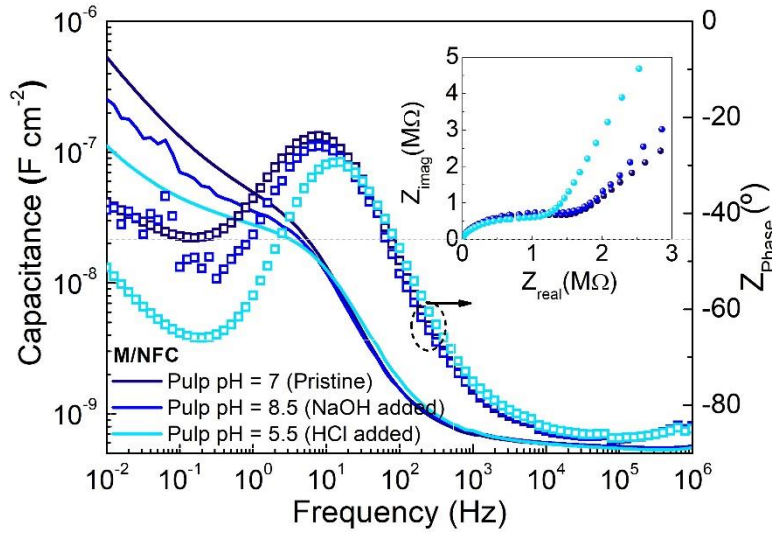


Figure 4.23 Electrochemical Impedance Spectroscopy of the M/NFC papers. Capacitance and phase as a function of the frequency. The inset shows the Cole-Cole plot to determine the papers' resistance.

The addition of ionic species to the pulp results in a variation of the frequency for which the transition from resistive to a capacitive regime occurs ($Z_{\text{Phase}} < -45^\circ$). The papers with $\text{pH} \neq 7$ enter their capacitive regime between 2 Hz (for $\text{pH}=5.5$), and 1 Hz (for $\text{pH}=8.5$), while for the pristine paper the transition only occurs for 0.2 Hz, suggesting higher ionic conductivity and polarizability for the papers with extra ionic species.

The Cole-Cole plot of the M/NFC papers produced with the different pulps is shown in the inset of Figure 4.23. All the papers present similar values of resistivity, varying from 0.7 GΩ cm for the case of the paper made with acid pulp, up to 0.89 GΩ cm, which does not represent a considerable variation.

4.5.1.2. M/NFC papers as a gate dielectric in field-effect transistors

The use of M/NFC paper as a gate dielectric in FET was demonstrated and discussed previously in this chapter. Here the influence of the ionic doping on the electrical characteristics will be in focus. Figure 4.24a shows the transfer characteristics of the M/NFC gated FETs. The devices on papers with extra ionic species show better electrical properties than those on the pristine M/NFC papers. The $I_{\text{On}}/I_{\text{Off}}$ ratio is improved reaching five orders of magnitude for the FETs produced with samples prepared from acid pulp (Table 4.10) mostly due to the increase of the maximum current reached in the device. However, the most impressive enhancement is observed in μ_{sat} , which are around 5 and 14 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, when using pulp with $\text{pH}=8.5$ and 5.5, respectively while for the pristine pulp the value is below 1 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$.

The output curves show that, despite some current crowding for low V_{DS} , suggesting some issues with the S/D contacts that may compromise a stable output to high V_{DS} , it is possible to verify that the FETs reach current saturation for a $V_{DS}=15$ V (Figure 4.24b).

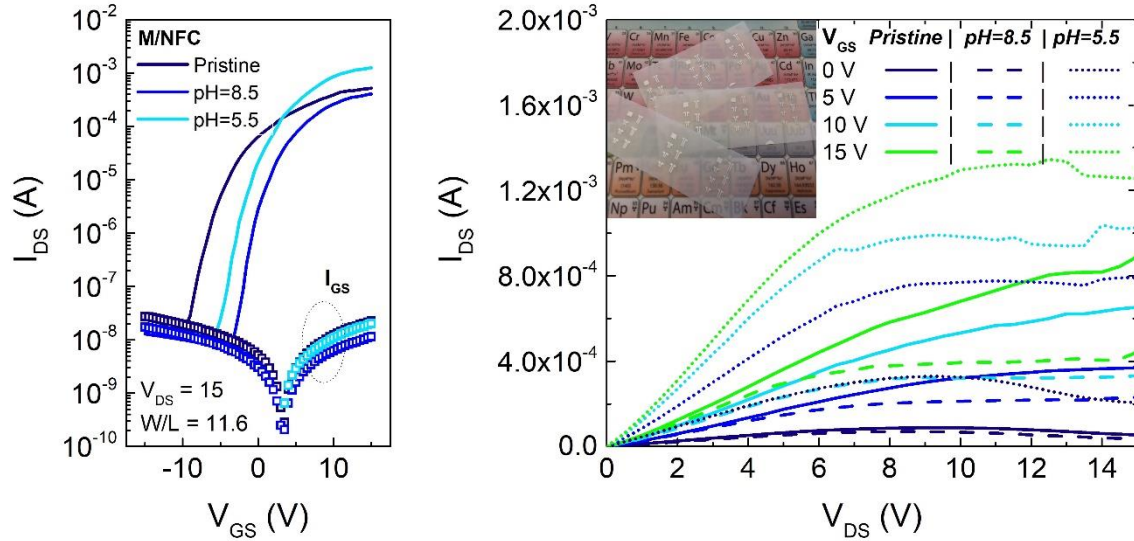


Figure 4.24 a) Transfer characteristics I_{DS} - V_{GS} , and b) output curves of the M/NFC gated transistors. In the inset a photograph of the FETs produced with the M/NFC papers is shown (from top to bottom: M/NFC pristine pulp, pulp with pH=8.5, and pulp with pH=5.5).

The existence of extra anions (Cl^- and OH^-) and cations (H^+ and Na^+) somehow varies the semiconductor's properties. In the case of the papers with lower pH, the maximum value of the On current is in the range of 1 mA. It is supposed that the extra density of protons (H^+) at the fibrils' surface can result in sorption of charges at the paper/IGZO interface, changing the channel's resistance. This phenomenon can occur through chemisorption or physisorption of H^+ at ZnO based materials induced by the applied bias during FET characterisation [9], [22].

Table 4.10 Summary of the electrical properties of IGZO based FETs for the M-NCF papers tested as a gate dielectric.

Properties	Pristine pulp	Pulp's pH=8.5	Pulp's pH=5.5
μ_{sat} ($cm^2 V^{-1} s^{-1}$)	0.62	5.59	14.12
V_{on} (V)	-10	-4	-6.5
I_{on}/I_{off}	3.3×10^4	8.9×10^4	1.1×10^5
S ($V dec^{-1}$)	1.34	1.26	1.20
C_{real} at 10 mHz ($\mu F cm^{-2}$)	0.53	0.25	0.11
Thickness (μm)	43	40	44

It is not expected that the alkalisation of the pulp has a bigger impact on the semiconductor properties as in the case of the protonation with H^+ . Both OH^- and Na^+ are supposed to have lower ionic mobility than H^+ . Moreover, they also have a larger ionic radius, which limits the chemisorption or physisorption of those species in the IGZO. Nevertheless, the presence of hydroxides on the fibrils' surface can result in a larger amount of negatively charged ions at the paper/semiconductor interface, which can result in a partial depletion of the electrons in the channel leading to a V_{On} shift to higher values.

4.5.1.3. FETs stability over time

In sub-section 4.3.6, it was seen that the M/NFC gated FETs had better electrical stability over time. The change in the pH of the pulp during the paper production through the addition of ionic species H^+ and Na^+ in the form of HCl and NaOH, results in a significant improvement of the devices' electrical performance together with better stability over time.

Some IGZO FETs without any passivation were produced in an early stage of this work (sub-section 4.5.1.2), and the electrical performance of those devices was again assessed four years after being stored at room temperature in a sample box at atmospheric conditions. Regardless of the M/NFC paper the transfer characteristics demonstrate the stability over time of these FETs. In general, the electrical parameters are similar to those obtained before for “fresh” devices (Figure 4.25 and Table 4.11).

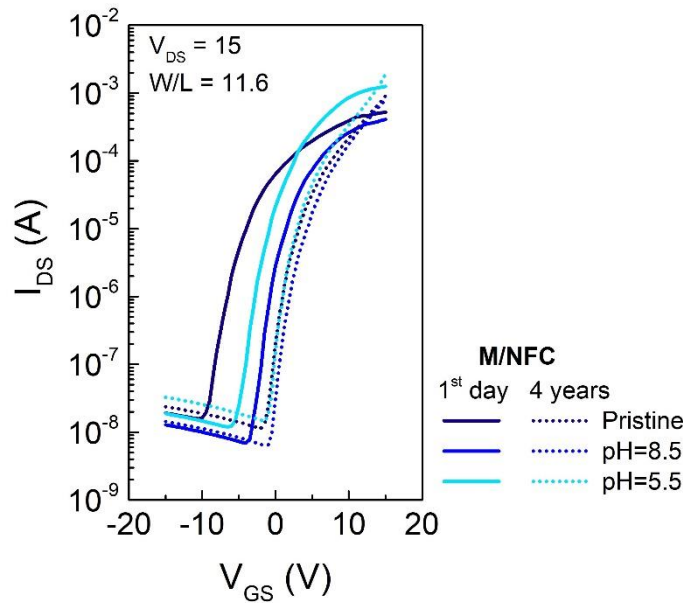


Figure 4.25 Aging effect of the M/NFC gated FETs: transfer characteristics I_{DS} - V_{GS} of the devices produced on M/NFC with different pH levels. The solid line represents “fresh” devices (1st day), while the dotted line stands for the devices aged for four years.

Despite the impressive electrical performance of the aged devices it is worth to mention two aspects: firstly, a positive V_{On} shift is observed. As discussed in sub-section 4.3.6 the shift is the consequence of the non-passivation of the channel allowing the adsorption of O_2 molecules that might form a depletion region through electron acceptor states in the channel surface [30], [38]. A second aspect is the steep increase of the I_{DS} for V_{GS} values above 10 V, whose behaviour is not in line with what was observed for new devices. However, it should be kept in mind that the presence of the ions in direct contact with the IGZO over the years may have resulted in chemisorption or physisorption of those species in the IGZO layer. Thus, it should not be disregarded that the high applied gate voltages during testing could result in a possible process of electrochemical doping of the IGZO [9]. Despite these two aspects, great stability for these non-passivated devices after such a long period is undeniable. As far as it is known, there is no report about the stability of cellulose-based FETs over time since the paper electronics is often referred to as a disposable and single-use technology. With this evaluation, it is not only possible to ensure that the cellulose-gated FETs retain proper operation over a considerable long period, but it is also demonstrated that selecting the most suitable fibre types and ionic doping, the performance is maintained.

Table 4.11 Summary of the electrical properties of aged IGZO FETs for the M-NCF membranes tested as a gate dielectric.

Properties		Pristine pulp	Pulp's pH=8.5	Pulp's pH=5.5
I_{On}/I_{Off}	Day 1	3.3×10^4	8.9×10^4	1.1×10^5
	After 4 years	8.9×10^4	1.3×10^5	1.3×10^5
μ_{sat} ($cm^2 V^{-1} s^{-1}$)	Day 1	0.62	5.59	14.12
	After 4 years	1.01	10.24	9.14
V_{on} (V)	Day 1	-10	-4	-6.5
	After 4 years	-2	-1.5	-1.5
S ($V dec^{-1}$)	Day 1	1.34	1.26	1.20
	After 4 years	1.06	1.04	0.95

4.5.2. Papers produced with TEMPO-mediated oxidised pulps

The 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation is one of the most commonly used treatments to enhance the fibrillation process, since it weakens the hydrogen bonding between the cellulose chains. The TEMPO system destroys the inter

fibrils hydrogen bonds and oxidises the C₆ hydroxyl groups to carboxyl groups or carboxylate depending on the reaction (Figure 4.26) [5], [37]. The most usual system includes TEMPO, sodium bromide (NaBr) and, sodium hypochlorite (NaClO) as oxidants and occurs in water at pH 10–11. Along this PhD, pulps with two oxidation levels were prepared through the TEMPO/NaBr/NaClO systems at UBI. In this process, the pH is monitored and kept at 10 through an aqueous solution of NaOH (0.1 M), as described elsewhere [37], [39].

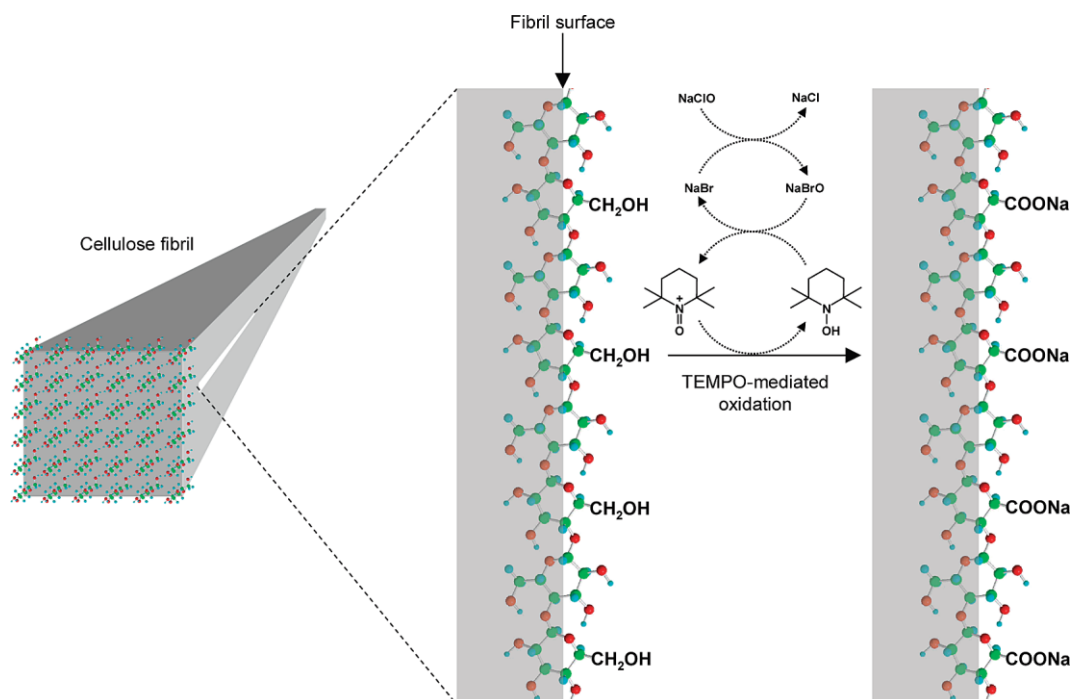


Figure 4.26 Schematic representation of the selective oxidation of mainly the C₆ primary hydroxyl groups to C₆ sodium carboxylate groups using the TEMPO/NaBr/NaClO system [40].

4.5.2.1. *TEMPO-mediated oxidised papers*

The papers with different oxidation levels were produced in the paper laboratory facilities at UBI, using commercial dry bleached eucalyptus kraft pulp (BEKP). This pulp was submitted to TEMPO-mediated oxidation, and then the oxidised pulps were directly used to produce paper hand-sheets, according to the standard procedures. The oxidation level can be tuned with the amount of added NaClO, whose main role is that of a primary oxidant. Two charges of NaClO were used (2 and 4 mmol per gram of cellulose) with the expectation that an increase of the oxidant agent amount would lead to the increase of the number of sodium carboxylate groups (COONa) linked to the C₆.

The TEMPO treatments performed in the scope of this PhD seem to have negligible influence on the structural and morphological characteristics of the formed paper samples. The TEMPO treatment did not change the cellulose crystallinity ($\text{CrI} \approx 80\%$) since just the XRD characteristic diffraction peaks for the $(1\bar{1}0)$, (110) and (002) crystallographic planes, assigned to semi-crystalline cellulose I, were observed (diffractograms not shown). The SEM images show that similar surface morphologies were obtained for the three tested TEMPO treatments, revealing a porous matrix (porosity near 56%) with randomly oriented fibres (Figure 4.27).

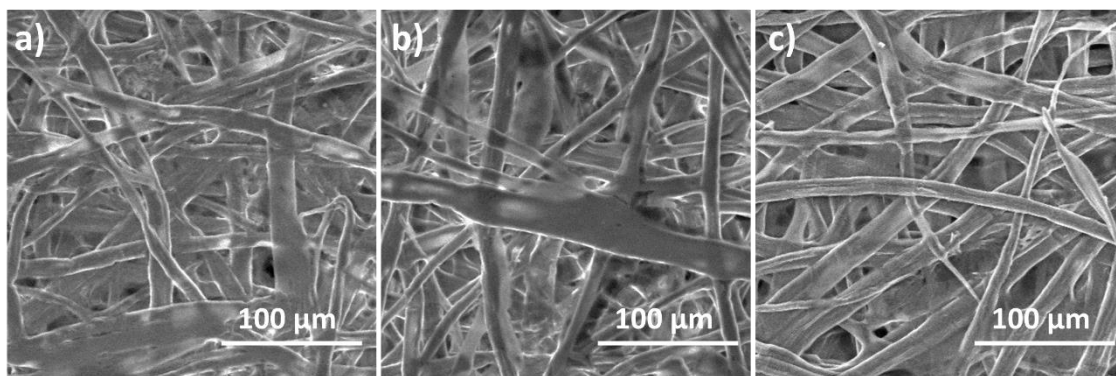


Figure 4.27 Micrographs of the bleached eucalyptus kraft pulp paper with different oxidation levels. a) no oxidation, b) oxidation with 2 mmol of NaClO, and c) oxidation with 4 mmol of NaClO.

4.5.2.2. *Influence of the oxidation level in the FETs' performance*

The transfer characteristic curves (Figure 4.28) of the FETs produced using BEKP paper (oxidised and not oxidised) demonstrates that the I_{GS} value is dependent on the oxidation level, and consequently determines the performance of the FETs.

For papers prepared with a lower amount of primary oxidant (2 mmol of NaClO), the performance of the devices is not affected, despite the higher value of I_{GS} when compared to the pristine not oxidised paper (Table 4.12). The increase of the I_{Off} is ruled by the I_{GS} and thus is also governed by the paper's resistivity that is close to $6 \text{ G}\Omega \text{ cm}$ with no oxidation, decreasing down to $2.2 \text{ G}\Omega \text{ cm}$ for the papers with low oxidation level, and to $\approx 0.13 \text{ G}\Omega \text{ cm}$ for the papers with higher oxidation levels. Therefore, the reduction of I_{On}/I_{Off} by more than one order of magnitude for the FETs on oxidised paper is understandable (4 mmol of NaClO).

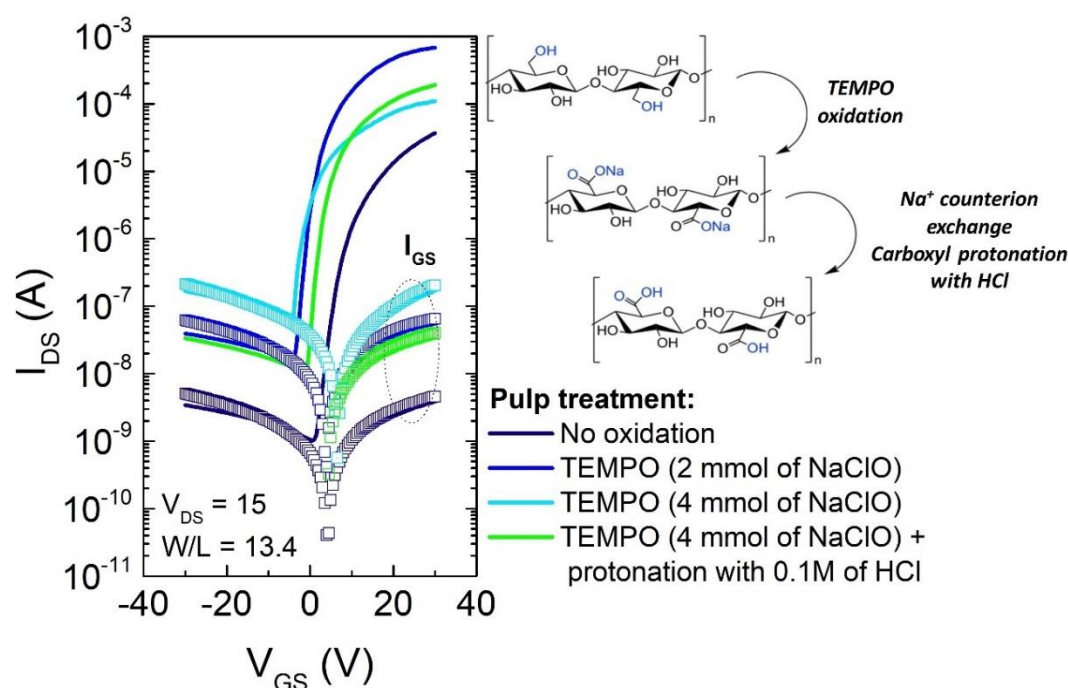


Figure 4.28 Transfer characteristics of the FETs on BEKP papers with different oxidation grades. On the top right the steps of the preparation of TEMPO-oxidized cellulose and counterion exchange with HCl is depicted.

Table 4.12 Summary of the electrical properties of IGZO based FETs for the BEKP papers tested as the gate dielectric.

Properties	No oxidation	TEMPO (2 mmol NaClO)	TEMPO (4 mmol NaClO)	TEMPO + Protonation (4 mmol NaClO and 0.1 M HCl)
μ_{FE} ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	0.26	0.21	0.11	0.02
V_{on} (V)	0.5	-5	-4.5	-1.5
I_{on}/I_{off}	3.6×10^4	4.3×10^4	1.8×10^3	1.8×10^4
S (V dec^{-1})	1.82	1.45	1.46	1.33
C_{real} at 10 mHz ($\mu\text{F cm}^{-2}$)	0.05	0.82	0.24	2.53
Resistivity ($\text{G}\Omega \text{cm}$)	6.2	2.2	0.13	0.67
Thickness (μm)	84	91	94	94

The increase of I_{GS} with the TEMPO treatment can be partially explained by the fibres' interaction. An increase of the oxidation grade of the cellulose leads to a replacement of hydroxyl groups by carboxylates. This leads to a decrease of the hydrogen bonding between fibres and the existence of COO^- groups, when non-neutralised, increasing the electronegativity of the fibres and consequently the electric double layer repulsion [41].

It was found that the I_{GS} of the devices could be reduced through protonation of the TEMPO-oxidized cellulose. The Na^+ counterion exchange in the carboxyl groups (Figure 4.28 – top right) was promoted by an aqueous solution of HCl (0.1 M), which was added to the suspension of the oxidised slurry, by keeping it under this condition for 12 hours.

Like Na^+ , the addition of H^+ ions to the cellulose, charges the fibres negatively. For the tested conditions it is expected that the larger amounts of charged sodium carboxylate groups cause higher electrostatic repulsion [37], while the addition of the second ones, which will replace the sodium carboxylates, can promote a better cohesion of the fibres through the creation of more hydrogen bonds.

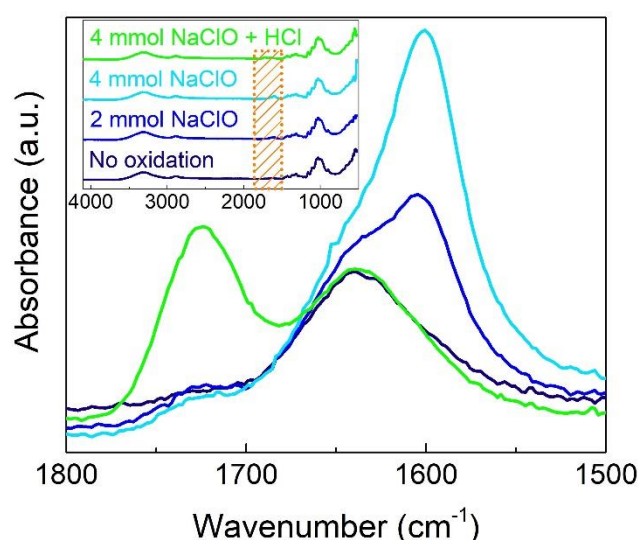


Figure 4.29 ATR-FTIR data of the BEKP papers with different oxidation grades. The inset shows the full spectra acquired with indication of the zoomed region.

The oxidation of the fibres influences the dielectric behaviour of the paper. High oxidation levels will lead to a large number of sodium carboxylates which become more pronounced with the concentration of the used oxidant (NaClO). This can be observed in the ATR-FTIR, where it is possible to identify the presence of the carboxylate groups at *ca* 1600 cm^{-1} (Figure 4.29). The large amounts of COONa groups will reduce the available hydrogen, which is responsible for the proton transfer from the hydroxyl groups to the water molecules (Grotthus-like mechanism) [26]. The hydrogen-bonds can be partially recovered through the Na^+ counterion exchange through protonation with H^+ , resulting in an annihilation of the carboxylate groups with the appearance of carboxylic acid groups at *ca* 1740 cm^{-1} (Figure 4.29) [42].

4.6. References

- [1] L. Segal, J. J. Creely, A. E. Martin, and C. M. Conrad, "An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer," *Text. Res. J.*, 1959.
- [2] V. L. D. Costa, A. P. Costa, M. E. Amaral, C. Oliveira, M. Gama, F. Dourado, and R. M. Simões, "Effect of hot calendering on physical properties and water vapor transfer resistance of bacterial cellulose films," *J. Mater. Sci.*, vol. 51, no. 21, pp. 9562–9572, Nov. 2016.
- [3] D. Le Bras, M. Strømme, and A. Mihranyan, "Characterization of dielectric properties of nanocellulose from wood and algae for electrical insulator applications," *J. Phys. Chem. B*, vol. 119, no. 18, pp. 5911–5917, 2015.
- [4] M. Schwanninger, J. C. Rodrigues, H. Pereira, and B. Hinterstoisser, "Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose," *Vib. Spectrosc.*, vol. 36, pp. 23–40, 2004.
- [5] F. Jiang and Y.-L. Hsieh, "Self-assembling of TEMPO Oxidized Cellulose Nanofibrils As Affected by Protonation of Surface Carboxyls and Drying Methods," *ACS Sustain. Chem. Eng.*, vol. 4, no. 3, pp. 1041–1049, Mar. 2016.
- [6] R. H. Marchessault, "Application of infra-red spectroscopy to cellulose and wood polysaccharides," *Pure Appl. Chem.*, vol. 5, no. 1–2, Jan. 1962.
- [7] J. Grdadolnik and Y. Maréchal, "Bovine serum albumin observed by infrared spectrometry. I. Methodology, structural investigation, and water uptake," *Biopolymers*, vol. 62, no. 1, pp. 40–53, 2001.
- [8] M. T. Kalichevsky, E. M. Jaroszkiewicz, S. Ablett, J. M. V. Blanshard, and P. J. Lillford, "The glass transition of amylopectin measured by DSC, DMTA and NMR," *Carbohydr. Polym.*, vol. 18, no. 2, pp. 77–88, Jan. 1992.
- [9] L. Pereira, D. Gaspar, D. Guerin, A. Delattre, E. Fortunato, and R. Martins, "The influence of fibril composition and dimension on the performance of paper gated oxide transistors," *Nanotechnology*, vol. 25, no. 9, p. 094007, Mar. 2014.
- [10] D. Gaspar, L. Pereira, A. Delattre, D. Guerin, E. Fortunato, and R. Martins, "Engineered cellulose fibers as dielectric for oxide field effect transistors," *Phys. Status Solidi Curr. Top. Solid State Phys.*, vol. 12, no. 12, pp. 1421–1426, Dec. 2015.
- [11] Y. Peng, D. J. Gardner, and Y. Han, "Drying cellulose nanofibrils: In search of a suitable method," *Cellulose*, vol. 19, pp. 91–102, 2012.
- [12] H. Theliander, *Pulping Chemistry and Technology Volume 2*, vol. 2. Berlin, New York: Walter de Gruyter, 2009.
- [13] V. I. Popa, Ed., *Pulp Production and Processing: From Papermaking to High-Tech Products*, 1st ed. Shawbury, Shrewsbury, Shropshire: iSmithers Rapra Publishing, 2013.
- [14] J.-L. Wertz, O. Bédué, and J. P. Mercier, *Cellulose Science and Technology*, 1st ed. Lausanne: EPFL Press, 2010.
- [15] A. Dufresne, *Nanocellulose: From Nature to High Performance Tailored Materials*, 1st ed. Berlin, Boston: De Gruyter, 2012.
- [16] M. Gama, F. Dourado, and S. Bielecki, *Bacterial Nanocellulose - From Biotechnology to Bio-Economy*, 1st ed., vol. 1. Elsevier, 2016.
- [17] L. Ma and Y. Yang, "Solid-state supercapacitors for electronic device applications," *Appl. Phys. Lett.*, vol. 87, no. 12, p. 123503, 2005.
- [18] O. Larsson, E. Said, M. Berggren, and X. Crispin, "Insulator Polarization Mechanisms in Polyelectrolyte-Gated Organic Field-Effect Transistors," *Adv.*

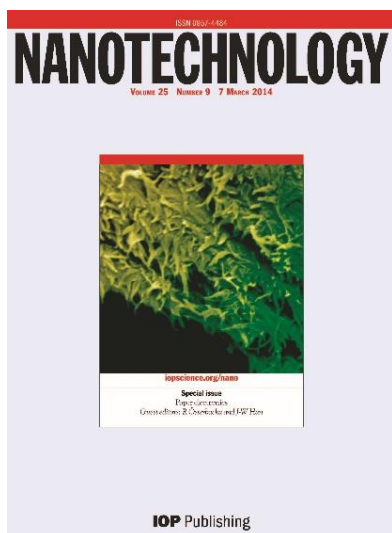
- Funct. Mater.*, vol. 19, no. 20, pp. 3334–3341, Oct. 2009.
- [19] H. G. O. Sandberg, T. G. Bäcklund, R. Österbacka, and H. Stubb, “High-Performance All-Polymer Transistor Utilizing a Hygroscopic Insulator,” *Adv. Mater.*, vol. 16, no. 13, pp. 1112–1115, Jul. 2004.
- [20] M. J. Panzer and C. D. Frisbie, “Exploiting Ionic Coupling in Electronic Devices: Electrolyte-Gated Organic Field-Effect Transistors,” *Adv. Mater.*, vol. 20, no. 16, pp. 3177–3180, Aug. 2008.
- [21] S. Dasgupta, S. Gottschalk, R. Kruk, and H. Hahn, “A nanoparticulate indium tin oxide field-effect transistor with solid electrolyte gating,” *Nanotechnology*, vol. 19, no. 43, 2008.
- [22] H. Yuan, H. Shimotani, A. Tsukazaki, A. Ohtomo, M. Kawasaki, and Y. Iwasa, “Hydrogenation-Induced Surface Polarity Recognition and Proton Memory Behavior at Protic-Ionic-Liquid/Oxide Electric-Double-Layer Interfaces,” *J. Am. Chem. Soc.*, vol. 132, no. 19, pp. 6672–6678, May 2010.
- [23] H. Xiao, L. Q. Zhu, Y. H. Liu, and R. Liu, “Proton gated oxide electric-double-layer transistors for full-swing low voltage inverter applications,” *RSC Adv.*, vol. 6, no. 2, pp. 1053–1057, 2016.
- [24] Z. Zheng, J. Jiang, J. Guo, J. Sun, and J. Yang, “Chitosan-gated low-voltage transparent indium-free aluminum-doped zinc oxide thin-film transistors,” *Org. Electron.*, vol. 33, pp. 311–315, Jun. 2016.
- [25] F. Shao, P. Feng, C. Wan, X. Wan, Y. Yang, Y. Shi, and Q. Wan, “Multifunctional Logic Demonstrated in a Flexible Multigate Oxide-Based Electric-Double-Layer Transistor on Paper Substrate,” *Adv. Electron. Mater.*, vol. 3, no. 3, p. 1600509, Mar. 2017.
- [26] G. Wu, J. Zhang, X. Wan, Y. Yang, and S. Jiang, “Chitosan-based biopolysaccharide proton conductors for synaptic transistors on paper substrates,” *J. Mater. Chem. C*, pp. 6249–6255, 2014.
- [27] J. Zhang, J. Dai, L. Zhu, C. Chen, and Q. Wan, “Laterally Coupled IZO-Based Transistors on Free-Standing Proton Conducting Chitosan Membranes,” *IEEE Electron Device Lett.*, vol. 35, no. 8, pp. 838–840, Aug. 2014.
- [28] R. Martins, D. Gaspar, M. J. Mendes, L. Pereira, J. Martins, P. Bahubalindrani, P. Barquinha, and E. Fortunato, “Papertronics: Multigate paper transistor for multifunction applications,” *Appl. Mater. Today*, vol. 12, pp. 402–414, 2018.
- [29] Z. Suo, E. Y. Ma, H. Gleskova, and S. Wagner, “Mechanics of rollable and foldable film-on-foil electronics,” *Appl. Phys. Lett.*, 1999.
- [30] K. Y. Shin, Y. J. Tak, W.-G. Kim, S. Hong, and H. J. Kim, “Improvement of Electrical Characteristics and Stability of Amorphous Indium Gallium Zinc Oxide Thin Film Transistors Using Nitrocellulose Passivation Layer,” *ACS Appl. Mater. Interfaces*, vol. 9, no. 15, pp. 13278–13285, Apr. 2017.
- [31] S.-H. Kim, K.-H. Choi, S.-J. Cho, J. Yoo, S.-S. Lee, and S.-Y. Lee, “Flexible/shape-versatile, bipolar all-solid-state lithium-ion batteries prepared by multistage printing,” *Energy Environ. Sci.*, vol. 11, no. 2, pp. 321–330, 2018.
- [32] S. Hong, S. P. Park, Y. Kim, B. H. Kang, J. W. Na, and H. J. Kim, “Low-temperature fabrication of an HfO₂ passivation layer for amorphous indium–gallium–zinc oxide thin film transistors using a solution process,” *Sci. Rep.*, vol. 7, no. 1, p. 16265, Dec. 2017.
- [33] M. Nogi, K. Handa, A. N. Nakagaito, and H. Yano, “Optically transparent bionanofiber composites with low sensitivity to refractive index of the polymer matrix,” *Appl. Phys. Lett.*, vol. 87, no. 24, p. 243110, Dec. 2005.
- [34] S. A. Paralikar, J. Simonsen, and J. Lombardi, “Poly(vinyl alcohol)/cellulose

- nanocrystal barrier membranes,” *J. Memb. Sci.*, vol. 320, no. 1–2, pp. 248–258, Jul. 2008.
- [35] H.-C. Liu, Y.-C. Lai, C.-C. Lai, B.-S. Wu, H.-W. Zan, P. Yu, Y.-L. Chueh, and C.-C. Tsai, “Highly Effective Field-Effect Mobility Amorphous InGaZnO TFT Mediated by Directional Silver Nanowire Arrays,” *ACS Appl. Mater. Interfaces*, vol. 7, no. 1, pp. 232–240, Jan. 2015.
- [36] P. Barquinha, R. Martins, L. Pereira, and E. Fortunato, *Transparent Oxide Electronics: From Materials to Devices*, 1st ed. West Sussex: Wiley, 2012.
- [37] A. Isogai, T. Saito, and H. Fukuzumi, “TEMPO-oxidized cellulose nanofibers,” *Nanoscale*, vol. 3, no. 1, pp. 71–85, 2011.
- [38] X. Du, B. T. Flynn, J. R. Motley, W. F. Stickle, H. Bluhm, and G. S. Herman, “Role of Self-Assembled Monolayers on Improved Electrical Stability of Amorphous In-Ga-Zn-O Thin-Film Transistors,” *ECS J. Solid State Sci. Technol.*, vol. 3, no. 9, pp. Q3045–Q3049, Jul. 2014.
- [39] A. F. Lourenço, J. A. F. Gamelas, T. Nunes, J. Amaral, P. Mutjé, and P. J. Ferreira, “Influence of TEMPO-oxidised cellulose nanofibrils on the properties of filler-containing papers,” *Cellulose*, vol. 24, no. 1, pp. 349–362, Jan. 2017.
- [40] Y. Okita, T. Saito, and A. Isogai, “Entire Surface Oxidation of Various Cellulose Microfibrils by TEMPO-Mediated Oxidation,” *Biomacromolecules*, vol. 11, no. 6, pp. 1696–1700, Jun. 2010.
- [41] J.-H. Chen, J.-G. Liu, Y.-Q. Su, Z.-H. Xu, M.-C. Li, R.-F. Ying, and J.-Q. Wu, “Preparation and properties of microfibrillated cellulose with different carboxyethyl content,” *Carbohydr. Polym.*, vol. 206, pp. 616–624, Feb. 2019.
- [42] Y. Jin, K. J. Edler, F. Marken, and J. L. Scott, “Voltammetric optimisation of TEMPO-mediated oxidations at cellulose fabric,” *Green Chem.*, vol. 16, no. 6, pp. 3322–3327, 2014.

Transistors on modified micro/nanocellulose membranes

The work presented in this chapter focuses on nanocellulose substrates and their application in FETs. Vegetal nanocellulose was prepared in CTP (France) that kindly provided the samples and at UBI facilities. The bacterial cellulose was produced and tailored for this work in Minho University at the Centre of Biological Engineering. The nanofibrillated cellulose membranes and FETs were produced in CEMOP while their characterisation was made in CENIMAT and CEMOP facilities.

Part of the content of **Chapter 5** was adapted from the publications:



D. Gaspar, S. N. Fernandes, A. G. de Oliveira, J. G. Fernandes, P. Grey, R. V. Pontes, L. Pereira, R. Martins, M. H. Godinho, and E. Fortunato, “Nanocrystalline cellulose applied simultaneously as the gate dielectric and the substrate in flexible field effect transistors”, *Nanotechnology*, vol. 25, no. 9, p. 94008, 2014.

E. Fortunato, **D. Gaspar**, P. Duarte, L. Pereira, H. Águas, A. Vicente, F. Dourado, M. Gama, R. Martins, Chapter 11 “Optoelectronic Devices from Bacterial NanoCellulose”, in *Bacterial Nanocellulose - From Biotechnology to Bio-Economy*, 1st ed. Elsevier, 179-198, 2016 (DOI: 10.1017/CBO9781107415324.004)

A. T. Vicente, A. Araújo, **D. Gaspar**, L. Santos, A. C. Marques, M. J. Mendes, L. Pereira, E. Fortunato, and R. Martins, Chapter 3 “Optoelectronics and Bio Devices on Paper Powered by Solar Cells,” in *Nanostructured Solar Cells*, 1st ed. InTech, 33–65, 2017 (DOI: 10.5772/66695).

D. Gaspar, P. Grey, J. Martins, R. Simões, F. Gama, R. Martins, E. Fortunato, and L. Pereira “Alkali-doped micro/nanofibrillated cellulose membranes applied as gate dielectric in FETs with improved electrical performance” (under preparation).

Transistors on modified micro/nanocellulose membranes

Chapter 5. Transistors on modified micro/nanocellulose membranes	163
Lightweight micro/nanocellulose membranes	163
5.1. Micro/nanofibrillated cellulose	164
5.1.1. Micro/nanofibrillated cellulose and influence of the alkaline ion doping	165
5.1.1.1. Structural and morphological characterisation	165
5.1.1.2. Electrochemical characterisation of the NFC-membranes	169
5.1.1.3. NFC-Membranes as gate dielectric in oxide FETs	174
5.1.1.4. Shelf time stability of the NFC-gated FETs	177
5.1.1.5. Flexibility, and electrical endurance of the pristine membranes	179
5.1.1.6. Recyclability	184
5.2. Nanocrystalline cellulose	187
5.2.1. Structural and morphological properties of NCC membranes	187
5.2.2. NCC-gated FETs	189
5.3. All-cellulose composites	191
5.3.1. Structure and morphology	191
5.3.2. All-cellulose composites as gate dielectric in FETs	193
5.4. Bacterial Cellulose	195
5.4.1. Alkali-doped BC membranes	195
5.4.1.1. Morphological and structural characterisation	196
5.4.1.2. Application of BC as dielectric in field-effect transistors	199
5.4.2. Highly pure membranes and pH influence	201
5.4.2.1. pH influence on oxide-based FETs performance	202
5.5. References	203

Chapter 5. Transistors on modified micro/nanocellulose membranes

In the previous chapter, the possibility of using “standard” paper as a gate dielectric was shown. However, the characteristics of those papers, such as roughness and porosity, impose some limitations on the operation of FETs, namely on the required voltage levels. Thus, in a sequence of Chapter 4, the focus here will be on the properties of different papers, produced with micro and nanofibrillated cellulose from different sources, as well as their application as dielectrics in FETs. Due to the specificity of the resulting paper-like substrates, such as much lower basis weight and thickness, from now they will be named as “membranes”.

Lightweight micro/nanocellulose membranes

Nowadays micro/nanocellulose captures a lot of attention in the research community due to its mechanical robustness, smoothness, and even optical properties, namely the possibility to form transparent membranes. Nanocellulose can be categorised as nanofibrillated cellulose (NFC) or cellulose nanofibrils (CNFs), nanocrystalline cellulose (NCCs), and bacterial cellulose (BC). The characteristics of these materials were already described in detail in Chapter 1, but it is worth to recall some relevant characteristics.

The CNF and CNC are obtained through a top-down process where the fibres are downsized and deconstructed to obtain different products according to the production method and crystalline content. Acid hydrolysis leads to microcrystalline bundles and nanocellulose crystals (or whiskers), while mechanical processes combined (or not) with enzymatic or chemical pre-treatments lead to micro and nanofibrillated cellulose (Figure 5.1) [1]–[3]. On the other hand, bacterial cellulose is obtained with a bottom-up approach, where long individual cellulose fibrils (with high length/width aspect ratio) are produced extracellularly through a biological extrusion mechanism made by the bacteria in an adequate medium.

These three nanocellulose substrates were studied during this PhD work and the following subsections will be discussed the modifications made to the fibres, membrane formation, their characterisation, and application as gate-dielectric in oxide-based FETs. Table 5.1 summarises the nanocellulose membranes used along this chapter.

Pulp/paper	Source	Supplier	Acronym
Bleached birch kraft pulp	Birch (hardwood)	CTP	BBKP and NFC-BBKP
Bleached sulphite eucalypt pulp	Eucalypt (hardwood)	UBI	BSEP and NFC-BSEP
Nanocrystalline cellulose	Cotton	FCT-UNL	NCC
	Unknown	CelluForce	
Bacterial Cellulose	<i>Komagataeibacter xylinus</i>	Minho University	BC

Among the different types of nanocellulose, the micro/nanofibrillated one is by far the most studied. The approach to obtain it can involve different types of mechanical processes, chemical or enzymatic pre-treatments, or a combination of them. During this work micro/nanofibrillated cellulose produced by CTP (obtained from bleached birch kraft pulp - BBKP) and UBI (produced with commercial bleached sulphite eucalypt pulp - BSEP) was used following the steps described in Chapter 2. The NFCs were received in the form of a gel (Figure 5.2) with a solid content of 2% and 1%, respectively.



Figure 5.2 NFC gel produced at CTP (on the left) and UBI (on the right) laboratories.

5.1.1. Micro/nanofibrillated cellulose and influence of the alkaline ion doping

In the previous chapter, the enhancement of the electrical properties of FETs through the intentional addition of ionic species to the pulp before paper formation was discussed. Having this in mind, after forming the pristine dried NFC membranes they were “doped” with lithium (Li), sodium (Na), and potassium (K) ions through infiltration of respective metal hydroxide solutions at 0.5 M. In the following sections, membranes prepared with NFCs from CTP are treated as BBKP-NFC (BBKP-NFC:Li, BBKP-NFC:Na, and BBKP-NFC:K when referring to the ion doped ones). The membranes formed with NFC produced at UBI will be denominated as BSEP-NFC.

5.1.1.1. Structural and morphological characterisation

The source used to obtain NFCs, combined with the pre-treatment made and the kind of mechanical disintegration, determines the morphology of the resulting fibrils and cellulose membranes formed. In the case of the NFC obtained from birch, which is a hardwood source, the fibrils in some cases can reach more than 1-2 μm in length and up to 50 nm in width (Figure 5.3), resulting in membranes with a surface roughness in the range of 44 to 69 nm (analysed area of $5 \times 5 \mu\text{m}^2$). When the source is eucalyptus, the “raw” fibres are smaller than the ones from the BBKP. TEMPO-oxidation was used as a pre-treatment combined with a two-stage homogenisation for a more efficient downsizing of the fibres, leading to finer and shorter fibrils than in the case of BBKP-NFC. In Figure 5.3 it is possible to verify that BSEP-NFC membranes have a smooth and homogenous surface, being possible to identify the existence of fibrils with a maximum width of 20 nm. The small dimensions of the fibrils lead to a surface’s roughness of 14 nm (determined by AFM).

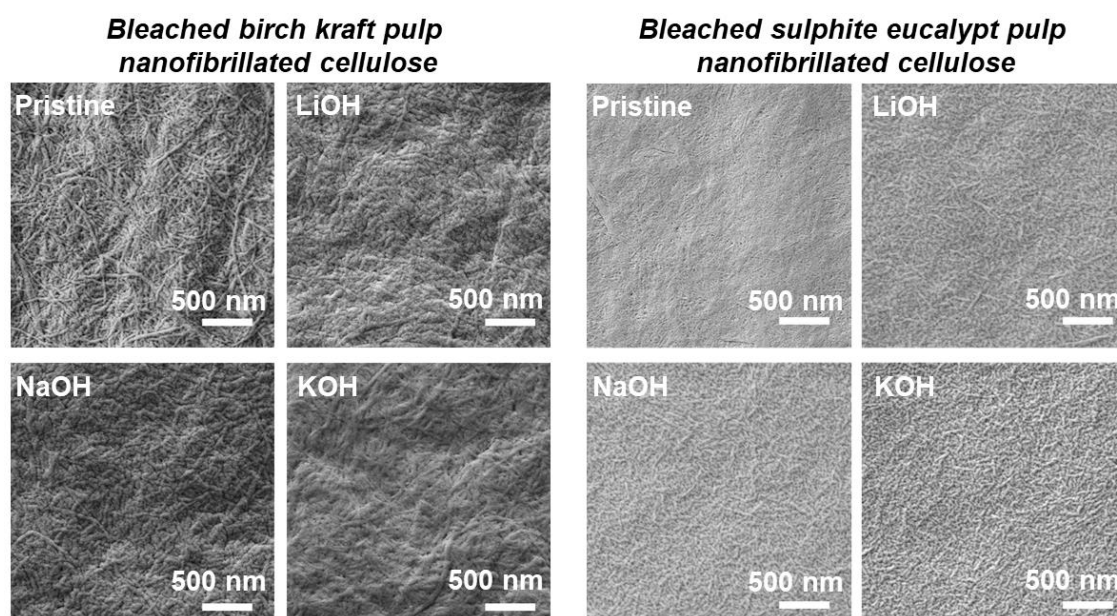


Figure 5.3 NFC membranes produced with bleached birch kraft pulp (BBKP), and bleached sulphite eucalypt pulp (BSEP), from CTP and UBI, respectively.

The morphology of the NFC membranes is substantially modified with the addition of alkaline ions to the pulp, although the cellulose structure is not dramatically changed. The XRD analysis of pristine membranes reveal the characteristic peaks of $(1\bar{1}0)$, (110) and (002) crystallographic planes related to cellulose I (Figure 5.4). Regardless of the treatment performed to the membranes, the crystalline index (CrI) remains nearly unaltered, being around 60% for both the BBKP and BSEP-NFC membranes.

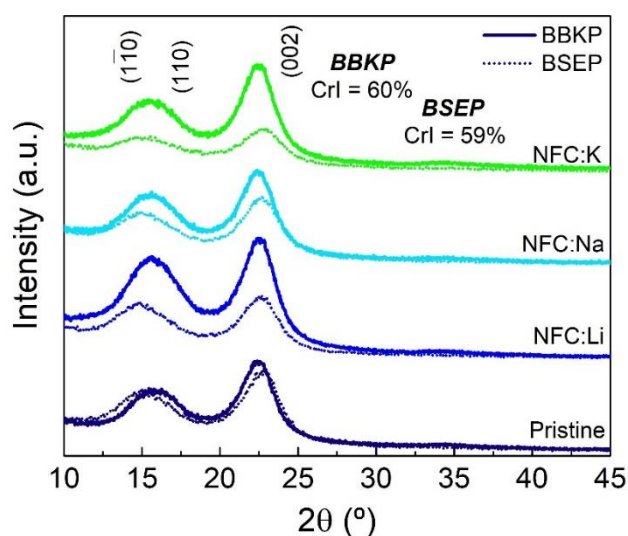


Figure 5.4 XRD diffractograms of the pristine and ion enriched BBKP-NFC and BSEP:NFC membranes.

In the literature some references can be found concerning alkaline treatments, designated as mercerisation, commonly made with highly concentrated NaOH solution. In this process, the cellulose is not dissolved being instead swollen through the action of the alkaline solution. In the case of highly concentrated alkaline solution cellulose I can be converted to the polymorph II, where the parallel chains are reconfigured to an anti-parallel order (cellulose II) [1], [4].

The diffractograms of the membranes formed from “doped” NFC pulp do not show any conversion of cellulose I to cellulose II since no splitting of the (002) peak is observed, typical in the presence of cellulose II [5]. Nevertheless, some changes may occur in the cellulose when modified with alkaline treatment, namely a counterion exchange on the carboxylic group at C₆ of the cellulose unit due to the high affinity of Li⁺, Na⁺, and K⁺ ions to it. The counterion exchange induces a swelling of the structure allowing better penetration of the hydrated hydroxide ions into the cellulose chains. High intercalation of those ions between the chains can result in disruption of the order and consequently in the decrease of the crystallinity, not observed in this case since the molarity of the hydroxide used was not enough to promote these structural changes generally observed at higher molarities [6]. However, this does not mean that some counterion exchange had occurred, as will be discussed further ahead in this chapter.

The morphology of the cellulose membranes after impregnation is different. The small entangled fibres possible to identify in pristine membranes turn into a matt of swelled fibres without a defined shape after being soaked in the hydroxide solution. This change is attributed to nonregular swelling along the fibres (also denominated as ballooning phenomenon) that is responsible for the decreasing of the membranes’ porosity by about 50%, compared with pristine ones (Table 5.2). The reduction of the porosity seems to follow the increase of the ionic radius of the alkaline impregnated ions. The alkaline ions impregnation of the membrane is confirmed by EDX analysis, which gives the estimated value of the atomic percentage for each element (except the lithium, whose presence was confirmed by XPS).

Table 5.2 Properties of the NFC membranes produced with the bleached birch kraft pulp and bleached sulphite eucalypt pulp.

Properties	Bleached birch kraft pulp				Bleached sulphite eucalypt pulp			
	Pristine	NFC:Li	NFC:Na	NFC:K	Pristine	NFC:Li	NFC:Na	NFC:K
C	50.97	48.36	48.85	51.77	50.70	50.50	50.68	50.21
O	48.87	51.64	50.46	47.28	49.30	49.50	47.77	47.90
Na	0.08	-	0.69	-	-	-	1.55	-
K	-	-	-	0.95	-	-	-	1.89
Thickness (μm)	12	11	11	12	10	11	12	11
Roughness (nm)	56	44	69	55	14	-	-	-
Basis weight (g m^{-2})	16.2	15.4	15.7	17.5	10.9	12.2	13.6	12.7
Apparent density (g cm^{-3})	1.35	1.40	1.43	1.46	1.39	1.41	1.44	1.47
Porosity (%)	16	12.8	10.6	8.8	13.1	11.7	10.3	8.1

The FTIR spectra for both NFC pulps tested (Figure 5.5), shows the existence of several characteristic bands of cellulose regardless of the post-treatment. In both sources, the typical absorption band between $3000\text{--}3600\text{ cm}^{-1}$ is found (related to the hydroxyl group -OH stretching in the cellulose molecules, including those involved in intra and intermolecular H-bonds). At 2890 cm^{-1} it is possible to identify the peak corresponding to asymmetrical and symmetrical C-H stretching vibration of methyl and methylene groups, the peak around 1430 cm^{-1} is associated with H-C-H and O-C-H in-plane vibration and finally the most intense band in the region of 1020 cm^{-1} , which is characteristic of the C-O-C pyranose ring vibration in cellulose [7]–[10].

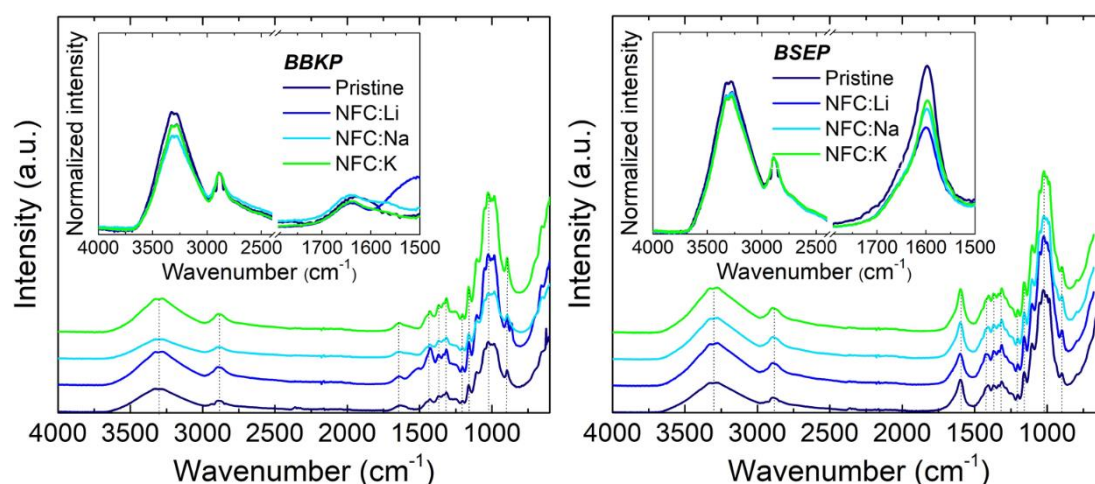


Figure 5.5 FTIR spectra of the pristine NFC and ion doped NFC membranes produced with bleached birch kraft pulp (BBKP – on the left), and bleached sulphite eucalypt pulp (BSEP – on the right).

At first glance, no deviations are found in these bands after the alkaline-doping of the NFC. The large band at $3000\text{--}3600\text{ cm}^{-1}$ assigned to the interaction of the OH of the cellulose chains, and also the band $1600\text{--}1635\text{ cm}^{-1}$ (related with the H-O-H bending vibration of the absorbed water molecules) can give some hints about the hydration of the fibres with and without the alkaline baths [9], [11]. The inset plots in Figure 5.5 show the spectra of both pulps normalised to the intensity of asymmetrical and symmetrical C-H stretching vibration band located at 2890 cm^{-1} , which is commonly used as a baseline for the study of water content in cellulosic substrates [11]. The first impression is that the ion-doped membranes have a reduced amount of the adsorbed water since the intensity of the $3000\text{--}3600\text{ cm}^{-1}$ band is slightly higher in pristine membranes. However, the decrease in the intensity in this band may also be an indication that the addition of the different alkaline ions decreases the intra or intermolecular hydrogen bonding, since contribution to this band come also from the OH groups involved in the hydrogen bonds between cellulose chains. For this reason alkaline systems combined with urea are often used for the dissolution of cellulose, since OH^- ions provided by the hydroxides reduce the hydroxyl groups which hinders inter-chain bonding [12].

The intensity of band near 1600 cm^{-1} is higher in BSEP membranes when comparing to the BBKP ones, which is related to the TEMPO-treatment made to the first. During the TEMPO-oxidation hydrophilic sodium carboxylate groups in the fibres are formed that may contribute to a higher amount of adsorbed water in BSEP [13]. In this case, it is clear that the hydration of the fibres decreases with the addition of the alkaline ions.

5.1.1.2. *Electrochemical characterisation of the NFC-membranes*

The electrochemical characteristics of the NFCs can be assessed by producing electrolytic capacitors with the membranes and making spectroscopic impedance measurements similarly to what was done with the papers in Chapter 4. In the following, just the characterisation for the BBKP-NFC will be presented and discussed in more detail, while the BESP-NFC characterisation will be summarised in Table 5.3

EIS measurements allow the determination of the capacitance (i.e. C_{real} or C_{eff} - effective capacitance) in a certain frequency range. However, the proper manner to calculate this value is not entirely consensual.

One of the proposed determination methods is through Equation 5.1:

$$C_{real} = -(Z_{Imag} \times \omega)^{-1} \quad \text{Equation 5.1}$$

where Z_{imag} is the imaginary part of the impedance and ω is the angular frequency ($\omega = 2\pi f$) [14]. This equation was questioned for high frequencies since the determined values could be overestimated, and the same authors proposed the determination of the capacitance through Equation 5.2 [14]:

$$C_{eff} = -\frac{Z_{Imag}}{\omega \times |Z|^2} \quad \text{Equation 5.2}$$

For simplification purposes, the capacitance determined using Equation 5.1 will be designated as C_{real} , while the C_{eff} stands for the capacitance calculated with Equation 5.2. Both approaches are valid, and its applicability ultimately depends on the frequency range. For solid state electrolytes, such as paper and the NFC membranes as gate dielectric in FETs, operation at high frequencies is not expectable. Therefore, and similarly to what was done in the previous chapter, the capacitance was extracted at low frequencies where the phase is close to -90° through Equation 5.1.

In Figure 5.6a the C_{real} and phase angle as a function of the frequency are presented (frequency range = [10 mHz - 1 MHz]). For all the membranes an increase of the capacitance at low frequencies is verified which evidences the formation of the EDL, leading to C_{real} values between $1.53 \mu\text{F cm}^{-2}$, for the pristine NFC, up to $2.94 \mu\text{F cm}^{-2}$, for the NFC:Li (values listed in Table 5.3). The significant difference between C_{real} and C_{eff} happens for an intermediate frequency range, while the values for low and high-frequency are very similar (Figure 5.6b and Table 5.3). The similar behaviour at low frequencies is understandable since EDL is formed (validated by the analysis of the phase of the NFC:Na, which will be addressed later). In a range of frequencies where the phase is higher than -45° , the difference is emphasised since the real part of the impedance (related to the resistance of the material) gradually dominates the total impedance, which results in overestimated values of C_{real} [14]. Depending on the frequency used to test the devices based on these solid electrolytes, both equations can be used taking into consideration the described limitation.

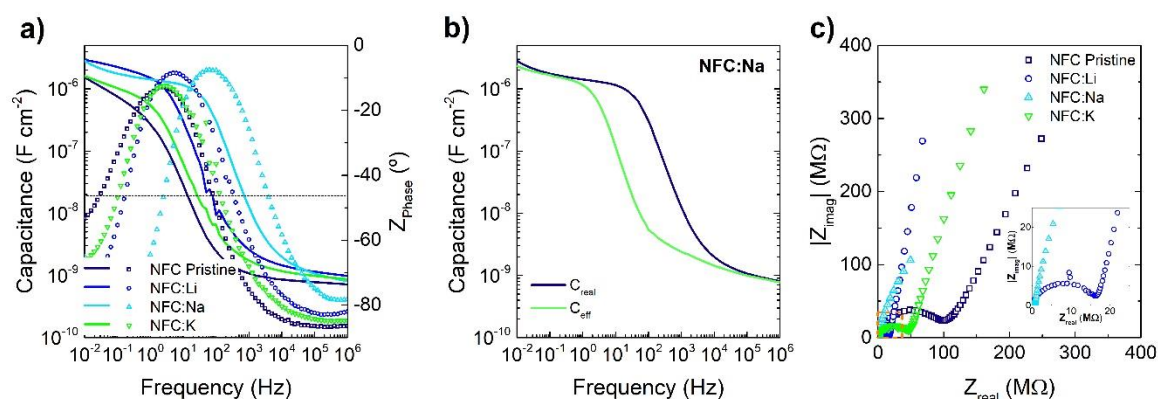


Figure 5.6 EIS of the BBKP-NFC membranes (pristine, Li, Na and K doped): a) C_{real} (solid line) and phase angle (open symbols) as function of the applied frequency, b) Comparison of the C_{real} and C_{eff} as a function of the applied frequency for NFC:Na, and c) Cole-Cole plot of the NFC membranes. The insets show a zoom of the indicated area for low resistance values from the NFC:Li and NFC:Na.

Table 5.3 Summary of the electrochemical and electrical properties of the tested NFCs.

<i>Properties</i>	<i>Bleached birch kraft pulp</i>				<i>Bleached sulphite eucalypt pulp</i>			
	<i>Pristine</i>	<i>NFC:Li</i>	<i>NFC:Na</i>	<i>NFC:K</i>	<i>Pristine</i>	<i>NFC:Li</i>	<i>NFC:Na</i>	<i>NFC:K</i>
<i>Capacitance*</i> ($\mu\text{F cm}^{-2}$)	1.53	2.94	2.84	1.61	2.84	3.56	5.97	2.57
<i>Effective capacitance*</i> ($\mu\text{F cm}^{-2}$)	0.98	2.77	2.33	1.35	2.36	3.08	4.00	2.37
<i>Double layer capacitance</i> ($\mu\text{F cm}^{-2}$)	0.54	2.53	2.16	1.30	-	-	-	-
<i>Resistivity</i> ($\text{M}\Omega \text{ cm}^{-1}$)	1740	311	40	853	2.37	1.19	0.4	0.9

*Values determined for $f = 10$ mHz.

Similarly to what was observed in the previous chapter, in the NFC membranes the phase vs frequency plot shows the existence of three domains, a dipole relaxation for high-frequency values denoted by a phase angle lower than -45° , followed by an increase of this value above -45° indicating an ionic relaxation and a transition to a resistive response. Finally, at low frequencies, the phase decreases again, indicating a capacitive response and consequent EDL formation. Considering the assumptions made previously about Equation 5.1, it is possible to validate its applicability for this particular case since all the BBKP:NFC membranes show phase angle lower than -45° for low frequency values.

The real part versus absolute imaginary part of the impedance (Figure 5.6c) for the NFC membranes shows a semicircle in the high-frequency range followed by a straight line in the low-frequency region. With the incorporation of alkaline species, the semicircles'

diameter tends to become smaller, which is an indication of the reduction of the resistance of the membranes. The addition of ions leads to an abrupt decrease of the resistance from $1700 \text{ M}\Omega \text{ cm}^{-1}$ down to $40 \text{ M}\Omega \text{ cm}^{-1}$ for the NFC:Na membranes.

The EIS data is often fitted in the literature with an equivalent electric circuit model (ECM) that considers the bulk impedance related to the intrinsic material properties, namely bulk electrical resistivity, ionic conductivity, bulk capacitance and EDL capacitance. Different ECMs were tested, namely the model proposed by Dasgupta *et al.*, which consists of a resistance associated to the contact resistance, in series with a RC circuit (associated with the bulk resistance and bulk capacitance) and a constant phase element (CPE). The use of a CPE is justified by the compressed semi-circles, indicating inhomogeneous charge distribution across the EDL at the NFC/electrode interfaces. Due to the nature of the membranes, the implementation of a model is challenging and can be doubtful due to the number of elements needed to have a good quality fitting, compromising the real meaning of those elements in the ECM [12], [14], [15]. Other models such as Maxwell-Wagner relaxation effect, could be considered to describe the dielectric response of heterogeneous materials as those presented in this thesis. This model also takes into consideration charge accumulation at the outer interfaces, considering the existence of a different relaxation times whenever an interface between two different materials exists [16], [17].

The use of NFC membranes as a dielectric in FETs is determined by the formation of a pair of EDLs; however, the determination of the double layer capacitance (C_{DL}) is not straightforward. The C_{DL} can be measured performing cyclic voltammetry (CV) with the capacitors, assuming that the increase of the current is linearly proportional to the scan rate for a range of voltages applied, as described by Equation 5.3:

$$I_c = \frac{I_a - I_b}{2} = C_{DL} \frac{dv(t)}{dt} \quad \text{Equation 5.3}$$

where I_a , and I_b , are the maximum and the minimum currents for the open circuit potential of the CV curve, I_c is the respective charging current, and $\frac{dv(t)}{dt}$ is the scan rate [18].

The CV scans at different scan rates of the BBKP-NFC membranes tested are plotted in Figure 5.7. In these measurements, the application of a potential with a specific scan rate can lead to one of two situations: the appearance of faradic currents, identified by the presence of peaks related with redox reactions, or the appearance of a capacitive current, which is associated to the double layer charging [12]. The first situation is quite expectable to happen in devices where electrodes are permeable to the ions in the electrolyte, while

the second one happens in capacitors and supercapacitors where a rectangular shape of cyclic voltammogram for those devices is desirable [19]. The addition of ionic species to the NFCs leads to an increase of the current, and simultaneously the shape of the cyclic voltammogram tends to become more rectangular, especially for the NFC:Na. Therefore, the absence of peaks suggests the inexistence of redox reactions, which is important due to the application aimed for these membranes.

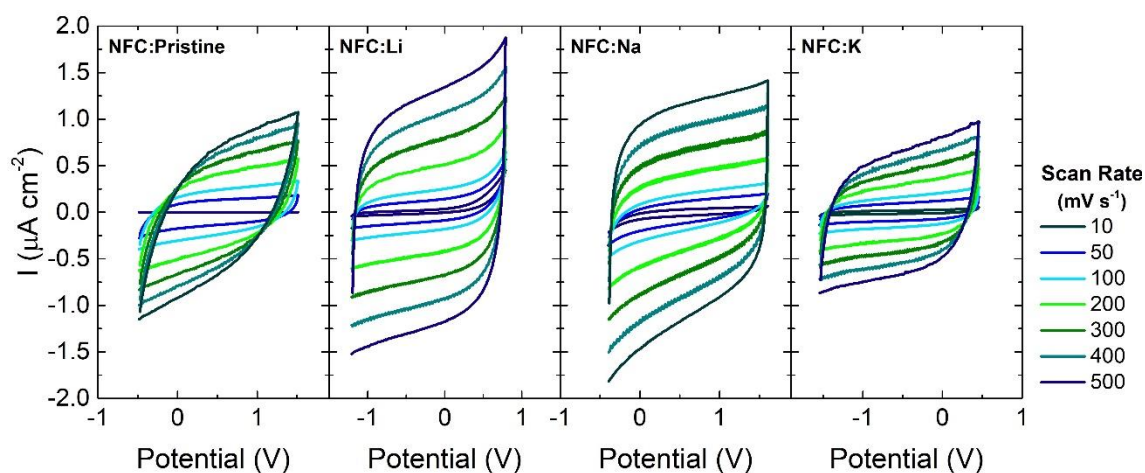


Figure 5.7 Cyclic voltammetry of the BBKP-NFC membranes (pristine, Li, Na and K enriched) at different scan rates.

The C_{DL} values calculated using CV are lower than the values determined using the EIS data. However, the C_{DL} values determined through CV could lead to underestimated or erroneous values. In liquid electrolytes, the formation of equivalent/symmetric EDL at each interface with the electrodes is not only expectable but also facilitated, which may not happen in solid-state electrolytes with low ionic conductivity and mobility as the NFC membranes.

Weighting the limitations and advantages for each method, it is believed that C_{eff} is the most accurate to use in this kind of solid-state electrolytes. Nevertheless, it should be emphasised that C_{real} , which is slightly higher than C_{eff} (Table 5.3 and Figure 5.8a), used in the previous chapter is not wrong since both follow the same tendency in low-frequency range, which was always the one considered ($f=10$ mHz) to calculate the mobility in the cellulose-based FETs.

When applied as the gate dielectric in FETs there is a need to evaluate the possibility that electrochemical reactions can take place at the semiconductor/NFC interface, since after the EDL formation/charging ionic diffusion or chemical doping of the IGZO with mobile

species coming from the membrane may occur. This possibility can be validated or discarded performing CV measurements using an electrochemical cell that can emulate the IGZO/NFC interface in the FETs. For this a metal/semiconductor/electrolyte structures with an IGZO thickness of ≈ 15 nm was used, and the same voltage range and scan rates as for the V_{GS} used in the characterisation of the transistors were applied. In Figure 5.8b the electrochemical behaviour of the IGZO/NFC interface for the different membranes is depicted. There are no evident peaks for a scan rate of 400 mV s^{-1} , allowing to conclude that in the present case no electrochemical reactions are occurring at the IGZO/NFC interface.

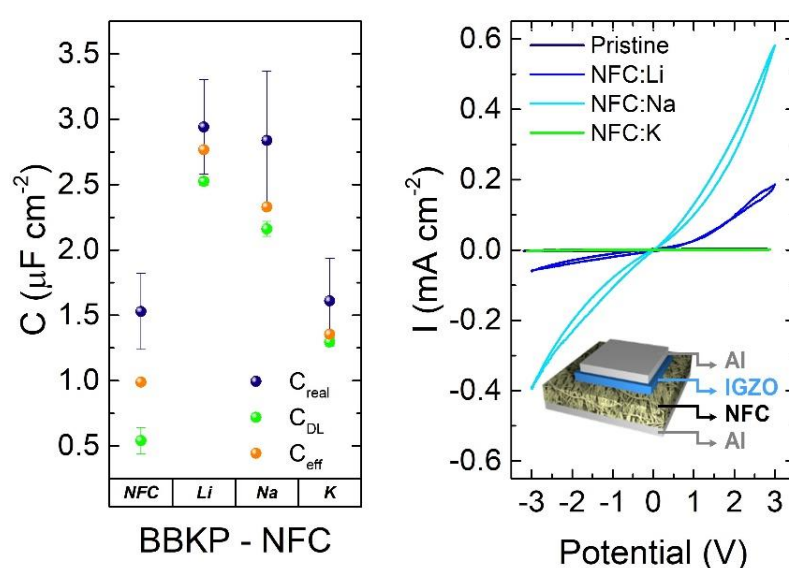


Figure 5.8 a) Comparison of the capacitances (C_{real} , C_{eff} and C_{DL}) obtained from EIS and CV measurements. b) CV of the Al/NFC/IGZO/Al structure produced to emulate the electrochemical behaviour in real FETs for a scan rate = 400 mV s^{-1} . The inset of b) shows a schematic representation of the cells produced to perform the respective measurements.

5.1.1.3. NFC-Membranes as gate dielectric in oxide FETs

IGZO FETs were produced at room temperature using the different NFC membranes as gate dielectrics. The IGZO channel and the Al source and drain electrodes were deposited using shadow masks on one side, while the IZO gate electrode was deposited on the other side.

The I_{DS} – V_{GS} transfer curves for those devices (measured in the dark at room temperature) with a $V_{DS}=1 \text{ V}$ and 2.5 V , and $V_{GS}=[-3;3] \text{ V}$ are plotted in Figure 5.9. The results show that the NFC membranes provide much better dielectric characteristics than the “conventional” paper as we named it. The main difference lays in the much lower V_{GS}

values required for the NFC-gated FETs when compared with those previously presented in Chapter 4.

FETs using pristine NFC as the gate dielectric have a good electrical response, reaching a modulation of four orders of magnitude, a steep sub-threshold slope of 0.29 V dec^{-1} , and a field effect mobility (μ_{FE}) on the order of $4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, the incorporation of alkaline ions lead to clear improvement in the devices' performance, such as the On/Off ratio, mobilities, sub-threshold slope, and the narrowing of the hysteresis value shift ($\Delta V_{\text{hysteresis}}$). The variation on the hysteresis it is assumed to be related with the presence of carboxyl groups and the capability to form close pairs with alkali ions, ($\text{Li}^+ > \text{Na}^+ > \text{K}^+$). This will affect the hydration of the ions resulting in a higher retention for Na^+ and K^+ , as shown in the FTIR data (Figure 5.5). The slightly higher hysteresis for the FETs on the NFC:K membranes might be related with the excess of ions non intereactiong with the carboxyl groups[20].

The FETs produced on the ion-doped membranes had a considerable enhancement of the saturation mobility (μ_{sat}) reaching $17 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, while $\Delta V_{\text{hysteresis}}$ decreases to 0 V for the NFC:Na. In the case of the NFC:K, the FETs reached five orders of magnitude current modulation with a considerable decrease of the sub-threshold slope down to 0.15 V dec^{-1} (Figure 5.9 and Table 5.4).

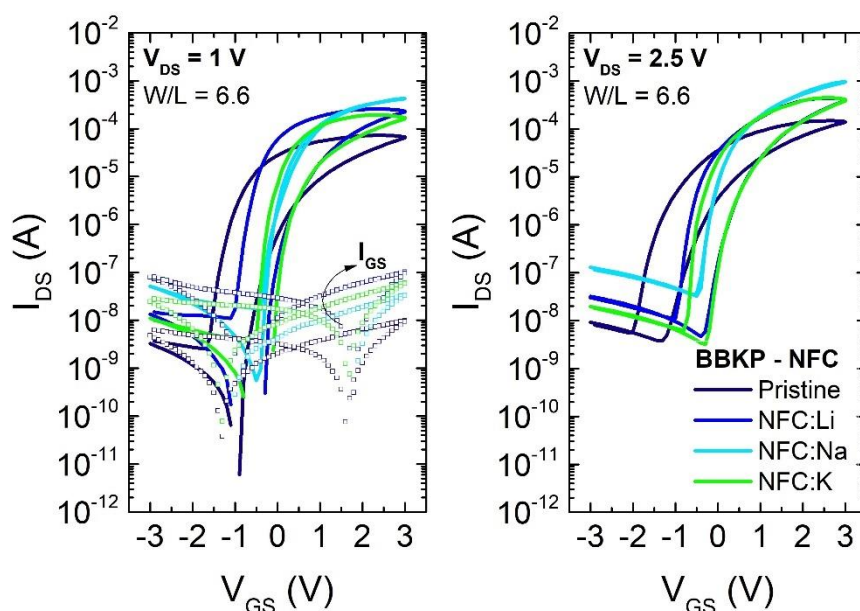


Figure 5.9 Transfer characteristics ($I_{\text{DS}}-V_{\text{GS}}$) with hysteresis of the NFC-gated FETs for $V_{\text{DS}} = 1 \text{ V}$ (on the left) and $V_{\text{DS}} = 2.5 \text{ V}$ (on the right). The scattered squares stand for the I_{GS} .

Among the doped membranes the NFC:Na ones present the lowest On/Off ratio, which is closely related to the electrical properties of the membranes. In the previous sub-section, it was verified by EIS that this membrane shows the lowest resistivity value, which is responsible for the accentuated increase of the I_{Off} in the FET (Figure 5.9). In fact, the trend observed for the FETs leakage current is fully aligned with the conclusions taken from the Cole-Cole plot, i.e. the resistivity decreases in the following order NFC:pristine>NFC:Li>NFC:K>NFC:Na, while the opposite tendency happens with the off current (I_{Off} - NFC:pristine<NFC:Li<NFC:K<NFC:Na).

Table 5.4 Electrical properties of NFC-gated FETs for $V_{\text{DS}}=2.5$ V.

	<i>Bleached birch kraft pulp</i>				<i>Bleached sulphite eucalypt pulp</i>			
<i>Properties</i>	<i>Pristine</i>	<i>NFC:Li</i>	<i>NFC:Na</i>	<i>NFC:K</i>	<i>Pristine</i>	<i>NFC:Li</i>	<i>NFC:Na</i>	<i>NFC:K</i>
μ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	4.32 (FE)	4.98	17.00	13.20	13.87 (FE)	14.55 (FE)	5.89 (FE)	19.09
V_{on} (V)	-1.4	-0.3	-0.6	-0.3	-2.5	-1.6	-1.4	-1
$\Delta V_{\text{hysteresis}}$	1.2	1	0	0.8	1.1	0.9	0.7	0.1
$I_{\text{on}}/I_{\text{off}}$	3.6×10^4	5.4×10^4	2.7×10^4	1.2×10^5	3.5×10^4	8.1×10^4	2.2×10^3	1.3×10^5
S (V dec^{-1})	0.29	0.18	0.17	0.15	0.36	0.19	0.58	0.14
<i>Effective capacitance*</i> ($\mu\text{F cm}^{-2}$)	0.98	2.77	2.33	1.35	2.84	3.56	5.97	2.57

*Values determined for $f = 10$ mHz.

Another effect of the alkaline ion incorporation is the shift of the V_{on} (Figure 5.9 and Table 5.4), although the devices presented here operate in depletion mode, which is the behaviour often seen in paper, NFC and NCC gated FETs [11], [21], [22]. Indeed, this is in line with the variation of the open circuit potential in the C-V in Figure 5.7. Another significant difference is the narrowing of the counterclockwise hysteresis, associated with the accumulation of ionic charges in the IGZO/membrane and membrane/IZO interfaces (Figure 5.9). One possible explanation for the decrease of the hysteresis may be the higher ionic conductivity of the NFC:Na membranes, suggested by the lowest resistivity determined from the EIS characterisation.

The output characteristic $V_{\text{DS}}-I_{\text{DS}}$ of the FETs (Figure 5.10) show a current saturation at $V_{\text{DS}}=2.5$ V for the ion enriched membranes, which is not observed in the pristine membranes. The smoothness of the surface of the membranes results in an improved contact quality but it is still possible to verify some current crowding in the low V_{DS} region.

The improved electrical performance of these devices allowed to go a step further, being possible to test them in inverters when combined with a load resistance. In Chapter 6 (devoted to more complex cellulose-based devices) results achieved with alkali-doped membranes will be presented. In the same chapter other applications of pristine NFCs in electronic devices will be investigated.

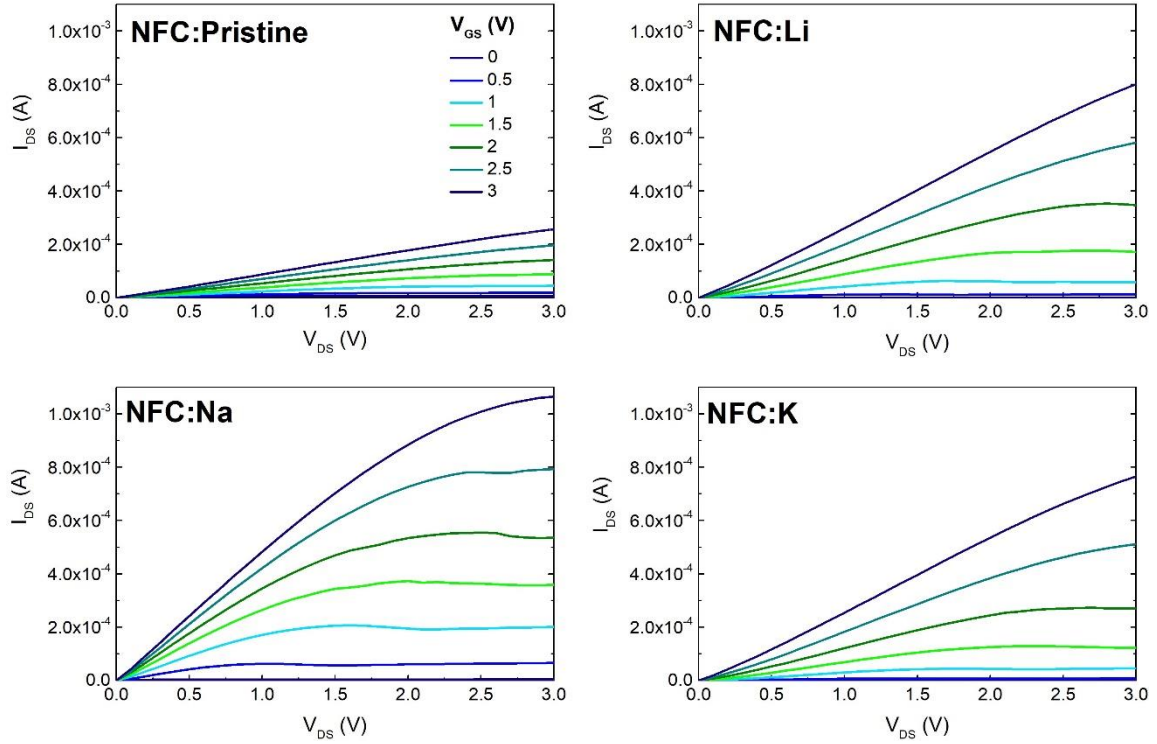


Figure 5.10 Output characteristics for the NFC-gated FETs.

5.1.1.4. Shelf time stability of the NFC-gated FETs

The devices produced with BBKP-NFC, whose results were presented and discussed in the previous sub-sections, were characterised in two different periods in order to verify their electrical performance over time. The devices were stored in a sample box without any encapsulation or other special care regarding temperature or relative humidity.

In Figure 5.11 the transfer characteristics obtained for the devices during different periods are plotted. Three months after production the performance of the devices on pristine membranes remained similar with just a small positive shift of the V_{On} . This behaviour is usually observed for devices submitted to positive gate bias stress for some time as a result of charge trapping at the dielectric/semiconductor interface [23]. For the present case, this

kind of stress is not expected due to the type of the measurements. The depletion of positive ionic species at the interface of the membrane/semiconductor at the beginning of each V_{GS} scan, can be a valid explanation to shift the V_{On} towards higher values. In parallel, the adsorption of O_2 can also occur at the surface of the non-passivated IGZO causing a depletion of the semiconductor layer [24].

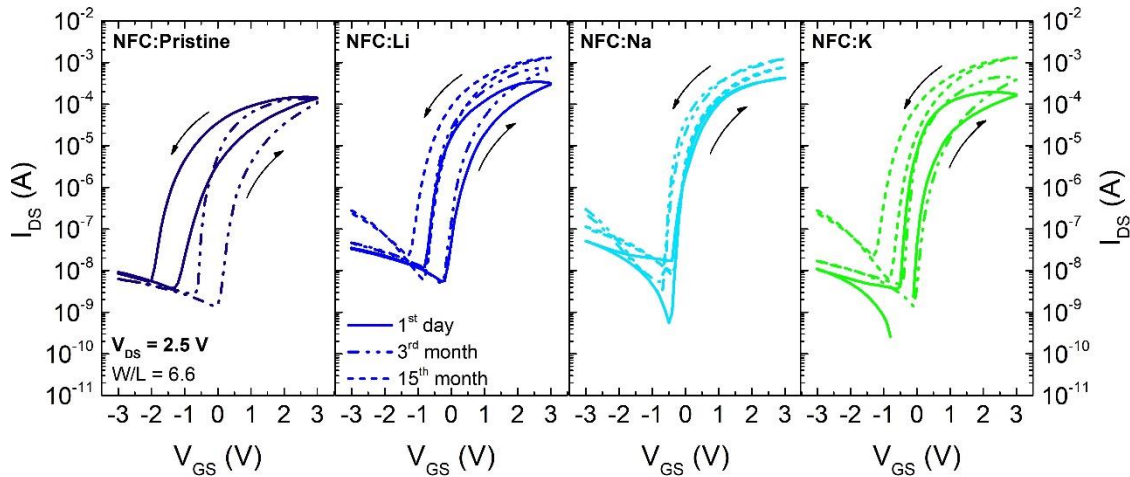


Figure 5.11 Transfer characteristics I_{DS} - V_{GS} of the NFC-gated FETs acquired one day, three months and fifteen months after production.

In the 15th month, more than 2/3 of the devices produced on the pristine membrane had the aluminium contacts irreparably deteriorated compromising their operation. From experience acquired during this PhD with different papers tested, this is associated with Cl^- present in the matrix (even if in small amounts) that destroys the semiconductor and metallic contacts. The BBKP-NFC membranes contain Cl^- in their composition, even though it is vestigial and not easily detected by EDX, coming from the bleaching during the pulping process.

On the other hand, the devices produced with alkali-doped NFC still show a proper operation at the 15th month. Indeed, an improvement in the electrical performance was observed as can be seen in the normalised parameters (On/Off ratio, S and μ) plot (Figure 5.12), regardless the used ions. The enhancement of the mobility and the decrease of S may be explained by an increase of the low-frequency capacitance of the membranes. The addition of the ions to these membranes, not only enhances the electrical performance of the devices but also seems to have a positive contribution to the stability of the membranes and oxide/aluminium thin films over time. It is assumed that this is associated to the

neutralisation of Cl^- that may exist in the membranes as the result of the bleaching step during the pulping process of the NFCs.

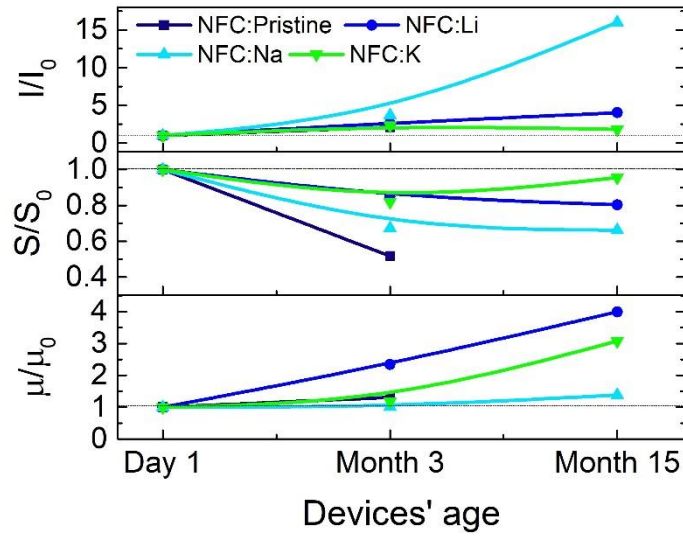


Figure 5.12 Normalized values of the $I_{\text{ON}}/I_{\text{OFF}}$ ratio (I/I_0), sub-threshold slope (S/S_0), and mobility (μ/μ_0) of the aged NFC-gated FETs. The parameters with the subscript “0” refer to the values determined in the first measurement of the device.

5.1.1.5. Flexibility, and electrical endurance of the pristine membranes

The stability of the devices can be defined in several domains. Besides the ageing factor, new devices were produced to assess the endurance of the FETs when submitted to a bending strain and their cyclability after consecutive gate voltage sweeps.

Flexibility of the NFC-gated FETs

The mechanical stability of fresh devices was evaluated under different bending strains. Two devices were selected and bent along the channel width direction with different inner radii (r) for outward (tensile strain) and inward (compressive strain) curvature, while measuring the transfer characteristics. Bending radii of 45, 25, 15, and 5 mm were used for outward and inward curvature which correspond to a strain of 0.02, 0.03, 0.05 and 0.16% as determined using Equation 4.3. The values of $I_{\text{ON}}/I_{\text{OFF}}$ ratio, S and μ determined for each curvature were then normalised to the parameters obtained for the unbent device, where the variation is represented in Figure 5.13.

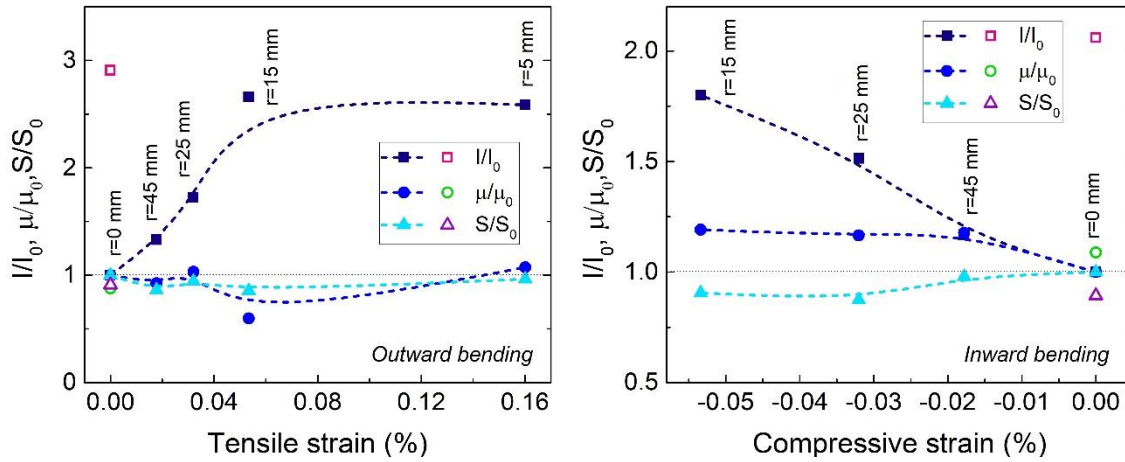


Figure 5.13 Normalized electrical parameters of the I_{ON}/I_{OFF} ratio (I/I_0), sub-threshold slope (S/S_0), and mobility (μ/μ_0) of the device for outward (on the left) and inward (on the right) bending strains. The open symbols represent the variation of the electrical properties after back to flat condition.

The strain applied to the devices is low due to the small thickness of the deposited thin films when compared to the dielectric. Thus, the electrical performance of the devices is not severely deteriorated during the bending or even when returning back to flat conditions. For the outward bending the On/Off ratio increases with the applied tensile strain. This variation is related to a decrease in I_{OFF} . In the literature, it is possible to find a report where IGZO TFTs were tested under different bending strains. The authors submitted the devices to several cycles and observed also a decrease in I_{OFF} . The observed phenomenon was justified with the moisture adsorbed in cracks formed during the bending that can work as charge trapping sites [25]. In the present work, the creation of small cracks and pockets in the semiconductor/cellulose membranes interface, where some moisture can be accumulated, is also a possibility. Nevertheless, it should be considered that permanent damage of the IZO gate electrode could partially be responsible for the decrease of the Off current, as suggested by the performance of the devices measured after returning back to the flat state (Figure 5.13).

On the other hand, compressive strains obtained through inward curvature lead to an enhancement of the device's performance (Figure 5.13) that can be justified with the compression of the fibres and consequently of the semiconductor layer. The strain applied to the device can induce cracks or partial detachment of the oxide layers, gate electrode and semiconductor. For the gate electrode, similarly to what was discussed for the outward bending, there is a strong possibility of damaging the IZO, leading to the decrease of the Off current. The amorphous character of the thin films obstructs the release of the applied

strain; thus, the material can be deformed resulting in layer cracking. According to the strain applied these cracks can be propagated (tensile strains), while for the compression the films may be delaminated [26]. For the semiconductor, despite the formation of cracks that might be induced due to the applied strain, it is still possible to have a continuous conducting channel(s) between the source and drain electrodes facilitating electron conduction and thus the devices' operation.

For flexible applications two variables should be considered that cannot be dissociated: on the one hand the substrate determines the applied strain to the devices, whereas the semiconductor and gate electrode layer quality and thickness will influence the endurance of the devices under a bending strain. The sputtered IGZO allows a good step coverage of the fibres, which is essential during this type of measurements once cracks or detachment of the surface are common and may severely compromise the proper operation of the devices. On the other hand, the smooth surface combined with the thickness of the NFC membranes, results in a low strain even for severe bending strains, making this material an excellent substrate for flexible/bendable electronics.

Electrical endurance

The electrical endurance of the devices can be measured in a static regime, where the transfer characteristics are obtained for a certain number of times. It can also be accessed by performing dynamic measurements applying a square wave gate voltage and monitoring I_{DS} . The static response of the devices will be presented and discussed in the following paragraphs, while the dynamic response will be addressed in Chapter 6 together with the integration of the NFC-FETs in a common source amplifier configuration using the FETs as the driving transistor and different commercial resistances as the load.

New devices produced in pristine BBKP-NFC were used to perform the static measurements in the dark and at atmospheric pressure (23 °C and relative humidity of 40%). The devices were submitted to 900 cycles where the V_{GS} was swept in the voltage range [-3;3]V with a step of 0.1 V, for V_{DS} =2.5 V. Then the devices were kept in the microprobe station to rest for 8 hours (in the dark), and further 200 cycles were applied. The influence of the scan rate was also checked by fixing it at 0.4 mV s⁻¹, and 4 V s⁻¹. After the 900 cycles, the devices still show proper current modulation, although the differences observed are highly related to the scan rate used. A successive decrease in I_{Off} and I_{GS} was monitored with the increase in the performed cycles (Figure 5.14). Parameters other than

On voltage such as S and μ remain nearly unchanged. After 8 hours of recovery, another V_{GS} scan was applied, where I_{Off} recovered to the initial value, being one order of magnitude lower than for the first curve (Figure 5.14).

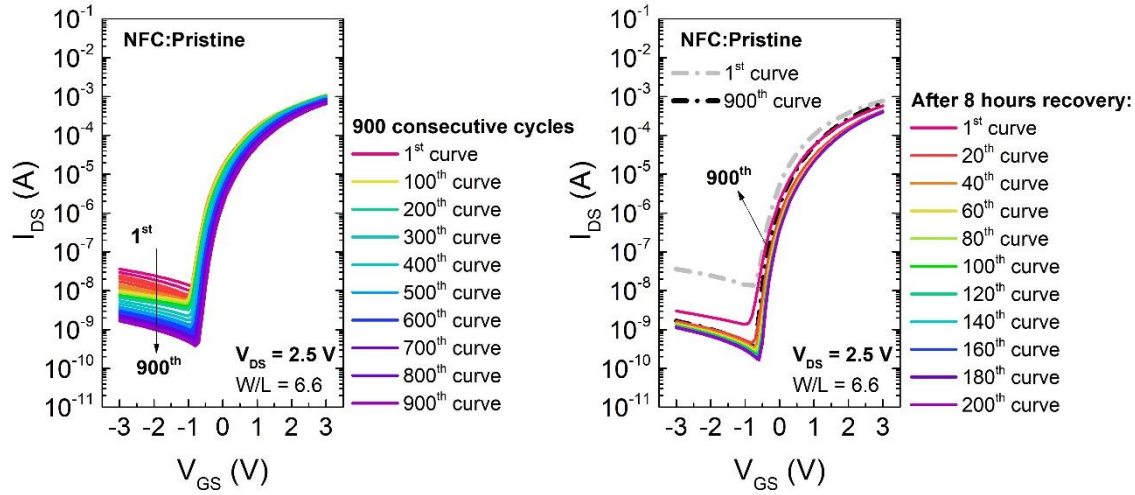


Figure 5.14 Transfer characteristic curves of the FETs characterised with a scan rate of 0.4 V s^{-1} . On the left the curves for the initial 900 cycles are represented, while on the right the 200 cycles after 8 hours recovery are plotted. The dash-dot lines are indicative of the 1st and 900th cycle of the FET before resting time.

For higher scan-rates the instability of the devices starts to be more evident, with a clear deviation of V_{On} towards higher values and an I_{On} decreases by 40% of the initial value (Figure 5.15a, b and d). The reason for both situations can be related with the scan speed. For such a fast acquisition an electron trapping mechanism is expected, but mostly the retention of negative fixed charges (ions) near the semiconductor/membrane interface or in the gate dielectric can be responsible. Regardless of the nature (ionic or electronic) of the negative charges trapped/retained near the membrane surface or immediately below the semiconductor, they will partially deplete the semiconductor interface and thus increase V_{On} [27]. Similar to what was observed for the lowest scan rate, the resting time is not sufficient to fully recover the initial state of the “fresh” device, and I_{Off} and I_{On} start to rapidly decrease again (Figure 5.15c and d).

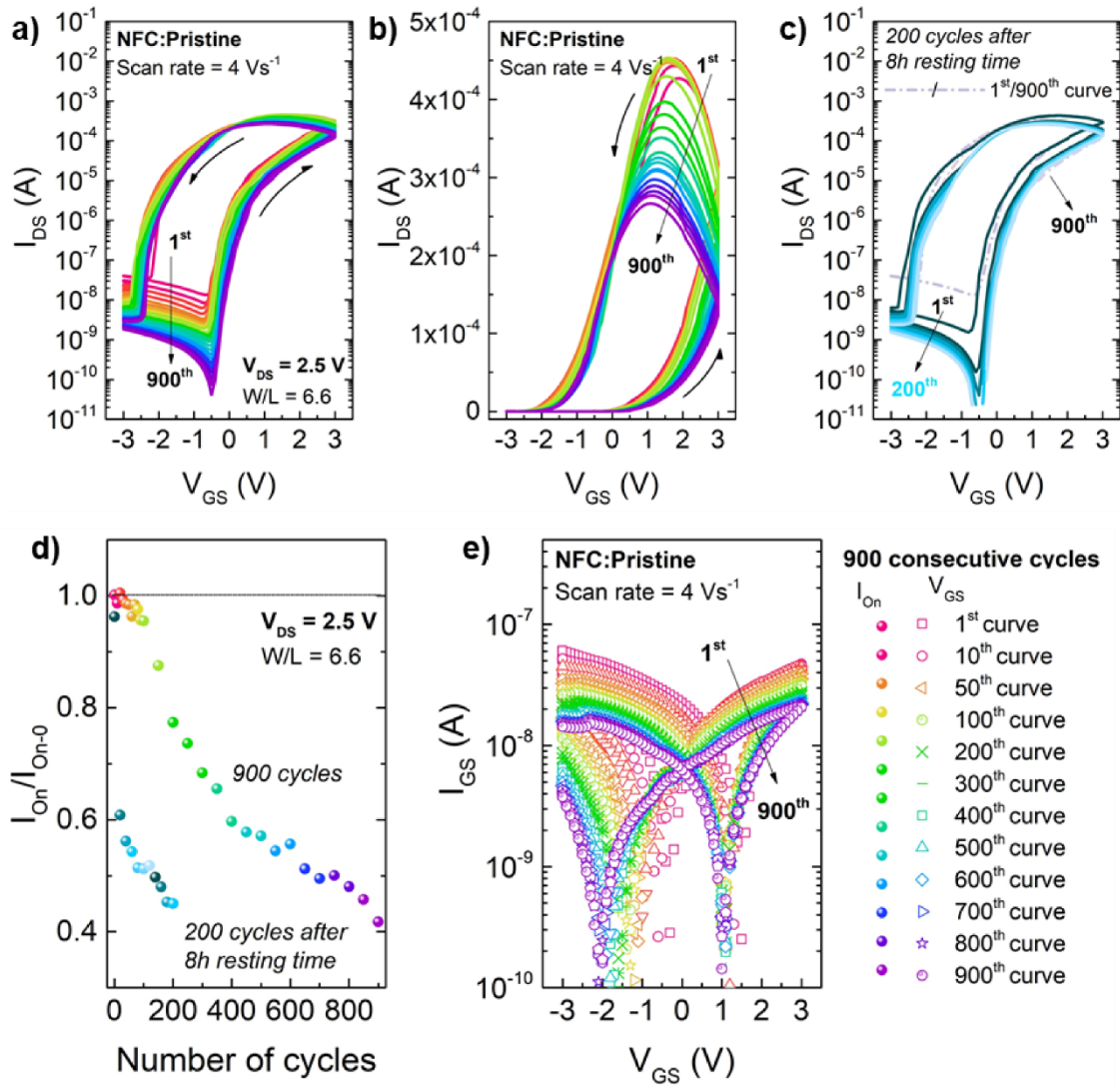


Figure 5.15 Electrical performance of the NFC-gated FETs for a scan rate of 4 Vs^{-1} . a) and b) transfer characteristics curves of the initial 900 cycles in semi-log and linear scale, respectively. c) devices behaviour after 8 hours of rest and an extra 200 cycles. d) Normalised On current as a function for the first 900 cycles and the following 200 cycles after an 8h recovering period. e) Leakage current (I_{GS}) variation for the 900 first cycles.

For both scan-rates, it is possible to verify that along consecutive acquisitions the On/Off ratio increases significantly (Figure 5.16). Despite the slight decrease in the I_{On} (Figure 5.15d), a continuous decrease in Off current is measured, resulting in an incremental improvement of the device's modulation. The Off current is ultimately dominated by I_{GS} , which also decreases over consecutive cycles (Figure 5.15e). The reason for the variation of I_{GS} is unclear but it is expected that a large number of cycles combined with the duration of the measurements may result in Joule heating able to promote water desorption. As has

been extensively discussed along this document, the water is a crucial element for the capacitive and resistive behaviour of the membranes, and thus I_{GS} would be affected immediately.

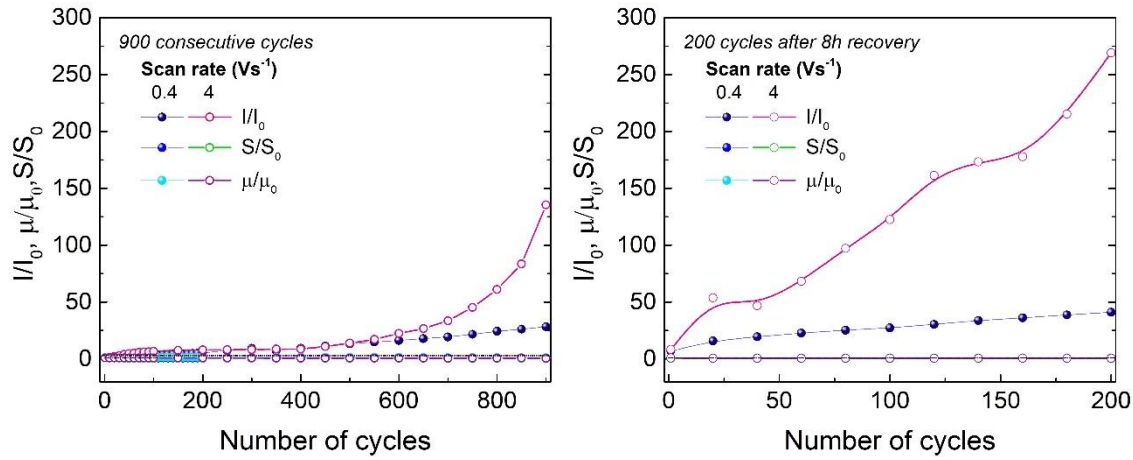


Figure 5.16 Normalised electrical parameters (I_{On}/I_{Off} ratio - I/I_0 , sub-threshold slope - S/S_0 , and mobility - μ/μ_0) of the devices for 900 cycles (on the left) and 200 cycles after 8 hours of recovery (on the right). The solid symbols represent the scan rate of 0.4 $V s^{-1}$, and the hollow symbols represent the scan rate of 4 $V s^{-1}$.

Overall, the current modulation is by far the most influenced parameter by the number of cycles and scan rate, while S and μ do not suffer significant changes (Figure 5.16). Thus, it is possible to state that the NFC-gate dielectrics have good electrical endurance over a large number of cycles, which is relevant for practical applications.

5.1.1.6. Recyclability

The considerable potential of cellulose-based electronics concerning reduced environmental impacts and recyclability processes are often mentioned in the literature as one of the advantages of this technology. Having this in mind, some of the devices produced during this work on pristine NFC membranes were used to fabricate recycled membranes that were reused as the gate dielectric in new devices. The recyclability was performed by starting to soak the “used” FETs in water, followed by a stirring step until obtaining a total dispersion of the fibres. The suspension was then poured in boxes left to dry to form the recycled membranes. Figure 5.17 presents the different steps involved in the reusing/recycling process.

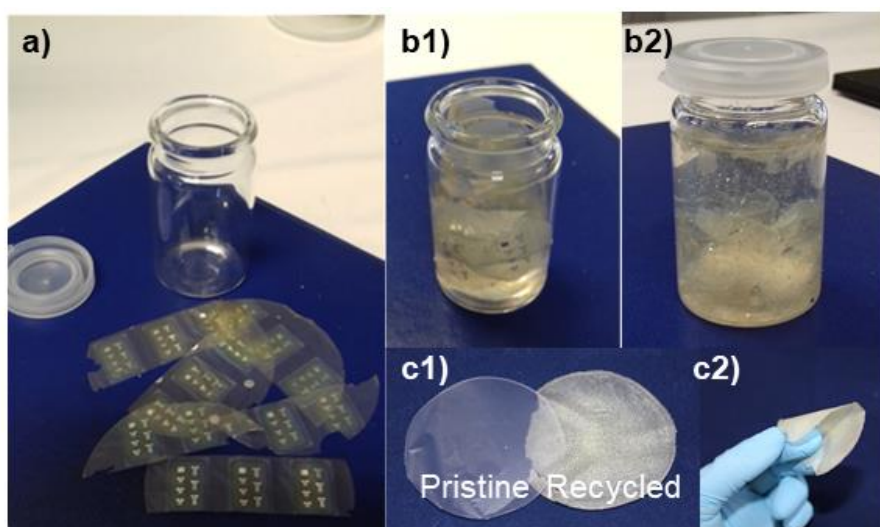


Figure 5.17 Steps involved in the NFC FETs recycling process. a) NFC-gated FETs used for the recycling before soaked in water (b1), and b2) after stirring for a few hours. c1) dried pristine and recycled membranes, also photographed in c2).

The recycled membranes are as flexible as the pristine ones, but the transparency decreases substantially due to the presence of oxide and aluminium particles that could not be appropriately disintegrated. This may limit the performance of the membranes as gate dielectric in the "new" FETs since: *i*) the incorporation of a large volume of conductive particles (IZO and Al) may lead to accentuated increase in the leakage current that ultimately hinders the devices' operation, *ii*) the inclusion of randomly dispersed aluminium particles with large dimensions can result in short-circuits in source/drain electrodes (Figure 5.18), and *iii*) the rough topography of the membranes which can result in poor coverage of the new layer to be deposited.

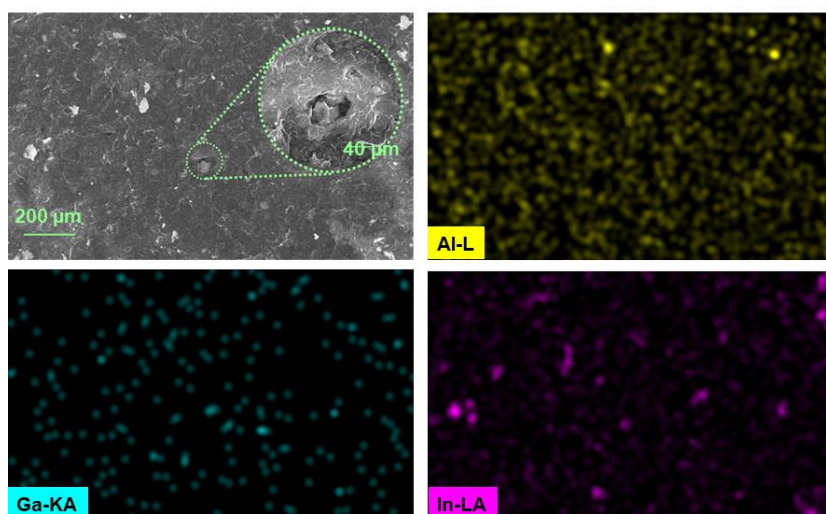


Figure 5.18 SEM micrograph of the recycled NFC membrane, and EDX elements identification for the Al, In, and Ga. The inset shows an IZO particle with a large dimension entangled in the NFC fibres.

The recycled membranes show different electrochemical behaviour when compared with the pristine ones. The capacitance value does not overcome 55 nF cm^{-2} at 0.01 Hz (Figure 5.19a), which is attributed to the inclusion of conductive particles within the matrix. This may indeed be related to the fact that the transition from a resistive to a capacitive behaviour seems to occur for frequencies lower than 0.01 Hz , indicating another limitation of FETs produced with recycled membranes. The possibility of electrochemical reactions in the semiconductor/recycled-NFC interface was disregarded, since no redox-reaction peaks (associated to faradaic currents) were observed during CV measurements (performed with the same scan rate and range of voltages used for the FETs) (Figure 5.19b). Nevertheless, it is not possible to discard entirely the occurrence of at least some electrochemical activity in the matrix due to the presence of IGZO and Al particles observed by SEM.

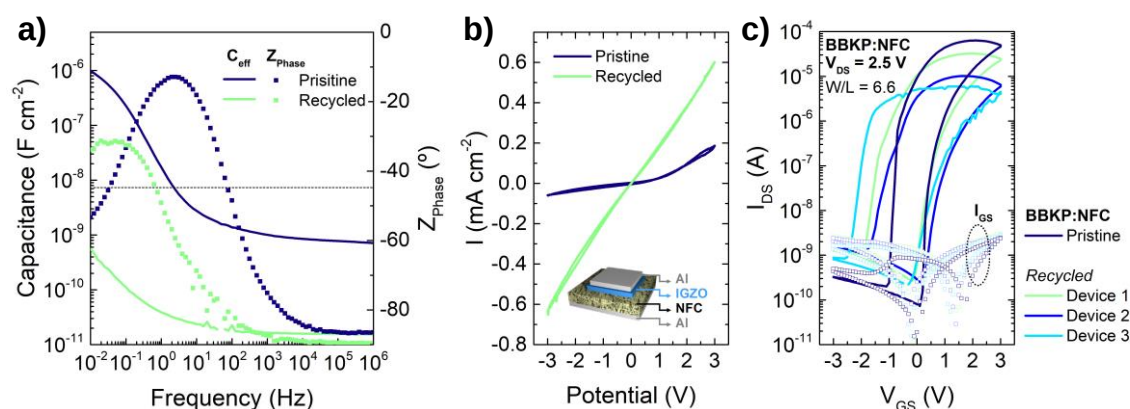


Figure 5.19 a) EIS characterisation of the NFC membranes (pristine and recycled), b) CV of the devices produced to emulate the electrochemical behaviour of real FETs (scan rate= 0.4 mV s^{-1}). The inset shows a schematic representation of the produced cells. c) I_{DS} - V_{GS} curves of the NFC-gated transistors using pristine and recycled membranes ($V_{DS}=2.5 \text{ V}$).

The performance of the FETs produced on the recycled membranes was compared with devices made on pristine ones. The devices produced on the pristine NFC show proper current modulation that reaches five orders of magnitude, which was also possible with the recycled-NFC membranes. The main difference lays in the variation of the performance when analysing several devices with the same dimensions produced on the recycled membranes (Figure 5.19c). As referred before, the roughness of the recycled NFC membranes can be a drawback for the reliability of the implemented FETs. Device #3 is an excellent example of this since a poor quality of the S/D contacts becomes clear, compromising the electrical performance of the devices.

The recyclability/reusability of NFC-membranes for new devices was successfully demonstrated with this proof-of-concept, validating one of the most defended ideas in the paper electronics field. Nevertheless, there are some improvements to be made in order to ensure better performance of the devices, namely the separation of the particles resulting from an inadequate disintegration of the thin films. This can, in principle, be done using centrifugation before recycled membranes formation.

5.2.Nanocrystalline cellulose

Among the different types of cellulosic materials discussed in Chapter 1, nanocrystalline cellulose (NCCs), often named in the literature as cellulose (nano)whiskers or cellulose nanocrystals, are the smallest product that can be produced through the downsizing of the cellulose fibres [1], [28].

NCCs can be obtained from many different sources. One of the purest possibilities is cotton, which simultaneously holds the highest amount of α -cellulose (90 wt.%) among vegetal sources, which usually vary from around 50 wt.% (wood) up to 80 wt.% (flax or hemp) [1], [4], [29]. The explanation for selecting cotton as an NCC source is based on the amount of cellulose found in the secondary wall. NCCs can be relatively easily extracted through acid hydrolysis from the secondary wall after the primary cell wall is removed [29].

The extraction of the cotton-based NCCs, as well as the preparation of the NCC membranes, was made in the laboratories of the Soft Materials group from the Materials Science Department, FCT/NOVA.

5.2.1. Structural and morphological properties of NCC membranes

The NCC membranes are highly crystalline (crystalline fraction of 81%), with XRD (data not shown here) revealing the characteristic peaks of the cellulose type I, for $2\theta = 14.7^\circ$, 16.8° and 22.7° equivalent to $1\bar{1}0$, 110 and 002 planes [29]. The morphology of this material is entirely different from paper like and NFC membranes. While NFCs have a very high aspect ratio, with a “spaghetti-like” appearance, NCCs are in scientific jargon described as “rice-like”. Looking at the SEM images, the analogy is immediate, since it is possible to distinguish small cellulose crystals in these membranes (Figure 5.20).

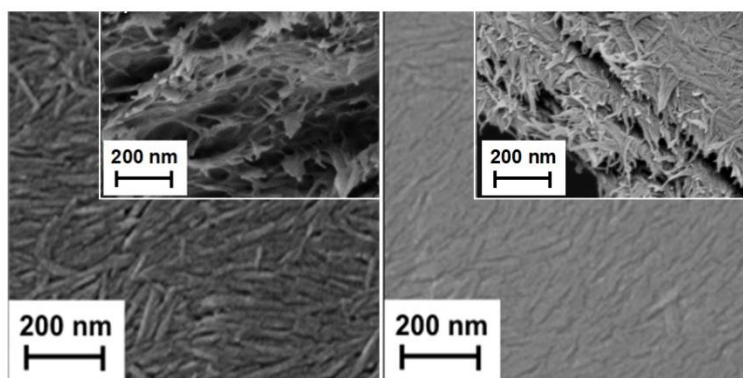


Figure 5.20 Micrographs of the free-standing NCC membranes produced by shear casting (on the left) and by evaporation. The insets show the corresponding cross-sections.

NCCs are a fascinating material with the particular characteristic of forming a lyotropic liquid crystal phase when dispersed in water. Two phases may be present: the isotropic one where the NCC concentration is low resulting in dried membranes with high transparency with randomly oriented crystals and the anisotropic phase where the NCC concentration is higher [1], [30]. The last lead to a chiral nematic arrangement by controlling the drying process, resulting in iridescent membranes with photonic properties; this particular feature can be explored for instance as circularly polarised light sensor [21].

The membranes used in this work were produced by evaporation from the isotropic suspension, where an ordered arrangement of the crystals is not expected. The shear-casted membranes were produced from the anisotropic phase, but the application of a directional shear force disrupts the chiral nematic self-assembly of the NCCs. Thus, it is not possible to identify a periodic arrangement of the crystals as shown in the cross-section of the membrane (inset of Figure 5.20). Chiral membranes produced with the anisotropic phase are currently being studied in the frame of another PhD work.

Regardless of the NCC membranes formation method, both membranes are highly transparent. The dense assembly of the NCCs reduces the porosity of the membrane, and consequently the voids within it, avoiding light scattering. This feature results in membranes with an average transmittance of 85% in the visible wavelength range (Figure 5.21).

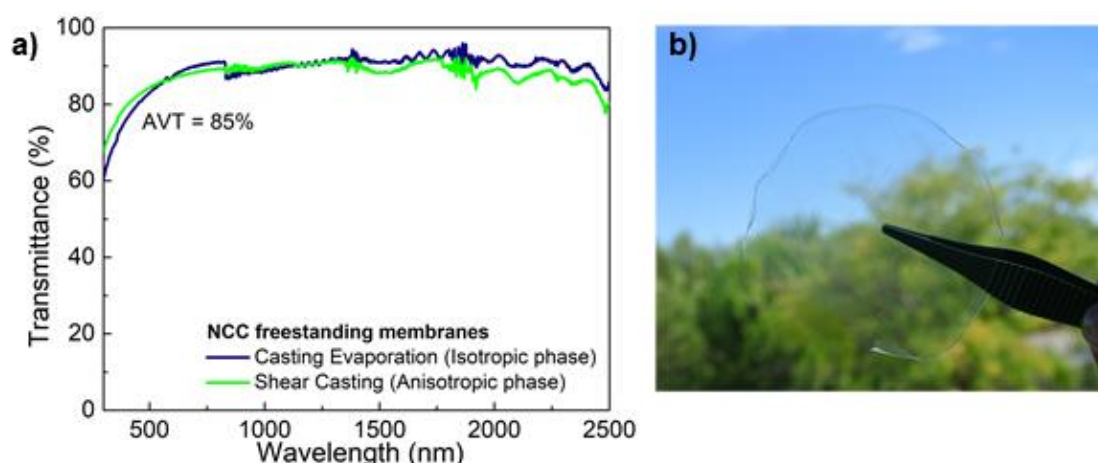


Figure 5.21 a) Optical characterisation of the NCC membranes reaching an AVT $\approx$ 85% (membranes with 30 μ m), and b) photograph of one NCC membrane produced by evaporation.

5.2.2. NCC-gated FETs

Figure 5.22 shows the transfer characteristics of FETs with different NCC membranes as gate dielectric. The difference in the behaviour of the evaporated casted one can be immediately realised. The On/Off modulation of those devices can reach five orders of magnitude, with μ_{Sat}^1 of $\approx 7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Table 5.5). The electrical performance of those devices is substantially better than the devices produced on shear-casted membranes. The difference in maximum current reached by the evaporated NCC gated devices is considerable. This is attributed partially to problems in S/D contacts resulting from higher surface roughness in shear-casted NCCs. Moreover, the thermal stability of the shear-casted membranes may also promote some interfacial reactions during semiconductor and aluminium electrodes deposition, limiting the drain current in the channel [29]. The non-ideal quality of the contacts is evidenced in the output characteristics. Although the saturation plateau is reached, it is possible to observe some current crowding for low V_{DS} caused by the electrical resistance of the S/D electrodes.

¹ Value determined for a capacitance of 0.14 $\mu\text{F cm}^{-2}$ (value measured for $f=0.01 \text{ Hz}$).

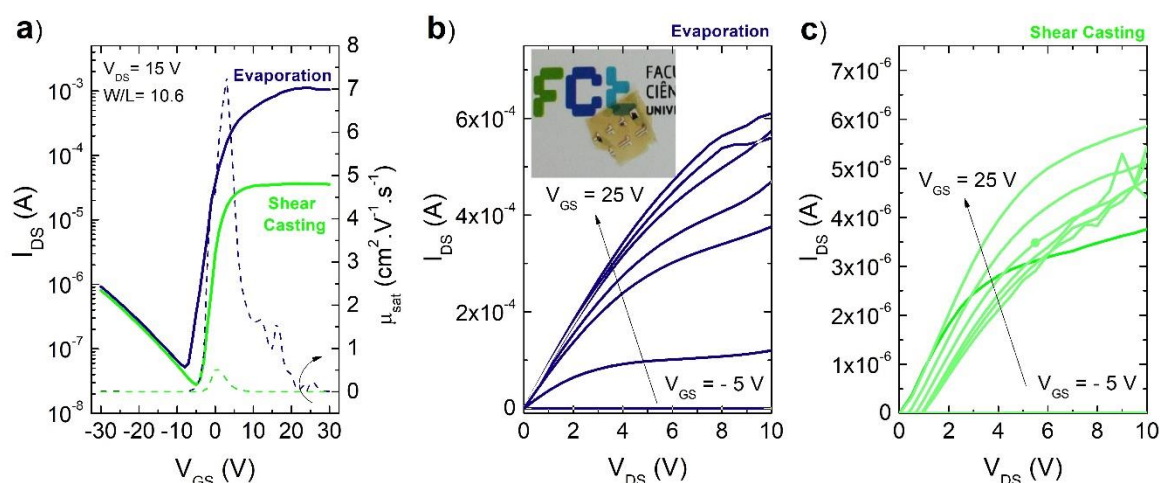


Figure 5.22 NCC-gated FET's electrical characteristics, a) I_{DS} - V_{GS} transfer and output characteristics of the FETs deposited on b) evaporated and c) shear casting NCC.

Table 5.5 Electrical properties of the FETs with cotton-based NCC as gate dielectric.

Properties	Evaporation	Shear casting
μ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	7.27	0.54
V_{on} (V)	-8	-5
I_{on}/I_{off}	2×10^5	1×10^4
S (V dec^{-1})	2.11	1.79

The FETs produced using NCC membranes as the gate dielectric have similar performance to those produced on membranes or paper made of "conventional" fibres without ionic doping [11], [31], [32]. In a recent work made in our group, it is reported that impregnation with an alkaline solution can dramatically improve the FETs' performance, also in NCC membranes, similarly to what was described in section 5.1.1.3 for NFC ones. The resulting increase of ionic polarizability of the NCCs, allows for a decrease of the operation voltage from a $V_{DS}=15$ V and $V_{GS}=[-30;30]$ V (same voltage values as for the discussed devices), to $V_{DS}=1.5$ V and $V_{GS}=[-2;2]$ V, reaching On/Off ratios of seven orders of magnitude and μ_{Sat} up to $9 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. These values are significantly improved by the alkali-doping of the NCC membranes [21].

5.3.All-cellulose composites

Both cellulosic materials presented in the previous sub-sections have distinct and interesting properties. On the one hand the NFC membranes are more robust, flexible and easier to handle, and the dimensions of the fibres lead to films with some transparency, however still with significant light scattering. The transparency of the cellulosic membranes can be improved preparing composites of NFC fibres combined with other cellulose derivatives. In a first stage, hydroxypropyl methy cellulose (HPMC) was the chosen derivative, since it is rapidly dispersed in water and after drying the combination of HPMC with the NFC resulted in robust and transparent membranes. The electrical performance of FETs using these membranes was satisfactory, reaching four orders of magnitude of current modulation. However, the remaining parameters were mediocre when compared to the ones obtained for the NFC-gated FETs.

The innovative approach tested in this PhD consisted thus of mixing two types of cellulose fibres with different dimensions (NFCs and NCCs) in order to benefit from the best properties provided by both. This is particularly interesting since pure NCC free-standing membranes are brittle, raising challenges, namely limiting the flexibility when used as a dielectric in FETs. The composites were prepared using BBKP-NFC gel with 2% of solid content (mass/mass - m/m), while for the NCCs a Na⁺ neutralised² NCC suspension in water with 2%wt (m/m) was used. Five samples were prepared: pure NFCs and pure NCCs using the same weight (m/m) (NFC weight=NCC weigh) for both, and three composites where the amount of NFCs was higher than the NCCs (75% of NFCs with 25% of NCCs), equal (50% of NFCs with 50% of NCCs) and lower than the NCCs (25% of NFCs with 75% of NCCs).

5.3.1. Structure and morphology

The membranes formed just with BBKP-NFCs, or just NCCs has a morphology similar to the ones already presented in section 5.1 and 5.2 (Figure 5.23).

With the SEM micrographs, it is possible to realise that the surface roughness of the NFC membranes becomes gradually smoother with the addition of NCCs that fill the small dimension voids between the larger fibres (Figure 5.23). In the SEM image for the composite with NFC=NCC a good example of the combination between these two

² Functional groups resulting from the acid hydrolysis made with H₂SO₄.

materials is highlighted where a fibril (green arrow), surrounded by small crystals that fill the empty spaces that naturally exist in an NFC membrane, is marked.

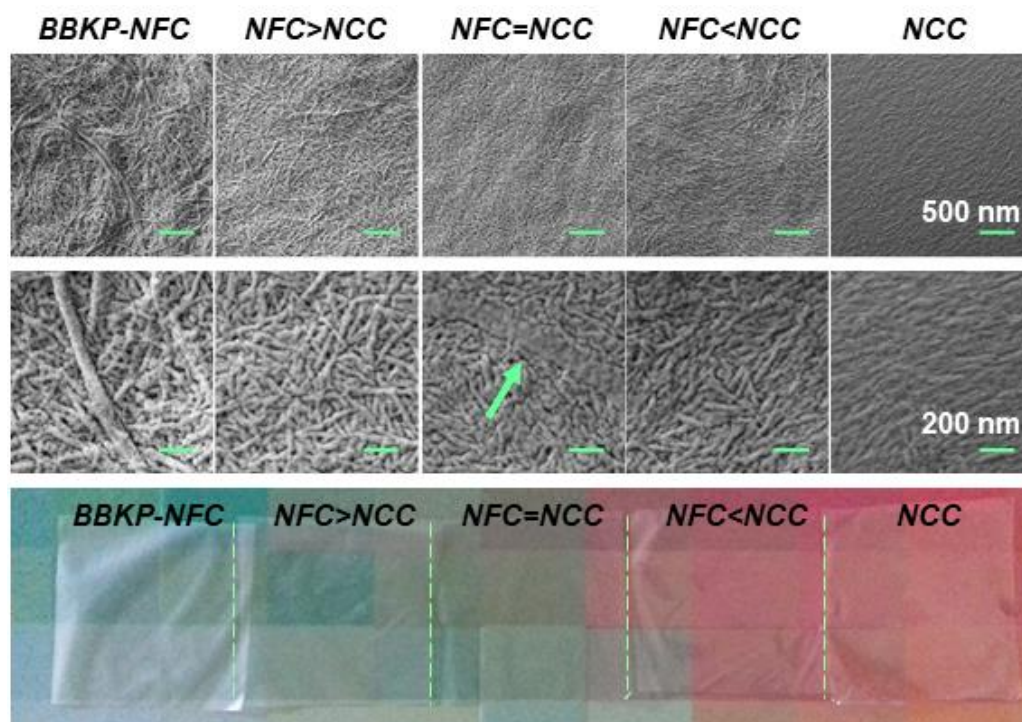


Figure 5.23 SEM images of the all-cellulose composites, NFC and NCC membranes.

In the last row are presented photographs of the casted membranes.

With the SEM micrographs, it is possible to realise that the surface roughness of the NFC membranes becomes gradually smoother with the addition of NCCs that fill the small dimension voids between the larger fibres (Figure 5.23). In the SEM image for the composite with NFC=NCC a good example of the combination between these two materials is highlighted where a fibril (green arrow), surrounded by small crystals that fill the empty spaces that naturally exist in an NFC membrane, is marked.

The changes made at the nanoscale result in a substantial decrease of the porosity of the films (Table 5.6). Voids in a pure NFC matrix represent nearly 17%, a value that is lower when compared to *regular* paper as seen in the previous chapter. With the gradual addition of the NCCs, the porosity is lowered to about 50% of the initial value, reaching 8% of porosity in the case where the volume of NFCs and NCCs is the same, with a further decrease for pure NCCs where the crystals are tightly packed (Table 5.6). The filling of the empty spaces through the addition of NCCs also attenuates the scattering of the light,

resulting in a tremendous improvement of the transmittance, from $\approx 17\%$ (pure NFCs) up to $\approx 77\%$ (pure NCCs) (Figure 5.23 and Figure 5.24).

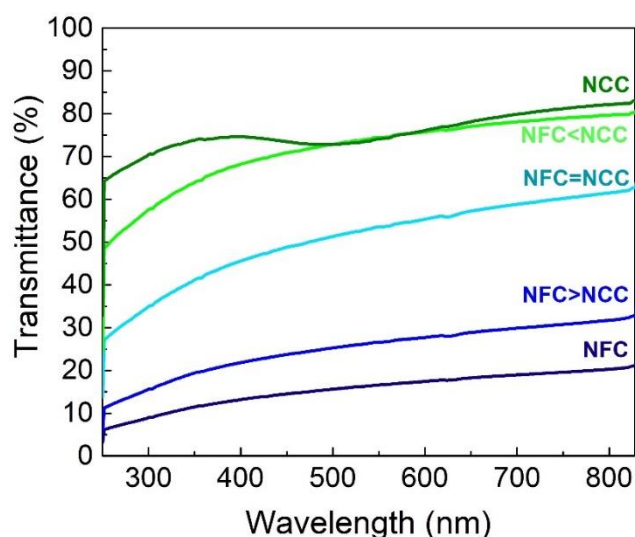


Figure 5.24 Specular transmittance of the all-cellulose composites.

Table 5.6 Properties of the all-cellulose composites prepared with the different amount of NFC and NCC.

<i>Properties</i>	<i>NFC</i>	<i>NFC>NCC</i>	<i>NFC=NCC</i>	<i>NFC<NCC</i>	<i>NCC</i>
Thickness (μm)	17	17	15	14	14
Apparent density (g cm^{-3})	1.33	1.45	1.47	1.51	1.54
Porosity (%)	17.2	9.3	8.0	5.3	3.6
Transmittance in the visible (%)	17.4	27.4	54.8	75.2	76.7

5.3.2. All-cellulose composites as gate dielectric in FETs

In Figure 5.25 the transfer characteristics curves (linear regime for a $V_{DS}=2.5$ V) for the all-cellulose composite gated IGZO FETs are depicted. The increase in leakage current becomes immediately evident. It depends directly on the resistivity of the membranes, as seen before, that gradually decreases with the addition of NCCs. This is explained by the resistivity measured for pure NCC membranes, ($\rho_{NCC} \approx 0.4 \text{ G}\Omega \text{ cm}^{-1}$) which is lower than the value measured for NFC membranes ($1.3 \text{ G}\Omega \text{ cm}^{-1}$). Another difference is the V_{on} shift towards more negative voltages, influenced by the ions inside the matrix and by the higher amount of absorbed water promoted by the NCC addition. (Table 5.7). It is reported in the literature that the absorbed water in the IGZO TFTs contributes to the formation of an accumulation layer through electron donor states [24].

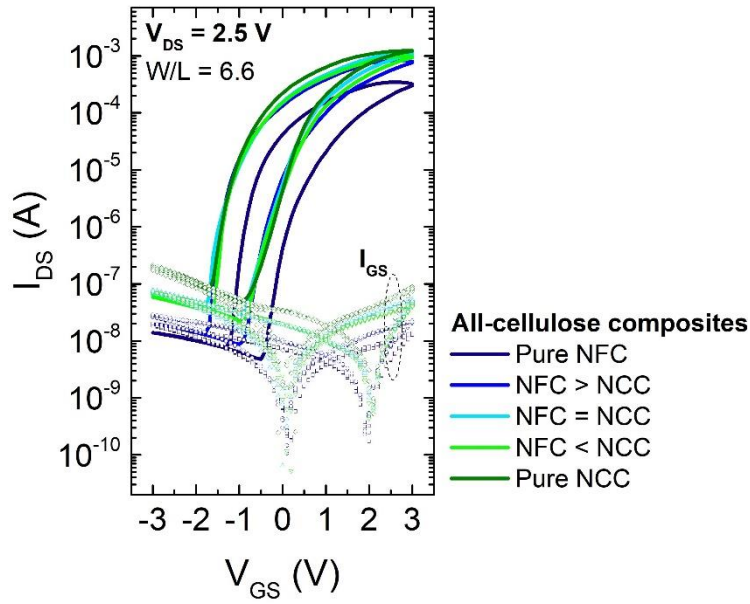
Figure 5.25 I_{DS} - V_{GS} transfer characteristics of the FETs with all-cellulose composites as gate dielectrics.

Table 5.7 Electrical properties of the FETs with all-cellulose composites as gate dielectrics.

Properties	NFC	NFC>NCC	NFC=NCC	NFC<CC	NCC
μ_{FE} ($cm^2 V^{-1} s^{-1}$)	13.9	62.1	41.7	38.7	65.9
V_{on} (V)	-0.5	-1	-1	-0.9	-1
I_{on}/I_{off}	6.3×10^4	8.8×10^4	4.3×10^4	4.2×10^4	2.5×10^4
S ($V dec^{-1}$)	0.21	0.22	0.37	0.29	0.36
C_{eff} ($\mu F cm^{-2}$)	98.8	40.9	7.47	3.65	4.39

The current modulation of these devices reaches at least four orders of magnitude, being higher for low content of NCCs in the membranes, also related to the lower Off current. The S increases with the addition of NCCs, which is explained by a decrease in the measured capacitance. However, a major improvement is obtained in μ_{FE} , which increase from $\approx 14 cm^2 V^{-1} s^{-1}$, for NFC membranes up to $66 cm^2 V^{-1} s^{-1}$, for pure NCC ones. The mobility values obtained here are higher than the ones presented in previous sections, and some factors must be considered since these values may be overestimated. One of the possibilities would be the underestimation of capacitance, a mistake often seen in publications dealing with ionic conductors as the gate dielectric. Having this in mind, the value used in the calculation of the mobility for all the devices in this PhD thesis was the C_{eff} determined for $f=0.01$ Hz, which should not lead to an underestimation of the values as would happen for the C_{DL} value obtained from CV. Thus, the possibility of electrochemical doping of the IGZO is foreseen (in case of ionic permeability of the

semiconductor) occurring at the interface with the membrane and promoted by the gate voltage applied during device characterisation.

Despite the early stage of the study of these all-cellulose composites, it is possible to foresee some possibilities brought by this mixture, namely the improved optical transmittance and robustness of the membranes without compromising the electrical performance of the devices, which can, in the future, be improved and better explored for application in electronic devices.

5.4. Bacterial Cellulose

The bacterial cellulose membranes used were kindly provided by the Centre of Biological Engineering of Minho University. The membranes were obtained from the cellulose-producing bacteria *Komagataeibacter xylinus* (in the literature often referred to as *Gluconacetobacter xylinum*) grown in a culture medium optimised for higher biopolymer yields [33].

In the previous sections, it was demonstrated that the electrical performance of the FETs could be significantly improved through the addition of specific ionic species. The pure character of the BC makes this material particularly interesting to study the interaction between the cellulose and the ions. In the present section, the results on a different type of BC membranes will be presented: highly pure and dried ones, membranes soaked with the aqueous alkaline solutions and membranes whose pH was adjusted with NaOH before the drying process.

5.4.1. Alkali-doped BC membranes

It was already demonstrated along this chapter that the incorporation of alkali ions affects the morphology of the cellulose, while the dielectric properties of the membrane are improved, resulting in FETs with better electrical performance. Bacterial cellulose is particularly useful in order to understand the role of these ions due to its purity, since it is harvested and no mechanical/chemical treatments are applied as usually required for a pulping process. To study the influence of alkaline ion doping, dried ultra-pure membranes were soaked during one hour in aqueous solutions of LiOH, NaOH, and KOH (0.5 M), and then rinsed and left to dry overnight. In the following subsections the results obtained for the alkaline membranes and reference pristine ultra-pure ones will be presented and discussed.

5.4.1.1. Morphological and structural characterisation

The diffractograms of pristine and ion-doped membranes (Figure 5.26) exhibit the characteristic peaks of cellulose type I, ($2\theta = 14.7^\circ$, 16.9° and 22.9°). The absence of lignin and hemicellulose have a tremendous impact on the crystallinity of the membranes, which present a CrI on the order of 88-89%, for the pristine BC. This value is well above the ones reported for wood-based paper, usually laying in the order of 70-80%, or even lower, depending on the performed treatments [11].

After the alkali soaking the CrI slightly decreases down to 81% for the BC soaked with LiOH (BC:Li), whereas the membrane with KOH (BC:K) presents a CrI=87% and for the NaOH soaked membrane (BC:Na) the CrI is 84%. It is known that cellulose can be dissolved in the presence of hydroxides, where LiOH is often reported as the most effective one, followed by NaOH and finally KOH [34], [35]. Thus, it is understandable that the crystalline fraction for the BC:Li is lower than for the other alkaline solutions used, meaning that dissolution of some parts of the cellulose may have occurred. Nevertheless, an eventual swelling of the fibres cannot be discarded, which may occur in parallel and also contribute to an apparent reduction of the CrI.

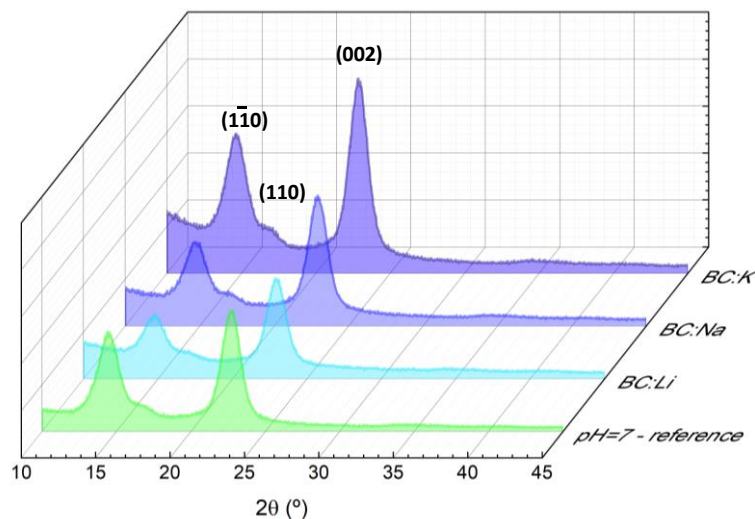


Figure 5.26 XRD diffractograms of the BC membranes with different metal alkaline ions.

These bacteria-produced membranes have a smooth three-dimensional structure of long entangled filaments of extruded cellulose fibrils (Figure 5.27). Hydrogen then promotes fine fibre-ribbons with an average width of 20 up to 100 nm that result in membranes with a surface RMS roughness on the order of 40 to 60 nm (value obtained from AFM measurements) [36]–[38].

The non-treated membranes have randomly organised but well-defined fine, and long bundles of fibres. With the addition of the alkaline solutions, the morphology of the fibres slightly changes especially for the Li and Na addition, remaining nearly unaltered for the K-doping (Figure 5.27a). In the BC:Li membranes the bundles have suffered a homogeneous swelling, although it is not possible to identify the formation of balloons. In addition, the fibres do not possess a well-defined shape, seeming to be partially dissolved, which may explain the decreasing of the crystallinity, resulting in a smooth surface with an RMS roughness of 32 nm. For the BC:Na the morphology is less affected, being still possible to identify a small swelling. The properties of the pristine and doped membranes are listed in Table 5.8.

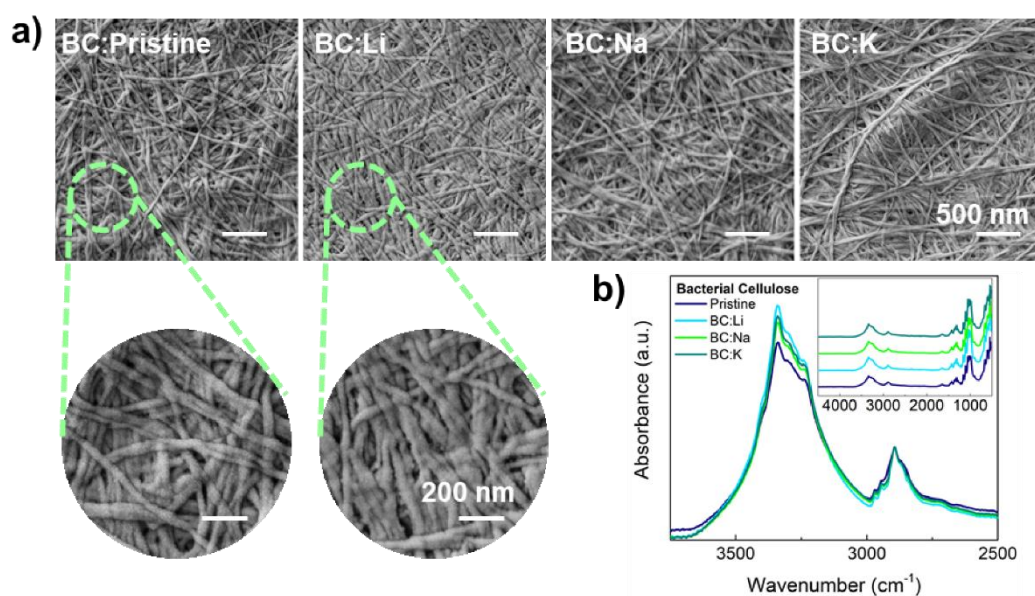


Figure 5.27 a) SEM Micrographs of the pristine BC and the alkali-doped membranes. b) FTIR spectra of the BC membranes (pristine and alkali-doped).

The doping of the membrane with alkali ions results in a variation of the adsorbed water (Figure 5.27b). The band assigned to the hydroxyl group -OH stretching in cellulose (3000-3500 cm⁻¹) shows higher normalised intensities for the doped membranes than for the pristine ones. This is indicative that in case of impregnation, the presence of different alkaline ions do not interfere with the intra or intermolecular hydrogen bonding. Thus, this should be related to an increase of adsorbed water caused by the addition of the ionic species that are highly susceptible to be hydrated.

The effective incorporation of alkaline ions was confirmed by EDX (Table 5.8). It is important to note that pristine membranes contain Na, which is the result of the purification

process. After being harvested and extensively washed, the BC slab is purified through alkaline treatment with a NaOH solution and rinsed with distilled water. The traces of Na detected by EDX result from this step, meaning that the intensive washing process does not remove all of the Na used during bacteria removal. Interestingly, when Li^+ and K^+ are intentionally incorporated no Na is detected. This may be due to an eventual ionic exchange in the membranes.

Table 5.8 Summary of the BC membranes' composition and thickness.

<i>Properties</i>	<i>Pristine</i>	<i>BC:Li</i>	<i>BC:Na</i>	<i>BC:K</i>
<i>C (at.%)</i>	52.78	52.91	53.01	53.75
<i>O (at.%)</i>	46.99	47.09	46.30	45.85
<i>Na (at.%)</i>	0.23	-	0.69	-
<i>K (at.%)</i>	-	-	-	0.39
<i>Thickness (μm)</i>	17	16	18	16

In Figure 5.28 the thermal analysis of a reference BC membrane is shown, which was extensively washed to reach a $\text{pH} \approx 7$. The thermogravimetric analysis measurement (TGA) shows a small mass loss due to the evaporation of adsorbed moisture in the membrane ($T \leq 100^\circ\text{C}$), followed by an abrupt mass reduction, starting around 300°C , indicating the extensive thermal degradation of the material. At the same time the derivative weight (DTA) shows that a significant weight loss occurs in the range of $300\text{--}350^\circ\text{C}$, reaching the maximum rate of transformation at 345°C .

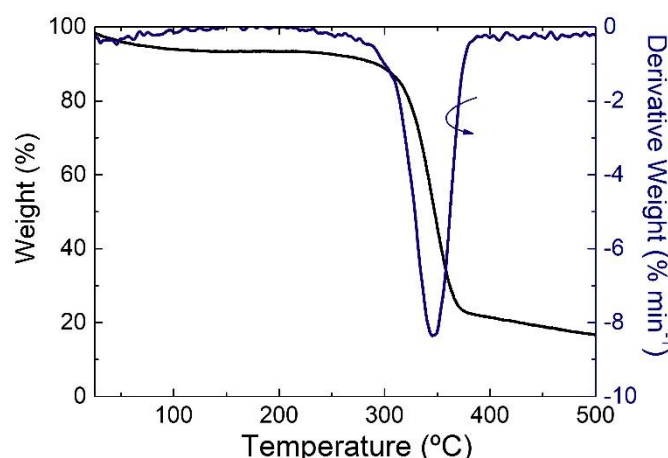


Figure 5.28 Thermal analysis of the reference BC membrane. The thermogravimetric analysis is represented in the left yy axis, and derivative weight is represented in the right yy axis.

The absence of hemicellulose, which would degrade at lower temperatures, results in improved thermal stability up to higher temperatures. Just for comparison purposes, in Chapter 4, a DSC/TGA for papers of different wood sources, shows a thermal degradation starting around 270 °C proceeding up to 350 °C.

5.4.1.2. Application of BC as dielectric in field-effect transistors

Despite the odd origin of these membranes, the principle that enables the use of *conventional* cellulose as dielectric remains the same; the existence of ions that are displaced under the application of an electric field. Electrochemical impedance spectroscopy measurements reveal a similar behaviour to that verified for membranes formed using other sources, which is a capacitance increase at low frequencies due to EDL formation at the membranes' interfaces (Figure 5.29). The capacitance is not largely affected by the alkali-doping, with values varying between 2.4 and 4.3 $\mu\text{F cm}^{-2}$ although the highest values are obtained through Na addition.

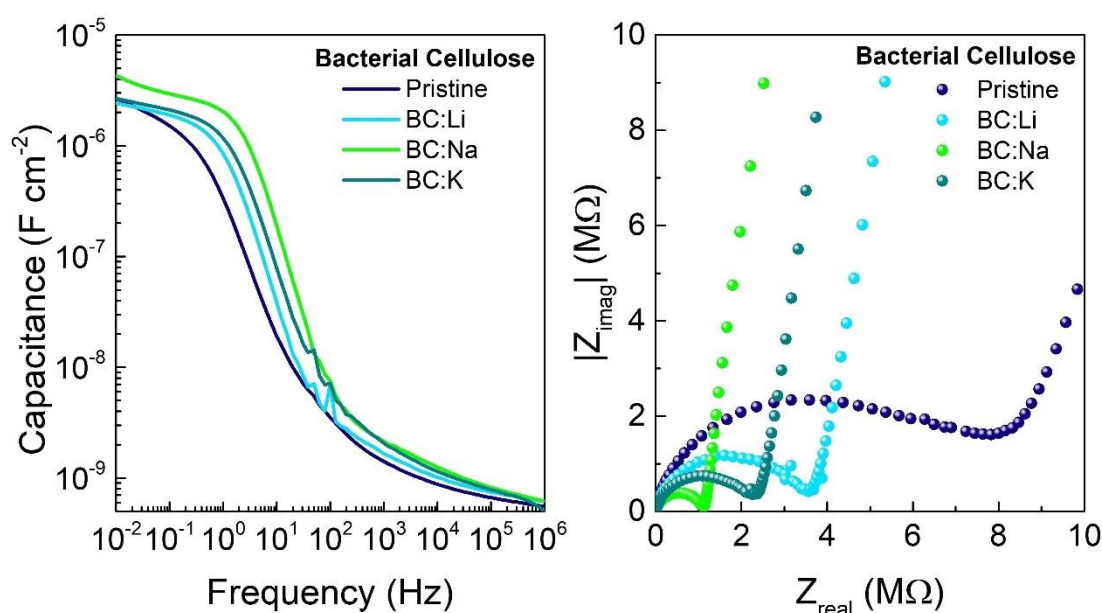


Figure 5.29 EIS characterisation of the alkali-doped BC membranes: C_{eff} as a function of the applied frequency (on the left) and determination of the BC resistance (on the right).

Similarly, to what was observed for the NFCs, the resistivity of the BC membranes is directly related to the intentional incorporation of alkaline ions. The pristine membrane has a resistivity of $\approx 97 \text{ M}\Omega \text{ cm}$ which is reduced to $14 \text{ M}\Omega \text{ cm}$, with a conductivity of $711 \mu\text{S cm}^{-1}$ for the BC:Na (Figure 5.29). For such low conductivity values, it is difficult to distinguish between electrical and ionic contributions. Indeed, the phase angle variation

indicates that the ionic relaxation behaviour dominates from 2.5 Hz to 10 kHz (CB:Na), where it is higher than -45° . Capacitive domains (phase angle lower than -45°) exist above 10 kHz being associated with dipole relaxation, and below 2.5 Hz when the EDL is formed (data not shown). This behaviour indicates that ionic relaxation dominates only up to 10 kHz, evidencing that paper is not a perfect ionic conductor and that the contribution of electrical conduction is relevant to the conductivity value determined by impedance spectroscopy.

The FETs produced using pristine BC as the gate dielectric show good electrical performance and low-voltage operation, with a current modulation above four orders of magnitude, $S=0.22 \text{ V dec}^{-1}$ and $\mu_{FE}=1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The electrical performance is improved with the addition of ions (Figure 5.30), accompanied by a significant narrowing of counterclockwise hysteresis from 1.5 V (pristine) to 0.1 V (BC:Na and BC:K).

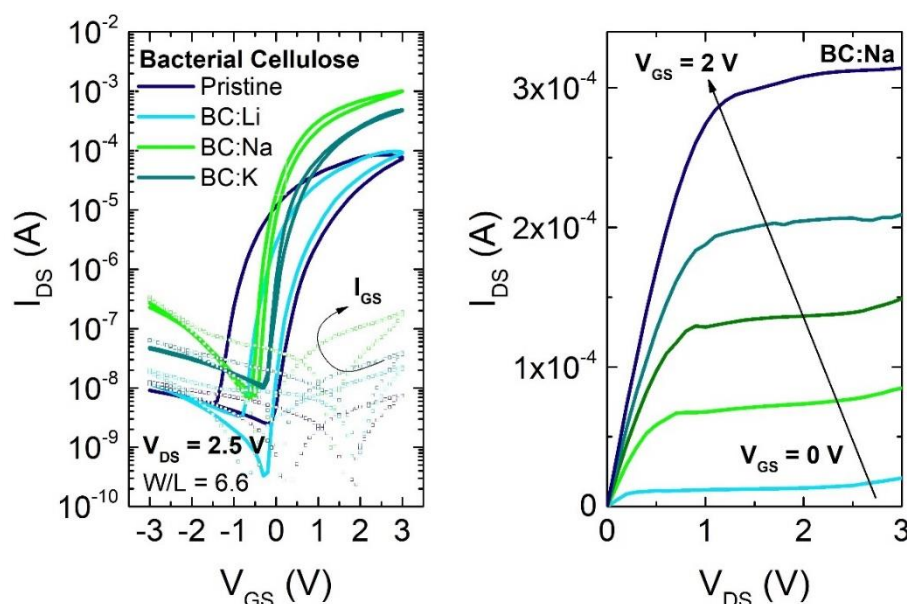


Figure 5.30 FETs using alkali-doped membranes as the gate dielectric. On the left the transfer characteristics I_{DS} - V_{GS} for a $V_{DS}=2.5 \text{ V}$. On the right, saturated output characteristic curves for the FETs on BC:Na.

Besides the hysteresis, a significant improvement on the electrical performance lies in the mobility. The FETs produced on the alkaline membranes reach the saturation regime (Figure 5.30), with μ_{sat} values varying between 1.8 and $25.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the BC:Li and BC:Na, respectively. The best electrical performance is by far obtained for the Na-doped membranes. The devices reach a current modulation above five orders of magnitude, while the sub-threshold slope is 0.12 V dec^{-1} , lower than what was obtained for the NFC

membranes. The increase of the leakage current is directly related to the variation (decrease) of the membranes' resistivity induced by the addition of ions to the matrix, as seen in the EIS measurements (Figure 5.29). Like what was observed for other membranes, such as the NFCs, the resistivity is lower in the membranes with Na addition, reinforcing the idea that Na could be an inexpensive and environmentally friendly option for suitable doping of the cellulose dielectric membranes.

5.4.2. Highly pure membranes and pH influence

The use of alkaline ion doping of the cellulose, regardless of the source, as a route to improve the electrical performance of the FETs is undeniable. Considering this, an alternative doping process of highly pure BC membranes was made by adjusting the pH with NaOH of the wet membranes in order to achieve pH=11. After this step, the membranes were dried in the oven. The preparation of the samples was entirely made in the Minho University laboratories.

The treated and pristine membranes consist of an entangled matrix formed by thin fibres (Figure 5.31a) with a high crystalline fraction ($\approx 89\%$). This represents a difference to ion impregnation, starting from dried membranes discussed in the previous section, where the CrI was reduced in the presence of NaOH. Again, the small dimension of the fibres lead to transparent membranes with average transmittance near 25% (pH=11) to 40% (pristine) for a thickness of 45 and 16 μm , respectively (Figure 5.31b). Like mentioned in the previous section, a dense and entangled matrix with low porosity results in an attenuation of the light scattering (Figure 5.31b).

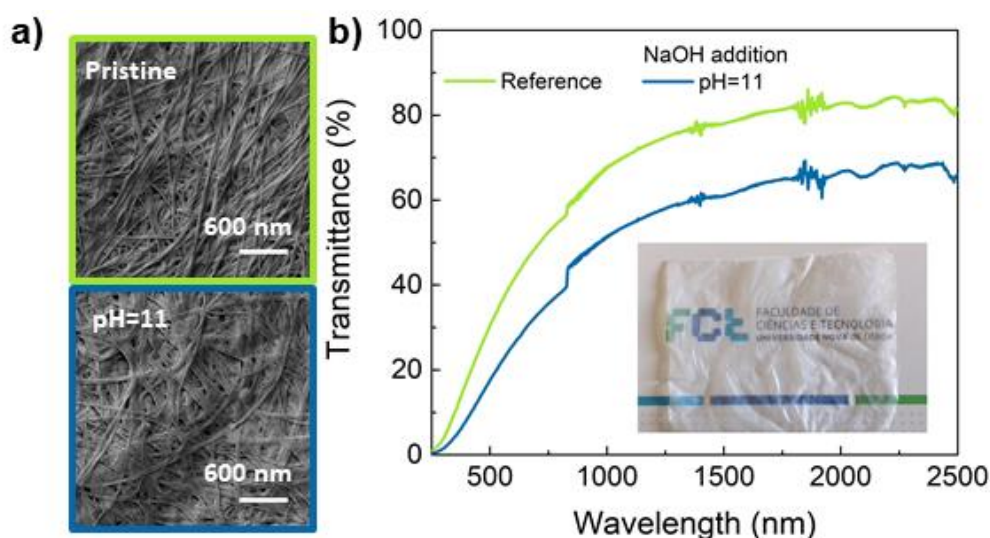


Figure 5.31 a) SEM of pristine BC and of a membrane with pH=11, b) Optical transmittance of the BC membranes with pH=11. The inset shows a photograph of a highly pure dried BC membrane.

5.4.2.1. pH influence on oxide-based FETs performance

The use of BC for electronic applications has been already reported for organic light emitting diodes or amorphous silicon solar cells [39]–[41]. The innovation brought by this work was the use of this material as gate dielectric, which was initially reported in 2016 [41].

The EDL formation in these membranes was verified in the capacitance vs frequency measurements (Figure 5.32a). The behaviour observed is very similar to what has already been presented and discussed, where it is possible to distinguish the three specific regions. In the high frequency regime, the dominant mechanism is mostly dipolar relaxation, while for intermediate frequencies the ionic relaxation is the expected mechanism. The most relevant domain in this specific case occurs for low frequencies, where an accentuated increase in the capacitance occurs, which is related to the EDL formation corroborated by a phase below -45° (Figure 5.32a). The C_{eff} determined for the pristine BC is $3.2 \mu\text{F cm}^{-2}$, while the C_{eff} for the doped membrane is slightly higher, reaching $5.4 \mu\text{F cm}^{-2}$ (Figure 5.32a).

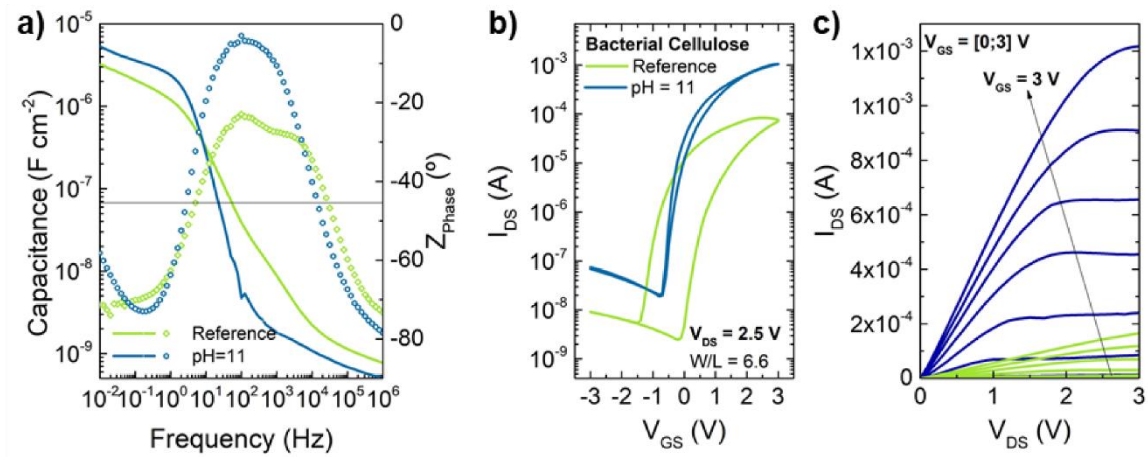


Figure 5.32 a) Impedance spectroscopy of the membranes produced with pH=11 showing C_{eff} and Phase as a function of frequency. b) Transfer ($I_{\text{DS}}-V_{\text{GS}}$) curves of the BC-gated FETs ($V_{\text{DS}}=2.5 \text{ V}$) and c) respective output characteristics.

The major difference lies in the performance of the produced FETs, using these membranes as gate dielectrics. The $I_{\text{ON}}/I_{\text{OFF}}$ reaches again four orders of magnitude with an increase to nearly five orders with the addition of Na^+ (Figure 5.32b). The improvement of the electrical properties goes beyond the $I_{\text{ON}}/I_{\text{OFF}}$ ratio, and the response of the device is significantly improved with an abrupt decrease in S from 0.29 to 0.17 V dec^{-1} , hysteresis

narrowed to ≈ 0.2 V, while μ_{Sat} reaches nearly $8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The output curves for these devices (Figure 5.32c) show that devices produced on doped-BC reach the saturation regime, which on the other hand is not confirmed for the pristine-BC membranes. The explanation for the improvement of the electrical performance of the FETs by increasing the pH in wet BC is the same as presented before for the doping of NFC and impregnation of pre-dried BC membranes.

5.5. References

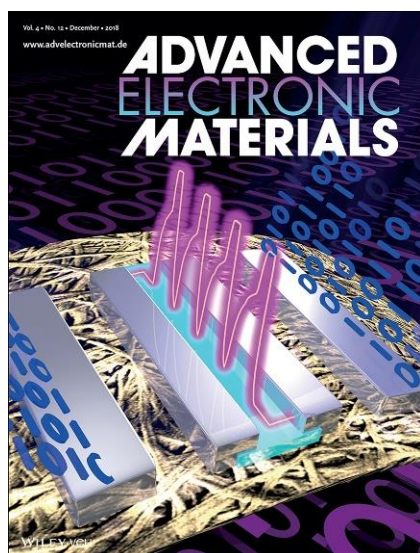
- [1] A. Dufresne, *Nanocellulose: From Nature to High Performance Tailored Materials*, 1st ed. Berlin, Boston: De Gruyter, 2012.
- [2] M. Toivakka, J. Peltonen, R. Osterbacka, M. (Mihai) Irimia-Vladu, E. D. Glowacki, N. S. Sariciftci, and S. Bauer, "Paper Electronics," in *Green materials for electronics*, 1st ed., M. Irimia-Vladu, E. D. Glowacki, N. S. Sariciftci, and S. Bauer, Eds. Wiley-VCH Verlag GmbH & Co. KGaA, 2017, pp. 163–189.
- [3] M. Pääkkö, M. Ankerfors, H. Kosonen, A. Nykänen, S. Ahola, M. Österberg, J. Ruokolainen, J. Laine, P. T. Larsson, O. Ikkala, and T. Lindström, "Enzymatic Hydrolysis Combined with Mechanical Shearing and High-Pressure Homogenization for Nanoscale Cellulose Fibrils and Strong Gels," *Biomacromolecules*, vol. 8, no. 6, pp. 1934–1941, Jun. 2007.
- [4] O. J. Rojas, Ed., *Cellulose Chemistry and Properties: Fibers, Nanocelluloses and Advanced Materials*. Springer International Publishing, 2016.
- [5] Y. Yue, "A comparative study of cellulose I and II and fibers and nanocrystals," Faculty of the Louisiana State University and Agricultural and Mechanical College, 2011.
- [6] S. Zhang, W. Wang, F. Li, J. Yu, and S. Zhang, "NaOH aqueous solvent systems," *Cellul. Chem. Technol.*, vol. 47, no. 9–10, pp. 671–679, 2013.
- [7] F. Jiang and Y.-L. Hsieh, "Self-assembling of TEMPO Oxidized Cellulose Nanofibrils As Affected by Protonation of Surface Carboxyls and Drying Methods," *ACS Sustain. Chem. Eng.*, vol. 4, no. 3, pp. 1041–1049, Mar. 2016.
- [8] M. Salajková, *Nanocelluloses - surface modification and use in functional materials*. 2012.
- [9] A. Khalid, R. Khan, M. Ul-Islam, T. Khan, and F. Wahid, "Bacterial cellulose-zinc oxide nanocomposites as a novel dressing system for burn wounds," *Carbohydr. Polym.*, vol. 164, pp. 214–221, 2017.
- [10] S. Dai, Y. Chu, D. Liu, F. Cao, X. Wu, J. Zhou, B. Zhou, Y. Chen, and J. Huang, "Intrinsically ionic conductive cellulose nanopapers applied as all solid dielectrics for low voltage organic transistors," *Nat. Commun.*, vol. 9, no. 1, p. 2737, Dec. 2018.
- [11] L. Pereira, D. Gaspar, D. Guerin, A. Delattre, E. Fortunato, and R. Martins, "The influence of fibril composition and dimension on the performance of paper gated oxide transistors," *Nanotechnology*, vol. 25, no. 9, p. 094007, Mar. 2014.
- [12] I. Cunha, R. Barras, P. Grey, D. Gaspar, E. Fortunato, R. Martins, and L. Pereira, "Reusable Cellulose-Based Hydrogel Sticker Film Applied as Gate Dielectric in Paper Electrolyte-Gated Transistors," *Adv. Funct. Mater.*, vol. 27, no. 16, 2017.

- [13] A. Isogai, T. Saito, and H. Fukuzumi, “TEMPO-oxidized cellulose nanofibers,” *Nanoscale*, vol. 3, no. 1, pp. 71–85, 2011.
- [14] S. Dasgupta, G. Stoesser, N. Schweikert, R. Hahn, S. Dehm, R. Kruk, and H. Hahn, “Printed and electrochemically gated, high-mobility, inorganic oxide nanoparticle FETs and their suitability for high-frequency applications,” *Adv. Funct. Mater.*, vol. 22, no. 23, pp. 4909–4919, 2012.
- [15] L. Santos, D. Nunes, R. Branquinho, D. Salgueiro, P. Barquinha, R. Martins, and E. Fortunato, “Solvothermal Synthesis of Gallium – Indium-Zinc-Oxide Nanoparticles for Electrolyte-Gated Transistors,” 2014.
- [16] M. Samet, V. Levchenko, G. Boiteux, G. Seytre, A. Kallel, and A. Serghei, “Electrode polarization vs. Maxwell-Wagner-Sillars interfacial polarization in dielectric spectra of materials: Characteristic frequencies and scaling laws,” *J. Chem. Phys.*, vol. 142, no. 19, p. 194703, May 2015.
- [17] M. Iwamoto, “Maxwell–Wagner Effect,” in *Encyclopedia of Nanotechnology*, vol. 50, no. 06, Dordrecht: Springer Netherlands, 2015, pp. 1–13.
- [18] B.-L. S. Instruments, “Measurements of the double layer capacitance,” no. Application note #21. BioLogic, p. 38568, 2010.
- [19] D. Nunes, A. Pimentel, L. Santos, P. Barquinha, L. Pereira, E. Fortunato, and R. Martins, “Oxide nanoparticles hybrid materials and applications,” in *Metal Oxide Nanostructures Synthesis, Properties and Applications*, 2018, pp. 235–281.
- [20] A. Salis and B. W. Ninham, “Models and mechanisms of Hofmeister effects in electrolyte solutions, and colloid and protein systems revisited,” *Chem. Soc. Rev.*, vol. 43, no. 21, pp. 7358–7377, Aug. 2014.
- [21] P. Grey, S. N. Fernandes, D. Gaspar, E. Fortunato, R. Martins, M. H. Godinho, and L. Pereira, “Field-Effect Transistors on Photonic Cellulose Nanocrystal Solid Electrolyte for Circular Polarized Light Sensing,” *Adv. Funct. Mater.*, vol. 1805279, p. 1805279, Oct. 2018.
- [22] F. Shao, P. Feng, C. Wan, X. Wan, Y. Yang, Y. Shi, and Q. Wan, “Multifunctional Logic Demonstrated in a Flexible Multigate Oxide-Based Electric-Double-Layer Transistor on Paper Substrate,” *Adv. Electron. Mater.*, vol. 3, no. 3, p. 1600509, Mar. 2017.
- [23] E. N. Cho, S. Member, J. H. Kang, and S. Member, “Analysis of Bias Stress Instability in Amorphous InGaZnO Thin-Film Transistors,” *IEEE Trans. Device Mater. Reliab.*, vol. 11, no. 1, pp. 112–117, 2011.
- [24] X. Du, B. T. Flynn, J. R. Motley, W. F. Stickle, H. Bluhm, and G. S. Herman, “Role of Self-Assembled Monolayers on Improved Electrical Stability of Amorphous In-Ga-Zn-O Thin-Film Transistors,” *ECS J. Solid State Sci. Technol.*, vol. 3, no. 9, pp. Q3045–Q3049, Jul. 2014.
- [25] Y. Kumaresan, Y. Pak, N. Lim, M. Park, S. Yoon, H. Yoon, H. Lee, B. H. Lee, and G. Y. Jung, “Highly Bendable In-Ga-ZnO Thin Film Transistors by Using a Thermally Stable Organic Dielectric Layer,” *Nat. Publ. Gr.*, no. August, pp. 1–10, 2016.
- [26] H. Gleskova, S. Wagner, and Z. Suo, “Failure resistance of amorphous silicon transistors under extreme in-plane strain,” *Appl. Phys. Lett.*, vol. 75, no. 19, pp. 3011–3013, 1999.
- [27] T. Mudgal, “Interpretation and Regulation of Electronic Defects in IGZO TFTs Through Materials & Processes,” Rochester Institute of Technology, 2017.
- [28] S. J. Eichhorn, “Cellulose nanowhiskers: promising materials for advanced applications,” *Soft Matter*, vol. 7, no. 2, pp. 303–315, 2011.
- [29] D. Gaspar, S. N. Fernandes, A. G. de Oliveira, J. G. G. Fernandes, P. Grey, R. V. V

- Pontes, L. Pereira, R. Martins, M. H. H. Godinho, and E. Fortunato, "Nanocrystalline cellulose applied simultaneously as the gate dielectric and the substrate in flexible field effect transistors," *Nanotechnology*, vol. 25, no. 9, p. 094008, Mar. 2014.
- [30] S. N. Fernandes, P. L. Almeida, N. Monge, L. E. Aguirre, D. Reis, C. L. P. de Oliveira, A. M. F. Neto, P. Pieranski, and M. H. Godinho, "Mind the Microgap in Iridescent Cellulose Nanocrystal Films," *Adv. Mater.*, 2017.
- [31] E. Fortunato, N. Correia, P. Barquinha, L. Pereira, G. Goncalves, and R. Martins, "High-Performance Flexible Hybrid Field-Effect Transistors Based on Cellulose Fiber Paper," *IEEE Electron Device Lett.*, vol. 29, no. 9, pp. 988–990, Sep. 2008.
- [32] W. Lim, E. a. Douglas, S.-H. Kim, D. P. Norton, S. J. Pearton, F. Ren, H. Shen, and W. H. Chang, "High mobility InGaZnO₄ thin-film transistors on paper," *Appl. Phys. Lett.*, vol. 94, no. 7, p. 072103, 2009.
- [33] A. C. Rodrigues, A. I. Fontão, A. Coelho, M. Leal, F. A. G. Soares da Silva, Y. Wan, F. Dourado, and M. Gama, "Response surface statistical optimization of bacterial nanocellulose fermentation in static culture using a low-cost medium," *N. Biotechnol.*, 2019.
- [34] J. Cai and L. Zhang, "Rapid dissolution of cellulose in LiOH/urea and NaOH/urea aqueous solutions," *Macromol. Biosci.*, vol. 5, no. 6, pp. 539–548, 2005.
- [35] I. Cunha, R. Barras, P. Grey, D. Gaspar, E. Fortunato, R. Martins, and L. Pereira, "Reusable Cellulose-Based Hydrogel Sticker Film Applied as Gate Dielectric in Paper Electrolyte-Gated Transistors," *Adv. Funct. Mater.*, vol. 27, no. 16, p. 1606755, Apr. 2017.
- [36] M. Gama, P. Gatenholm, D. Klemm, and E. Al, *Bacterial NanoCellulose*. 2013.
- [37] Y. Luo, J. Zhang, X. Li, C. Liao, and X. Li, "The Cellulose Nanofibers for Optoelectronic Conversion and Energy Storage," *J. Nanomater.*, vol. 2014, pp. 1–13, 2014.
- [38] M. Iguchi, S. Yamanaka, and A. Budhiono, "Bacterial cellulose - a masterpiece of nature's arts," *J. Mater. Sci.*, vol. 35, no. 2, pp. 261–270, 2000.
- [39] C. Legnani, C. Vilani, V. L. Calil, H. S. Barud, W. G. Quirino, C. A. Achete, S. J. L. Ribeiro, and M. Cremona, "Bacterial cellulose membrane as flexible substrate for organic light emitting devices," *Thin Solid Films*, 2008.
- [40] E. R. P. Pinto, H. S. Barud, R. R. Silva, M. Palmieri, W. L. Polito, V. L. Calil, M. Cremona, S. J. L. Ribeiro, and Y. Messaddeq, "Transparent composites prepared from bacterial cellulose and castor oil based polyurethane as substrates for flexible OLEDs," *J. Mater. Chem. C*, vol. 3, no. 44, pp. 11581–11588, 2015.
- [41] E. Fortunato, D. Gaspar, P. Duarte, L. Pereira, H. Águas, A. Vicente, F. Dourado, M. Gama, and R. Martins, "Optoelectronic Devices from Bacterial NanoCellulose," in *Bacterial Nanocellulose*, Elsevier, 2016, pp. 179–197.

Logic operations with transistors on cellulose substrates

Some of the results presented in this chapter are part or partially adapted from the following publications:



D. Gaspar, J. Martins, P. Bahubalindrani, L. Pereira, E. Fortunato, and R. Martins, “Planar Dual-Gate Paper/Oxide Field Effect Transistors as Universal Logic Gates,” *Adv. Electron. Mater.*, vol. 1800423, p. 1800423, 2018.

R. Martins, **D. Gaspar**, M. J. Mendes, L. Pereira, J. Martins, P. Bahubalindrani, P. Barquinha, and E. Fortunato, “Papertronics: Multigate paper transistor for multifunction applications,” *Appl. Mater. Today*, vol. 12, pp. 402–414, 2018.

D. Gaspar, P. Grey, J. Martins, R. Simões, F. Gama, R. Martins, E. Fortunato, and L. Pereira “Alkali-doped micro/nanofibrillated cellulose membranes applied as gate dielectric in FETs with improved electrical performance” (under preparation).

Logic operations with transistors on cellulose substrates

Chapter 6.	<i>Logic operations with transistors on cellulose substrates</i>	211
6.1.	Dual-gate oxide-based field effect transistors	211
6.1.1.	Architecture and devices' conception	212
6.1.2.	DG-FGFETs electrical characteristics	213
6.1.2.1.	Influence of the electrodes' separation and yield of fabrication	220
6.1.3.	Logics in a single DG-FGFET	223
6.1.4.	Tensile Bending Strain Tests	226
6.2.	Low voltage logic on NFC membranes	227
6.2.1.	NFC-gated dual-gate transistors	228
6.2.2.	Alkali-doped NFC membranes in inverters	230
6.3.	References	236

Chapter 6. Logic operations with transistors on cellulose substrates

The knowledge acquired along this PhD work, on modified cellulose substrates for their application as dielectric in FETs, allowed to implement more complex device architectures that evolved from a typical staggered bottom gate structure to planar dual-gate oxide-based transistors. Similar to the FETs, the working principle of the devices proposed here relies on the formation of electric double layers at the semiconductor/paper and paper/back floating electrode interfaces (associated to ions displacement within the paper). The novelty is that the EDL can be “disturbed” by a voltage applied at a secondary gate that determines the potential established at the back-floating electrode, that can itself be used as a fifth electrode.

The uniqueness of these devices allows the control of the transistors’ on-voltage, from depletion to enhancement mode, for instance. This specific characteristic permits the implementation of five logic functionalities using just one transistor, by setting the proper combination of the voltage level applied at each gate. This way a simple and universal device architecture can be envisaged towards the simplification of the production of low power electronic systems on paper.

Besides the dual-gate FETs, in this chapter devices produced with alkali-doped nanofibrillated cellulose will be presented, where it the influence of those ions in the dynamic response of the inverters using NFC membranes as gate dielectric will be addressed.

6.1. Dual-gate oxide-based field effect transistors

During this PhD a small step further was taken by implementing dual-gate in-plane oxide-based field effect transistors with a back floating gate electrode (DG-FGFETs) on paper, enabling multi-logic functionalities. The concept of dual gate FETs has been already tested on Si technology with SiO₂ based gate dielectrics [1], [13]. It has also been explored with organic semiconductors on paper surfaces [1], and even with other ionic dielectrics, such as chitosan or alginate, to create artificial synapses to emulate biological synaptic functions, which are often referred to as synaptic transistors in the literature [2], [3]. However, reports of such architectures using paper or other protonic conductors as gate dielectrics were scarce and poorly explained. The on-voltage (V_{On}) modulation through the second gate

electrode and the ability to perform logic operations with these devices using oxides as active semiconductors has not been thoroughly reported. Indeed, the existing reports on logics with oxide FETs have been mainly limited to demonstrate logic operations for OR and AND, using devices with different threshold (or V_{On}) voltages [4]. Moreover, the output logic is usually the drain current of the transistor while voltage is used as the input [16], while in many real-world applications it is essential to have voltage as the output logic to drive the next stages.

6.1.1. Architecture and devices' conception

The DG-FGFETs have a similar structure to the conventional paper-gated FETs which were described in the previous chapter, consisting of 30 nm thick sputtered indium-gallium-zinc oxide IGZO ($\text{In}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-ZnO}$; 1:2:2%mol) channel layer¹ and evaporated aluminium source (S), drain (D) (Figure 6.1a). However, the DG-FGFETs have two gates placed parallel to the source and drain electrodes, i.e. in the same plane, and also a conductive IZO floating electrode deposited on the back side of the paper.

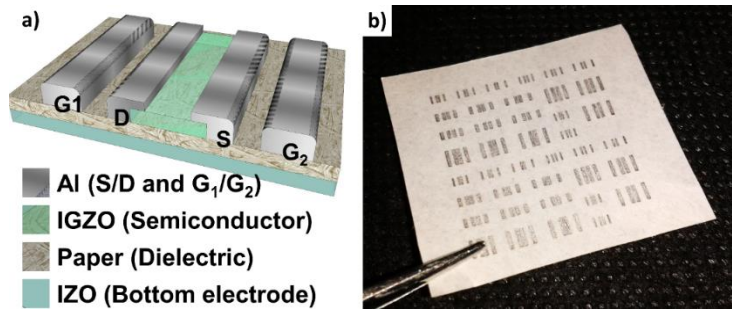


Figure 6.1 a) Schematic illustration of the architecture of IGZO paper DG-FGFETs using the tracing paper as the gate dielectric. G_1 and G_2 stand for the primary and secondary gate, respectively, while S and D are the source and drain, respectively.

b) Photograph of the produced DG-FGFETs.

The paper used for this work consisted of a commercial one with the same properties as the CSP analysed in Chapter 4. This paper had a capacitance of $0.23 \mu\text{Fcm}^{-2}$, at 10 mHz, a thickness of $75 \mu\text{m}$, and a bulk resistance $\approx 1.1 \text{ M}\Omega$, which corresponds to an estimated conductivity of $3.96 \times 10^{-9} \text{ S cm}^{-1}$.

¹ The channel length (L) and width (W) are 170 and $1035 \mu\text{m}$, respectively, resulting in a W/L ratio of 6.1 (theoretical values).

6.1.2. DG-FGFETs electrical characteristics

The transfer characteristics of the DG-FGFETs were measured at room temperature and relative humidity of $\approx 45\%$, for a V_{DS} of 1 V and 15 V, while the voltage applied at the secondary gate (V_{GS2}) was swept from -15 to 5 V, in 5 V steps (Figure 6.2a). It was observed that the carrier density modulation in the channel layer is possible only when the back electrode is present and kept at a floating potential; otherwise (when absent or when grounded) it is not possible to modulate the current in the channel through the primary gate voltage (V_{GS1}) (see Figure 6.2b). The current mapping resulting from the combination of different V_{GS1} and V_{GS2} is shown in Figure 6.2 c and d.

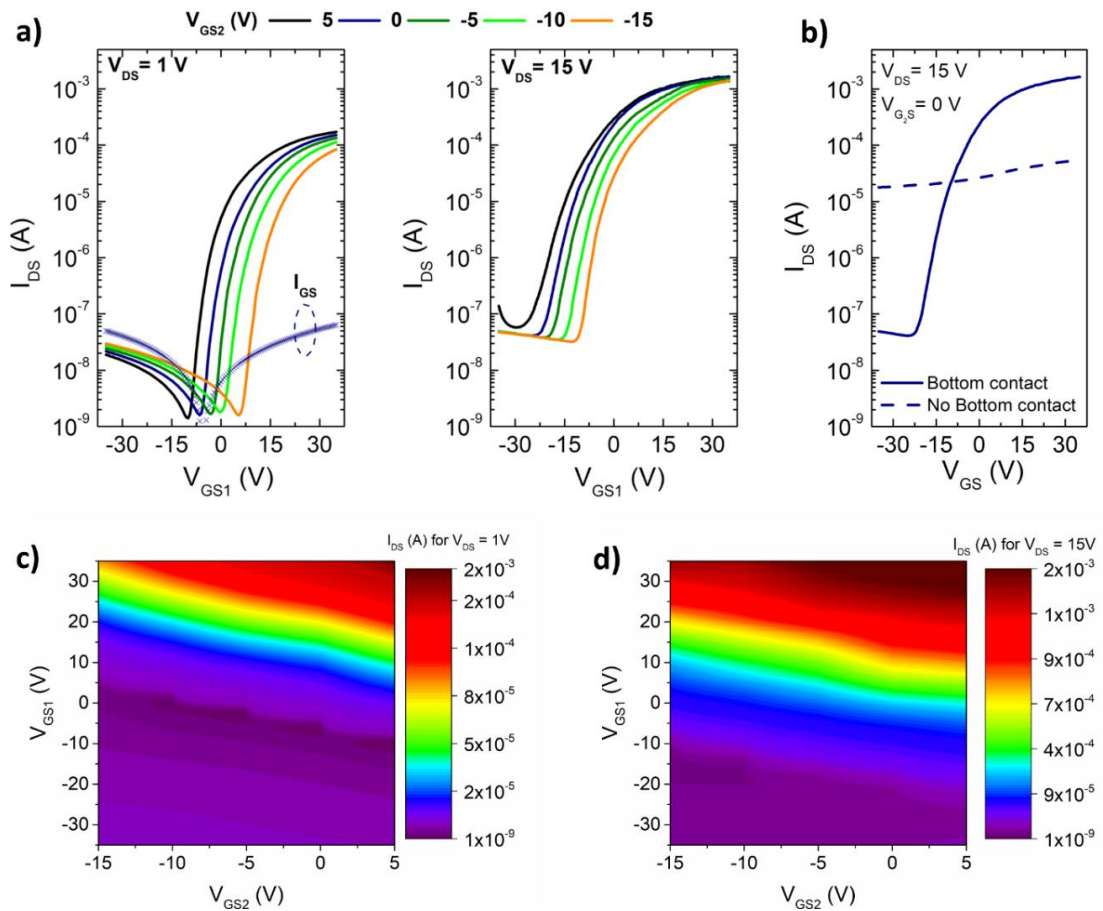


Figure 6.2 a) I_{DS} - V_{GS} transfer characteristics of the paper gated IGZO DG-FGFETs at $V_{DS}=1$ and 15 V (linear and saturation regime). I_{GS} for $V_{DS}=1$ V and $V_{GS2}=0$ V is also plotted, b) I_{DS} - V_{GS} transfer characteristics of DG-FGFETs with and without floating gate ($V_{DS}=15$ V and $V_{GS2}=0$). c) and d) Two-dimensional current map obtained from transfer curves, as a function of V_{GS1} and V_{GS2} , for $V_{DS}=1$ and 15 V, respectively.

In the architecture proposed here, V_{On} of the DG-FGFETs depends on V_{DS} since the voltage applied to the top electrodes will determine the potential established at the back electrode, that behaves indeed as the effective gate of these DG-FGFETs, as will be discussed and demonstrated further below. For $V_{DS}=1$ V (linear regime), it is possible to move from the depletion to the enhancement mode when V_{GS2} changes from 5 to -15 V. On the other hand, for $V_{DS}=15$ V (saturation regime), V_{On} is shifted towards high negative values, and the same range of V_{GS2} is not enough to reach the enhancement mode. In this case, V_{On} stays between -30 and -12.5 V. Regardless of the used V_{DS} , a shift of the transfer curves towards negative voltages is always obtained, when V_{GS2} becomes positive. A linear dependency of V_{On} on V_{GS2} was verified, both in linear and saturation regime, as shown in Figure 6.3.

When there is no voltage applied at G_2 , V_{On} is shifted towards high negative voltages (from nearly -7 V to around -25 V) just by changing V_{DS} from 1 V to 15 V (Figure 6.3), while the Off current also increases by about one order of magnitude. Ionic displacement in the paper and the establishment of a charge neutrality condition that lead to the formation of the EDL at the channel and floating gate interfaces (see Figure 6.5) [5] are responsible for the operation mode, as well as the maximum and minimum source to drain current.

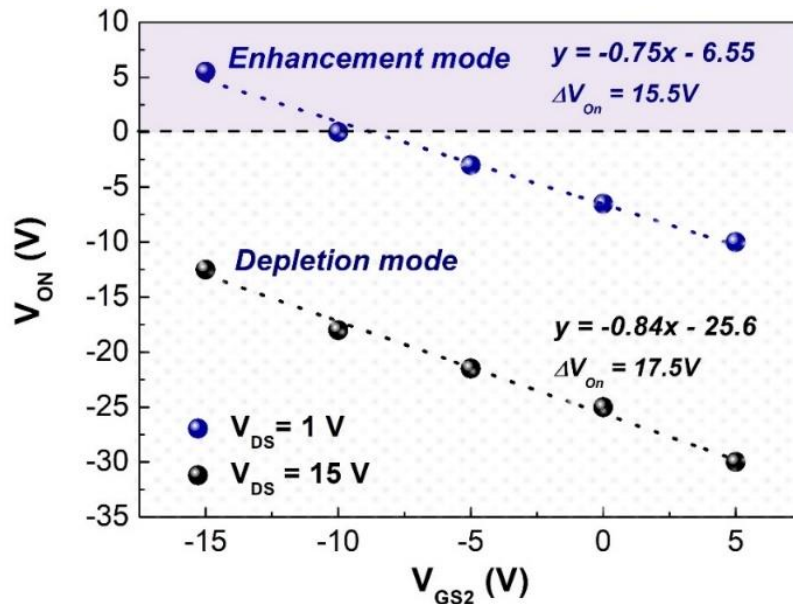


Figure 6.3 V_{On} dependence on V_{GS2} , respectively for a V_{DS} of 1V and 15 V. The variation of V_{On} follows a linear tendency that was fitted according to the equations presented in the figure.

A comparison of the main electrical parameters, such as On/Off current ($I_{\text{On}}/I_{\text{Off}}$) ratio, V_{On} , sub-threshold slope (S), field effect and saturation mobility (μ_{FE} and μ_{SAT} , respectively), determined for the DG-FGFETs, is plotted in Figure 6.4. For low V_{DS} ($V_{\text{D}} = 1\text{ V}$) the $I_{\text{On}}/I_{\text{Off}}$ ratio is about 8×10^{-4} , which increases when V_{GS2} changes from negative to positive. However, this is just an apparent variation once it is dictated by the current achieved at $V_{\text{GS1}} = 30\text{ V}$ (the maximum value used in the measurements), which decreases with an increase in V_{On} as a result of V_{GS2} becoming negative. On the other hand, the Off current is insensitive to V_{GS2} and is ruled by the paper resistivity. For a $V_{\text{DS}} = 1\text{ V}$ and $V_{\text{GS1}} = 30\text{ V}$, the gate leakage current (I_{GS1}) is around $5 \times 10^{-8}\text{ A}$, representing electrical resistance of about $600\text{ M}\Omega$. Considering the overlap area of the gate and source electrodes ($1.76 \times 10^{-3}\text{ cm}^2$), this compares well to the bulk resistivity of the paper determined by impedance spectroscopy, which is around $1.1\text{ M}\Omega$ for an electrode area of 1.77 cm^2 .

Since V_{On} is always negative for $V_{\text{DS}} = 15\text{ V}$, the maximum I_{DS} current obtained for $V_{\text{GS1}} = 30\text{ V}$ becomes similar, and the $I_{\text{On}}/I_{\text{Off}}$ ratio stays around 4×10^4 . The Off is limited by I_{GS1} , which is proportional to the applied V_{DS} . Consequently, higher V_{DS} results in increased I_{Off} , which in turn decreases the $I_{\text{On}}/I_{\text{Off}}$ ratio. The fact that the I_{GS1} limits the minimum values of I_{DS} just below V_{On} also dictates the increase of S when V_{GS2} moves from negative to positive since it tends to become higher as I_{Off} increases. On the other hand, the S values are unresponsive to V_{GS2} when $V_{\text{DS}} = 1\text{ V}$ because I_{Off} is much lower. The influence of I_{Off} on the S values was also observed when measuring the devices under bending.

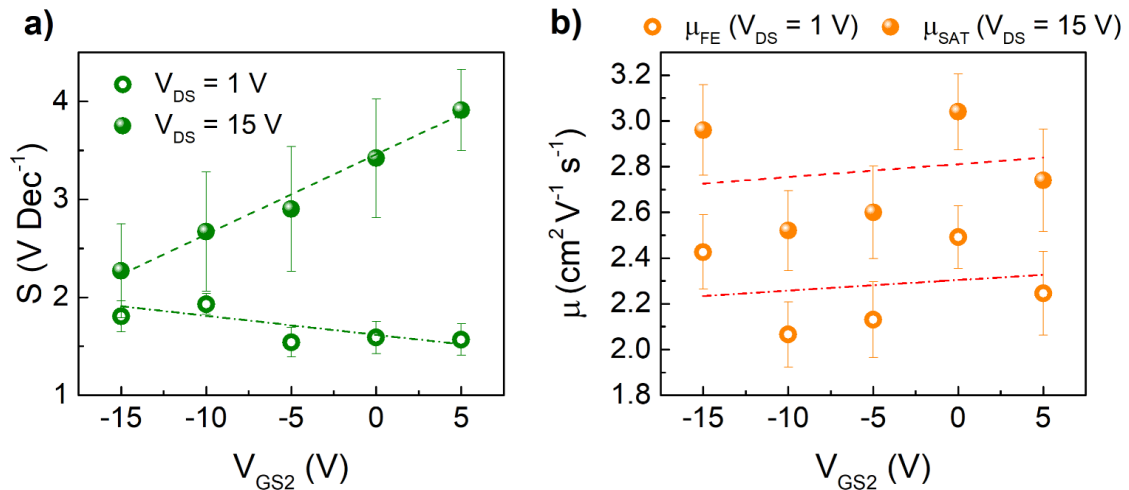


Figure 6.4 Comparison of electrical parameters of the paper-based DG-FGFETs for different V_{GS2} : a) sub-threshold slope (S), and b) mobility (μ_{FE} and μ_{SAT}) (open symbols for $V_{\text{DS}} = 1\text{ V}$ and solid symbols for $V_{\text{DS}} = 15\text{ V}$) (The lines are merely guides for the eyes.)

Finally, the maximum μ_{sat} is in the range of $2\text{-}3\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, being roughly constant for different V_{GS2} (see Figure 6.4b). The mobility is here mainly determined by the EDL associated capacitance, being its spatial extension determined only by the combinations of all the voltages applied at the four electrodes in the device. The μ_{sat} values obtained for $V_{\text{DS}}=15\text{ V}$ are always higher than the mobility for $V_{\text{DS}}=1\text{ V}$, which can be associated with the reduced influence of contact resistance.

A simplified model for the potential established at the floating back electrode is presented in Figure 6.5. The shift observed in the transfer characteristics of the DG-FGFETs is explained by the asymmetry of the electrical fields associated with G_1 , G_2 and V_{DS} in relation to the grounded source electrode. This determines the potential established along the floating electrode (V_{FG}) that behaves as the effective gate voltage responsible for the differences in the free carriers accumulated or depleted in the oxide channel layer. This means that an electrically-like doping effect occurs similarly to dual gate silicon-based structures [6], [7], determining how channel resistance modulation occurs.

Considering the case when only G_2 is negatively biased ($V_{\text{GS2}} < 0$) (solid blue curve), the V_{FG} is negative, leading to a partial depletion of the electronic charges existing in the channel, resulting in enhancement mode transistors. Nevertheless, the range of V_{GS2} , where the carrier depletion occurs, will also depend on V_{DS} , as already explained, meaning that both voltages will determine the V_{On} of the DG-FGFETs. When applying a sufficiently high voltage at G_1 , the V_{FG} established at the floating back electrode will become positive, resulting in electron accumulation in the channel and a current flow between source and drain (Figure 6.5). On the other hand, a positive V_{GS2} establishes a positive V_{FG} at the floating electrode, which promotes carriers' accumulation turning the channel conductive, even without any applied V_{GS1} , which effectively shifts the V_{On} towards negative values [4], [8], resulting in depletion mode FETs regardless of the used V_{DS} (1 and 15 V).

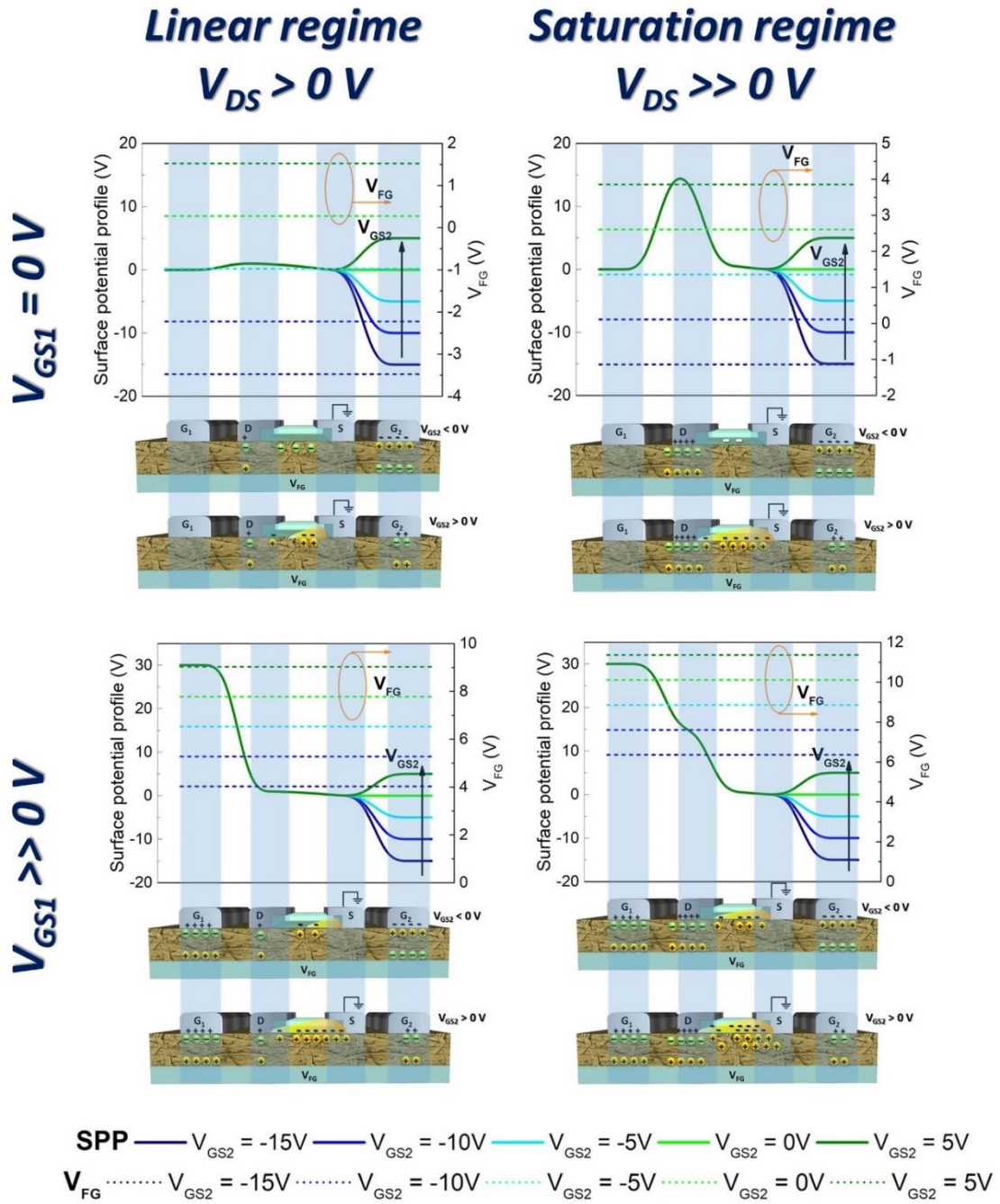


Figure 6.5 Schematic representation of the operation mode of the paper DG-FGFETs as a function of the V_{GS2} , and its influence on the accumulation of carriers in the channel, showing the depletion region (in orange). The plots depict the Surface Potential Profile (SPP, solid lines) for different $V_{GS1}/V_{DS}/V_{GS2}$ combinations and the resulting Floating Gate potential (V_{FG}) determined for each case (dashed lines). In each situation, a simplified schematic diagram of the ions' distribution in the paper dielectric is presented, aiming to understand better the potential's intensity established at the floating electrode that depends on the balance established by $V_{GS1}/V_{DS}/V_{GS2}$.

Table 6.1 presents the V_{FG} values obtained through this simplified model as well as the ones resulting from the simulation using SILVACO software. A close relationship between the obtained values is evident, supporting the discussion presented here. The differences result primarily from the surface potential profile that is assumed to change monolithically between the top electrodes, while simulation in SILVACO software shows a slightly more complex potential profile since it considers the dielectric characteristics of the paper, working function of the back-electrode material, the spacing between top electrodes and the semiconductor thickness (see Figure 6.6).

Table 6.1 V_{FG} values obtained for the simplified operation mode of the paper DG-FGFETs as a function of the V_{GS2} and the ones obtained using SILVACO software and measured.

V_{GS1} (V)	V_{DS} (V)	V_{GS2} (V)	V_{FG} (V)		
			Silvaco simulation	Simplified model	Measured
0	1	-15	-4.01	-3.45	-4.32
0	1	-10	-2.60	-2.23	-2.27
0	1	-5	-1.20	-0.98	-1.32
0	1	0	0.17	0.28	0.20
0	1	5	1.43	1.53	2.02
0	15	-15	-0.97	-1.14	-1.40
0	15	-10	0.38	0.11	1.02
0	15	-5	1.66	1.36	2.18
0	15	0	2.94	2.61	3.31
0	15	5	4.21	3.86	4.76
30	1	-15	3.76	4.023	1.92
30	1	-10	4.94	5.28	4.10
30	1	-5	6.11	6.53	5.62
30	1	0	7.28	7.78	6.84
30	1	5	8.45	9.03	8.35
30	15	-15	6.74	6.36	5.25
30	15	-10	8.00	7.61	7.25
30	15	-5	9.26	8.86	8.84
30	15	0	10.52	10.11	9.69
30	15	5	11.78	11.36	11.04

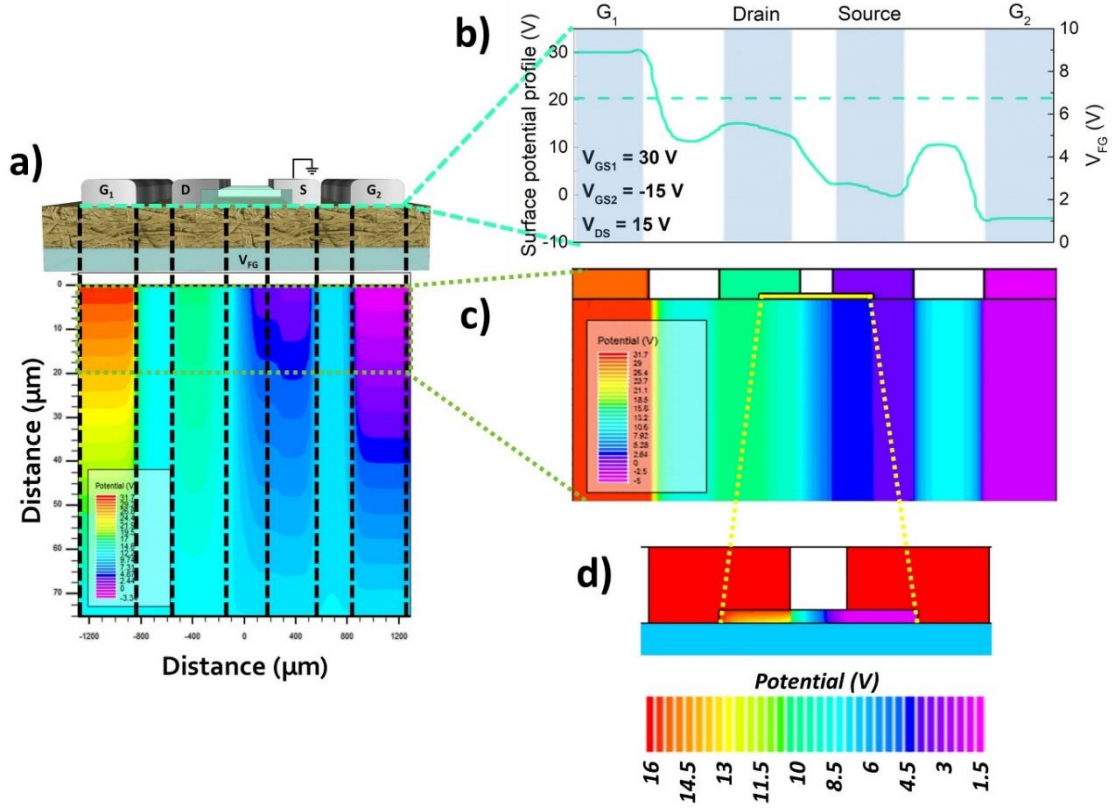


Figure 6.6 V_{FG} potential simulation using SILVACO software for a DG-FGFETs with $V_{GS1}=30\text{ V}$, $V_{DS}=15\text{ V}$, and $V_{GS2}=-5\text{ V}$, a) Cross-section of the potential profile, b) Surface potential profile at the interface paper/electrodes and respective V_{FG} for the applied voltages, c) Zoom-in of the region near the electrodes, and d) Detail of the potential variation in the IGZO channel.

The V_{FG} values were measured experimentally by monitoring the open-circuit voltage as a function of V_{GS1} and V_{GS2} with a fifth probe while obtaining the transfer characteristics of the DG-FGFETs (Figure 6.7a). The measured values follow the trend determined by simulation, validating the proposed model. By plotting the transfer characteristics as a function of V_{FG} (Figure 6.7b), it is possible to verify that V_{On} is nearly the same, staying between -2 and -1.4 V, for the different V_{GS2} tested. This is also valid for different distances between the inner S/D and the outer G_1/G_2 electrodes (as will be discussed in the following sub-section). Figure 6.7b also demonstrates that when considering V_{FG} as a reference (instead of V_{GS1}) V_{On} becomes essentially independent of V_{DS} , as expected for a FET with the dimensions used in this work.

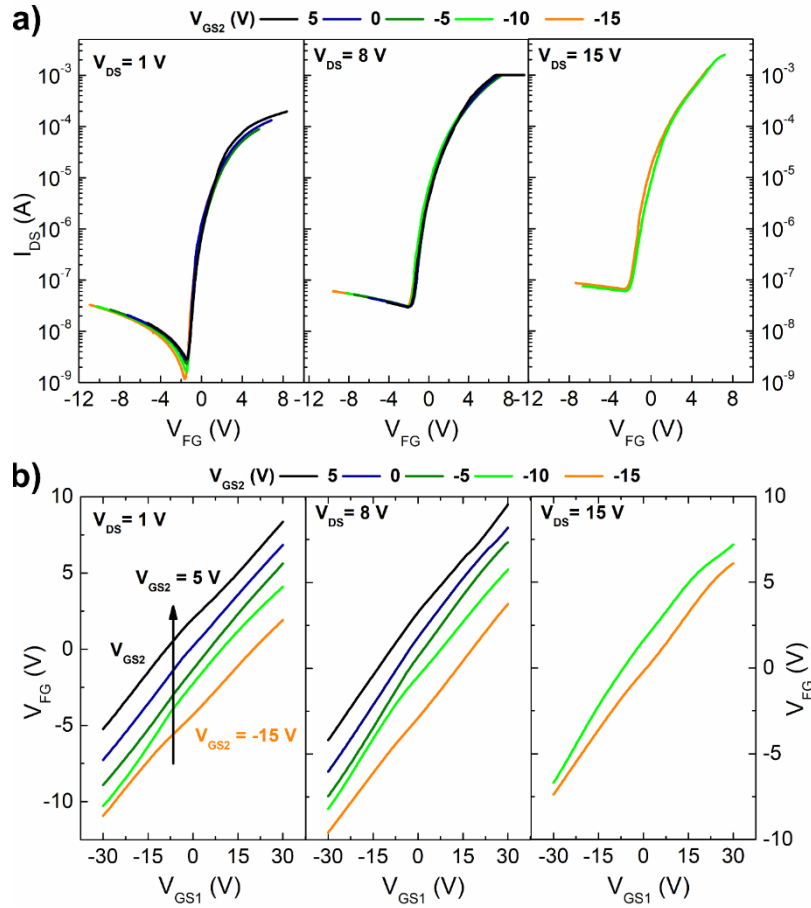


Figure 6.7 a) I_{DS} - V_{FG} transfer characteristics of the paper gated IGZO DG-FGFETs at $V_{DS}=1, 6$, and 15 V for different V_{GS2} , b) V_{FG} variation as a function of V_{GS1} and V_{GS2} for different V_{DS} .

6.1.2.1. Influence of the electrodes' separation and yield of fabrication

The influence of the electrode's separation on the electrical performance of the DG-FGFETs was investigated by producing devices with three different distances between the inner S/D and the outer G_1/G_2 electrodes. The data in the previous section was obtained for transistors with a separation of $365 \mu\text{m}$, and here the results for $570 \mu\text{m}$ and $770 \mu\text{m}$ are discussed (Figure 6.8a), maintaining the same W/L. All the devices were fabricated in the same batch and characterised in the same day with similar environmental conditions (atmospheric pressure, 27°C and relative humidity of 50%).

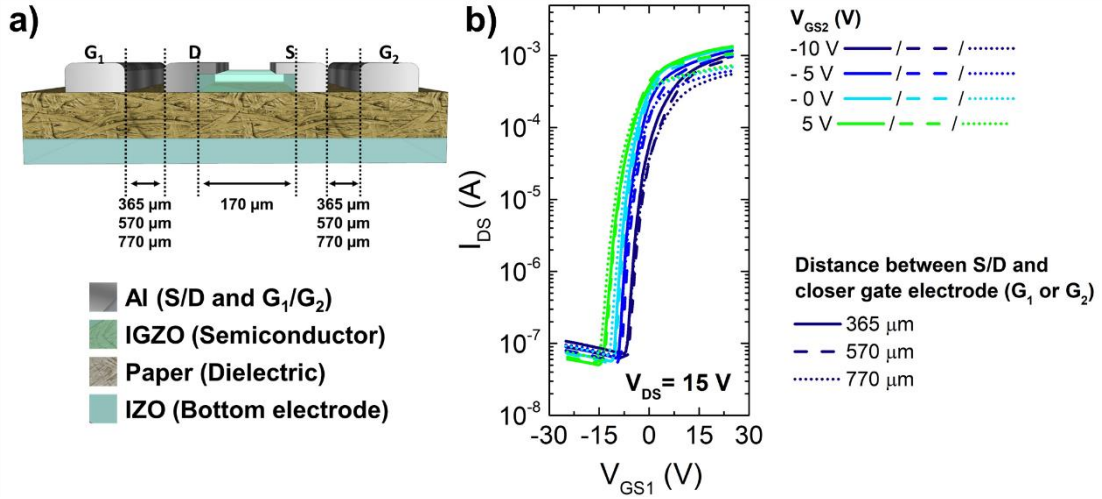


Figure 6.8 a) Schematic representation of the separation of the electrodes, and b) respective transfer characteristics for DGFG-FETs for $V_{DS}=15$ V.

Analysing the transfer curves (I_{DS} - V_{GS} for $V_{DS}=15$ V) of the new devices (Figure 6.8b), it is clear that the separation between the S/D and the outer G_1/G_2 electrodes does not affect the V_{On} shifting amplitude as V_{GS2} is modified. This fact was expected, since device operation relies on the potential established at the floating back electrode (V_{FG}), which results, as shown and discussed beforehand, from the voltage applied on both gates and S/D electrodes. Thus, in principle, V_{FG} should strongly depend on the electrodes' separation. Nevertheless, the maximum current extracted at high V_{GS} is reduced as the distance increases.

The transfer curves plotted as a function of V_{FG} (Figure 6.9a) show an almost perfect overlap, regardless of the used V_{G2} , confirming that the potential established at the back electrode is the effective gate voltage of these devices. The distance between S/D and G_1/G_2 seems to only have a small influence on the measured V_{FG} values as a function of V_{GS1} , for different V_{GS2} (Figure 6.9b). The observed tendency confirms that the floating potential established at the bottom electrode is not strongly affected by the distance. Thus, the difference observed in I_{DS} , and V_{FG} can be attributed to some lateral movement of ions between the G_1 and D electrodes, which will establish a distant dependent capacitance. This capacitance is in parallel with that established between the floating electrode and the channel layer, which may increase the effective gate capacitance and also improve carrier injection at the drain, by reducing the contact resistance.

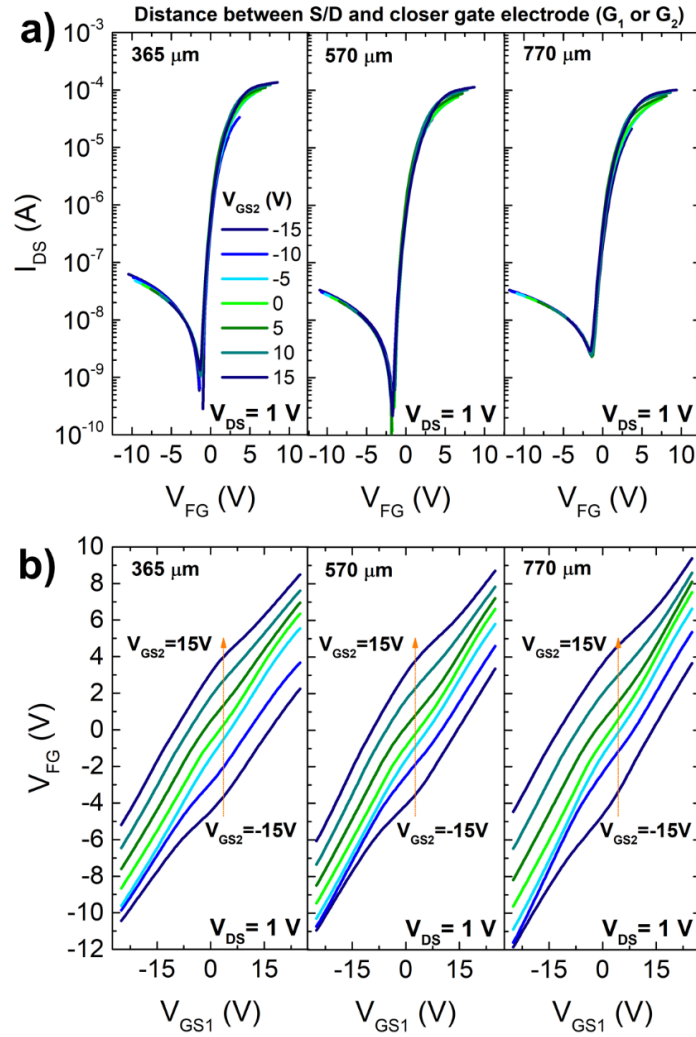


Figure 6.9 a) Transfer characteristics for DGFG-FETs with three different distances between S/D and G_1/G_2 (365, 570, and 770 μm) as a function of V_{FG} , and b) respective variation of V_{FG} with V_{GS2} as a function of V_{GS1} ($V_{GS2} = [-15; 15]$ V, and $V_{DS} = 1$ V)

For application on more complex circuits which may combine more than one device, the yield of device fabrication, as well as the electrical performance reliability are quite important. Due to size limitations in the employed vacuum deposition tools, the maximum area used was 10 cm x 10 cm. Several devices with the same W/L, and the same electrodes' separation (365 μm) were tested. The electrical performance is very similar for all the devices, namely how V_{On} changes as a function of the V_{GS2} applied, as shown in the transfer characteristics for six randomly chosen devices (Figure 6.10).

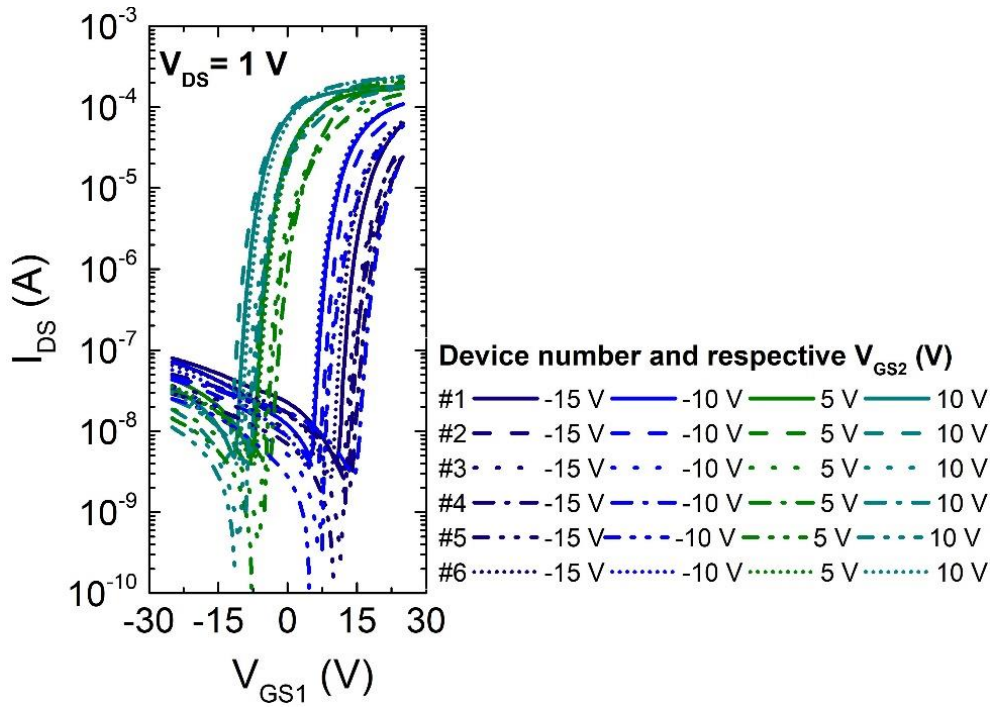


Figure 6.10 I_{DS} - V_{GS} transfer characteristics of six IGZO DG-FGFETs at $V_{DS}=1$ V.

The uniformity of the obtained characteristics allowed the selection of five transistors (with the same W/L ratio) to be implemented in a logic circuit. Each one was selected concerning its “low” and “high” levels for a proper circuit function. This will be discussed in the following section.

6.1.3. Logics in a single DG-FGFET

The flexibility in terms of operation voltage of the DG-FGFETs allows for the implementation of other logic functionalities directly through the variation of the input gate signals, permitting a unique combination of five logic operations [9].

For the OR and AND operation the logic levels *low* or logic “0” and *high*, the logic “1” can be rapidly chosen through the selection of the applied voltage at V_{GS1} and V_{GS2} , designated as V_{In1} and V_{In2} , respectively.

Figure 6.11 demonstrates the AND and OR logic for a frequency of 20 mHz and 40 mHz. The AND operation (Figure 6.11a) is obtained by using -13 V (*low*) $< V_{In1} \&_2 < 0$ V (*high*). In this logic gate at least one of the inputs should be *low*, this way no conductive channel is formed in the transistor. On the other hand, when V_{G1} and V_{G2} are both *high*, a conductive channel is formed, turning it On, and thus an increase in I_{DS} , by more than 4 times, is measured, which corresponds to a logic “1”. The OR operation (Figure 6.11b) is obtained

using $-12\text{ V (low)} < V_{In1} \& V_{In2} < 8\text{ V (high)}$ as logic levels. Here, when V_{In1} and V_{In2} are low, there is no current flowing in the device. Therefore, I_{DS} is at logic “0”. On the other hand, when the voltage applied at any of the gates (either V_{In1} or V_{In2}) is *high*, a conductive channel is formed, and I_{DS} is at logic “1”. In this state, I_{DS} is four times higher than the Off current, showing robust OR logic operation.

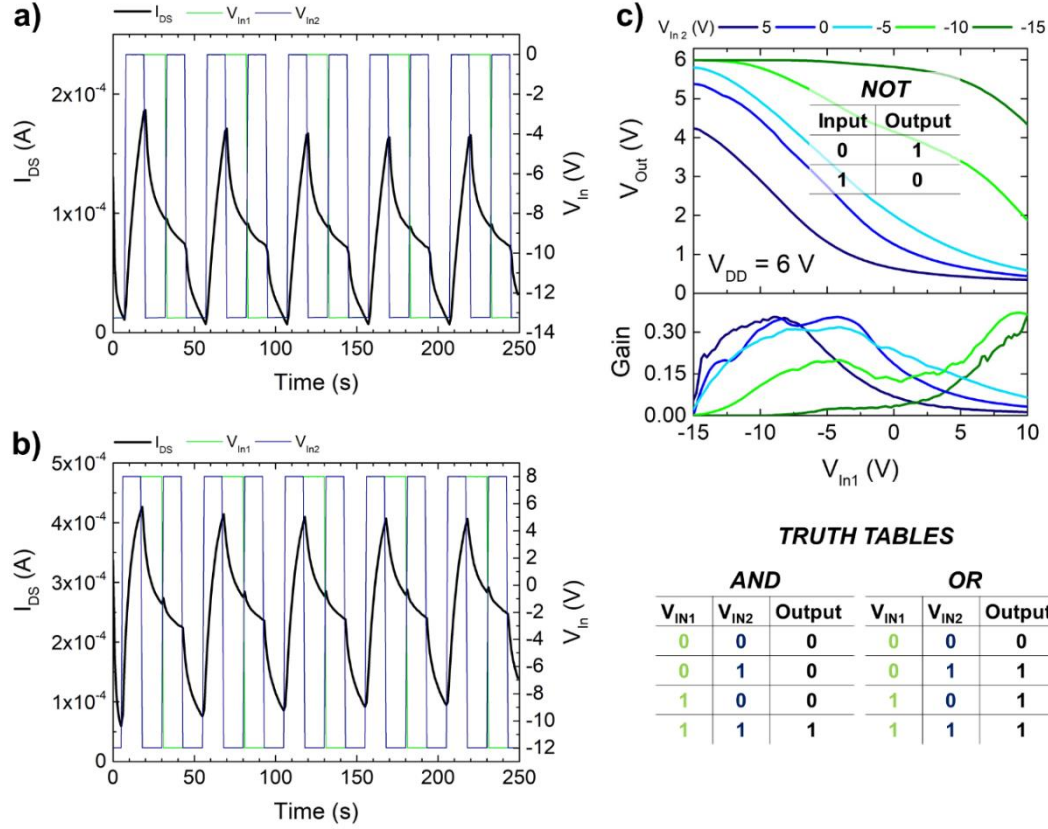


Figure 6.11 Demonstration of a) AND, and b) OR logic in DG-FGFETs on paper substrates with a single device, for an applied frequency of 20 mHz and 40 mHz in V_{GS1} and V_{GS2} , respectively. c) Static behaviour of the inverter for different V_{DD} values and corresponding voltage gain.

When combining a DG-FGFET with a pencil-drawn load resistance, it is possible to operate an inverter or a NOT logic gate. In this case, there is only a single input (V_{In1}) while a second one (V_{In2}) is fixed at a constant voltage, resulting in the transfer curves shown in Figure 6.11c. For these devices, a high load resistance value is employed to achieve a quick transition between logic states (high gain) as the gain is proportional to this resistance ($Gain \propto \frac{R_{Load}}{g_m}$), allowing to achieve low voltage levels for the logic “0”.

However, V_{Out} for the logic “1” decreases with the load resistance value as:

$$V_{Out} = V_{DD} - R_{Load} \cdot I_{DS} \quad \text{Equation 6-1}$$

Since I_{DS} will always have a significant current level as the DG-FGFET cannot be properly turned off, due to several reasons such as the used frequency, high I_{off} current, or hysteresis.

The versatility of the IGZO DG-FGFETs allows for the implementation of universal logic gate operations (NAND and NOR), using a single versatile device together with a resistive load, whose circuit schematic is shown in Figure 6.12a. The on-chip load resistance, with 140 k Ω was deposited by hand using a commercial pencil (Figure 6.12b). It should be noticed that a single DG-FGFET is used for these circuits, unlike the conventional single gate based TFTs, which typically need multiple transistors to demonstrate the same logic operation. Both logic gates were characterised using a power supply (V_{DD}) of 6V while dynamic characterisation was conducted using a semiconductor parameter analyser, together with an oscilloscope, and a wave generator. Under this test setup, the load capacitance driven by these logic gates is very high (≈ 175 pF – almost 160 pF from the probing and another 15 pF from the oscilloscope cable), which typically impose a limitation on the frequency of operation. Isolating this high capacitive load with the help of a buffer, an improvement in the frequency of operation can be achieved.

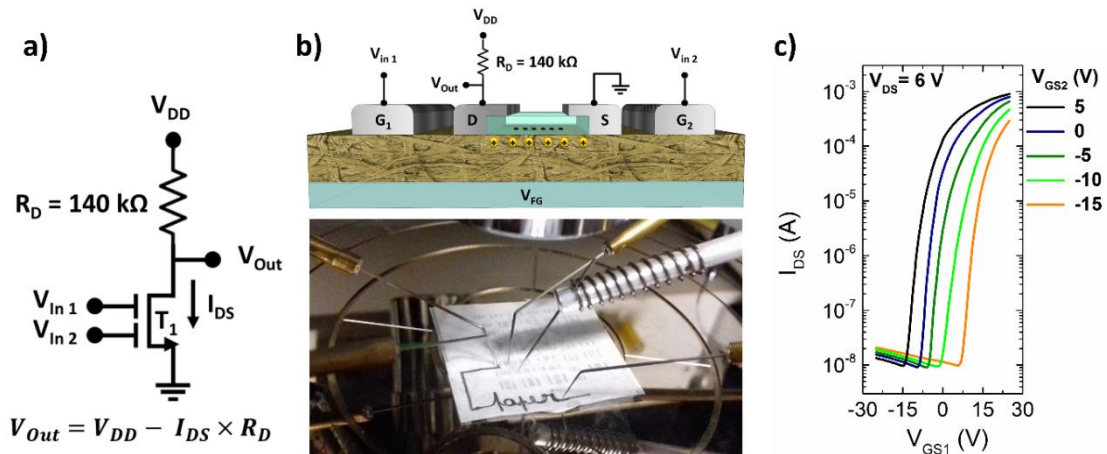


Figure 6.12 Universal logic gates: a) Circuit schematic, b) On-chip implementation, and c) I_{DS} - V_{GS} transfer characteristics DG-FGFETs at $V_{DS}=6$ V.

To illustrate the NOR operation, both the input signals (V_{In1} and V_{In2}) logic low and high levels were set to -12 and 8 V at a frequency of 20 and 40 mHz, respectively. These signals are applied at two gates of the DG-FGFETs, as can be seen from Figure 6.12b. When the input voltage levels are at logic '0', I_{DS} is lowest (see Figure 6.12c), and V_{Out} will be close to V_{DD} since the voltage drop across R_D is small. On the other hand, when any of the inputs is logic '1', significant I_{DS} flows through R_D and the voltage drop increases, which results in low V_{Out} . This expected operation with good output voltage swing can be seen in the measured data (Figure 6.13a).

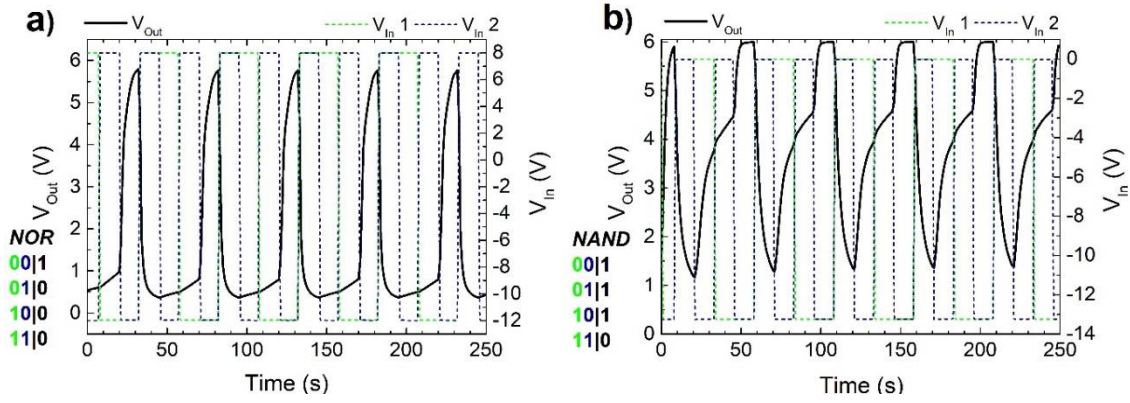


Figure 6.13 Dynamic response of the universal logic gates: a) NOR functional demonstration from measurements, and b) NAND functional demonstration from measurements.

Selecting different values for the logic ‘1’ and ‘0’ levels, the same circuit resulted in NAND operation for the same frequencies. In this case logic ‘1’ and ‘0’ are set to be 0 and -13V, respectively. When any input is logic ‘0’, I_{DS} is very small as can be noticed from Figure 6.12c (transfer characteristics), which in turn results in high V_{Out} due to a small voltage drop across R_D . On the other hand, when both inputs are at logic ‘1’, I_{DS} is high, and V_{Out} is small, due to a high voltage drop across R_D . This behaviour can be observed in Figure 6.13b. This thus demonstrates the possibilities for these type of devices to be implemented with on-chip universal logic gate functionalities, using merely a single dual gate paper FET together with a resistive load, where inputs and outputs of these logic gates are voltage levels.

6.1.4. Tensile Bending Strain Tests

The endurance of the DG-FGFETs, when submitted to tensile bending strain (ϵ), was checked by measuring the transfer characteristics under different curvatures, keeping the bias at the secondary gate ($V_{GS2} = 0$ V) constant and sweeping V_{GS1} from -30 to 30 V. The devices were tested with convex bending radii of 45, 25, 15 and 5 mm, resulting in an equivalent strain of 0.08, 0.15, 0.25 and 0.75% that was determined considering the equation 4.3 $\epsilon = \frac{d_f - d_s}{2r}$, where d_f and d_s are the film and substrate thicknesses, respectively (assuming $d_f \ll d_s$, for simplification), and r the bending radius [10].

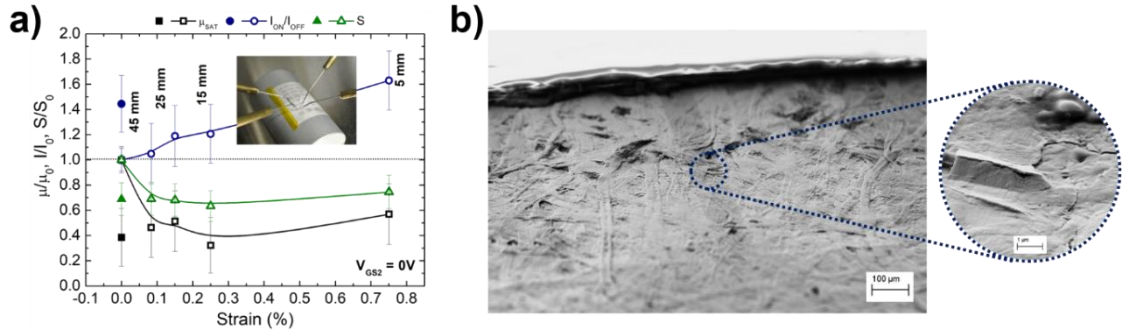


Figure 6.14 a) Normalized values of μ_{sat} (μ/μ_0), $I_{\text{ON}}/I_{\text{OFF}}$ ratio (I/I_0) and S (S/S_0) for DG-FGFETs determined after measuring the transfer characteristics under tensile bending strain. The bending radius is presented next to the symbols. Solid symbols represent the values calculated for the flat condition after bending. The inset shows a picture of the FETs being measured under bending conditions. b) SEM magnification of the surface of the DG-FGFET channel after bending with a tensile strain of 0.75% (equivalent to 5 mm radius).

Figure 6.14a represents the relative variation of μ_{sat} (μ/μ_0), S (S/S_0) and $I_{\text{ON}}/I_{\text{OFF}}$ (I/I_0) for devices measured with $V_{\text{GS2}} = 0$ V. The changes on these parameters under bending become permanent when returning to the flat condition. The mobility deterioration to about 40% of its initial value can be associated to cracks/voids promoted during bending, taking the stiffness differences between paper and the nanoscale oxide layer used for the channel (Figure 6.14b) and one of the back gates into account, which may promote associated resistances. This also contributes to a reduction in the I_{OFF} from 4.11×10^{-8} A to 1.65×10^{-8} A, resulting in an increase in $I_{\text{ON}}/I_{\text{OFF}}$ ratio under tensile strain, which remains after bringing the transistor back to the flat condition. This may explain the positive effect on the S values that decrease about 30% as a result of the I_{OFF} reduction.

6.2.Low voltage logic on NFC membranes

In the previous chapter, it was discussed and shown how the substitution of conventional paper with microscale fibres by micro-nanofibrillated cellulose membranes enabled two unique advantages: the operation of FETs at a lower voltage and the implementation of devices working at higher frequencies. In the following section, the advantage of using NFC membranes also on DG-FGFETs and logic circuits will be presented.

6.2.1. NFC-gated dual-gate transistors

The NFC-gated DG-FGFETs were produced following the same principle as for the DG-FGFET in commercial standard paper. Similarly to what was observed previously, it is possible to see the shift of the V_{on} voltage towards negative values when the bias applied to the secondary gate is changed from -5 V to 0 V, corresponding to a $\Delta V_{on} \approx 3$ V (Figure 6.15a).

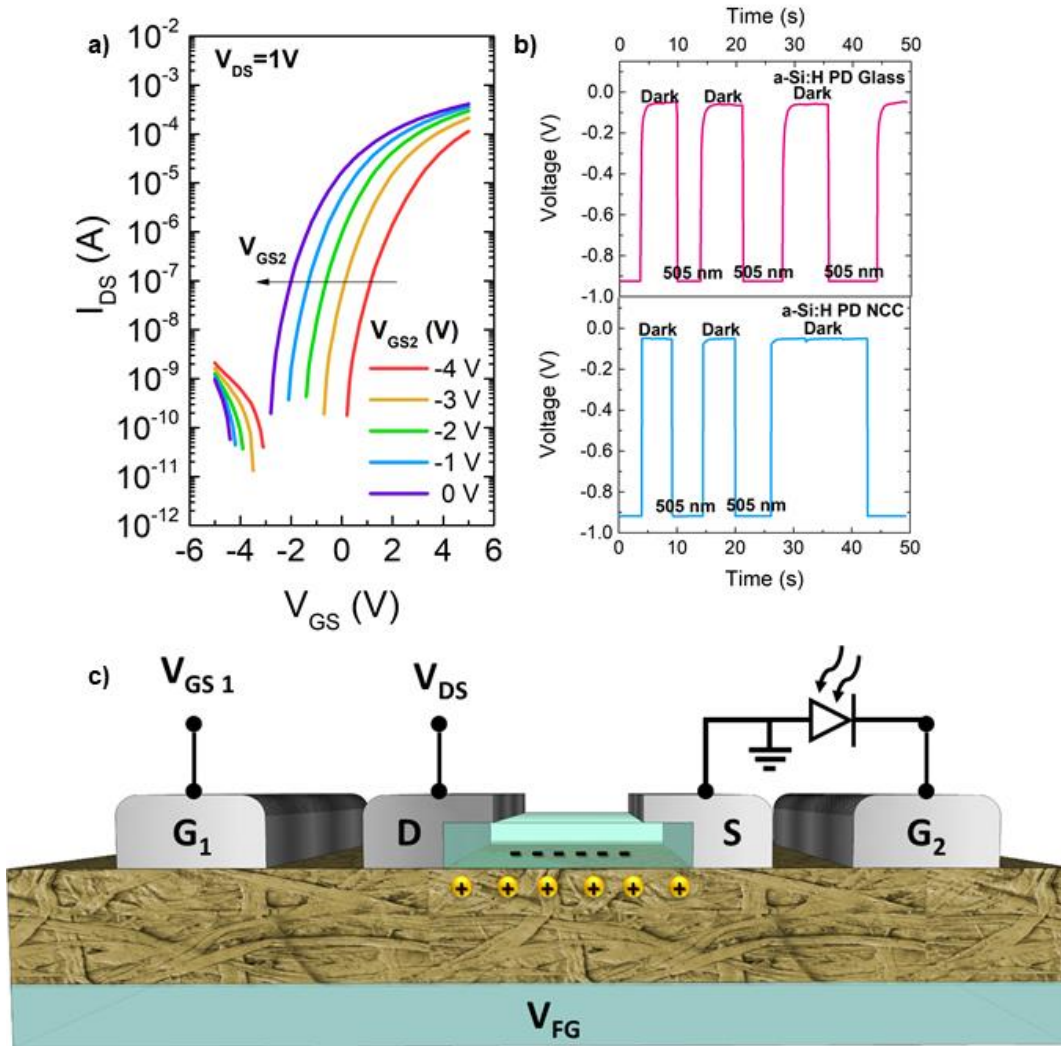


Figure 6.15 a) I_{DS} - V_{GS} curves of the NFC-gated DG-FGFETs with $V_{DS}=1$ V. b) Voltage output for the a-Si:H PD produced on glass and on NCC in the dark and when irradiated with $\lambda=505$ nm. c) Schematic representation of the integration of the DG-FGFETs with the a-Si:H PD.

The structure of the DG-FGFET revealed to be a versatile architecture due to the possibility of adjusting the V_{FB} with the voltage level at both gates. This feature allows for new applications and integration of different devices capable of providing an external voltage for sensing applications. This is demonstrated here by combining a DG-FGFET with a

hydrogenated amorphous silicon photodetector (a-Si:H PD) produced by plasma enhanced chemical vapour deposition (PECVD) on glass or on top of an NCC membrane. These photodetectors consist of a p-i-n junction behaving as a solar cell, being capable to convert the electromagnetic radiation into an electrical current accordingly to the photovoltaic effect. When illuminated with a light of $\lambda=505$ nm, the a-Si:H PD on top of glass or on the NCCs have an output voltage of ≈ -0.9 V (Figure 6.15b). The cathode and anode terminals of the a-Si:H PD were connected to the secondary gate and to the source, respectively, as schematically represented in Figure 6.15c.

When the photodetector is not illuminated no voltage is supplied to the secondary gate of the DG-FGFETs, thus the transfers characteristic curves overlap with the curves obtained for the devices when characterised with $V_{GS2} = 0$ V (Figure 6.16). The voltage generated under illumination of the a-Si:H PD with $\lambda=505$ nm results in a shift of the $I_{DS}-V_{GS}$ curve towards higher V_{GS1} , either for the photodetectors on glass or NCC, nearly reaching the values obtained for $V_{GS2}=-1$ V when the photodetector is not connected (Figure 6.16).

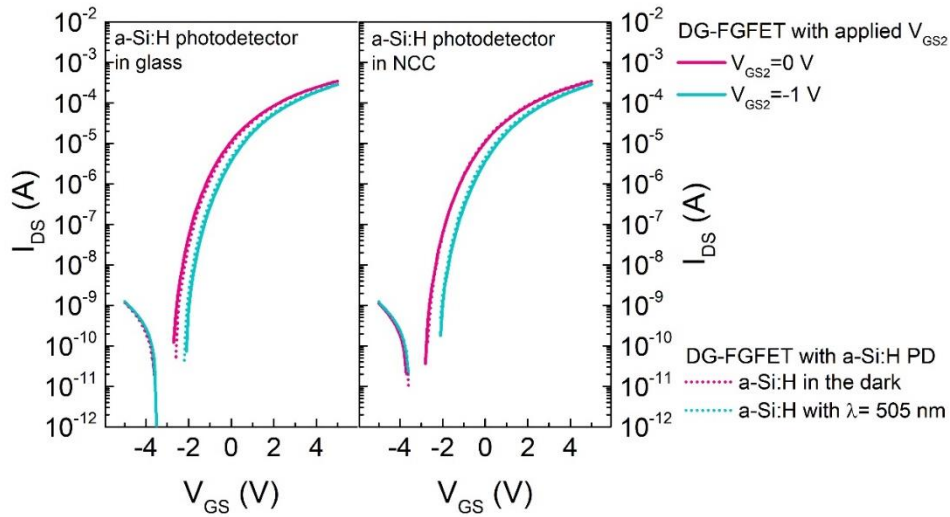


Figure 6.16 $I_{DS}-V_{GS}$ transfer characteristic curves for the DG-FGFETs using an a-Si:H PD produced on glass (on the left) and produced on NCC (on the right) as external bias at V_{GS2}

The good performance of the a-Si:H PD deposited on cellulose combined with the DG-FGFETs successfully demonstrates that these transistors can be integrated with other devices that can work as sensors/detectors, allowing to explore the ability to tune the V_{on} of the transistor. In the future the goal will be the integration of both devices on the same substrate, without the need of wires to connect them (Figure 6.17).

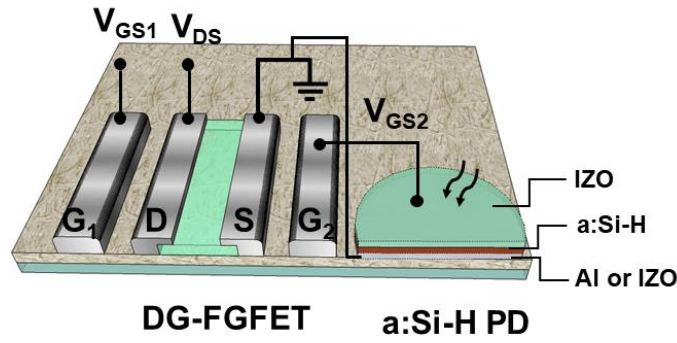


Figure 6.17 Representation of the integration of a DG-FGFET with an a:Si-H photodetector.

6.2.2. Alkali-doped NFC membranes in inverters

The doping of the NFC membranes with alkaline ions dramatically improves the electrical performance of the devices, as already demonstrated in the previous chapter. The benefits of the presence of those ions in the membranes used as dielectric in oxide FETs goes beyond than just decreasing the hysteresis or improving the mobility. Dynamic characterisation of FETs on ion-doped NFC membranes was performed by applying a square wave potential as gate voltage. The I_{On}/I_{Off} ratio was monitored according to the expected V_{On} , when using pristine or doped membranes (V_{GS} between -3 and 3 V and between -2 and 1 V, respectively), keeping V_{DS} constant ($V_{DS}=3$ V).

The devices produced on NFC:Pristine, show proper current modulation for low frequencies. It is possible to distinguish a current modulation higher than two orders of magnitude up to 0.5 Hz, decreasing to nearly 10 for 1 Hz (Figure 6.18a). The trend observed for the I_{On}/I_{Off} ratio decays with the frequency, which allows to conclude that the operation of the FETs produced with pristine membranes is limited to 2-3 Hz.

Usually, the maximum operation frequency is determined by the value when it is no longer possible to discriminate the maximum and minimum current, i.e. when I_{On}/I_{Off} equals 1. However, in this work this approach was not used since a clear discrimination between the two states was aimed. Consequently, the cut-off frequency for these FETs was defined as an I_{On}/I_{Off} of two orders of magnitude.

The response of the FETs on doped membranes is quite different (Figure 6.18a). The addition of alkaline ions results in a tremendous improvement in the operating frequency that can go from 7 Hz for NFC:K up to 50 Hz for NFC:Na, where it is still possible to have an I_{On}/I_{Off} ratio of about two orders of magnitude. Thus, it was expected to have those

membranes (NFC:Li and NFC:Na) enable devices at operating frequencies above 50 Hz by using the tested conditions ($V_{DS}=3$ V and V_{GS} between -2 and 1 V).

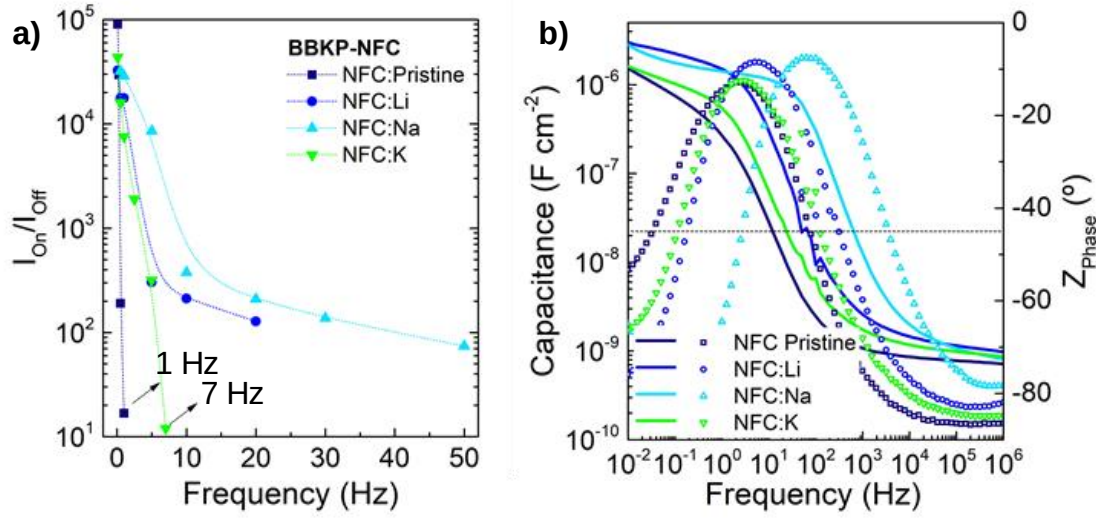


Figure 6.18 a) I_{on}/I_{off} ratio as a function of the frequency applied to the gate of the NFC-membrane FETs ($V_{DS}=3$ V). b) Electrochemical characterisation of the NFC membranes - capacitance and phase as a function of frequency.

The behaviour observed for the FETs is intrinsically related to the ionic character of the membranes. The electrochemical characterisation (Chapter 5), namely the phase angle explains those differences. The frequency at which the transition from the resistive to the capacitive domain occurs (EDL formation) is an indication of the threshold frequency for the FETs on such membranes. In Figure 6.18b it can be seen that the transition to the capacitive domain occurs in a wide range of frequencies, depending on the membrane. The Na doped one has this transition at frequency values, above 1Hz, comparing to 30 mHz for pristine membranes. Thus, the best dynamic response for devices produced using NFC:Na as the gate dielectric is expected.

The electrical reliability under a dynamic stimulus allows the implementation of those devices into simple circuits, such as an inverter. Inverters are one of the simplest logic operations and can be fabricated using a single transistor, combined with a resistance. In a slightly more complex setup, the load resistor can be replaced by a load transistor, where both transistors can be either n-type or a combination of n-type and p-type [11], [12]. In this work, the same NFC-gated FETs characterised in Chapter 5 were used, which were combined with a load resistor as schematically represented in Figure 6.19a.

In these inverters, V_{Out} should ideally have the same value as V_{DD} when the transistor is off, which corresponds to a logic “1”, once this value is determined by $V_{Out} = V_{DD} - R_{Load} \cdot I_{DS}$ (Equation 6-1). For the logic “0”, the applied V_{in} increases the current level of the transistor. Therefore, when coupled to a proper load resistor, its product with I_{DS} should be the same as V_{DD} , resulting in the decreasing of the V_{Out} . The transition between logic states defines the gain of those devices, which is proportional to the promptness that the circuit transacts from logic “1” to logic “0”, i.e. $Gain \propto \frac{R_{Load}}{g_m}$, being determined as:

$$Gain = -\frac{\partial V_{Out}}{\partial V_{in}} \quad \text{Equation 6-2}$$

The gain of the inverters relies on the V_{Out} which is directly determined by two factors: the I_{DS} of the FETs, which depends on the applied V_{DD} and the R_{Load} (Equation 6-1 and Equation 6-2). In Figure 6.19b the gain for the inverters produced on the different membranes is traced.

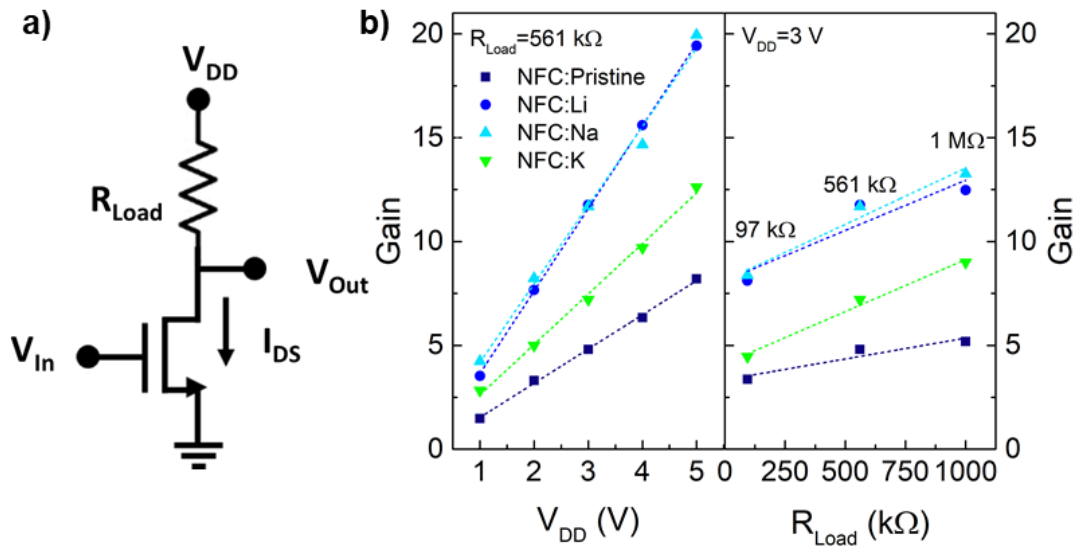


Figure 6.19 a) Schematic diagram of the inverter. b) Gain as a function of the applied $V_{DD}=[1;5]$ V (on the left) and as function of the load resistance used for a constant $V_{DD}=3$ V and $-3 \leq V_{in} \leq 3$ (on the right).

Regardless of the used membrane, the increase of the gain is linearly related to the applied V_{DD} . The pristine membrane shows the lowest gain, which can be enhanced from ≈ 1.5 up to 8, depending on the applied V_{DD} . Likewise, the alkaline membranes have the same response. In this case, the presence of the ions results in a steeper transition between the two logic states, which is in line with the improved dynamic response of the FETs. The fast shift from logic “1” to logic “0” results in gains that can go up to 20 for the NFC:Li or NFC:Na membranes for $V_{DD}=5$ V.

Considering the parameters used for the characterisation of the FETs (Chapter 5) and since these devices have a good electrical response (static and dynamic) for low operation voltages, the V_{DD} was fixed at 3 V. In addition, a low V_{DD} assures that the device does not reach a very high current which can induce additional electrical stress.

The second aspect tested was the R_{Load} applied to the circuit for $V_{DD}=3$ V (Figure 6.19b). All the membranes show a linear behaviour with an increasing Gain for a higher load resistance ($R_{Load}=97$ k Ω , 561 k Ω and 1 M Ω), which corroborates the premise that $Gain \propto \frac{R_{Load}}{g_m}$.

In the voltage transfer characteristics (VTCs) it is possible to observe a large discrimination between the two logic states, indicating a good performance of the inverters for a $V_{DD}=3$ V and $R_{Load}=561$ k Ω (Figure 6.20). For this condition the inverters on the Li and Na doped membranes have a sharp transition between the two states, resulting in a gain of nearly 12. This value is higher than the values reported for complementary organic inverters using NFCs as gate dielectrics, with a gain of 8 for low-voltage operation [11], or CMOS produced on paper and operating with much higher voltages ($V_{DD}=17$ V and gain $\approx$ 16) [12].

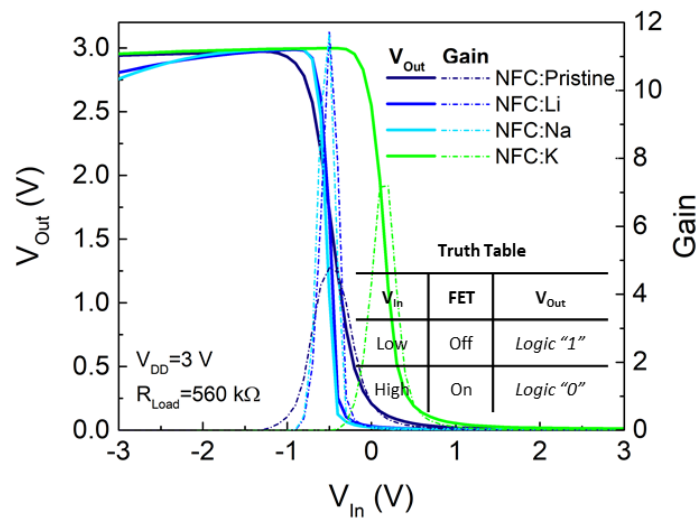


Figure 6.20 Voltage transfer characteristics (VTCs) of the resistor-loaded inverters on NFC measured with $V_{DD}=3$ V. In the inset the truth table for the logic operations is shown.

In some membranes, V_{Out} does not reach the V_{DD} value since the I_{DS} value is slightly higher on those membranes than for the NFC:Pristine or NFC:K. These difference can be related to two aspects: either the devices were not properly turned off, or they yielded increased I_{GS} (higher than for the NFC:Pristine or NFC:K – Figure 5.9).

Ideally, the R_{Load} should be integrated by replacing the load resistor by a second transistor. The concept is feasible and was previously demonstrated; in the future, it is expected to have this circuit integrated on NFCs working in a low voltage range, with proper optimisation of the FETs aspect ratio.

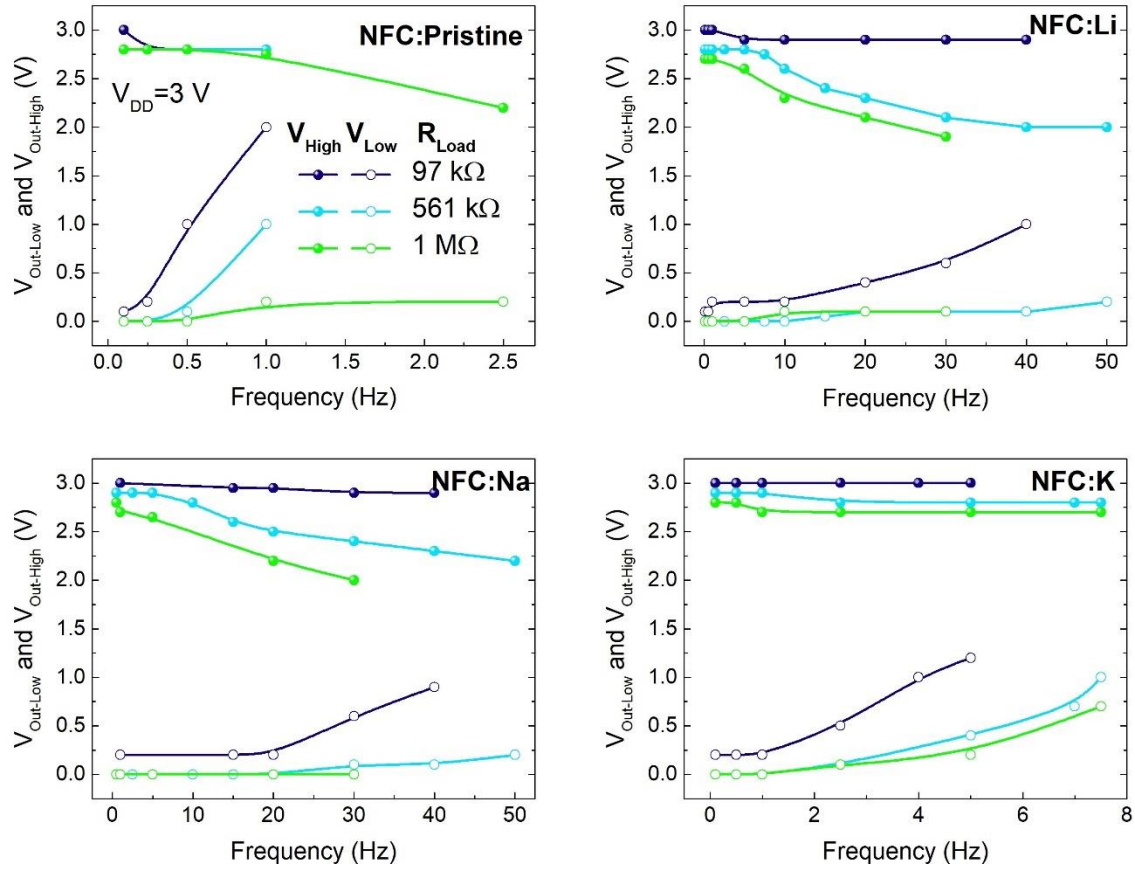


Figure 6.21 Voltage output for high and low states of the different NFC based inverters with a fixed V_{DD} ($V_{DD}=3$ V) and variable load resistances ($R_{Load}=97$ k Ω , 561 k Ω and 1 M Ω).

The dynamic response of the inverters is highly influenced by the implemented resistor (Figure 6.21). The inverters were characterised using the same square wave as for the dynamic response of the FETs, V_{In} between -3 V and 3 V for the pristine membrane and V_{In} between -2 V and 1 V for the doped NFC. The operation of the NFC:Pristine and NFC:K is in line with the dynamic response of the FETs. For the pristine membranes, it is possible to have a proper distinction between logic states up to 1 Hz when integrated with a load resistance of 1 M Ω . Above 1 Hz the $V_{Out-High}$ became slightly lower since the device is not properly switched off, whereas the $V_{Out-Low}$ starts to increase, indicating some limitation on the maximum obtained I_{DS} value. The response of the inverters on NFC:K have some resemblances to what was described for the pristine NFC membranes. Low load

resistances do not allow to fully reach the logic “0” ($V_{Out}=0$ V), indicating that the 97 k Ω is insufficient to isolate the I_{DS} supplied by the FET. For higher resistances, the same behaviour is observed for higher frequencies, where a good discrimination between high and low states for up to 7.5 Hz is possible. The best performance is achieved for the NFC:Li and NFC:Na membranes (Figure 6.21). These inverters show a good discrimination between the high and low state for input square-wave signals with frequencies that can go up to 40-50 Hz. For frequencies in the order of 10 Hz, the maximum and minimum output signals are identical to the values in the static VTC curves (Figure 6.20).

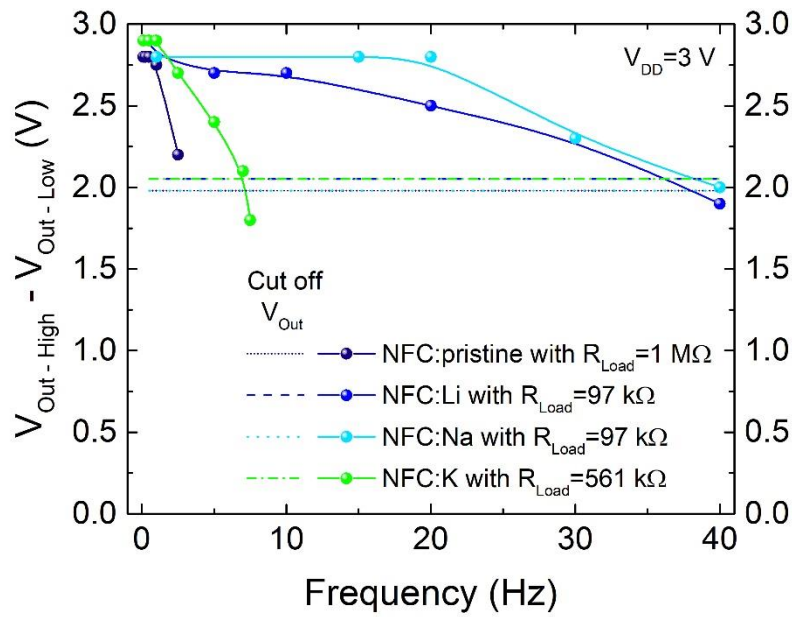


Figure 6.22 Voltage output of the different NFC based inverter with a fixed V_{DD} ($V_{DD}=3$ V) as a function of the frequency.

The cut-off frequency for these inverters can be established at 70.7% (-3dB) of the $V_{Out_High}-V_{Out_Low}$, determined for the lowest frequency, i.e. $Cut\ off = \frac{V_{Out_High}-V_{Out_Low}}{\sqrt{2}}$. For the different membranes this threshold varies between 1.98 and 2.05 V. The dynamic response of these devices (Figure 6.22), especially the ones produced with the Li and Na doped membranes, shows that these inverters yield a good performance and a fast switching between states, enabling these NFC inverters for several applications where a logic response combined with light weight and low cost is aimed for.

6.3. References

- [1] W. Dou, L. Zhu, J. Jiang, and Q. Wan, “Flexible Dual-Gate Oxide TFTs Gated by Chitosan Film on Paper Substrates,” *IEEE Electron Device Lett.*, vol. 34, no. 2, pp. 259–261, Feb. 2013.
- [2] Y. H. Liu, L. Q. Zhu, P. Feng, Y. Shi, and Q. Wan, “Freestanding Artificial Synapses Based on Laterally Proton-Coupled Transistors on Chitosan Membranes,” *Adv. Mater.*, vol. 27, no. 37, pp. 5599–5604, Oct. 2015.
- [3] C. Wan, L. Zhu, Y. Liu, Y. Shi, and Q. Wan, “Laterally coupled synaptic transistors gated by proton conducting sodium alginate films,” *IEEE Electron Device Lett.*, vol. 35, no. 6, pp. 672–674, 2014.
- [4] W. Dou, L. Qiang Zhu, J. Jiang, and Q. Wan, “Flexible protonic/electronic coupled neuron transistors self-assembled on paper substrates for logic applications,” *Appl. Phys. Lett.*, vol. 102, no. 9, p. 093509, 2013.
- [5] F. Pettersson, D. Adekanye, and R. Österbacka, “Stability of environmentally friendly paper electronic devices,” *Phys. status solidi*, vol. 212, no. 12, pp. 2696–2701, Dec. 2015.
- [6] J. W. Jin, A. Nathan, P. Barquinha, L. Pereira, E. Fortunato, R. Martins, and B. Cobb, “Interpreting anomalies observed in oxide semiconductor TFTs under negative and positive bias stress,” *AIP Adv.*, vol. 6, no. 8, p. 085321, Aug. 2016.
- [7] R. K. Sharma, R. Gupta, M. Gupta, and R. S. Gupta, “Dual-material double-gate SOI n-MOSFET: Gate misalignment analysis,” *IEEE Trans. Electron Devices*, vol. 56, no. 6, pp. 1284–1291, 2009.
- [8] J. Jiang, J. Sun, L. Zhu, G. Wu, and Q. Wan, “Dual in-plane-gate oxide-based thin-film transistors with tunable threshold voltage,” *Appl. Phys. Lett.*, vol. 99, no. 11, p. 113504, Sep. 2011.
- [9] R. Martins, D. Gaspar, M. J. Mendes, L. Pereira, J. Martins, P. Bahubalindrani, P. Barquinha, and E. Fortunato, “Papertronics: Multigate paper transistor for multifunction applications,” *Appl. Mater. Today*, vol. 12, pp. 402–414, 2018.
- [10] L. Pereira, D. Gaspar, D. Guerin, A. Delattre, E. Fortunato, and R. Martins, “The influence of fibril composition and dimension on the performance of paper gated oxide transistors,” *Nanotechnology*, vol. 25, no. 9, p. 094007, Mar. 2014.
- [11] S. Dai, Y. Chu, D. Liu, F. Cao, X. Wu, J. Zhou, B. Zhou, Y. Chen, and J. Huang, “Intrinsically ionic conductive cellulose nanopapers applied as all solid dielectrics for low voltage organic transistors,” *Nat. Commun.*, vol. 9, no. 1, p. 2737, Dec. 2018.
- [12] R. Martins, A. Nathan, R. Barros, L. Pereira, P. Barquinha, N. Correia, R. Costa, A. Ahnood, I. Ferreira, and E. Fortunato, “Complementary Metal Oxide Semiconductor Technology With and On Paper,” *Adv. Mater.*, vol. 23, no. 39, pp. 4491–4496, Oct. 2011.

Conclusions and future perspectives

Chapter

7

Conclusions and future perspectives

CHAPTER 7. Conclusions and future perspectives	241
7.1. Main conclusions	241
7.2. Future perspectives	247
7.3. References	249

Chapter 7. Conclusions and future perspectives

The experimental part of this work was divided into three main themes (as schematised in Figure 7.1): optimisation of oxide thin films sputtered at room temperature (TCOs for application as gate electrode and IGZO semiconductor), the study of cellulose-based substrates, and finally, integration of these materials into cellulose-based FETs. In addition to this, a new transistor architecture was implemented along this work, also using cellulose as gate dielectric. The main conclusions of all the work are presented in the following paragraphs, as well as some perspectives and suggestions for future developments.

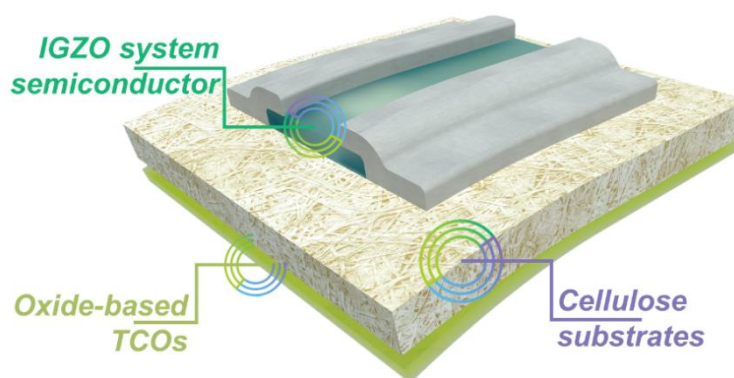


Figure 7.1 Developments made along this PhD work towards high-performance cellulose-based field-effect transistors.

7.1. Main conclusions

This PhD work aimed to develop hybrid FETs combining oxide-based thin films with cellulose-based substrates, that are simultaneously the gate dielectric of such devices.

Although it is a well-established technology at CENIMAT/I3N and CEMOP/UNINOVA [1]–[4], the oxide thin films had to be optimised to overcome the challenges imposed by the rough and heterogeneous surface of fibre based substrates, such as paper.

Magnetron sputtering was chosen as deposition technique for the oxide layers to be used as semiconductor (IGZO) and gate electrode due (IZO) due to its versatility. In conventional substrates, as glass or silicon, the electrical properties of the oxide thin films can be easily improved through different approaches, such as substrate heating or post-deposition annealing. However, the use of cellulosic substrates requires low processing temperatures, and 150 °C was defined as the maximum temperature able to be used in this type of substrates in order to guarantee its integrity. Thus, all the films were produced

without intentional substrate heating followed by a final annealing step of the final device at 150 °C in air.

The optimised IGZO films resulted in devices with proper current modulation (four orders of magnitude in the $I_{\text{On}}/I_{\text{Off}}$ ratio). The most critical parameter for IGZO deposition is the oxygen content during deposition (D_{O_2}), that lead to a shift in the turn-on voltage of the devices shifts towards positive values, with a simultaneous decrease of the swinging voltage (SS) meaning less defective semiconductor layer.

Two types of oxide conductors were tested as gate electrode: zinc oxide-based and indium oxide-based TCOs. In this case, the focus was on the effect of hydrogen incorporation in the improvement of the electro-optical properties of the TCOs deposited at low temperature. It was verified that in ZnO based conductor oxides the hydrogen behaves as a shallow donor effect enhancing the n-type conductivity. However, the higher carrier density for the ZnO:H (for $D_{\text{H}_2} \approx 1.5\%$ with $\mu_{\text{H}} = 47.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a $\rho = 3 \times 10^{-3} \Omega \text{ cm}$) films was partially related to the favouring of defects as zinc interstitials (Zn_i) when H_2 is added during the deposition process, meaning that shallow donor effect of hydrogen is not the only responsible for the enhancement of the electrical properties of ZnO:H.

Hydrogenation of binary systems as AZO and GZO has a similar effect and, for both cases it was observed a significant decrease of the resistivity and improvement of the mobility for an optimal $D_{\text{H}_2} = 1.5\%$. For the AZO ρ decreases to $9.2 \times 10^{-4} \Omega \text{ cm}$ while for GZO ρ is almost unaffected ($\sim 8 \times 10^{-4} \Omega \text{ cm}$). The best electro-optical properties in ZnO based TCOs were obtained for co-sputtered AZO+GZO thin films. Highly transparent ($\text{AVT}_{\text{AGZO}} = [85-87] \%$) Al and Ga co-doped ZnO (AGZO) with higher Al content compared to Ga, resulted in a decrease of the resistivity down to $5.6 \times 10^{-4} \Omega \text{ cm}$, for an n of $6.9 \times 10^{20} \text{ cm}^{-3}$.

Is undeniable that ZnO-based TCOs are an excellent option to substitute critical raw materials as indium. However, the indium-based TCOs, such as IZO and ITO, combine excellent optical and electrical properties that until the moment no other oxide system was able to equate.

During this work was rapidly pointed as a drawback the inferior electrical performance of the crystalline ZnO-based thin films when deposited in cellulose substrates. The alternative was on amorphous IZO TCOs, whose electrical performance remained similar when deposited on cellulose substrates. The IZO films sputtered in a reactive atmosphere with Ar, O_2 and H_2 exhibited better electrical parameters than the ones sputtered in a mixture of

Ar and O₂. For a D_{O₂}(%)/D_{H₂}(%)=1.44(%) / 2.87(%) the resistivity decreases to $4.95 \times 10^{-4} \Omega \text{ cm}$ for $n=3.08 \times 10^{20} \text{ cm}^{-3}$ and $\mu_H=40.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The addition of hydrogen to the sputtering atmosphere lead to the increase of n , suggesting that hydrogen behave a shallow donor in In₂O₃ as predicted in theoretical studies [5].

The D_{O₂}(%)/D_{H₂}(%)=1.44(%) / 2.87(%) dilution proved to be the best condition to be transferred to cellulose substrates. IZO films produced in smooth and homogenous NFC membranes (raw and pristine) show similar electrical properties to those deposited on glass during the same run, with neglectable variation in the resistivity (Chapter 3 section 3.2.3). The IZO thin films were also successfully deposited on top of papers with rough topography, as the commercial standard paper, being possible to have a good step coverage of the fibres. Even though the electrical resistivity decreased nearly one order of magnitude these were the films with the best combination of electro-optical properties.

The amorphous character of the films allows a good interface semiconductor/cellulose, regardless of the topography of the paper, which could represent an issue for the electrical properties of the FETs. During this work different cellulose substrates were tested, being observed that smooth micro/nanofibrillated cellulose membranes establish the best interface with the oxide layers. The small dimension of the fibres used to form the substrates have significant relevance since the degradation of the FETs performance under bending is more severe for papers with high roughness as was seen for the commercial standard papers (Chapter 6 section 6.1.4). Moreover, in general, the overall performance of FETs produced on thick non-fibrillated papers (Chapter 4) tend to be worse than when smooth cellulose membranes are used.

The core of this thesis was cellulose and the approaches to turn that it a functional material able to serve as physical support and gate dielectric layer in field-effect transistors (FETs). The approaches to improve the properties were made through physical modification of the fibres, playing with the size and source, beating index, density/porosity and preferential orientation of fibres. While chemical modification of the pulp/fibres can be achieved with oxidation processes (i.e. TEMPO-mediated oxidation), modification of the pulp pH or even ionic “doping” of dried membranes through impregnation with alkaline solutions.

The study of traditional paper was extremely important to establish new approaches and outline strategies to tackle some bottlenecks of this technology. The study developed in chapter 3 was extensive and made clear two main aspects that determined the direction of this thesis. The tailoring of the fibres shown that the fibrillation of the cellulose could result

in devices with better performance mostly due to the smooth surface and dense matrix formed by the smaller fibres. Moreover, the chemical modification of the pulp (pH adjustment) allowed for improved electrical performance and stability of the transistors over time. Regardless of the treatment made, or type of fibre used, the high operation voltage required was pointed as a significant drawback.

Considering this, it was necessary to evolve to a different architecture for the paper-based FETs. In this case planar dual-gate oxide-based field effect transistors with a back floating electrode used paper simultaneously as substrate and dielectric. Similar to the other FETs, the working principle of these transistors is based on the formation of electric double layers at the semiconductor/paper and paper/back floating electrode interfaces that can be disturbed by a voltage applied at a secondary gate, by the back floating potential or by the combination of both. The DG-FGFETs were produced using regular paper as gate dielectric. Thus the required operation voltage was high ($V_{DS}=15$ V), but with similar electrical properties comparable to the ones obtained in a staggered-bottom gate FETs structure previously reported by the group [6]–[8]. The new devices presented I_{ON}/I_{OFF} ratio in the range of 10^4 and saturation mobilities around $3\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$. The most interesting feature of these devices was the possibility to control the on-voltage of the transistors, making them interesting for logic circuits. Moreover, it was possible to implement five logic operations: AND, OR, two universal logic gates (NAND and NOR), and also an inverter using only one transistor, by setting the proper combination of the voltage level applied at each gate [9], [10].

The turning point of this thesis was the transfer of the knowledge acquired with “conventional paper” (Chapter 4) to membranes formed with smaller fibrils (micro/nanofibrillated cellulose and bacterial cellulose) (Chapter 5). The use of these cellulosic substrates as the gate dielectric in FETs brings a unique feature: the operation voltages required are considerably lower than the ones used for the papers discussed in Chapter 4.

Chapter 5 was dedicated to the implementation of micro/nanofibrillated cellulose membranes obtained by downsizing fibre (top-down approach), as the vegetal NFC and NCC (Chapter 5 section 5.1 and 5.2) and with a bottom-up approach as the case of bacterial cellulose (Chapter 5 section 5.4). The pristine NFC membranes without any treatment, lead to highly stable FETs capable of maintaining their electrical performance under severe electrical endurance tests, and yet having much better performance than the devices

produced with regular paper. The smooth and compact matrix of these membranes makes them an excellent substrate for flexible/bendable electronics. However, the highlight of the study with these membranes was the ionic “doping” with hydroxide alkaline solutions (LiOH, NaOH, KOH). This procedure resulted in a notorious improvement of the electrical performance of the devices. The operation voltage of the transistors produced on these infiltrated membranes is much lower when compared with the papers discussed in Chapter 4. The V_{DS} is reduced from 15 V to less than 5 V, while the gate voltage narrowed for the range [-3;3] V. Despite the ion doping used, the FETs showed I_{ON}/I_{OFF} ratios that surpasses five orders of magnitude and saturation mobilities close to $14\text{--}17\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, while the swinging voltage is decreased down to of 0.15 V dec^{-1} . The excellent electrical performance of the devices is deeply related to the good interface between the membrane and the oxide semiconductor layer. In fact, the quality of semiconductor/membrane interface was verified with the tensile and compressive strains, where it was possible to verify that the devices are not severely deteriorated since they had proper current modulation, during the bending or after returning to flat conditions.

The ionic doping has a broader influence than the electrical improvement of the FETs like it was verified for the long shelf time stability, with the devices working properly after more than fifteen months, and also faster dynamic response. The aged devices showed good dynamic response where the operation frequency could go from less than 1 Hz for pristine membranes, up to 7 Hz for the NFC:K and 50 Hz for NFC:Na, being possible to have an I_{ON}/I_{OFF} ratio of about two orders of magnitude. Thus, it was possible to have those (NFC:Li and NFC:Na) membranes enabling devices’ logic operations at frequencies close to 50 Hz (Chapter 6 section 6.2.2). Indeed it was possible to reach gains up to 20 for the NFC:Li or NFC:Na membranes for $V_{DD}=5\text{ V}$ for an $R_{Load}=561\text{ k}\Omega$, exceeding some reference values reported in the literature for CMOS [11], [12]. These two membranes not only reach the highest gain values but also had good discrimination between the high and low state for input square-wave signal with frequencies that can go up to 40-50 Hz.

The potential of the NFC membranes is undeniable, and the good performance obtained with NFCs as active material lead to an ultimate test: to produce a large number of devices (more than 1600) ensuring the electrical performance reliability. The goal to fulfil? Produce devices for the International Physics Olympiads 2018 (IPhO2018) held in Lisbon. This can be translated into numbers: more than 30 NFC membranes produced ($12\times 12\text{ cm}$), more

than 25 IGZO sputtering cycles made and nearly 50 aluminium thermal evaporation runs.

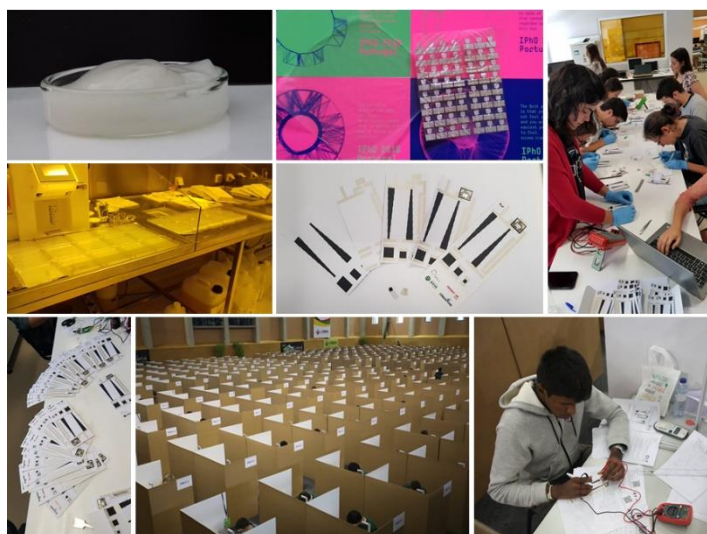


Figure 7.2 Photographs of the several steps involved in the production of the NFC membranes, FETs and final circuits on paper for the IPhO2018.

The interest of the work developed using NFC as gate dielectric in FET was validated during the International Physics Olympiads in 2018, where over 400 high-school school students from 87 countries were engaged in two experimental exercises, one of them devoted to paper electronics, and later highlighted in the Nature Electronics editorial “A lesson on paper” (Figure 7.3) [13]. For the exercise the students had a commercial silicon-based junction field effect transistor (JFET) and paper board circuit with silver conductive lines and carbon resistors. The aim was to perform a characterization of the devices, plotting the transfer and output curve and the determination of several typical electrical parameters. The paper transistor was used to create and characterise a unipolar inverter using an additional load resistor that should be drawn by the students using a graphite pencil.

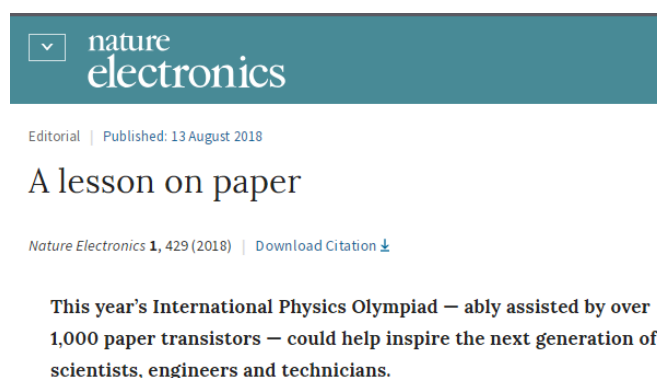


Figure 7.3 Nature Electronics editorial “A lesson on paper” featuring the IPhO2018.

7.2.Future perspectives

The need low-cost, eco-friendly, disposable but yet reliable electronic devices will be the driving force for the further coming years. It is unquestionable that cellulose-based electronics will be one of the technologies able to partially fulfil those demands, and this work has indeed demonstrated it. Doing so, some of the points that must be further investigated are:

❖ *Dual-gate transistors: Floating gate as sensing element*

FG-DGFETs can be further improved and better explored. At the moment bio-chemical sensor is one of the applications foreseen for paper-based devices, mainly due to its simplicity in the modulation of the On voltage [14], [15]. The sensing element reported in the literature is typically the semiconductor where antigens are immobilised for bio-sensing purposes, and the detection sensitivity can be enhanced through the voltage applied in the second gate [15]. Some works also report the use of an extended gate as sensing element [14].

The cellulose-based FG-DGFETs implemented in this PhD work have a great potential to be used as biosensor since the floating electrode itself can act as a sensing element. Preliminary tests using FG-DGFETs produced in paper, shown that the On voltage can be modulated just by performing an O₂ plasma treatment to the IZO floating gate.

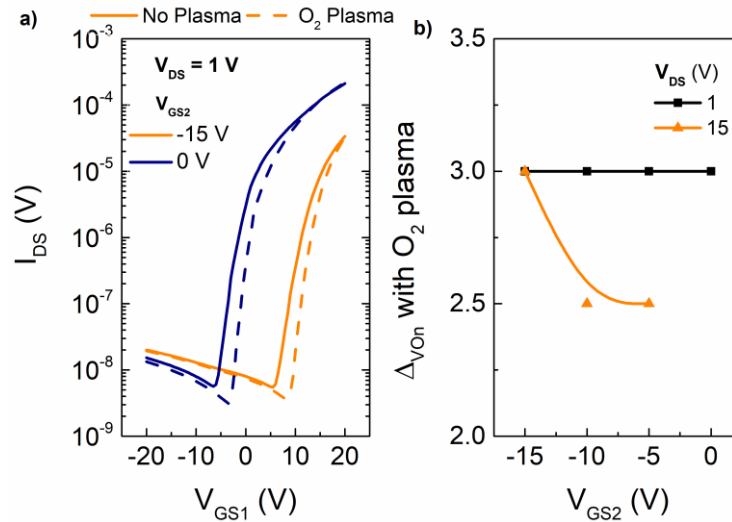


Figure 7.4 a) Transfer (I_{DS} – V_{GS}) characteristics measured at $V_{DS}=1$ V for as-deposited devices (solid line) and after 1 minute of O₂ plasma treatment to the IZO floating gate, and b) ΔV_{On} after O₂ plasma treatment (V_{DS} of 1, and 15 V) with different V_{GS2} applied.

In Figure 7.4a are represented transfer curves of the pristine device and then after 1 minute of plasma treatment to the floating electrode, being possible to verify a V_{On} shift toward higher values independently of the V_{GS2} applied. For the tested V_{DS} (1, 8 and 15 V – values for $V_{DS} = 8$ V not shown) the O_2 plasma resulted in a similar variation of the on voltage (ΔV_{On}), with a ΔV_{On} variation between 2.5 and 3 V (Figure 7.4b).

It is expected that during the O_2 plasma several reactions can occur and active species may be formed, as O_2^+ , O^- , O_3 , among others (Figure 7.5) [16], [17]. The interaction of these ionic and radical species with the IZO strongly affect the surface of the thin film, increasing the surface potential. The enhancement of the surface potential can be explained with the increase of the carrier density, which results in a negative “plasma-induced” polarisation of the floating gate, what reinforces the effect of the second gate which controls the conduction in the channel. Like it was seen in chapter 6, when the $V_{GS2} < 0$, the potential of the floating gate is negative, and it was observed the depletion of carriers in the channel, hereupon is expected that a pre-existence of a negatively biased floating gate ($V_{FG} < 0$) also results in carrier depletion leading to the ΔV_{On} towards positive values.

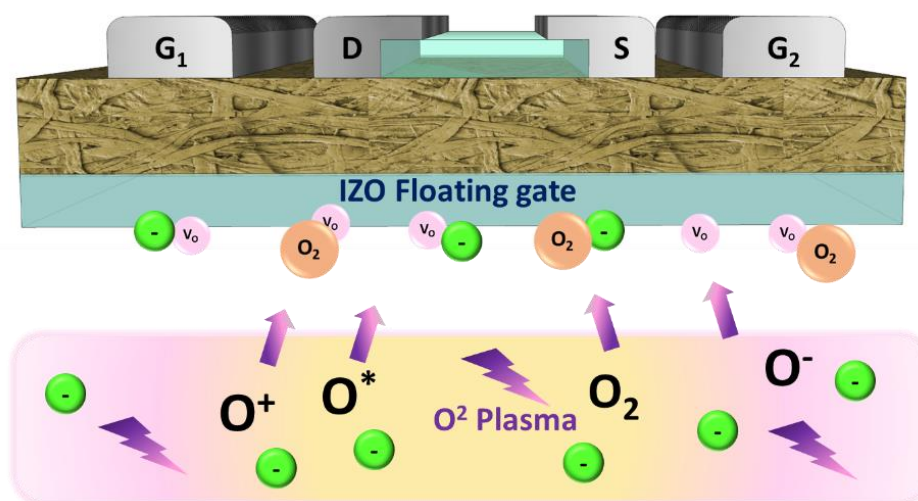


Figure 7.5 Schematic representation of reactions occurring between the IZO floating gate and O_2 plasma treatment responsible for the V_{ON} shift.

❖ *Dual-gate transistors: Integration of photodetector*

As discussed in Chapter 6, another device, such a photodetector, can be integrated into the same cellulose substrate to control the gate voltage in DG-FGFETs. In this work, the demonstration was made with the devices in different substrates. The integration of both devices in the same substrate will be the “natural” next step, without the need of wires to

connect them, aiming higher and more complex integration also combining sensors or using the floating gate as sensing element.

❖ *NFC membranes: n-MOS, p-MOS, CMOS and Ring oscillators*

The perspectives for this material are ambitious. Due to the faster response of the FETs produced with ion-doped membranes, it will be possible to evolve to other devices to replace the R_{Load} in the inverters by a second transistor. Besides another n-FET, some options towards “fully” CMOS logic are p-MOS using a p-type semiconductor, such as copper oxide, tin oxide or even perovskite materials deposited at low temperature. The implementation of ring oscillators will be “straightforward” through the integration of more n-FETs. At the moment, some tests are being made aiming the integration of at least three n-FETs where the most challenging point lies in the connection between the inverters. Despite this issue, it is expected that cellulose-based ring oscillators will be successfully demonstrated in a very near future.

7.3. References

- [1] P. Barquinha, A. M. Vila, G. Gonçalves, L. Pereira, R. Martins, J. R. Morante, and E. Fortunato, “Gallium–Indium–Zinc-Oxide-Based Thin-Film Transistors: Influence of the Source/Drain Material,” *IEEE Trans. Electron Devices*, vol. 55, no. 4, pp. 954–960, Apr. 2008.
- [2] P. Barquinha, L. Pereira, G. Gonçalves, R. Martins, and E. Fortunato, “Toward High-Performance Amorphous GIZO TFTs,” *J. Electrochem. Soc.*, vol. 156, no. 3, p. H161, 2009.
- [3] P. M. C. Barquinha, “Transparent Oxide Thin-Film Transistors: production, characterization and integration,” Universidade Nova de Lisboa, 2010.
- [4] P. Barquinha, R. Martins, L. Pereira, and E. Fortunato, *Transparent Oxide Electronics: From Materials to Devices*, 1st ed. West Sussex: Wiley, 2012.
- [5] C. G. Van De Walle, “Universal alignment of hydrogen levels in semiconductors and insulators,” *Phys. B Condens. Matter*, vol. 376–377, no. 1, pp. 1–6, 2006.
- [6] E. Fortunato, N. Correia, P. Barquinha, L. Pereira, G. Goncalves, and R. Martins, “High-Performance Flexible Hybrid Field-Effect Transistors Based on Cellulose Fiber Paper,” *IEEE Electron Device Lett.*, vol. 29, no. 9, pp. 988–990, Sep. 2008.
- [7] R. Martins, L. Pereira, P. Barquinha, N. Correia, G. Gonçalves, I. Ferreira, C. Dias, N. Correia, M. Dionísio, M. Silva, and E. Fortunato, “Self-sustained n-type memory transistor devices based on natural cellulose paper fibers,” *J. Inf. Disp.*, vol. 10, no. 4, pp. 149–157, 2009.
- [8] R. Martins, B. Brás, I. Ferreira, L. Pereira, P. Barquinha, N. Correia, R. Costa, T. Busani, A. Gonçalves, A. Pimentel, and E. Fortunato, “Away from silicon era: the paper electronics,” *Proc. SPIE*, vol. 7940, p. 79400P–79400P–10, Feb. 2011.
- [9] R. Martins, D. Gaspar, M. J. Mendes, L. Pereira, J. Martins, P. Bahubalindrani, P.

- Barquinha, and E. Fortunato, “Papertronics: Multigate paper transistor for multifunction applications,” *Appl. Mater. Today*, vol. 12, pp. 402–414, 2018.
- [10] D. Gaspar, J. Martins, P. Bahubalindrani, L. Pereira, E. Fortunato, and R. Martins, “Planar Dual-Gate Paper/Oxide Field Effect Transistors as Universal Logic Gates,” *Adv. Electron. Mater.*, vol. 4, no. 12, p. 1800423, Dec. 2018.
- [11] S. Dai, Y. Chu, D. Liu, F. Cao, X. Wu, J. Zhou, B. Zhou, Y. Chen, and J. Huang, “Intrinsically ionic conductive cellulose nanopapers applied as all solid dielectrics for low voltage organic transistors,” *Nat. Commun.*, vol. 9, no. 1, p. 2737, Dec. 2018.
- [12] R. Martins, A. Nathan, R. Barros, L. Pereira, P. Barquinha, N. Correia, R. Costa, A. Ahnood, I. Ferreira, and E. Fortunato, “Complementary Metal Oxide Semiconductor Technology With and On Paper,” *Adv. Mater.*, vol. 23, no. 39, pp. 4491–4496, Oct. 2011.
- [13] “A lesson on paper,” *Nature Electronics*, vol. 1, no. 8, pp. 429–429, 13-Aug-2018.
- [14] N. Liu, Y. Hui Liu, P. Feng, L. Qiang Zhu, Y. Shi, and Q. Wan, “Enhancing the pH sensitivity by laterally synergic modulation in dual-gate electric-double-layer transistors,” *Appl. Phys. Lett.*, vol. 106, no. 7, p. 073507, Feb. 2015.
- [15] J.-H. Ahn, S.-J. Choi, J.-W. Han, T. J. Park, S. Y. Lee, and Y.-K. Choi, “Double-Gate Nanowire Field Effect Transistor for a Biosensor,” *Nano Lett.*, vol. 10, no. 8, pp. 2934–2938, Aug. 2010.
- [16] M. Liu and H. K. Kim, “Ultraviolet detection with ultrathin ZnO epitaxial films treated with oxygen plasma,” *Appl. Phys. Lett.*, vol. 84, no. 2, pp. 173–175, Jan. 2004.
- [17] J. S. Meena, M.-C. Chu, Y.-C. Chang, H.-C. You, R. Singh, P.-T. Liu, H.-P. D. Shieh, F.-C. Chang, and F.-H. Ko, “Effect of oxygen plasma on the surface states of ZnO films used to produce thin-film transistors on soft plastic sheets,” *J. Mater. Chem. C*, vol. 1, no. 40, p. 6613, 2013.