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Mestre em Engenharia Física

**Development of copper and nickel based
oxide thin-films: design and fabrication
of thin-film transistors**

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ABSTRACT

Thin-films of copper and nickel oxides films were successfully produced using two different methods (thermal oxidation and RF sputtering) and characterized using a wide range of techniques to determine their electrical, optical, structural and morphological properties.

The production of copper oxide (Cu_xO) thin-films by thermal oxidation was achieved using different temperatures (150 – 450 °C). The films produced at 200, 250 and 300 °C showed high Hall mobilities of 2.2, 1.9 and 1.6 $\text{cm}^2 \text{V}^{-1}\text{s}^{-1}$, respectively. Single Cu_2O phases were obtained at 200 °C and its conversion to CuO starts at 250 °C. For low thickness films of ~40 nm oxidized at 250 °C showed a complete conversion to CuO. Successful thin-film transistors (TFTs) were produced by thermal oxidation of a 20 nm Cu film, obtaining p-type Cu_2O (at 200 °C) and CuO (at 250 °C) with On/Off ratios of $\sim 10^2$.

The Cu_xO films deposited by RF-sputtering were produced using different oxygen partial pressures (O_{PP}) to study its impact in the properties of the films. A metallic Cu film with cubic structure obtained from 0% O_{PP} has been transformed to cubic Cu_2O phase for the increase in O_{PP} to 9% and then changed to monoclinic CuO phase (for $O_{\text{PP}} \geq 25\%$). The films deposited with O_{PP} of 9, 25 and 50% shown evident p-type conductivity with values around 2.70×10^3 , 2.93×10^2 and $6.39 \Omega \text{ cm}$, respectively, also confirmed by Seebeck measurements. The resistivity and mobility decreased with the increase of O_{PP} . The films produced with higher O_{PP} showed lower resistivity values, ranging between 4.21×10^{-2} - $9.09 \times 10^{-2} \Omega \text{ cm}$. Post-annealing (at 200 °C) was effective inducing changes in the films. The major evidence was visible for the films produced with 9% O_{PP} , where the mobility increased from 0.65 to $18.5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ with annealing temperature. Bottom-gate TFTs were produced with this condition showing p-type behaviour with an On/Off ratio of $\sim 10^3$ and a V_{On} around 7 V.

Nickel samples deposited with both methods were also characterized, showing promising properties (high transmittance up to 80% and low resistivity 10^{-2}). TFTs were also

produced but no effective field effect was observed in these devices.

RESUMO

Filmes finos de óxido de cobre e níquel foram produzidos com sucesso (usando oxidação térmica e pulverização catódica) e caracterizados usando um vasto conjunto de técnicas para estudar as suas propriedades eléctricas, ópticas, estruturais e morfológicas.

Na produção de filmes finos de Cu_xO através de oxidação térmica, foram usadas temperaturas entre 150 – 450 °C. Os filmes produzidos a 200, 250 e 300 °C mostraram os mais altos valores de mobilidade de efeito de Hall de 2.2, 1.9 e 1.6 $\text{cm}^2 \text{V}^{-1}\text{s}^{-1}$, respectivamente. A fase Cu_2O foi obtida por oxidação a 200 °C, observando-se a sua conversão para CuO a partir de 250 °C. Para filmes mais finos (usados em TFTs) a oxidação a 250 °C revela uma conversão completa do Cu_2O para CuO . Transístores de filme fino (TFTs) foram produzidos com sucesso usando Cu_2O (oxidado a 200 °C) e CuO (oxidado a 250 °C) como canal dos TFTs, com razões $On/Off \sim 1 \times 10^2$.

Os filmes de Cu_xO depositados por pulverização catódica RF foram produzidos usando pressões parciais diferentes de oxigénio (O_{PP}). Filmes fino de cobre metálico foram obtidos para 0% O_{PP} . Com o aumento de O_{PP} é observado uma mudança de fase para Cu_2O e depois para o CuO ($O_{\text{PP}} \geq 25$). Os filmes produzidos com 9, 25 e 50% O_{PP} apresentaram claramente uma condutividade tipo-p, com valores de resistividade de 2.70×10^3 , 2.93×10^2 e $6.39 \Omega \text{cm}$, respectivamente. O tipo de condução foi também confirmado por medidas de efeito de Seebeck. Os filmes produzidos com maior O_{PP} apresentaram os mais baixos valores de resistividade de 4.21×10^{-2} - $9.09 \times 10^{-2} \Omega \text{cm}$. Posteriores tratamentos em temperatura (200 °C) induziram mudanças nos filmes. A condição de 9% foi aquela em que o recozimento teve maior impacto, obtendo-se aumentos de 0.65 para $18.5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. Foram produzidos TFTs “Bottom-gate” que comprovaram a condutividade tipo-p com razões On/Off de $\sim 10^3$ e um V_{On} de $\sim 7 \text{ V}$.

Filmes de Ni depositados pelos dois métodos descritos foram também caracterizados, mostrando resultados promissores (elevada transparência $\sim 80\%$ e baixa resistividade 10^{-2}). No entanto os TFTs produzidos usando NiO não evidenciaram claro efeito campo.

SYMBOLS

α	Absorption coefficient
Z	Acoustic impedance
E_G	Bandgap
k_B	Boltzmann constant
θ	Bragg angle
C	Capacitance
q	Carrier charge
n_0, N	Carriers concentration
L	Channel length
w	Channel width
g_d	Conductance
F	Correction factor
σ_{CS}	Crosse section of collision
D	Crystallite size
I	Current
I_D	...current in the drain
I_G	...current in the gate (usually called leakage current)
I_S	...current in the source
	Density
ρ_d	...material density
n_T	...filled traps density
n_C	...density of free electrons in the conduction
ρ^A	...density of the material A
N_T	...density of traps
ρ_{Sol}	...solvent Density
d_{TS}	Distance between target and substrate
m_0	Effective mass of a free electron
m	Effective mass of the carriers
$\mathbf{F}_E$	Electric force
σ	Electrical conductivity
c	Electron affinity
ΔH	Enthalpy
ΔS	Entropy
R_{ev}	Evaporation rate of the solvent
E_F	Fermi level

ΔG	Gibbs free energy
R	Growth rate
R_H	Hall coefficient
K	Kinematic factor
$\mathbf{B}$	Magnetic field
$\mathbf{F}_M$	Magnetic force
μ	Mobility
μ_{AVG}	...average mobility
μ_{EFF}	...effective mobility
μ_{FE}	...field effect mobility
μ_{INC}	...incremental mobility
μ_H	...Hall mobility
μ_{SAT}	...saturation mobility
E_N	Neutrality level
O_f	Oxygen ratio of flows
O_{PP}	Oxygen ratio of partial pressures
P	Pressure
P_{Ar}	...argon partial pressure
P_B	...base pressure
P_D	...deposition pressure
P_{O_2}	...oxygen partial pressure
τ	Relaxation time (time between two scatterings)
ρ	Resistivity (bulk)
ρ_s	Resistivity (sheet)
S	Subthreshold swing
Q	Symmetry factor
T	Temperature
T_0	...initial Temperature
$P(\text{hkl})$	Texture coefficient
t	Thickness of the film
g_m	Transconductance
$T(\%)$	Transmittance
$T_{400-750}$	...average transmittance
E_T	Trap ionization Energy
$\mathbf{v}$	Velocity
η	Viscosity (liquid)
V	Voltage
V_{ON}	...turn-on-voltage

V_D	...drain voltage
V_G	...gate voltage
V_H	...Hall voltage
V_{DSAT}	...saturation voltage (drain)
V_{trap}	...voltage needed to fill empty traps
V_S	...source voltage
V_T	...threshold voltage
λ	Wavelength
Φ_M	Work function (metal)
Φ_S	Work function (semiconductor)
F_{O_2}	Flow of oxygen
F_{Ar}	Flow of Argon

ABBREVIATIONS

ATO	Alumina–titania nanolaminates
AFM	Atomic force microscopy
CEMOP	Center of excellence in microelectronics optoelectronics and processes
CENIMAT	<i>Centro de investigação dos materiais</i>
CMOS	Complementary metal oxide semiconductor
CB	Conduction band
CO	Copper oxides
DC	Direct current
FCC	Face centred cubic
FDP	Flat display panel
FIB	Focused ion beam
FTIR	Fourier transform infrared spectroscopy
FPP	Four-point configuration
ITO	Indium tin oxide
IZO	Indium zinc oxide
IC	Integrated circuits
LED	Light emitting diode
LCD	Liquid crystal display
NIR	Near infrared
OLED	Organic light emitting diode
RF	Radio-frequency
RBS	Rutherford backscattering spectrometry
SEM	Scanning electron microscopy
TFT	Thin film transistor
TCO	Transparent conductor oxide
TSO	Transparent semiconductor oxide
UV	Ultraviolet
VB	Valence band
VIS	Visible

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Chapter I

Motivation

CONTENTS

In this section some motivation aspects for the development of this work are presented, substantiated with economic figures that illustrate the importance of the research and development of p-type semiconductor oxides.

1 Motivation

1.1 Transparent electronics

1.2 Market size and abundance

1.3 References

1 MOTIVATION

1.1 TRANSPARENT ELECTRONICS

Transparent electronics is a new and emergent science and technology field focused on the production of ‘invisible’ electronic circuits and optoelectronic devices, which is only possible due to the appearance of transparent conducting oxides (TCOs) and transparent semiconducting oxides (TSOs). The applications can be the same as those produced with silicon, with great advantages in terms of production and costs, but more important, this technology will allow new and disruptive products or solutions that are only possible due to the fantastic combination of properties that are available in those materials (transparency + electric conduction). In the future it will be possible to find TCOs and TSOs (with n and p-type conduction) in consumer electronics, new energy sources, transportation, telecommunication systems, etc, for civilian and military purposes. TCOs have already been used as a passive layer or optical coatings in many applications such as solar cells, front electrodes for flat panel displays (FDP), low emissivity windows (“Low-e”), electrochromic materials for “smart windows”, light emitting diodes (LEDs), gas sensors, bio-sensors, thin-film transistors (TFTs), among others [1-3]. However, the use of this class of materials in active layers (functional part of the device), is still a challenge. Tremendous efforts have been made to develop new active materials for functional transparent electronics including conducting, dielectric and semiconducting oxides (TSOs). Thanks to those efforts, dielectrics and n-type TSOs with good properties for commercial applications are already available. In the case of n-type TCOs and TSOs today’s research is mostly focused in finding a substitute to indium due its low availability and high price.

Today, as it was when this research started (2008), the lack of p-type TSOs with good enough properties (similar to the n-type counterparts) is one of the major limitations to the development of this exciting “new era” of electronics, where complementary metal oxides semiconductors (CMOS) or photovoltaic cells, can be built fully transparent in any window.

Another inspiration for this work was the absence of reports on p-type semiconductor oxides applied successfully in TFTs. In fact, the first paper of a p-type TFTs appeared in the second half of 2008, using metal oxides of copper and tin [4, 5] as a TFT channel.

Despite the major effort done worldwide for the synthesis and application of these materials in devices, more research is needed using new material combinations or new deposition methods, to try to approximate the performance of p-type semiconductor oxides to the performance of their n-type counterparts.

1.2 MARKET SIZE AND ABUNDANCE

One of the major proofs about the importance of these classes of materials, TCOs and TSOs (n and p-type) are their market size of already available products (mainly related with passive applications) and its forecast for the near future.

The basic device structure for the majority of applications, such as conventional Si/III–V-based electronics, it is based on semiconductor junctions and transistors. To build this type of block materials device, all the component layers: the semiconductor, the electric contacts, and the dielectric/passivation layers, must now be transparent in the visible region of the electromagnetic spectrum. This represents a true challenge and as explained before, a huge effort is being done worldwide by scientists and engineers, within several research groups, to make it possible.

The first step to make this technology a reality is the discovery, the understanding and implementation of new high-performance electronic materials (TCOs and TSOs). The second step will be the implementation and evaluation of those materials in the development of transistors and circuits. The final step is the achievement of stable properties and application-specific materials that will allow their implementation into common or new solutions (devices), integrated in sellable products.

The oxide materials used in these developments (conductors, semiconductors and dielectrics) are in some cases used since ancient times, mainly based in SiO_2 , Al_2O_3 , CaO , MgO and Fe , due to their abundance in the Earth's crust [3]. To quantify the elements in

the Earth's upper continental crust Figure 1.1 compares it to the silicon (Si) abundance.

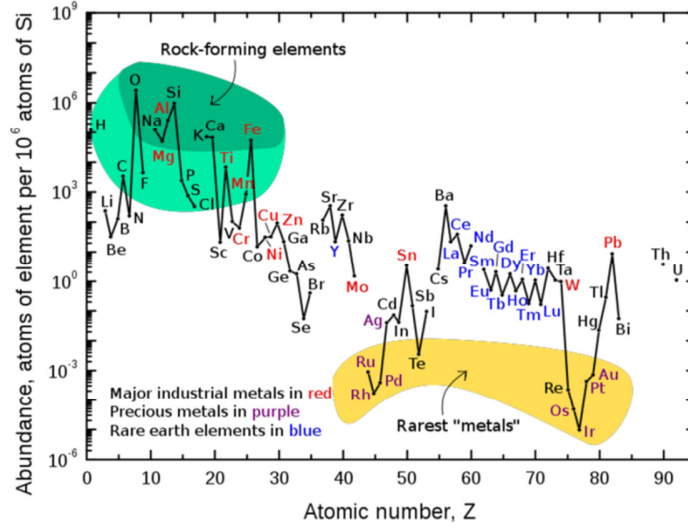


Figure 1.1 – Elements abundance in the Earth's upper continental crust[6].

In Figure 1.1, it is easy to understand that the major goal of this research on TCOs and TSOs is not the replacement of Si. In fact Si is one of the top available elements in the earth's crust, and despite the high temperature processes associated to its synthesis, the maturity and stability of the technology used for this purpose, makes it a high reliable material hard to replace. However, without TCOs and TSOs it is very difficult to produce transparent electronic circuits. Today, most of the ordinary circuits are made of conventional materials like Si that are known to be opaque. Transparent electronics, as mentioned before, can replace Si technology but the most important consequence is the possibility of new and disruptive applications, only possible due to the conjunction of their notable optical and electrical properties.

In fact, technology that uses transparent materials in electronic equipment has been around for a while, mainly as transparent electrodes (such as indium tin oxide - ITO) in touch panels, LCD panels, solar cells and others. The Japanese "Nikkei Electronics Asia" magazine calls it the "second wave" of transparent electronic market (Figure 1.2) where some applications have reached the commercial level, using high performance n-type semiconductors oxides. The "first wave" started with the use of transparent TCOs, like ITO

and other materials, mainly as electrodes in some devices. The “third wave” will be based on the existence of high performance p-type semiconductor oxides that will be integrated widely in more complex applications and systems.

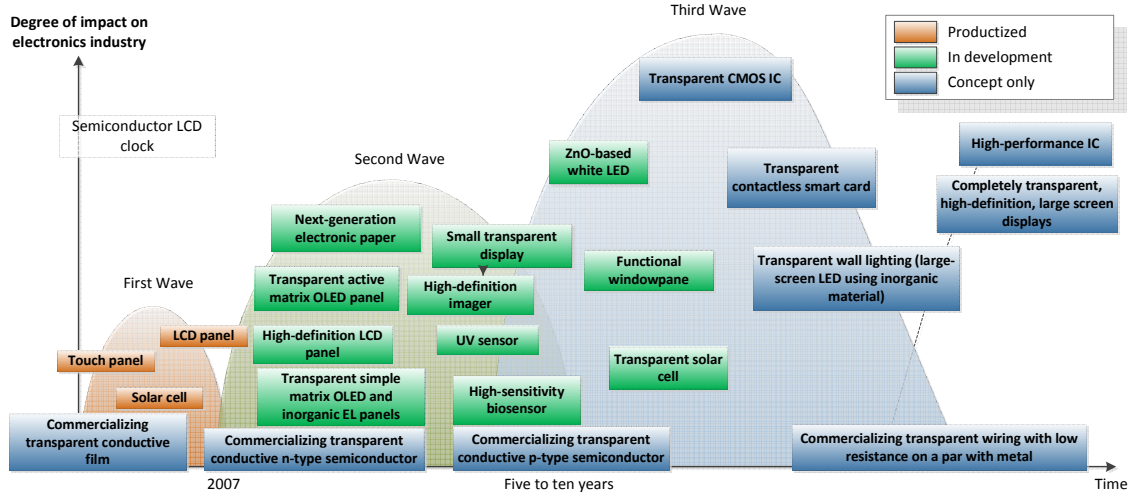


Figure 1.2 – Degree of impact of TCOs and TSOs in the electronic industry (some acronyms: LCD - *liquid crystal display*, (O)LED - (*organic*) *light-emitting diodes*, CMOS - *complementary metal-oxide-semiconductor*, IC - *integrated circuits*). Adapted from [7].

Today, economy acts as a driving force with major implications in society, and science is not an exception. In this point of view, as observed before/above, p-type semiconductors are still a “hot-topic” and a key in the development of new products in this emergent but already large market of transparent electronics. This market was worth US\$76400 million in 2010 and is expected to grow 10% in the next five years. Only inorganic materials were worth US\$74000 million in 2010 and are expected to grow 6.7% by 2015 at an estimated US\$103000 million (Figure 1.3)[8].

With the arguments presented before, it is clear that p-type semiconductors oxides are a prominent area with high potential impact in the economy, in the society and of course in our daily life. The research of this type of material is truly challenging. Progress is slow but every small step has a high impact.

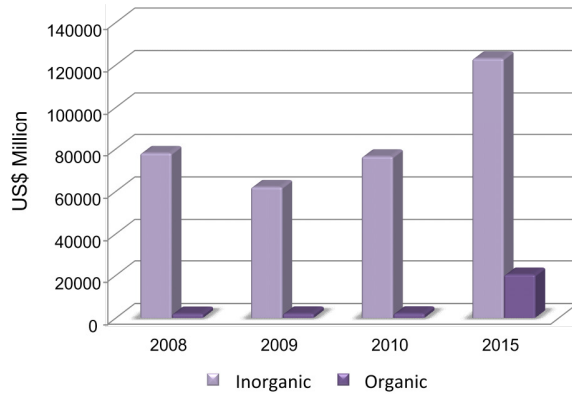


Figure 1.3 – Market Size of Transparent Electronics Components Market Size (2008-2015)[8].

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Chapter II

Review and technical background

CONTENTS

This chapter presents a technical and theoretical background and literature review of several topics studied in this thesis. Transparent conductors are discussed and also a review on p-type oxides semiconductors with special attention for copper and nickel oxides. The operation mode of thin-film transistors are also discussed and analysed.

2	Review and technical background
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2 REVIEW AND TECHNICAL BACKGROUND

2.1 BRIEF REVIEW ON TCOs* AND TSOs†

Normally there is an association between material transparency to the inability of current conduction. In fact all the traditional materials used by their optical properties are insulators. This means that photons with energy below 3.1 eV ($\lambda > 400$ nm) do not have enough energy to excite an electron from the valence band (VB) to the conduction band (CB), through a bandgap (E_G , by definition a region where no electron states can exist) [1]. The amount of energy needed to excite an electron from one band to another, can be correlated to the optical transparency. In a simple way, if a solid doesn't absorb energy in the visible region (400 nm – 700 nm, in the range of energy between 1.77 to 3.10 eV) is called transparent (see Figure 2.1).

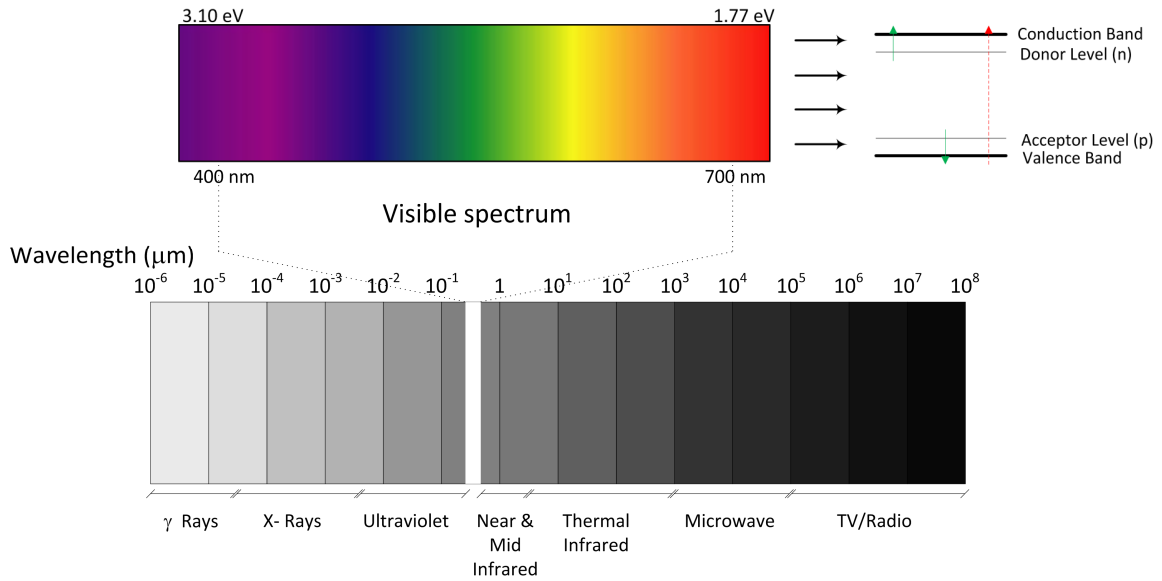


Figure 2.1– Representation of the electromagnetic spectrum. Photons of visible radiation (1.77 – 3.1 eV) do not have enough energy to excite electrons directly from the VB to the CB, but are able to excite electrons from acceptor level (for p-type materials) to de VB or from the donor level to the CB (n-type materials)[2].

Optical transparency requires materials with a large enough bandgap, ideally there is a

* TCO – Transparent conducting oxide.

† TSO – Transparent semiconducting oxide.

minimum value which is considered of 3.1 eV (~ 375 nm) eV [3]. Although high electrical conductivity (σ), traditionally, requires a narrow bandgap (in case of metals there is an overlap between the VB and the CB). The union of both excellent conduction and good optical properties in a material is a true challenge, and only possible recently due to an outstanding new “class” of materials, called “transparent conducting oxide” (TCO). The most studied TCOs are n-type, where electrons (which are responsible for the charges flow associated to an electronic current) are originated in defects such as oxygen vacancies, impurity substitutions and interstitials. In the case of p-type TCOs, ionized cation, impurity acceptor ion substitutions and/or oxygen interstitials, act as electron acceptors, which in general are responsible for hole doping in these materials [4, 5]. They can have a carrier concentration (N) above 10^{20} cm $^{-3}$, the resistivity can be as low as 10^{-4} Ω cm, with values of 10^{-5} Ω cm reported in controlled laboratory conditions [6-9]. It is important to lower the resistivity (ρ) of TCOs without the reduction of their optical transmission in the VIS-NIR region. This is possible by playing with other parameters in the relation [1]:

$$\sigma = \frac{1}{\rho} = e \cdot \mu \cdot N \quad (2.1)$$

where, e is the electronic charge given by 1.602×10^{-19} C and μ is the carrier mobility. Observing the values of N and ρ presented before, and the relation (2.1), one can verify that these values, will lead to a high (μ). In fact mobility ranging from 1 to 358 cm 2 V $^{-1}$ s $^{-1}$ has already been reported by different authors for n-type TCOs [3, 4, 10, 11].

Most of the n-type TCOs are binary or ternary compounds, containing one or two metallic elements (usually Zn, Sn, Cd and In) [4, 6, 12]. Sn doped In $_2$ O $_3$ (ITO) is the most common material for present TCO applications, with mobility higher than 100 cm 2 V $^{-1}$ s $^{-1}$, low resistivity $\sim 10^{-5}$ Ω cm, and with $E_G > 3$ eV. The expanding use of TCO materials, especially for the production of transparent electrodes for optoelectronic device applications, depends on the high price of TCOs, especially those based on scarce elements such as In (as shown in the Chapter 1, Section 1.2, In is a relatively rare element, which today is more demanded than ever and consequently expensive). Then there is a need to find substitute materials. The alternatives includes the pure and impurity doped ZnO, SnO $_2$, CdO and

Ga_2O_3 [12] and also multi-component materials based on its elements. For example, ZnO is a well-known TCO (with major advantages related to availability and non-toxicity) with high values of resistivity around $10^{-4} \Omega \text{ cm}$ and mobility up to $50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, obtained already by different techniques [13, 14]. Other materials such as cadmium oxide (CdO) are well known with even higher reported mobility ($>200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [15, 16].

Although the TCOs have a vast range of applications, that can be found described in detail elsewhere [2-4, 6, 12, 17-19], very little work has been done on active device fabrication using TCOs. This was because of the lack of high performance p-type transparent semi/conducting oxides.

The combination of the two types of TCOs (and also TSOs) will allow p-n junctions and will definitively lead to new applications (as shown in Chapter I). A “functional” window which transmits visible portion of solar radiation generating electricity by the absorption of the UV part [20] is one of the most famous example of such applications. NiO and Cu_2O are two examples of the first reported p-type conducting thin films. Nowadays the production of high performance p-type TCOs and TSOs is a constant endeavour. Besides Cu_xO and NiO (and their doping), other materials have been studied for TCOs and TSO including: ZnO doped (Mg, N, In), and perhaps the most notorious examples are the delafossite structure materials such as CuAlO_2 , Cu_2SrO_2 , and CuGaO_2 , among others. In the next section will be presented more details about the p-type materials studied in this dissertation.

2.2 P-TYPE SEMICONDUCTOR OXIDES

In the Chapter I was presented some reasons concerning the importance of p-type TCOs and also TSOs in the next-generation electronics. Cu_xO and NiO are among the most antique and important p-type metal oxides used today in a large number of compounds.. Copper oxides (CO), being naturally cation-deficient and hole conductors, are promising materials to be applied as binary p-type CO semiconductors, but also in Cu based delafossite structures such as CuMO_2 (where $\text{M} = \text{Al, Ga, In, etc.}$), LnCuOX (where $\text{Ln} = \text{lanthanide}$,

X = chalcogen) and SrCu_2O [21, 22]. In Table 2.2 some of the most reported p-type semiconductor oxides are presented.

Table 2.2 – Some of the most reported p-type oxides and characteristics.

Material	T (%)	σ (S cm ⁻¹)	n (cm ⁻³)	μ (cm ² V ⁻¹ s ⁻¹)	E_G (eV)	Ref.
NiO:(Al, Li)	60-80	10 ⁻² - 1.5	1.91×10 ¹⁷	-	3.50 – 4.30	[23-27]
Cu _x O	66	10 ⁻⁴ - 10 ⁻³	10 ¹³ - 10 ¹⁶	1.56 – 18.50	1.30 – 2.60	[28-30]
Ag ₂ O	-	10 ⁴	10 ²¹	127.80	3.70-4.00	[31]
SnO _x : (Li, Al, In, Co, Fe, Y)	60 - 80	10 ⁻² - 6.9	10 ¹⁶ -10 ¹⁸	25.90	3.61 – 4.10	[32-36]
ZnO:(N, Cr, P, Mg, Co)	60 - 90	10 ⁻¹ – 1.8	10 ¹³ – 10 ²⁰	0.8 -111	2.30 – 2.50	[37-42]
CuAlO ₂	65 - 80	10 ⁻³ – 2.4	10 ¹⁵ - 10 ¹⁹	0.13 – 39.50	3.43 – 3.75	[43-50]
SrCu ₂ O ₂ :(K, Ca)	50 - 80	10 ⁻³ -10 ⁻²	10 ¹⁷	0.27 – 3.82	3.12 - 3.30	[51-54]
CuCrO ₂ :(Mg)	32 - 80	10 ⁻² – 50.0	10 ¹⁹	0.10 - 0.25	2.58-3.19	[47, 55-57]
CuScO ₂ :(Mg)	40 - 65	10 ⁻² - 30.0	4.50×10 ¹⁶	1.40×10 ⁻¹	3.30 – 3.7	[58-60]
LaCuO ₂	-	-	10 ¹⁷	3.50×10 ⁻⁷	2.77	[61]
CuGaO ₂	60 - 80	10 ⁻² - 10 ⁻³	10 ¹⁷ - 10 ¹⁸	<1	3.40 – 3.60	[43, 62, 63]
CuInO ₂ :Ca	50	10 ⁻³	-	-	3.90	[64]
AgCoO ₂	~50	0.2	-	-	4.15	[65]
CuYO ₂ :(Ca)	40 - 45	1.0 – 8.0	10 ¹⁹	<1	3.15 - 3.60	[66, 67]
BaCu ₂ S ₂	~60	17.0	10 ¹⁹	3.50	2.30	[68]
BaCuQF (Q=S, Se, Te)	65	43.0 – 167.0	10 ²⁰	8.00	3.00 - 3.20	[69, 70]
BiCuOSe	-	176.0	10 ²⁰	2.00	-	[70]
LaCuO:(S, Se, Mg)	70	10 ⁻¹ – 140.0	10 ¹⁹ 10 ²⁰	4 - 16	2.80 - 3.10	[71, 72]
Cu-Nb-O	70	116.0	10 ²¹	0.36	2.60	[73]
TiO ₂ :Pd	-	10 ³	-	-	~1.25	[74]

The copper and nickel oxides studied, belong to a group of elements called transition metals. Transition metals have a number of properties shared that are not found in other elements, due to their partially filled d shell (Table 2.2). They usually form several compounds in many oxidation states and many paramagnetic compounds in result to their unpaired d electrons [75]; the colour of those compounds is attribute to $d - d$ electronic transitions. Many attempts have been made to investigate these $3d$ transition-metal oxides in an experimental and theoretical point of view. Cu_2O , CuO and NiO are examples of the simplest case of compounds in this group, called binary compounds. The actual number of

compounds obtained using transition metals (usually divided in binary, ternary and complex oxides) is already large having insulator, magnetic, semiconductor and metallic characteristics. The properties of these materials are dependent of the state of its d shell. According to conventional band theory, if a material has an empty or a completely filled shell it will behave as insulator (there are no electrons that could be easily delocalized). This is the case of Cu_2O with a $3d^{10}$ electron configuration. The electrical properties of closed shell insulators like Cu_2O and others are usually understood as deviations in stoichiometry originated by slightly differences of copper/oxygen in the structure. Partially-filled shells usually result in partially-filled bands usually associated to metallic conductivity. This is the case of CuO and NiO , they have respectively a partial filled $3d$ shell $3d^9$ and $3d^8$ electronic configurations. However they do not have metallic conductivity as explained in further sections.

Table 2.2.1 – Electron configuration of O, Cu and Ni.

Element	Electronic configuration
O	$1s^2 2s^2 2p^4$
Cu	$[\text{Ar}] 3d^{10} 4s^1$
Ni	$[\text{Ar}] 3d^8 4s^2$

2.3 BRIEF REVIEW ON CO

Copper is known from ancient times and used in different ways for different purposes. In the 21st century it is used alone or combined in different compounds from medical applications to spatial technology.

In the recent era of electronics its utilization is mainly due to its high electrical and thermal conductivity, respectively $59.6 \times 10^6 \text{ S m}^{-1}$ ($T = 20 \text{ }^\circ\text{C}$) and $401 \text{ W m}^{-1} \text{ K}^{-1}$. Only silver has a higher electrical conductivity of $63.0 \times 10^6 \text{ S m}^{-1}$ ($T = 20 \text{ }^\circ\text{C}$). The two main copper oxides are known as copper (I) oxide (Cuprous, Cuprite, Cu_2O) and copper (II) oxide (Cupric, Tenorite, CuO), and are shown in Figure 2.3. However, other form of CO, known as Paramelaconite (Cu_4O_3) was discovered in 1870 as a mineral in the Copper Queen mine

located in Bisbee (Arizona, USA). This copper phase is a very rare secondary mineral in hydrothermal copper deposits [76]. Nevertheless, reports of copper oxides of compositions other than Cu_2O , Cu_4O_3 and CuO have appeared in literature, such as Cu_2O_3 and Cu_3O_2 [77-79], falling into one of two categories: (a) Cu-rich thin-films and (b) O-rich thin films [76].

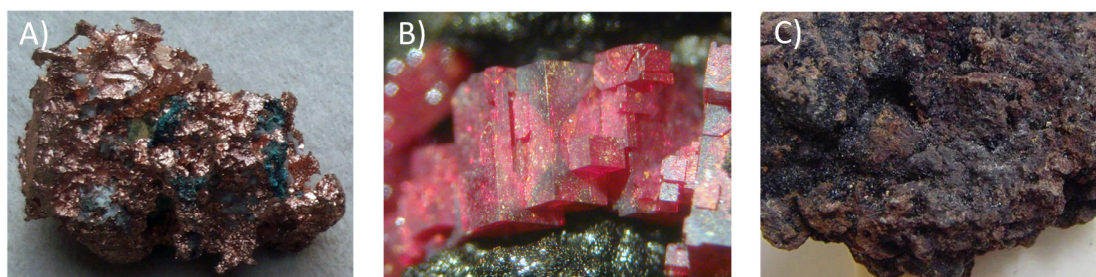


Figure 2.3 – Images of ores of Copper (A), Cuprite (B) and Tenorite (C).

The main interest in copper oxides is due to the promising properties of Cu_2O and CuO . The Cu_2O was the first substance known to behave as a semiconductor, together with selenium, even before the interest in materials like germanium and silicon [80]. In fact, in the early's 1920 was fabricated the first real solar cell based on Cu_2O [81, 82].

Much research was done in this semiconductor material between the years 1920 – 1940, but in this period, the energy production using the photovoltaic effect was just a scientific curiosity. In the other hand, the electronic devices based on Cu_2O , like rectifiers [82, 83] had a relatively short life, and its attention declined in the early fifties after the discovery of the doping of silicon and germanium.

Later, in the first oil crisis (1973-1974) a renewed interest was given to copper oxides, due to their low cost and their different possible applications, mainly in photovoltaic cells [84]. It was always been considered a material suitable for the development of low cost solar cells, with a maximum theoretical efficiency of about 20%. However, current experimental data show results that are very below this value around 2% [85]. In fact Cu_2O shows several interesting characteristics for both device and photovoltaic applications, having high absorption coefficient for light above the energy gap.

In case of CuO the major interest was its remarkable large and almost constant paramagnetic susceptibility at low temperatures. The discovery of the superconducting

mixed-valence copper oxides, facilitating the high T_c has intensified the interest in binary oxides [76]. In case of CuO it is still currently the subject of intense theoretical and experimental study that aims to solve the failure of different theoretical models in the prediction of its semiconductor ground state [86].

CO as described before, have many advantages and are attractive in terms of abundance, sustainability, non-toxicity (or negligible for main purposes), and the numerous methods available for its production (specifically as thin-film coatings) facilitating their low cost production [80, 87]. Many studies were published concerning the deposition of CO with a wide set of techniques such as: thermal oxidation of a copper thin-film [80, 87, 88], DC sputtering [46, 89], RF sputtering [29, 90], electrochemical techniques [91-94], thermal evaporation [20], etc. Cu₂O together with CuO were already used in several applications such as inorganic solar cells [84], high- T_c superconductors [95], as catalyst to convert hydrocarbons into carbon dioxide and water [96], in fabrication of lithium batteries [97] and more recently, in nanowire transistors [98], gas sensors, [99, 100], etc. Large areas can be produced using low cost methods (some of them explained in this thesis). The use of metallic oxidation in specific regions of a metallic film, makes possible to have both metal and semiconductor phases in a same device. More specific about the subject developed in this dissertation, recent reports on Cu₂O and CuO showed p-type conductivity in case of Cu₂O exceeding 100 cm²/V.s [101]. These promising results highlight the CO properties, and in particular Cu₂O as promising candidate to be used as channel in p-type thin-field transistors (TFTs). Relatively to the application in p-type TFTs the results are very recent, existing few reports based on Cu₂O [29, 90, 102-105] and CuO [106] as a p-type channel, produced mainly using PLD and RF sputtering techniques. Recently, a Cu₂O channel was also used in a copper wire transistor using an oxidation process [98], speculating the application of this technique in nanowire based devices. In case of the application of CuO as a p-type channel, only few published work exists using this oxide alone or in a mixture with Cu₂O as p-type channel for TFTs [104, 106].

2.3.1 STRUCTURE, ELECTRONIC AND OPTICAL PROPERTIES

As described before, Cu_2O and CuO are the two most common and stable phases of the three well established copper oxide compounds [76]. In Figure 2.2 it is presented the crystalline structure of Cu and both CO phases. Cu_2O crystallizes in a simple cubic lattice with the symmetry of 224^{th} space group ($\text{Pn}\bar{3}\text{m}$). The CuO has a monoclinic structure with symmetry of the 15^{th} space group ($\text{C}2/\text{c}$). More details about their structural and crystallographic parameters can be found in Table 2.3.1.

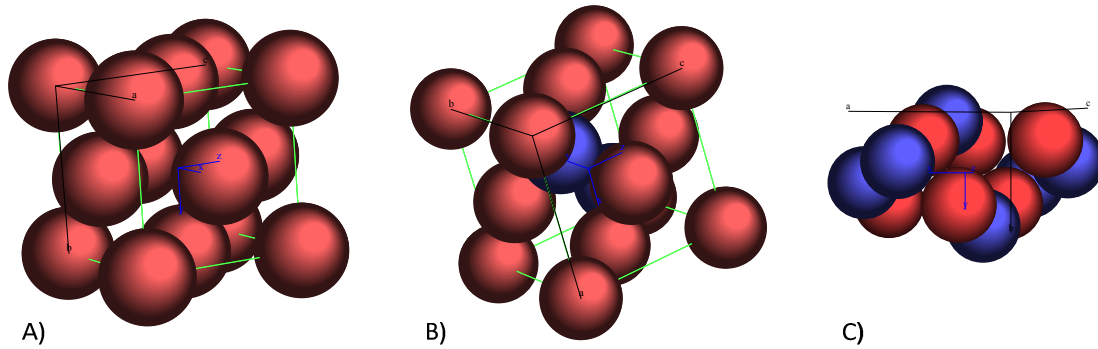


Figure 2.2 – Crystalline structure of Cu (A) Cu_2O (B) and CuO (C).

The p-type conduction in Cu based oxides arises from its electronic structure, in which the top of the valence band (VB) is composed of fully occupied Cu $3d^{10}$ states [22]. In Figure 2.3 (A) is illustrated the chemical bond between an oxide and a cation that has a closed-shell configuration.

The p-type characteristics of Cu_2O were attributed mainly to the presence of negatively charged Cu vacancies (represented as $\text{V}_{\text{Cu}}^{1-}$, with a defect charge -1) and interstitial oxygen [22]. However from other works is generally accepted that $\text{V}_{\text{Cu}}^{1-}$ formation is the dominant process responsible for the origin of p-type characteristics in Cu_2O . The $\text{V}_{\text{Cu}}^{1-}$ is believed to be also responsible for the introduction of an acceptor level about 0.3 eV above the VB. In Figure 2.3 (B) it is illustrated the simple electronic model proposed by Brattain[83]. It was also proposed by some authors the co-existence of both intrinsic, acceptor and donor levels. However, the nature of the donor levels is not completely clear being even controversial [83, 107, 108]. Soon *et al.*[109] and Raebiger *et al.*[21] from

calculations of the enthalpies of formation of different defects[‡] (representation of these native defects can be found in [109]) determined that in Cu₂O the lowest formation energy (<1 eV) is attributed to the copper vacancies (Figure 2.4 (A), represented as V_{Cu}), even in copper-rich or oxygen-rich conditions. Figure 2.3 (C) presents a scheme of the most important defects on CO.

Table 2.3.1 – Structure details of copper and copper oxide films (FCC – face centred cubic; A.P.F. – atomic packing factor for the ideal structures).

	Structure	Lattice parameters (Å)	Unit cell volume (Å ³)	A.P.F.	Density (g/cm ³)
Cu	FCC	$a = 3.6149$	47.24	0.74	8.94
Cu ₂ O	Simple Cubic	$a = 4.2690$	77.80	0.52	6.10
CuO	Monoclinic	$a = 4.6809$ $b = 3.4176$ $c = 5.1220$ $\beta = 99.78$	80.75	0.42	6.32

In case of CuO (with 3d⁹ electronic configuration), and also in NiO (with a 3d⁸ electronic configuration), the explanation of their p-type nature (and also some of their magnetic properties) was challenging, and many theoretical models have failed in this attempt [22, 86]. As explained before, CuO with its partially filled band should behave as a conductor. These materials are included in a particular class of compounds known as Mott insulators, where the conventional band theory generally fails.

Wu *et al.* [86] and Peng *et al.* [110] used the Hubbard correction in their model, enabling them to predict some of the properties of this important material. They found in their study of CuO, that the V_{Cu}²⁻ (where the superscript refers to the charge $q(-2)$ of the defect) is always the most stable defect as observed in Figure 2.4 (B). In fact V_{Cu}²⁻ has the lowest formation energy (among other charged states, less than 1.0 eV), indicating their spontaneous formation during the growth of the CuO crystal. Consequently they conclude that CuO should be dominated by acceptors. Meaning that intrinsically CuO is a p-type

[‡] Some of the native point defects considered in these studies: copper vacancies (here represented as V_{Cu}) oxygen vacancies (V_O), copper (Cu_O) and (O_{Cu}) antisites, and copper (Cu_i) and (O_i) interstitials.

semiconductor, which agrees with many experimental results [86]. They also predict that this material is not expected to be intrinsically n-type [110].

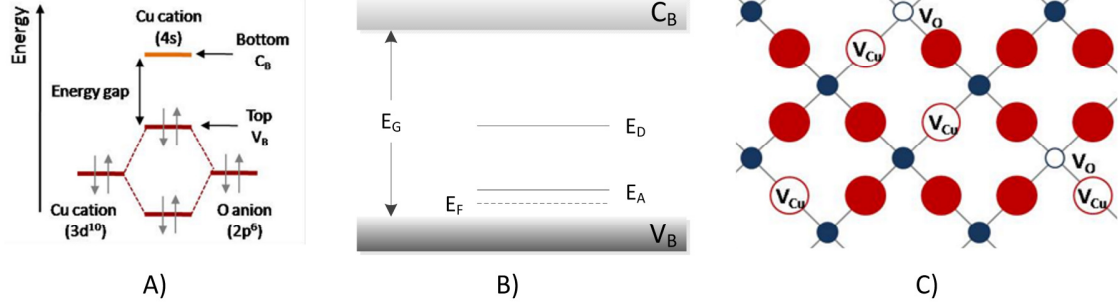


Figure 2.3 – (A) Illustration of the chemical bond between an oxide ion and a cation that has a closed-shell electronic configuration. (B) Representation of the simple electronic model for Cu_2O proposed by Brattain[83] consisting of a compensated semiconductor with one acceptor level at 0.3 eV and a deep donor level at 0.9 eV from VB. (C) Presents a scheme of the more important defects in both Cu_2O and CuO .

Wu *et al.* [86], also calculated the effective mass of the longitudinal and transverse electrons respectively $0.78 m_0$ and $3.52 m_0$, where m_0 is the rest mass of a free electron. In average the hole effective mass was estimated around $1.87 m_0$. In case of silicon, for example, the electron and hole effective mass are around $0.26m_0$ and $0.39m_0$, respectively. Small effective masses are generally associated to high mobility by the equation:

$$\mu = \frac{e\tau}{m} \quad (2.2)$$

where e is the electron charge, m the effective mass of the carrier and τ the relaxation time (the time between two scatterings). This means that the carrier mobility in CuO are smaller compared to Si.

The mobility of free carriers is one of the most important parameters to describe the electrical properties of a material. In case of CO exists a wide scattering on the mobility values, associated to the morphology of the crystal and consequently to the morphology of the film.

Relatively to their optical properties, CO have in general a narrow bandgap around 2.1 to 2.6 eV for the Cu_2O phase and 1.35 to 1.9 eV for CuO [22, 111-113]. According to Elliot theory, Cu_2O is a direct forbidden bang gap semiconductor. However, the inefficiency

of a $\alpha^{2/3}$ fit[§] in the energy interval range between 2.09 to 2.64 eV, to the experimental data, makes this not an ideal method to estimate the energy gap as explained by Malerba *et al.* [112]. A possible explanation also given by these authors, states that the superposition of several different absorption mechanisms above the bandgap is the reason of the inadequacy of the $\alpha^{2/3}$ fit. Nevertheless, many authors have considered the direct allowed transition using the Tauc model, due to the excellent fit obtained for the α^2 transition.

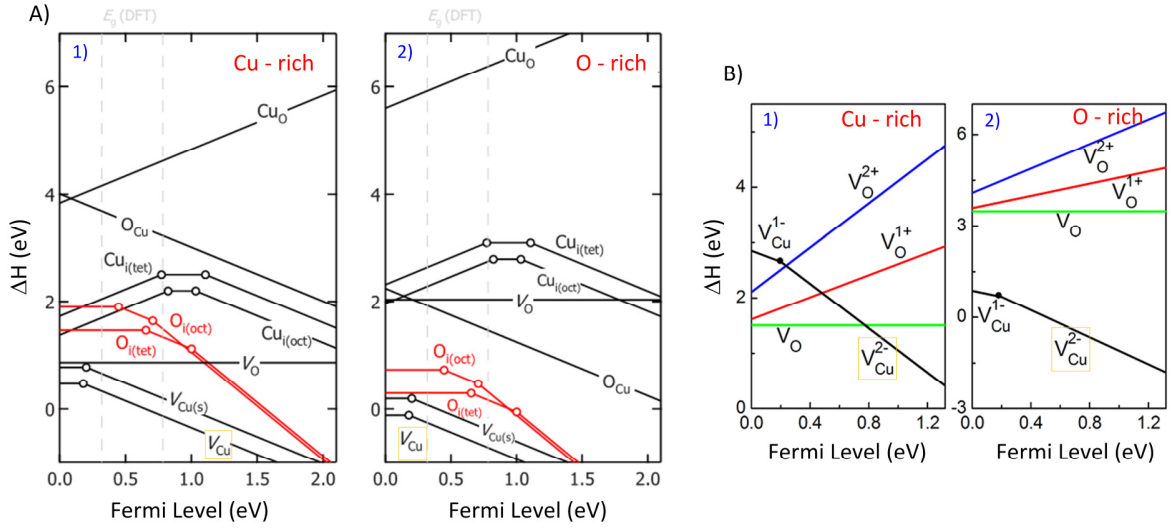


Figure 2.4 – Formation energies for intrinsic defects for rich Cu (1) and rich oxygen (2) contents for Cu_2O (A) and CuO (B). Adapted from [109, 110].

In case of CuO phase, Wu *et al.*[86] predicted an indirect allowed bandgap. However, the problem of the inadequacy of the $\alpha^{1/2}$ transition to the experimental data observed to Cu_2O appears to happen once again in CuO .

2.4 BRIEF REVIEW ON NiO

Nickel is a silvery-white hard metal, used since ancient times, but always in an unintentional way, mixed with other metals or mistaken with silver (Figure 2.5). It is a readily available material and very abundant in the world (see Chapter I, Section 1.2, Figure

[§] α is the absorption coefficient. Discussion about the different transitions and other considerations are provided in Chapter III, Section 3.3.

2.1). This metal has a good electrical and thermal conductivity $\sim 14.43 \times 10^6 \text{ S m}^{-1}$ ($T = 20^\circ\text{C}$) and $90.9 \text{ W m}^{-1} \text{ K}^{-1}$. Nickel (II) often called bunsenite is the most common form of nickel oxide, but other forms such as Ni_2O_3 and NiO_2 , have been claimed but not very much studied and characterized.

Nickel and nickel oxides (NiO) are used in many applications due to their excellent chemical stability, electrical, magnetic and optical properties, allowing a large number of possible applications. NiO is a wide bandgap semiconductor with energy gap ranging 3.5 to 4.0 eV [24, 26, 114-117]. They can be found in superalloys [118], p-type transparent conducting films [119], materials for electrochromic displays [120], OLED applications [3], automobile mirrors [121], in heterojunction solar cells [122], as anti-ferromagnetic materials [123], functional layer materials for chemical sensors [124], spin-valve films [125], gas sensors [126], etc. It is evident that the improvement of material properties can be reached by the optimization of the preparation conditions.

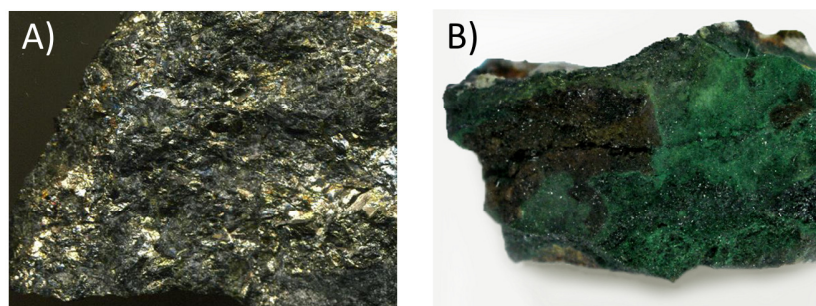


Figure 2.5 – Nickel (A) and NiO (B) ores.

There are several methods reported to prepare NiO films, which include DC sputtering [127], RF Sputtering [128], electron beam evaporation [129], resistive evaporation [117], sol-gel deposition [130], spray pyrolysis [131], pulsed laser deposition [132], plasma-enhanced chemical vapour deposition [133], etc. The sputtering technique, which is also used in this thesis, has been extensively used to fabricate NiO films essentially because of high film quality (allowing high uniformity over large areas with an easy control over the composition of the deposited films) and the relatively high deposition rates. The properties of the deposited films, as usual, will depend on the deposition parameters.

2.4.1 STRUCTURE, ELECTRONIC AND OPTICAL PROPERTIES

Ni has a simple face-centred cubic (FCC) structure with a symmetry of 225^{th} space group ($\text{Fm}\bar{3}\text{m}$) (ICCD: 00-004-0850), with a twelve-fold coordination (Figure 2.6 (A)), NiO frequently crystallizes in a FCC structure with symmetry of 225^{th} space group ($\text{Fm}\bar{3}\text{m}$) like FCC Ni (ICCD: 00-047-1049). This structure has a six-fold coordination and a simple crystallographic rock salt structure (NaC) presented in Figure 2.6 (B).

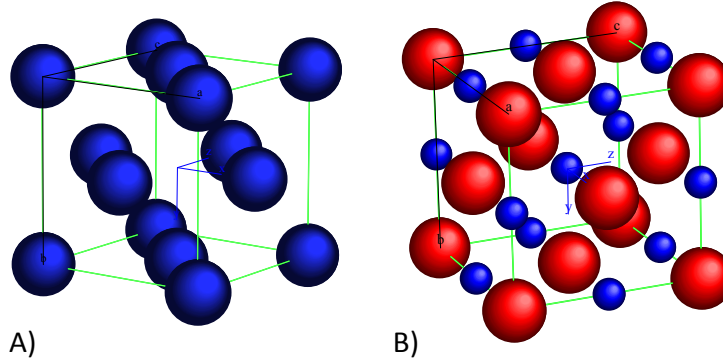


Figure 2.6 – A) Nickel and B) NiO structures (red spheres are referred to oxygen and blue to nickel).

Table 2.4.1 – Structure details of nickel and NiO.

	Structure	Lattice parameters ($\text{\AA}$)	Unit cell volume ($\text{\AA}^3$)	Density (g cm^{-3})
Ni	FCC	$a = 3.52380$	43.76	8.91
NiO	FCC	$a = 4.17710$	72.88	6.67

In terms of their physical properties, NiO is a $3d$ transition-metal oxide with partially occupied 3-d orbitals (as discussed before) being expected a metallic electrical behaviour. However, NiO is known to be an excellent insulator having a resistivity (room temperature) up to $10^{13} \Omega \text{ cm}$ [25, 134-136]. Like CuO, it was a true challenge to explain the electronic structure and correspondent properties of this material [22]. In NiO a filled oxygen $2p$ -band and an empty nickel $4s$ -band are involved in the explanation of their electronic properties. To form the nickel $3d$ -bands needed for conduction, quantum mechanics requires a substantial overlap between the $3d$ -wave functions [134]. However, band structure calculations show that these interactions will not take place. Instead, are observed in the forbidden band (close to the upper edge of the valence band) deep-lying localized electron

states. Thus, no $3d$ -band conduction can take place, resulting in a stoichiometric NiO insulator [134]. However, NiO appears to be always non-stoichiometric (Ni_{1-x}O) and metal deficient. The oxygen atom is too large to allow any considerable concentration of interstitial oxygen (O_i) atoms in its structure. As a result, excess of oxygen in NiO creates nickel vacancies ($\text{V}_{\text{Ni}^{2-}}$), each of which leads to the formation of two Ni^{3+} ions to obtain neutrality [26, 117, 136]. Osorio-Guillén, *et al.* [137] calculated the formation enthalpies (ΔH) for the intrinsic defects in NiO (Figure 2.7).

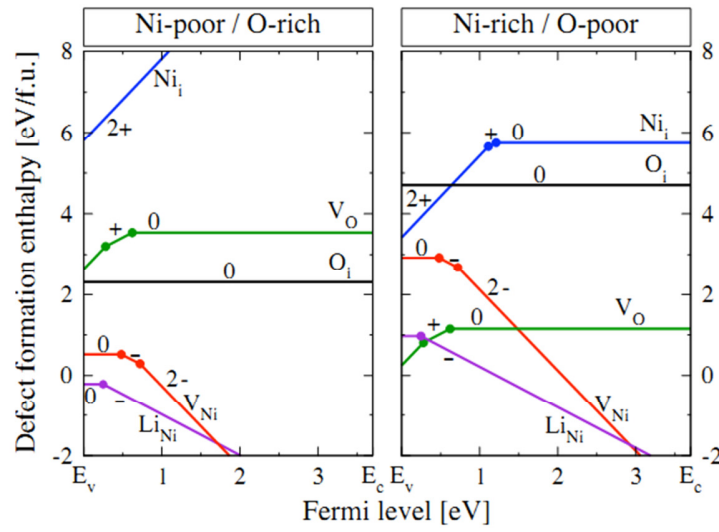


Figure 2.7 – Defect formation enthalpies for NiO [137].

For Ni-poor/O-rich condition is visible that the most important defect is the Ni vacancy (in figure represented as V_{Ni}) which has $\Delta H < 1$ eV. These authors also considered other defects in their model such as oxygen vacancies (V_o), interstitial nickel (Ni_i) and interstitial oxygen (O_i). All of these defects have higher formation energy above 2 eV. They concluded that, $\text{V}_{\text{Ni}^{2-}}$ (V_{Ni} in figure) is the cause of nonstoichiometric NiO. In the case of Ni-rich/O-poor, the main defect is V_o , with an enthalpy of formation close to 1 eV. However, its deep donor levels is the reason for the non-production of free-electrons [137]. Appropriate doping with extrinsic acceptors like Li, could lead to high concentration of free-holes.

In conclusion, a number of defects are usually present in NiO samples which cause it's deviation from stoichiometry. Therefore, their electrical transport properties are dominated by impurity states and extra carriers introduced by the defects. In terms of its

optical properties, and more specific its optical gap, NiO is a wide bandgap semiconductor with optical E_G reported between 3.25 – 4.3 eV [23, 27, 117, 119, 138-140].

2.5 METAL OXIDATION

Most metals are oxidized by oxygen in air by a process known as oxidation (but also corrosion). In a general way, this process occurs at the metal interface when the electrons leap from the metal to the oxygen molecules originating negative ions which penetrate into the metal, causing the growth of an oxide surface. The oxide layer formed serves the purpose of an ionic conductor (electrolyte) at which oxygen is reduced, and as a diffusion barrier through which electrons flow, and ions must migrate over defect lattice sites, indicated as V_M and V_O in Figure 2.8.

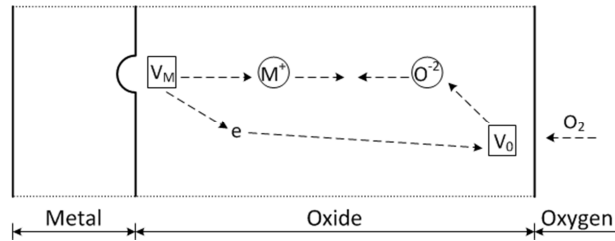


Figure 2.8 – Schematic illustration of an oxidation process.

To describe the oxidation process in metals, there are two major paths to discuss: thermodynamics and kinetics. The reaction between metallic elements and oxygen only occurs if it's energetically favourable. Thermodynamics shows if a reaction can or cannot take place. The oxidation kinetics tells how fast the reaction will occur (see Appendix A and B for more details). For practical purposes, oxidation kinetics is more important because it allows the determination of the extent of metal consumption, and consequently, lifetimes.

The products of metals oxidation are ionic compounds, in which the metal and the oxide ions are arranged in the crystal lattices. If the metal oxide contains excess of metal ions in interstitial positions they are known as n-type (negative carrier type), if they contain vacant sites in the lattice they are called p-type (positive carrier type) [141]. As explained before, two different diffusion processes can occur in the formation of metal oxides: the

oxygen diffusion inwards through the metal film as well the metal diffusion outwards. The copper-oxide system exemplifies a case of diffusion of metal outwards from the metal/oxide interface. The mechanism of oxidation of copper to produce Cu_2O is represented in Figure 2.9. The oxygen molecule reacts with cuprous ions, Cu^+ , at the air/oxide interface as shown in Figure 2.9 (A). The positive charge will move inward and electrons outward to maintain the electron-neutrality. This type of mechanism requires that the metal under consideration should have dual oxidation states (like Cu (I) and Cu(II) in the case of copper) [141].

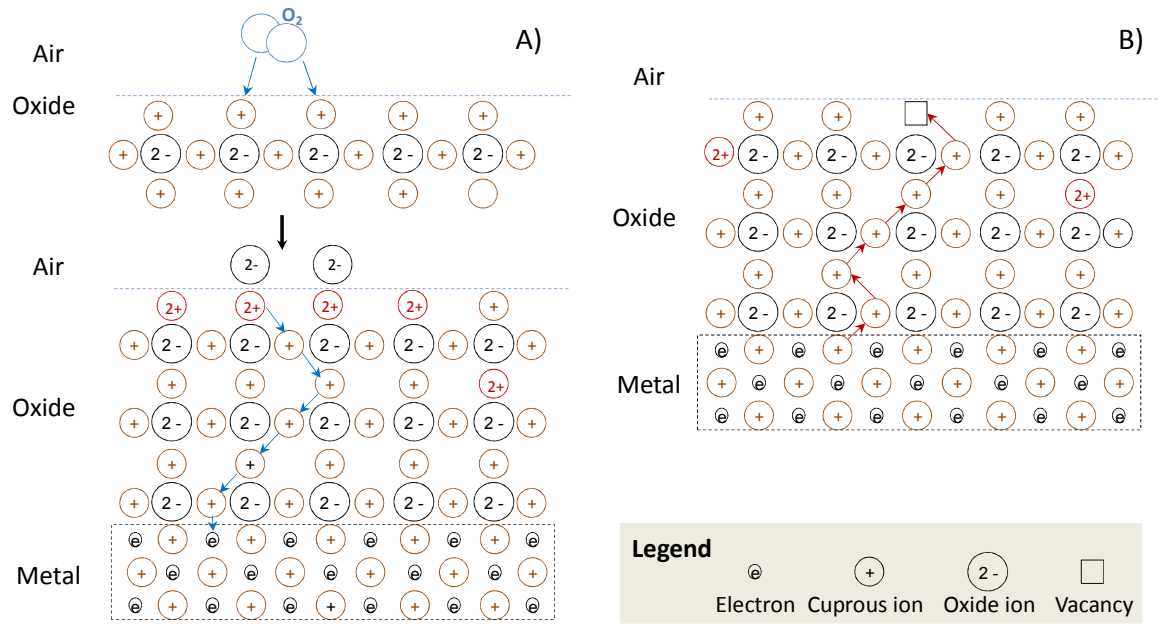


Figure 2.9 – Schematic diagram of the mechanism of oxidation of copper. (A) reaction of oxygen molecules with Cu^+ ions at the air/oxide interface and diffusion of positive charge inwards to neutralize the excess of electrons in the metal. B) Diffusion of Cu^+ ions from the metal to the air/oxide interface via cation vacancies; (Adapted from [141]).

NiO , as already discussed before, is also a p-type metal-deficient material having a structure with Ni^{2+} , O^{2-} and Ni^{3+} in nickel vacancy sites. Addition of lithium ion impurity to NiO improve its p-type conductivity, reducing its oxide growth rate when compared to the Ni-O_2 system alone [141].

2.5.1 COPPER THERMAL OXIDATION

In 1962 Wieder and Czanderna [142] published a detailed study about the oxidation of

copper films. In that study, they observed five temperature regions, ranging from the room temperature to 330 °C, in an atmosphere around 1.3×10^{-4} Pa of oxygen (Figure 2.10). The region (a) (before 70 °C) shows an oxidative growth typical of an amorphous oxide. The regions (b) (70 to 110 °C) and (d) (200 - 270 °C) are abrupt regions of sudden changes in the films composition, followed by an increase of the thickness. The region (e) (270 to 330 °C) is related to the existence of a major CuO phase.

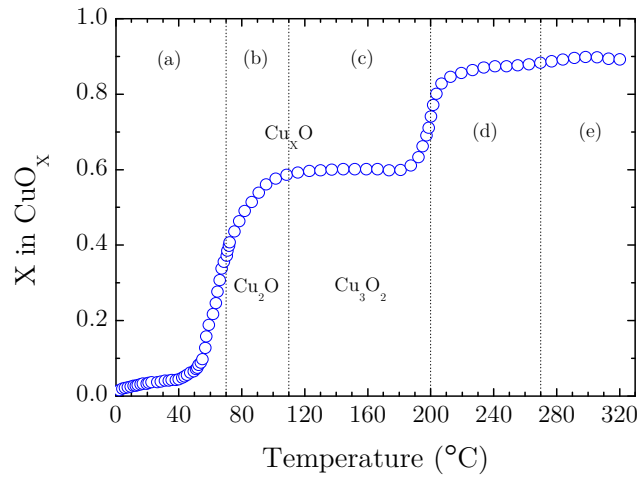


Figure 2.10 – Copper oxidation with temperature in a 13.3 kPa (100 torr) atmosphere of oxygen (Adapted from [142]).

The plot shows a region (c) with an unusual copper composition $\text{CuO}_{0.67}$ (Cu_3O_2), when it was expected to find the composition $\text{CuO}_{0.5}$ (Cu_2O). The authors found significant differences in the growth of the copper oxide depending on the history of the copper samples.

Relatively to the Cu_3O_2 is appointed to be a gross defect structure of Cu_2O [78] although very difficult to detect. Other authors reported only the formation of Cu_2O and CuO with the annealing temperature [20, 28, 80, 88, 143]. One of the reasons assumed to complicate the detection of this phase is the very small difference of the XRD diffractograms ($\sim 1\%$ expansion in the lattice of Cu_3O_2) comparing to the Cu_2O ones [78], giving rise to some controversy. Another difference claimed by some authors, is its bigger bandgap when compared with Cu_2O [142]. An increase in the number of structural defects on Cu_2O , apparently, facilitates the formation of the Cu_3O_2 .

In this work only the conversion from Cu to Cu_2O and then to CuO was detected,

following these reactions:



The Table 2.5.2 presents some standard thermodynamic properties for copper, copper oxides and oxygen. Applying the Gibbs free energy for each reaction ($\Delta G = \Delta H - T\Delta S$, where ΔH is the enthalpy, T the absolute temperature and ΔS is the entropy), it is possible to predict the behaviour of the copper oxidation with the temperature, assuming a dry atmosphere. It will also allow the representation of each reaction in an Ellingham diagram (shown in Figure 2.11).

Table 2.5.1 – Standard thermodynamic properties of copper, copper oxides and oxygen [144] ($\Delta_f H^\ominus$ and $\Delta_f G^\ominus$ are the standard enthalpy and Gibbs free energy of formation, respectively. $S^\ominus$ is the standard molar entropy)**.

	$\Delta_f H^\ominus$ (kJ mol ⁻¹)	$\Delta_f G^\ominus$ (kJ mol ⁻¹)	$S^\ominus$ (J mol ⁻¹ K ⁻¹)
Cu (s)	0		32.2
Cu ₂ O (s)	-168.6	-146.0	93.1
CuO (s)	-157.3	-129.7	42.6
O ₂ (g)	0		205.2

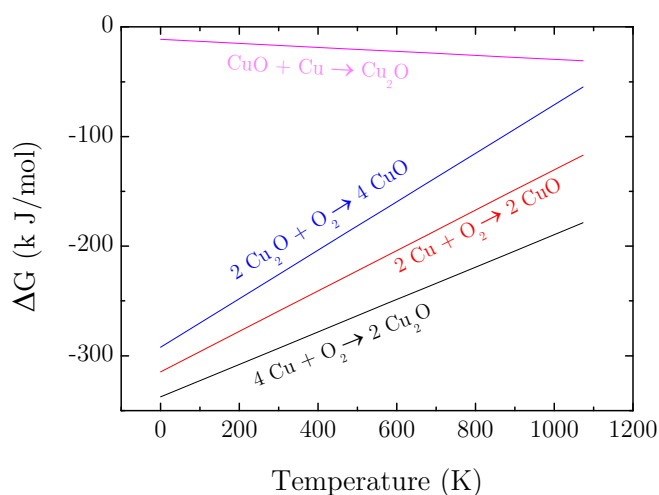


Figure 2.11 – Gibbs free energy versus temperature in the copper oxidation process.

** The symbol $\ominus$ is referred to standard quantities.

From the diagram it is expected that while Cu phase is present, between the CuO and the Cu, is stable a layer of Cu_2O , since $\Delta G < 0$ (around $-16.3 \text{ kJ mol}^{-1}$). The conversion from a fully formed CuO layer to Cu_2O is also expected to happen at higher temperatures than the ones used in this work [145].

2.5.2 NICKEL THERMAL OXIDATION

Oxidation of the nickel has been a topic of great interest during almost a century, due to its application in several technologies. Bunsenite (NiO), as explained before, is one of the most common phases of nickel oxides. Other phases such as Ni_2O_3 and NiO_2 have also been claimed [24, 146]. These investigations, as shown before, concluded that NiO is a metal deficient p-type semiconductor, in which nickel vacancies are the predominating defects.

In the Table 2.5.2 some standard thermodynamic properties for nickel and NiO are presented. It is also possible to plot the behaviour of ΔG in an Ellingham diagram (Figure 2.12) for the reaction (2.7).

Table 2.5.2 – Standard thermodynamic properties of nickel and NiO .

	$\Delta_f H^\ominus (\text{kJ mol}^{-1})$	$\Delta_f G^\ominus (\text{kJ mol}^{-1})$	$S^\ominus (\text{J mol}^{-1} \text{K}^{-1})$
Ni(s)	0		29.9
NiO(s)	-239.701	-211.539	37.991

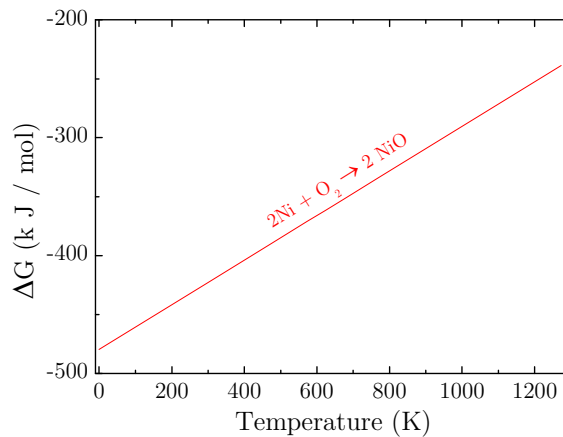


Figure 2.12 – Gibbs free energy versus temperature in nickel oxidation process for the formation of NiO .

The conversion of nickel that occurs in the oxidation process is expected to follow the

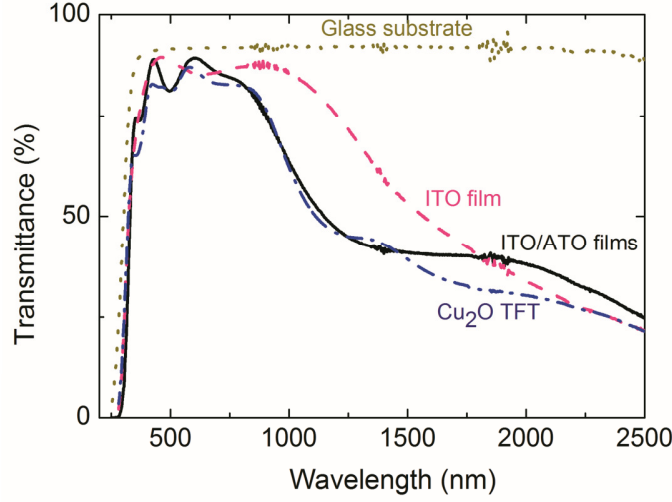
reaction:



Using the Gibbs free energy and the data shown in the Table 2.5.2, it is possible to conclude that the reaction (2.7) is favourable ($\Delta G < 0$) and the NiO phase is formed.

2.6 THIN-FILM TRANSISTORS (TFTs)

Thin-film Transistors (TFTs) are electronic devices, which importance is rising in recent years due to their main use as *On-Off* switches in active matrix backplanes of flat panel displays (FPDs). TFTs are composed by three electrodes: gate, source and drain. The semiconductor comprised between the source and drain electrodes and the insulator (or dielectric). The concept behind this device, is the control of the current between drain and source, by the variation of the voltage applied in the gate contact. This is not a new principle, the first references are attributed to Lilienfeld in the early thirties [147]. Literature devoted to device physics, categorized the TFTs operation in three major eras: the 1960s, the 1980s and relatively recent [148]. These three eras reflect the birth of TFTs, the realization of amorphous silicon TFTs for display applications and the development of polycrystalline silicon TFTs for display and other applications, as well a resurgent interest in TFTs for emergent applications involving large-area, low-cost, printed, flexible, and/or transparent electronics [148]. These last examples, concern inorganic materials are only possible using semiconductor oxides. This was one of the major innovations in the last few years, where the fabrication of TFTs using semiconductor oxides with high optical gap, originate devices with high transparency [149-152]. One example of such high transparent p-type TFT is shown in Figure 2.13. This device was produced in a glass substrate during this work, having a Cu_2O , ITO and ATO as a channel, gate contact and dielectric of the TFT, respectively. In this study, a huge effort was done in the research of such devices, using p-type semiconductor oxides. It is important to underline that the first report of p-type semiconductor oxide TFTs was published only in 2008, when this work was started. Today, this is still a “hot-topic” due to the reasons presented in the Chapter I.

Figure 2.13 – Transmittance of a p-type Cu_2O TFT [29].

In this section some relevant background concerning the structure and physics of these devices will also be provided. Table 2.6.1 shows a summarized state of the art on p-type semiconductor oxide TFTs.

Table 2.6.1 – State of the art on p-type semiconductor oxide TFTs.

Material	Technique	$ V_T $ or V_{ON}	On/Off	$\mu_{FE}(\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1})$	Year
SnO [153]	PLD	4.8	1×10^2	1.3	2008
SnO [154]	RF-Sputtering	30	1×10^2	0.24	2010
SnO [155]	RF-Sputtering	5	1×10^3	1.1	2010
SnO [156]	e-beam	-	1×10^2	0.87	2010
Cu_2O [29]	RF-Sputtering	12	2×10^2	1.2×10^{-3}	2010
CuO [106]	RF-Sputtering	-	1×10^4	0.4	2010
Cu_2O [104, 157]	PLD	0.8	3×10^6	4.3	2011
SnO:Y [36]	EBE	13 - 21	$9 \times 10^1 - 4 \times 10^2$	0.8 – 3.9	2011
Cu_2O [90]	RF-Sputtering	7	1×10^3	7×10^{-3}	2012

2.6.1 DEVICE STRUCTURE AND OPERATION

TFTs are usually categorized in four structures represented in (Figure 2.14). They can be staggered or coplanar as well bottom- gate and top-gate devices.

In a coplanar configuration, the source/drain contacts and the insulator are in the same side of the channel. In this arrangement, the current flows in a single plane, since the

source/drain contacts are in direct contact with the induced channel.

In a staggered configuration, the source/drain contacts and the insulator are in opposite sides of the channel. This means that there is no direct connection to the induced channel. Current must flow vertically to the induced channel before continue horizontally to the drain. In this configuration the contact area is very large, resulting in a minimal contact resistance [148].

In addition to this staggered and coplanar configurations, and as already mentioned, TFTs can also be bottom-gate and top-gate devices. In a top-gate configuration the insulator is located on top of the channel, covering and inherently perform a passivation of the TFT. The gate is located on the top of the insulator. In a bottom-gate configuration, the insulator and gate electrodes are located beneath the channel. The top surface of a TFT in this configuration is exposed to air. Passivation can also be done by coating the top of the surface with a protective layer [148, 158].

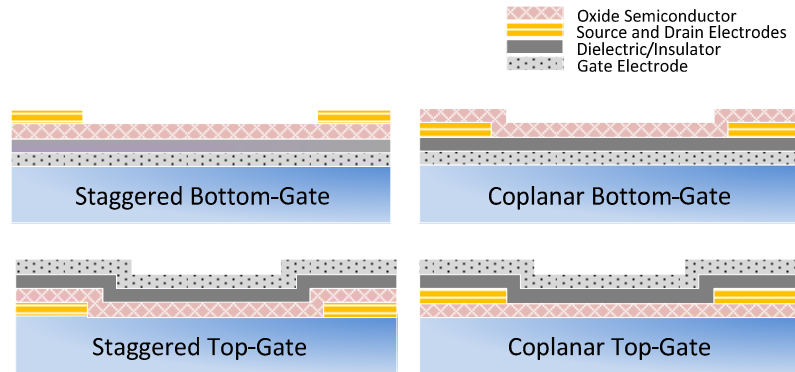


Figure 2.14 – Common TFT structures.

In this work the Staggered Bottom-Gate configuration was used, mainly due to the simplicity of this structure and because the films were deposited in glass substrates with already deposited a gate contact (ITO) and the dielectric (ATO).

It is possible to describe the ideal operation of a TFT, analysing the energy band diagram of the capacitor comprised by the gate electrode, dielectric and semiconductor (Figure 2.15), under the application of different gate voltages (V_G). The energy band diagram showed in Figure 2.15 (A), shows the device at equilibrium (when V_G , V_S , $V_D = 0$

V).

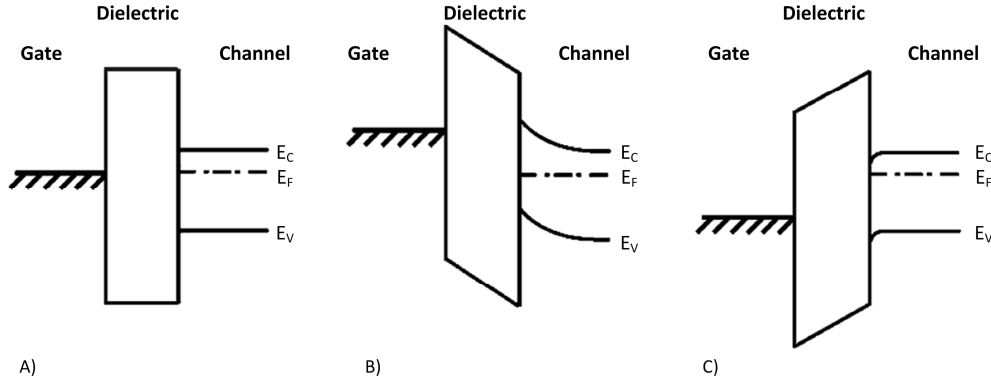


Figure 2.15 – Ideal energy band diagrams (neglecting any passivation layer) as viewed through the gate of an n-channel TFT for several biasing conditions: equilibrium ($V_G, V_S, V_D = 0$ V), (B) depletion ($V_G < 0$ V), and (C) accumulation ($V_G > 0$ V) (Adapted from [148]).

When it is applied a negative voltage to the gate, the negative bias will repel the electrons from the channel/dielectric interface, creating a depletion layer near that region as shown in Figure 2.15 (B). When compared with the equilibrium represented in Figure 2.15 (A), this biasing condition reduces the conductance due to a reduced number of mobile electrons in the channel. Even if a large drain to source voltage (V_{DS}) is used, a very low current flows between the drain and the source. This region corresponds to the *Off*-state of the transistor. Finally, when a positive voltage is applied in the gate electrode, the positive bias will attract mobile electrons, forming an accumulation region near the dielectric/channel interface. This excess of mobile electrons will lead to an increase in the conductance. As V_{DS} increases from 0 V, the channel is initially modelled as a resistor, and the current increases linearly with increase of V_{DS} . This increase on V_{DS} leads to a decrease of the accumulation near the drain contact, and in a limit situation, the region near the drain eventually begins to deplete. The voltage at which the channel region near the drain is fully depleted of electrons is called V_{DSAT} . This means that the application of $V_{DS} \geq V_{DSAT}$ results in saturated drain current characteristics. This region corresponds to the *On*-state of the transistor.

2.6.2 SQUARE LAW MODEL

Borkan and Weimer published their analysis of the behaviour of a TFT device in 1963, based on Shockley's gradual channel approximation of the junction field-effect transistor [147, 148]. This approximation assumes that the lateral change in the electric field along the channel (x-component) is much less than the change in the electric field perpendicular to the channel (y-component). With this assumption the two-dimensional electric field problem is simplified in two separated one-dimensional problems: the voltage modulation of the carriers along the channel and the drain voltage-induced transport of carriers along the channel. More considerations about this can be found in the review paper of Hong *et al.* [148]

This model can be used to predict the current I_D (often called drain to source current I_{DS}) to the saturation point visible in Figure 2.18 (C) and (D). For a brief explanation, regard Figure 2.16.

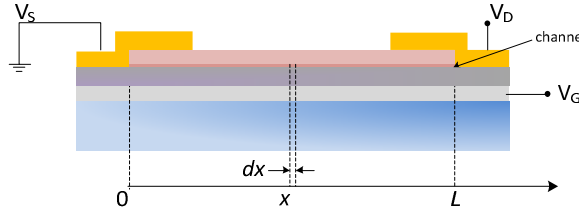


Figure 2.16 –Transversal section of TFT.

Considering the infinitesimal section, dx , from the represented TFT and an arbitrary distance from the source designated as x , the charge per unit of area induced by the gate electrode applied (V_G) is given by,

$$q \cdot n(x) = C(V_G - V(x)) \quad (2.8)$$

where C is the capacitance per unit of area and $V(x)$ is the gate voltage in the point x . The potential $V(x)$ is then dependent on the distance x , varying in a continuous way along the channel from $x = 0$ (being $V(0) = V_S$) to $x = L$ ($V(L) = V_D$). In the case of V_G is maintained constant along L . Considering the initial number of free carriers per unit of surface in the semiconductor n_0 , the charge density in the channel can be represented as [147],

$$q \cdot n(x) = n_0 \cdot q + C \cdot (V_G - V(x)) = C(-V_T + V_G - V_x) \quad (2.9)$$

where $V_T = n_0 \cdot q / C$ is the *threshold voltage*, correspondent to limit V_G necessary to the onset of conduction. The current I_d can be expressed by,

$$I_D = w \cdot \mu \cdot [-V_T + V_G - V_x] \frac{dV_x}{dx} \quad (2.10)$$

where V_x is a simplified representation of $V(x)$, w is the width of the channel, μ is the mobility (assumed to be constant along the channel) and dV_x is the potential difference in the infinitesimal section dx . Proceeding with the separation of variables dependent of x and V_x the equation (2.10) takes the form:

$$I_D \int_0^L dx = Cw\mu \int_0^{V_D} [-V_T + V_G - V_x] dV_x \quad (2.11)$$

$$I_D = \frac{C \cdot w \cdot \mu}{L} \left[(-V_T + V_G)V_D - \frac{V_D^2}{2} \right] \quad (2.12)$$

This equation has validity for $V_D \in [0, V_G - V_T]$, with $V_G > V_{ON}$, known as pre-pinch-off regime (or triode). Is not applicable in the cut-off region (when $V_G < V_T$) or in the saturation also known as post-pinch-off region ($V_D > V_G - V_T$). Saturation is defined to occur when $V_D = V_G - V_T = V_{DSAT}$. Is possible to estimate the maximum of I_D (I_{DSAT}) that corresponds to the saturation, differentiating (2.12) with respect to V_D ,

$$\frac{dI_D}{dV_D} = 0 \rightarrow V_D = V_G - V_T \quad (2.13)$$

and inserting this result in the equation (2.12):

$$I_{DSAT} = \frac{Cw\mu}{L} \frac{(V_G - V_T)^2}{2} \quad (2.14)$$

For higher values of V_D , ($V_D > V_G - V_T$), as already said, the model is not applicable and I_D is assumed to be constant and equal to I_{DSAT} with V_D .

It is often observed in some literature the definition of another region for values of $V_D \ll V_G - V_T$, for $V_G > V_T$. In this region V_G is enough to form the channel and the current I_D (after the formation of the channel) is then proportional to the voltage applied in the drain (V_D) (resistor behaviour). Using $V_D \ll V_G - V_T$ in the equation (2.12), is possible to determine an estimation of the value for I_D for the linear region:

$$I_D \approx \frac{C \cdot w \cdot \mu}{L} [(-V_T + V_G)V_D] \quad (2.15)$$

This result does not bring any relevant information, is just a simplification of (2.12) for a

particular case.

Other considerations can be made about the value of V_T :

	n-type TFT	p-type TFT
Enhancement mode	$V_T > 0$, $I_D \approx 0$ until $V_G > V_T$	$V_T < 0$, $I_D \approx 0$ until $V_G < V_T$
Depletion mode	$V_T < 0$, $I_D \approx 0$ if $V_G = -V_T$	$V_T > 0$, $I_D \approx 0$ if $V_G = V_T$

A summary of the square-law model is presented in the Table 2.6.2. It is often to represent V_D , V_G , I_D and I_G having the source electrode grounded (V_S), but these notations have the same meaning as V_{GS} , V_{DS} , I_{GS} and I_{DS} . This will be the designation used throughout this dissertation.

Table 2.6.2 – Summary of the square-law model

Regime of operation	Equation	Constrains
Cut-off	$I_D = 0$	$V_G < V_T$
Linear regime	$I_D \approx \frac{C \cdot w \cdot \mu}{L} [(-V_T + V_G)V_D]$	$V_D \ll V_G - V_T$
Pre-pinch-off /Triode	$I_D = \frac{C \cdot w \cdot \mu}{L} \left[(V_G - V_T)V_D - \frac{V_D^2}{2} \right]$	$V_G \geq V_T$ $V_D \leq V_{DSAT}$
Pinch-off	$I_{DSAT} = \frac{Cw\mu}{L} \frac{(V_G - V_T)^2}{2}$	$V_G \geq V_T$
		$V_D = V_{DSAT}$
Post-pinch-off/Saturation		$V_G \geq V_T$ $V_D > V_{DSAT}$

In this ideal model, that neglects the effect of traps and of diffusion current, the V_T can be replaced by the turn-on voltage (V_{ON}). As visible in the inset of the Figure 2.17, $V_T = V_{ON}$. In a more general overview, V_T and V_{ON} can have two main interpretations concerning the quantification on the onset of drain current conduction. Although, V_{ON} has a more concise physical interpretation.

Differences in these two parameters could be observed for a real device in Figure 2.18 which is shown two transfer and output curves for a n-type TFT based on ZnO (adapted from [151]). In the pictures is observed a real modulation of the current by a application of a voltage V_{GS} . As shown in figure, V_T can be extrapolated by a simple linear fit of an $I_{DS} - V_{GS}$ transfer curve. In the other hand in a log scale, a fit of $\log(I_{DS}) - V_{GS}$ near the subthreshold

region gives a lower value: V_{ON} .

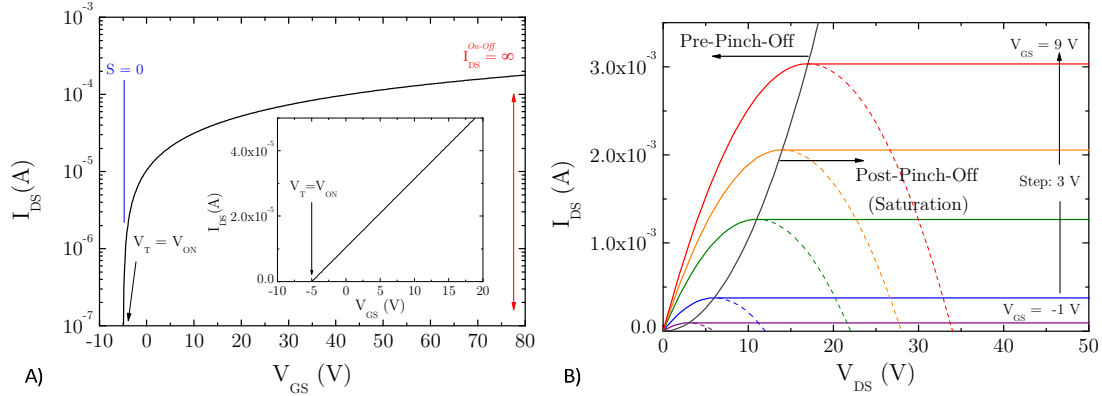


Figure 2.17 – Ideal square law model simulations for the transfer curve $\text{Log}(I_{DS}) - V_{GS}$ A) and output curve $I_{DS} - V_{DS}$ B) for a n-type channel, depletion mode TFT using the. The dark curve identifies the pinch-off I_{DSAT} current. (Square-law model parameters: $V_{ON} = -5$ V, $C = 70$ nF / cm^2 , $\mu = 30$ $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and $W/L = 10/1$.)

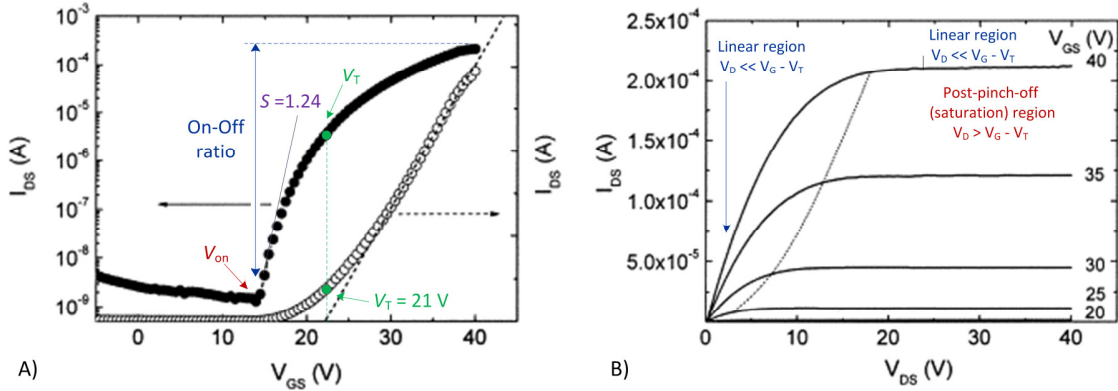


Figure 2.18 – Transfer (A and C) and output curves (B and D) of an n-type (A and B) and p-type (C and D) transistor.

As observed in Figure 2.18, V_{ON} is a more precise parameter to quantify the drain current onset than V_T , being proposed as the preferred drain onset parameter to characterize TFTs. The concept of threshold voltage, as explained by Hoffman [159], contains a certain amount of ambiguity (also shown before) and becomes quite ill-defined for thin-film transistors in general. This ambiguity rises from the fundamental definition of V_T as a model parameter in the drain current equation or as phenomenological parameter used to characterize the gate voltage for which the initial TFT turn-on is observed. In the other hand, V_{ON} is simply identified as the gate voltage at which the increase on I_D begins in the

transfer curve (Figure 2.18 (A)). The disadvantage of using V_{ON} is that it requires a low leakage current in the *Off* region, since a high I_G can obscure the real value of V_{ON} [159]. Since V_{ON} characterizes the gate voltage directly to fully “turn-off” the transistor in a switching application, is also preferable than V_T as a practical device performance metric. One of the physical reasons that could explain the differences between V_{ON} and V_T are explained using the interface traps model.

2.7 BULK AND INTERFACE TRAPS

Traps are present everywhere in the semiconductor affecting the TFT operation, with consequences to its characteristic parameters [160]. However, the traps that are located in the insulator-semiconductor interface played the major role. Interface traps are formed because of unsatisfied dangling bonds, impurities, and other defects at the interface [158]. Considering acceptor-like and donor-like traps, with ionization energies E_{TA} and E_{TD} , respectively, present in the bulk semiconductor (Figure 2.19.). The following considerations can be done:

Donor-like trap (with ionization energy close to the conduction band minimum, E_C):

1. If the Fermi level (E_F) is located above E_{TD} ($E_F > E_{TD}$) the trap is filled with an electron, and will be electronically neutral.
2. If E_F is located below E_{TD} ($E_F < E_{TD}$) the trap will lose an electron being ionized (positively charged).

Acceptor-like trap (with ionization energy close the valence maximum, E_V):

1. If E_F is located below E_{TA} ($E_F < E_{TD}$) this trap is neutral, since it is not filled with an electron.
2. If E_F is above E_{TA} ($E_F > E_{TD}$) the trap will be negatively charged since it is filled with an electron.

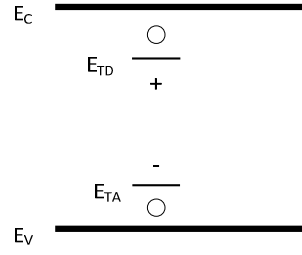


Figure 2.19 – Energy band diagram of a bulk-semiconductor with a donor-like trap (with ionization energy E_{TD}) and an acceptor-like trap (with ionization energy E_{TA}).

Table 2.7.1 – Charge of the donor-like and acceptor-like traps, with the location of the Fermi level.

	Donor-like trap	Acceptor-like trap
$E_F > E_{TD}$	0	–
$E_F < E_{TD}$	+	0

The Figure 2.20 illustrates the acceptor or the donor-like nature of the interface traps, considering the charge neutrality level (E_N).

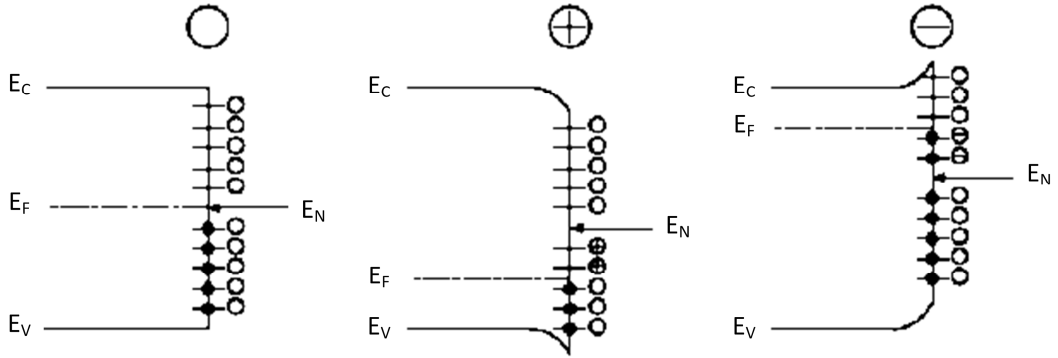


Figure 2.20 – Energy band diagram considering interface states and the resultant effect of the modulation of the Fermi level position (E_F), with respect to the charge neutrality level, E_N (Adapted from [161]).

Considering interface states and the resultant effect of the modulation of the Fermi level position (E_F), with respect to the charge neutrality level, E_N :

1. If $E_F = E_N$, the net charge at the insulator-semiconductor interface is zero → “flat band condition”.
2. If $E_F < E_N$, a net positive charge is present due to ionized donors at the interface → donor-like interface^{††}.

^{††} This net positive interface charge is balanced by negative space charge in the semiconductor, originating a negative

3. If $E_F > E_N$, a net negative charge is present at the interface $\rightarrow$ acceptor-like interface^{‡‡}.

2.8 DISCRETE TRAP MODEL

The use of the discrete trap model is a simplification of the interface-traps problem. This model elucidates the primary device physics consequences of carrier trapping, previously introduced by Sze [158]. A discrete trap is assumed to interact only with conduction band electrons (not with holes in the valence band), having ionization energy (E_T), a capture cross section^{§§} (σ_n), and density (N_T). Being n_t the density of filled traps (equal to the density of trapped electrons) is possible to define a density of empty traps as ($N_T - n_t$). Note that in this case and using a parallelism to the ideal case (without traps) the density of carriers (n_0) is the sum of the density of filled traps or trapped electrons (n_t) and the density of free electrons presented in the conduction (n_c).

Using this model reviewed in a simple way by Hong *et al.* [148], it is possible to correlate the distribution of the total charge induced in the channel by the application of V_{GS} , into both conduction band and trap states:

$$q (n_c + n_t) = C[V_{GS} - V(x) - V_{ON}] \quad (2.16)$$

V_{ON} is defined as:

$$V_{ON} = -\frac{q}{C}(n_{c0} + n_{t0}) \quad (2.17)$$

where n_{c0} and n_{t0} are initial zero-bias densities of free conduction band electrons and trapped electrons, respectively.

V_T can also be quantitatively defined in this context, being equivalent to the gate voltage required to fill all the traps.

$$V_T = \frac{q}{C}(N_T - n_{t0}) + \frac{q}{C}(n_1 - n_{c0}) = V_{TRAP} + V_{ELECT} \quad (2.18)$$

where V_{TRAP} is associated to the gate voltage needed to fill the empty traps ($N_T - n_{t0}$) and

curvature of the energy bands.

^{‡‡} This net negative charge is balanced by positive charge in the semiconductor, as is evident from the positive curvature of the energy bands.

^{§§} Described as the effective area of a trap. It is related to the capability of the trap to capture free charge carrier.

V_{ELECT} is related to the change in conduction band density with the applied voltage. In the equation is also visible a parameter n_1 that is the conduction band electron density when $E_F = E_T$.

With this brief exposition, it was possible to illustrate the influence of the trap density at the interface, but also within the semiconductor, used to explain the differences between V_{ON} and the V_T .

2.9 TFT CHARACTERISTIC PARAMETERS

In the characterization of TFTs it is very common to see a parameter typically referred to as the subthreshold swing (S) that characterizes the effectiveness of the gate voltage in reducing the drain current to zero. This parameter was already presented in Figure 2.17 (for the ideal square law model) and in Figure 2.18 (for a real device). S is defined as:

$$S = \frac{\partial V_{GS}}{\partial (\log I_{DS})} \quad (2.19)$$

A small value of S is desirable, since corresponds to a very sharp transition from the *Off* to the *On* stage (see the Figure 2.17 (A), with $S = 0$). The On-Off ratio, often represented as $I_{DS}^{\text{on-off}}$, is also another very important parameter in the characterization of TFTs. A large $I_{DS}^{\text{on-off}}$ ratio corresponds to a more effective switch, being desirable.

Considering what was expressed above, the mobility (μ) of the TFT channel was regarded as a constant parameter, what should be true in an ideal TFT. Although, in reality there are various reasons why μ may not be constant (e.g., scattering, electron trapping, interface roughness) [148]. The mobility of a real TFT usually increases with V_{GS} above the threshold voltage, and then either saturates or peaks and decreases. There are few manners to determine this parameter, based on its dependence on V_G (V_{GS}) and V_D (V_{DS}): the effective mobility (μ_{EFF}), the field effect mobility (μ_{FE}) and the saturation mobility (μ_{SAT}). V_T was used in the classical formulation of μ_{EFF} , μ_{FE} and μ_{SAT} .

2.9.1 MOBILITY ESTIMATED IN THE LINEAR REGION (μ_{EFF} AND μ_{FE})

The effective mobility (μ_{EFF}) is calculated differentiating the equation (2.15) with respect to V_D ,

$$\left. \frac{\partial I_D}{\partial V_D} \right|_{V_G} = \frac{Cw\mu}{L} (V_G - V_T) = g_d \quad (2.20)$$

$$\Rightarrow \mu_{\text{EFF}} = \frac{L}{Cw} \frac{g_d}{(V_G - V_T)} \quad (2.21)$$

where g_d is the conductance. This methodology requires the estimation of V_T that is associated to some error. In the other hand the plot of $g_d(V_G)$ can be also used to estimate V_T .

The Field effect mobility (μ_{FE}), also determined in the linear region, is obtained by differentiation (2.15) with respect to V_G :

$$g_m = \left. \frac{\partial I_D}{\partial V_G} \right|_{V_D} = \frac{Cw\mu}{L} V_D \quad (2.22)$$

$$\Rightarrow \mu_{\text{FE}} = \frac{L}{Cw} \frac{g_m}{V_D} \quad (2.23)$$

where g_m is the transconductance. This is the most common “mobility” used in TFTs characterization and does not require the determination of V_T .

2.9.2 MOBILITY ESTIMATED IN THE SATURATION (μ_{SAT})

The saturation mobility (μ_{SAT}) is determined in the saturation region, differentiating the square root of I_D with respect to V_G :

$$\mu_{\text{SAT}} = \frac{2L}{Cw} \left(\frac{d\sqrt{I_D}}{dV_G} \right)^2 \quad (2.24)$$

In this region it is also possible to determine V_T by extrapolation of $I_D^{1/2}$ with V_G :

$$I_D^{1/2} = \sqrt{\frac{Cw\mu}{4L}} (V_G - V_T) \quad (2.25)$$

This is the more common method to determine V_T since is not very sensitive to the contact resistance effects.

2.9.3 AVERAGE AND INCREMENTAL MOBILITY

Besides the methodologies presented before for the estimation of the channel mobility, others are taking relevance, designated by average (μ_{AVG}) and incremental (μ_{INC}) mobility proposed by Hoffman [159]. The growing preferences on these two new methodologies are based on the precise physical interpretation, what does not happen with the previous methodologies.

The average mobility (μ_{AVG}) is similar to the expression used to determine μ_{EFF} , except V_T that is represented by V_{ON} , and corresponds to the average mobility of the total carrier concentration in the channel,

$$\mu_{\text{AVG}} = \frac{L}{Cw} \frac{g_d}{(V_G - V_{\text{ON}})} \quad (2.26)$$

The incremental mobility, (μ_{INC}), corresponds to the mobility of the carriers that are incrementally added to the channel with the increase of magnitude of the gate voltage:

$$\mu_{\text{INC}} = \frac{L}{Cw} \frac{dg_d}{dV_{\text{GS}}} \quad (2.27)$$

This physical interpretation assumes that the mobility of carriers already present in the channel does not change.

2.10 METAL-SEMICONDUCTOR CONTACTS

Another concern in the device production is the nature of the contacts. In the case of TFTs application and regarding the bias conditions in the device, it is desirable to have an Ohmic contact between the contacts drain/source and the semiconductor, to ensure (ideally) a zero contact resistance. However, in real applications this is not always true. If the contact resistance is small, most of the applied drain-source voltage drops across the channel as desired. Although an improper selection of the contacts can result in a Schottky barrier. This type of contact has high resistance that compromises the TFT performance.

In this section a brief overview of the ideal and non-ideal theories will be presented in order to describe the metal-semiconductor contacts.

2.10.1 IDEAL THEORY

In the ideal metal-semiconductor theory, a metal-semiconductor junction may form either an Ohmic contact or a Schottky barrier, depending on the value of the metal work function (Φ_M) relatively to the semiconductor work function (Φ_S) (Figure 2.21 (A) and (C)) [158, 162].

For a p-type semiconductor, if $\Phi_M > \Phi_S$ the contact will be Ohmic (Figure 2.21 (B)) and holes will be able to flow freely either under a forward or reverse bias (positive bias to the p-type semiconductor or positive bias to the metal, respectively). In the other hand, if $\Phi_M < \Phi_S$ a Schottky barrier will be formed in the metal-semiconductor contact as shown Figure 2.21 (D). With this contact, holes flow from the semiconductor to the metal, lowering their energies. This is the most thermodynamically favourable process. As the holes transfer from the semiconductor to the metal, a barrier V_{Bi} prevents further hole migration to the semiconductor. The Schottky barrier height for holes (Φ_{Bp}) will be given by:

$$\Phi_{Bp} = \frac{E_G}{q} - (\Phi_M - \chi) \quad (2.28)$$

where E_G is the semiconductor bandgap and χ is the semiconductor electron affinity. For a Schottky barrier, if a forward bias is applied (connecting the metal to a negative terminal) V_{Bi} decreases and the holes are able to flow from the semiconductor to the metal. However, if a reverse bias is applied (connecting the metal to a positive terminal) V_{Bi} increases preventing the hole flow.

The contact between a metal and a p-type semiconductor will be Ohmic if the $V_{Bi} = 0$. Substituting this in the equation (2.28), is possible to say that if $\Phi_M > \frac{E_G}{q} + \chi$ the contact will be ohmic, else if $\Phi_M < \frac{E_G}{q} + \chi$ it will be a Schottky contact.

In an ideal contact, the charge balance across the metal-semiconductor interface can be expressed as:

$$Q_M + Q_{SC} = 0 \quad (2.29)$$

where Q_M and Q_{SC} are the metal charge per unit area and the semiconductor space charge region per unit area, respectively.

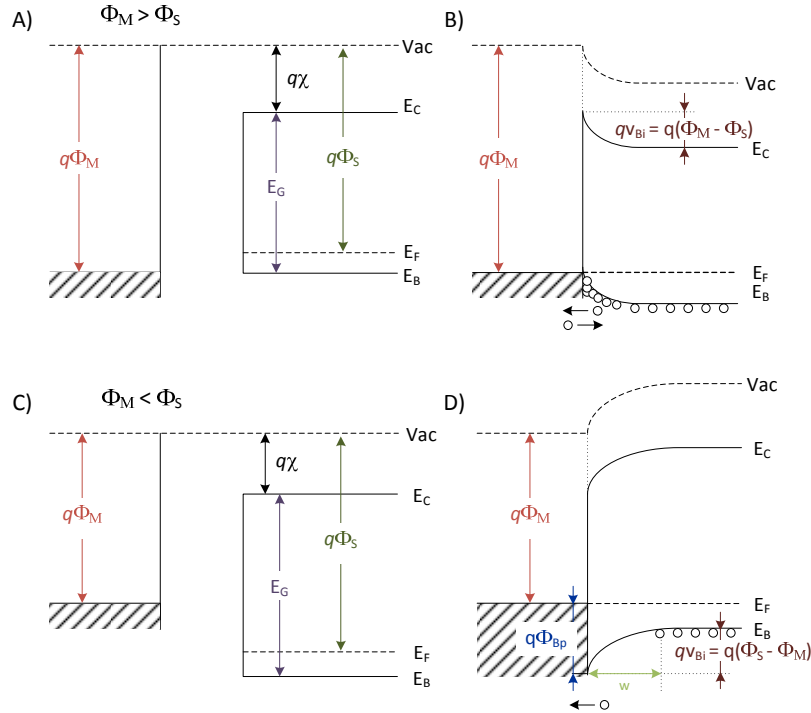


Figure 2.21 – Energy band diagram for a metal-semiconductor contact in which the semiconductor is p-type: before contact is formed (A and C); after contact formed (B and D).

The type of the contacts considering the work functions of both metal and semiconductor is summarized in the Table 2.10.1.

Table 2.10.1 – Summary of the type of contacts determined by Φ_M and Φ_S relationship (ideal theory).

	n-type	p-type
$\Phi_M > \Phi_S$	Rectifying	Ohmic
$\Phi_M < \Phi_S$	Ohmic	Rectifying

2.10.2 NON-IDEAL THEORY

The ideal metal-semiconductor contact theory assumes that the metal and the semiconductor are in intimate contact on atomic scale, the barrier height is only dependent on the metal work function and semiconductor electron affinity, ignoring any chemical reactions occurring at the interface. This model explains all the experimental results in a satisfactory way. However, the observed discrepancies to the experimental results were addressed by Bardeen [163] with the introduction of interface traps concept (historically

called surface or interface states). As already explained before, these traps are localized electronic states within the bandgap, they are chargeable, and they can be acceptor- or donor-like [158] (see section 4.2.1).

Regardless of the metal-semiconductor work function alignment, if there is a large density of interface traps, the Fermi level at the semiconductor surface may be pinned at a given energy level in the bandgap. For a non-ideal contact, the charge balance for the metal-semiconductor contact yields,

$$Q_M + Q_{ss} + Q_{sc} = 0 \quad (2.30)$$

where Q_{ss} is the interface traps charge per unit area. This pinning of the Fermi-level is present in some degree in metal-semiconductors contacts. To determine the degree of pinning in a barrier, a pinning parameter (S^*) can be defined by [164-166]:

$$S^* = \frac{1}{1 + 0.1(\epsilon_\infty - 1)^2} \quad (2.31)$$

where ϵ_∞ is the high-frequency dielectric constant of the semiconductor. Using S^* the barrier height for holes (Φ_{Bp}) can be calculated in a more accurate way by [164, 165]:

$$\Phi_{Bp} = (E_G + \chi - \Phi_{CNL}) - S^*(\Phi_M - \Phi_{CNL}) \quad (2.32)$$

where the Φ_{CNL} is the charge neutrality level of the interface states measured from the vacuum level. There are two limit cases of interest. The first for $S^* = 0$, for a barrier height independent of the choice of the metal, defined as:

$$\Phi_{Bp} = (E_G + \chi - \Phi_{CNL}) \quad (2.33)$$

This result is known as the Fermi-level pinning limit. The other limit of interest is found for $S^* = 1$, reducing the equation (2.32) to,

$$\Phi_{Bp} = (E_G + \chi - \Phi_M) \quad (2.34)$$

This is the same result as given by the ideal theory.

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Chapter III

Deposition and characterization techniques

CONTENTS

In this chapter some considerations about characterization techniques and the experimental procedure adopted in this dissertation will be presented.

- 3 Deposition and characterization techniques
 - 3.1 Deposition techniques
 - 3.2 Supplementary techniques
 - 3.3 Characterization techniques
 - 3.4 Surface and morphologic characterization
 - 3.5 Semiconductor parameter analyzer (TFTs)
 - 3.6 References

3 DEPOSITION AND CHARACTERIZATION TECHNIQUES

Regarding the productions of thin-films, two main techniques were used: radio frequency magnetron sputtering and electron beam thermal evaporation, simply called RF sputtering and e-beam, respectively. These techniques were preponderant in the production of all the semiconductor oxides: Cu_2O , CuO , NiO , and others*. They were also used in the deposition of electrodes, mainly based on nickel/gold (by e-beam) and TCOs like IZO (by RF sputtering). Conventional patterning techniques will be briefly discussed, as they were required for the production of different structures for thin-films characterization (Hall effect and DC dark conductivity in temperature) and a fundamental technique in TFTs production.

In the study of both materials and devices, a broad range of characterization techniques were used and will be described in this chapter.

3.1 DEPOSITION TECHNIQUES

Today a variety of deposition techniques are available for the production of thin-films, in research environments and also in several industry segments. Thin-films, are classified as thin material layers ranging from few nanometres to several micrometres thickness [1], are available almost everywhere, from simple optical coatings in mirrors to complex thin-film multilayers in electronic devices. Despite of this more or less ambiguous classification of “thin-films”, some of the techniques that allow their production are also used for thicker films.

Any thin-film deposition process, in general, involves three main steps: production of the appropriate atomic, molecular or ionic species; transport of these species through a medium to the substrate; form a solid deposit through condensation on the substrate, either directly or via a chemical and/or electrochemical reaction [1]. The most important deposition technologies can be divided in four categories [2]:

1. Evaporation methods (vacuum evaporation);
2. Glow-discharge processes (sputtering and plasma processes);
3. Gas-phase chemical processes (chemical vapour deposition and thermal forming

* Other oxides were studied such as CuAlO_2 , $\text{CuO}:\text{ZnO}$ and $\text{CuO}:\text{SnO}$. Although the promising preliminary results achieved they will not be presented here.

processes);

4. Liquid phase chemical techniques (electro processes and mechanical techniques);

In this thesis two main methods were used: evaporation (such as resistive and electron beam assisted thermal evaporation) and glow-discharge processes (such as RF magnetron sputtering).

3.1.1 THERMAL EVAPORATION

In the development of this work two techniques of thermal evaporation were used: electron-beam and resistive. Both techniques use different processes to achieve the same effect, the evaporation of the material by the increase of its temperature (Figure 3.1). E-beam evaporation was the most used technique and therefore, will be described below.

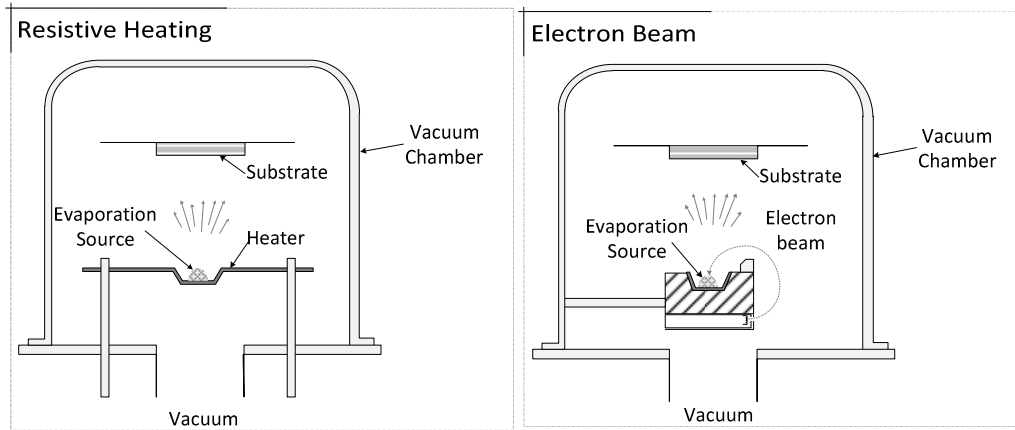


Figure 3.1 – Schematic of thermal evaporation processes (resistive heating and electron beam).

3.1.1.1 E-BEAM THERMAL EVAPORATION

E-beam thermal evaporation is a technique that uses the heat generated by an electron beam of high energy (up to 15 keV) that collides to the desirable material held in a graphite crucible [3]. The electron beam is generated by thermionic emission (Edison effect) of electrons emitted by an incandescent filament (cathode) usually made from tungsten that are connected to a high current and low voltage power supply, which is controlled by the user. The deposition usually occurs at low pressures, commonly below 1×10^{-2} Pa, to increase the medium path of the evaporated species, ensuring that they reach the substrate. The vacuum also prevents contaminations and non-wanted reactions that can occur with the gas contained in the chamber [4].

The emitted electrons are accelerated to the anode by a potential difference (usually in the order of 10 – 30 kV), and deflected to the crucible by a magnetic field. One of the main advantages of this technique is the possibility of focusing the e-beam in small areas, tuning precisely the growth-rate of the film avoiding waste of material and making possible to deposit a wide range of materials with different fusion points. This high focusing feature allows a high control of the deposition process, limiting the risk of contamination. The usual way to perform the monitoring of the deposition rate is through the use of a quartz crystal, which is covered by the evaporating material during the deposition. The resonant frequency of the crystal shifts in proportion to the film thickness. Monitoring the resonant frequency is then possible to estimate a deposition rate with accuracy better than $1 \text{ \AA s}^{-1}$ [3].

In some e-beam systems it is possible to have a dual electron beam to co-evaporate different materials. It is also possible the introduction of reactive gases into the chamber during the evaporation process, allowing (for instance) the production of oxide thin-films from metal sources. Deposition of compounds is possible, but not reliable, since each component has a different vapour pressure, therefore different deposition rates, being difficult to keep the stoichiometry of the source. One of the drawbacks of electron-beam evaporation is associated to high beam acceleration voltages (with energy above 5 - 10 keV) that can cause some radiation damage from energetic electrons and X-rays to the substrates [3, 4].

The applied current can be AC or DC, although a more stable beam is achieved with a DC current, which is usually the preferable condition to apply in e-beam evaporator systems of high power. The thermionic emission of the electrons from the tungsten filament is described by the Richardson equation [5]:

$$J = AT^2 e^{-B/T} \quad (3.1)$$

where J is the current density emitted by the filament, A is the Richardson constant and T is the filament absolute temperature. B is a quantity that characterizes the electron work-function (φ) that is defined by:

$$B = \frac{e\varphi}{k_B} \quad (3.2)$$

where e is the electron charge and k_B is the Boltzmann constant ($1.3806 \times 10^{-23} \text{ J K}^{-1}$). The A and B are quantities are strongly dependent of the material used in the filament.

The e-beam evaporation system used for this study of thermal oxidation of copper and also

to deposit Ni/Au contacts is shown in Figure 3.2. This system has a rotative holder to fix 4 crucibles water cooled.

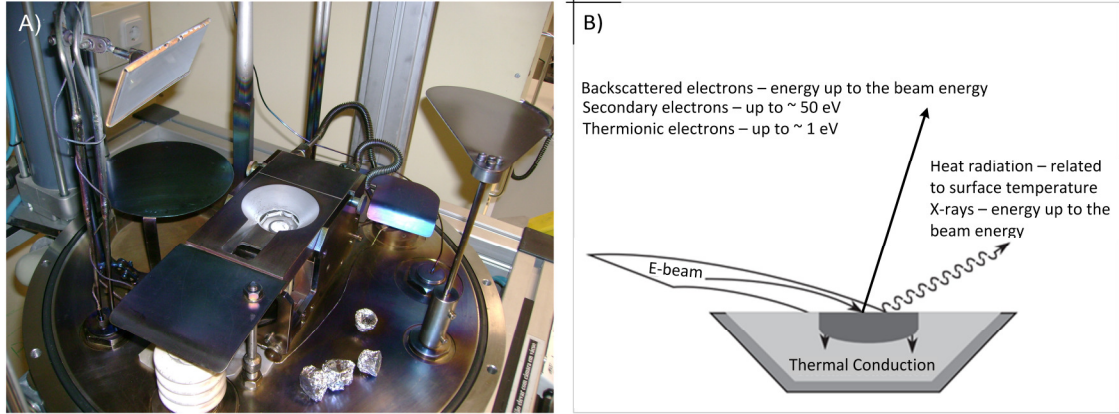


Figure 3.2 – A) E-beam evaporation system used in this work; B) Schematic drawing showing the interactions that occur as the electron beam hits the source material (adapted from [4]).

EXPERIMENTAL DETAILS

In the study of the films produced by e-beam evaporation was used glass (Marienfeld from Laboratory Glassware), corning 1737 and silicon substrates of 25×25 mm dimensions. For thin-film transistors was used standard substrates coated with tin-doped indium oxide[†] (ITO) and alumina–titania nanolaminates[‡] (ATO) produced by Planar Systems, Inc. [6-8]. The materials to deposit (Cu, Ni and Au) were used in the form of pellets and the distance from the target to the substrate fixed around 25 cm. Table 3.1 summarizes the parameters used in the deposition of thin-films of copper, nickel and gold.

Table 3.1 – Deposition parameters used in the e-beam evaporation system. The parameters represented by ρ_d and Z are the material density and the acoustic impedance, respectively. P_B is the base pressure, T_0 the initial temperature, I_F is the filament current and R the growth rate.

Material	Cu	Ni	Au
P_B (Pa)		$10^{-4} - 10^{-3}$	
T_0 (°C)		17 - 22	
ρ_d (g cm ⁻³)	8.93	8.91	19.3
Z ($\times 10^5$ g cm ⁻² s ⁻¹)	20.21	26.68	23.18
I_F (A)	0.05 – 0.11	0.05 – 0.07	0.045 – 0.07
R (Å s ⁻¹)	1 – 5	1 – 2	2 – 4
Purity (%)	99.999	99.997	99.999

[†] ITO is compound based typically of 90% of indium (III) oxide (In₂O₃) and 10% of tin (IV) oxide (SnO₂), by weight.

[‡] The Alumina-titania nanolaminates are an engineered dielectric composed of Al₂O₃ and TiO₂ alternative coatings.

3.1.2 RF MAGNETRON SPUTTERING

The RF magnetron sputtering (for simplicity called RF sputtering) was one of the main techniques used in this work. Alongside with two different systems of RF sputtering were used in the research work. In the first part (Part I) of the study a home-made system was used. In the second part (Part II) of this thesis a new and more efficient sputtering system from AJA International, Inc, was available allowing several depositions in short time (among other things). For this reason was needed for the conclusion of this thesis, a new optimization of the deposition conditions found previously.

Sputtering is one of the most well-known and used techniques for the deposition of thin-films that use the complex plasma physics in a very practical and engineered way. However, the concept employed in the deposition of a material is simple: an inert gas is introduced in the chamber, typically argon due its low cost and high cross section [3], and an external RF signal is used to achieve the ionization of the gaseous species. This high energetic ionized species will be accelerated, colliding with the target and injecting atoms/molecules that will reach the substrate being deposited there. In the sequence of this bombardment, electrons will be emitted and then accelerated by the electric field in a region often called cathode dark space (region near the cathode where there is no luminescence) [4, 9, 10]. In their trajectory to the negative *glow* electrons will collide with the inert gas (in this case argon) originating new ions that will be accelerated to the target, originating the injection of new atoms/molecules and the emission of new electrons (secondary electrons). The new injected atoms/molecules will reach the substrate being deposited there. Secondary electrons will be accelerated colliding with the inert gas originating a new cycle (Figure 3.3) [9, 10]. This explanation is valid for other gas mixtures, influencing their physical properties, being used depending on the application. A DC signal can also be used instead of a RF, although these systems are restricted to the usage of conductive targets (mostly metals), because insulating materials are not able to supply the target surface with sufficient secondary electrons to maintain the glow discharge[1]. Insulating targets, in the other hand, are not a problem with RF sputtering. The use of a magnetron will increase the sputtering's efficiency, confining the electron movement to the region immediately above the target surface without changing significantly the ions movement. This confinement reduces the

bombardment of the target by electrons, increasing the probability of ionization of neutral gaseous molecules and increasing the growth rate [10]. A disadvantage of the use of a magnetron is the poor target utilization, since sputtering will occur with more probability in the path defined by the magnetic field.

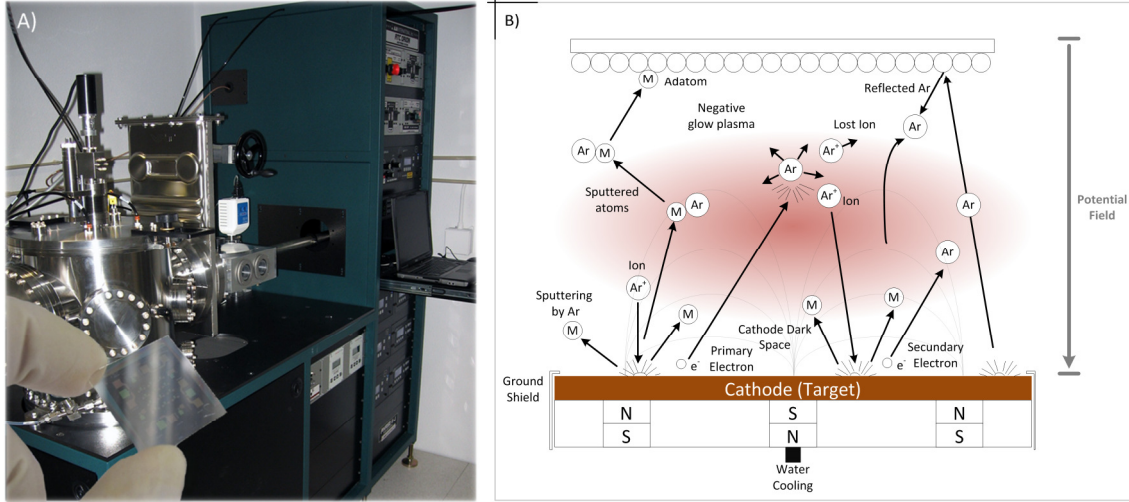


Figure 3.3 – A) RF Magnetron Sputtering (from AJA International, Inc.) with a glass substrate containing transparent TFTs; B) Schematic of the interactions in a magnetron sputtering process.

Ferromagnetic materials will affect the magnetic field presented in the chamber, affecting the plasma. This happened with nickel (in this thesis) and to avoid this problem a ceramic target of NiO was used.

Sputtering, in comparison with the evaporation techniques, does not depend on the material evaporation temperature, enabling the deposition of alloys and other complex materials, ensuring higher control on the stoichiometry of the deposited films that should be equivalent to the precursor targets. Such attribute is very difficult to achieve with the evaporation technique, since different materials have different evaporation temperatures. Relatively to other thin-film deposition techniques, sputtering has many advantages, allowing low substrate temperatures, good adhesive strength, good control of the growth ratio and film composition, highly compact films, possibility to deposit a broad range of materials and allowing a good scalability to large areas [1, 3, 11].

The deposition pressure, P_D , plays an important role in the growth-rate of the films, since it influences the plasma density, the mean-free path of the ions and the effectiveness of the deposition. In a general way, growth rate is inversely proportional to the distance between the target and the substrate (d_{TS}) and P_D ,

$$R \propto \frac{1}{d_{TS}P_D} \quad (3.3)$$

High P_D is suitable to maintain the plasma, and small P_D to maintain a good deposition rate and reduce random scattering. However, if P_D is small enough, an etching process can take place.

The mean-free path (λ_m) is related to the deposition pressure by the equation [12-14]:

$$\lambda_m = \frac{1}{\sqrt{2}} \frac{k_B T}{\sigma^{cs} P} \quad (3.4)$$

where k_B is the Boltzmann constant, T the absolute temperature, $\sigma^{cs} = \pi d^2$ is the cross section[§] and P is the gas pressure (in Pa units). For example using Ar with cross section of $\sim 0.36 \text{ nm}^2$, it is possible to understand the impact of the pressure in the mean-free path of atoms. Figure 3.4 represents the variation of λ_m for an oxygen atmosphere.

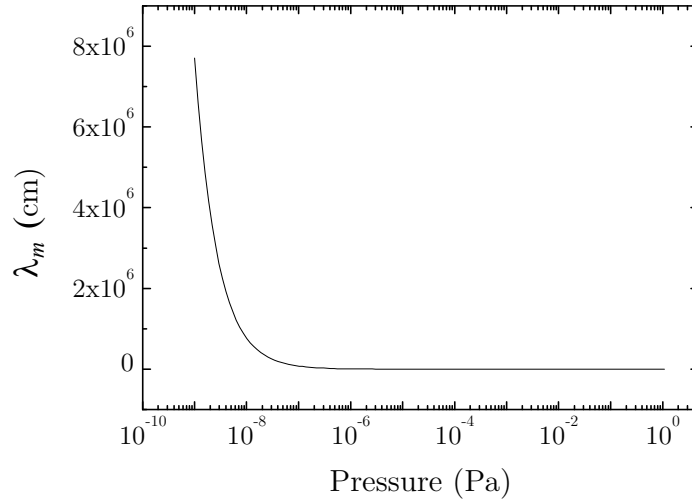


Figure 3.4 – Variation of the free-mean path with the pressure for an oxygen atmosphere.

The growth rate is sensitive to d_{TS} not only due to the mean-free path, but also because of the dispersion of the particles in their travel to the substrate. A large d_{TS} is associated to a small growth rate and a small d_{TS} can originate less uniformity in the film. Equilibrium should be found.

The power is also another important factor in the sputtering parameters settings. There is a direct relation between the power density applied in the target and the growth rate. The atmosphere in the chamber and the temperature of the substrate will either influence the physical properties of the plasma, the growth rate and the physical properties of the film [15].

[§] In the collision of two species of diameter d_1 and d_2 , $d = (d_1 + d_2)/2$.

EXPERIMENTAL DETAILS

During the development of this work, different metallic and ceramic targets were used trying to achieve the ideal conditions to produce p-type semiconductor oxides. Some of the deposition parameters are presented in Table 3.2. The Cu_2O and CuO films were deposited using a 2" diameter metallic Cu target (99.99 % purity). The NiO and IZO^{**} were deposited from a 2" diameter ceramic target (99.99 % purity) of NiO and IZO , respectively.

Table 3.2 – Resumed RF magnetron sputtering parameters used in this work. All the depositions were performed without intentional annealing of the substrate (Cu^1 is related to the first part of the work and Cu^2 to the second part, using RF sputtering). The parameters O_{PP} and O_t are the oxygen ratio percentage in terms of partial pressures and flows, respectively. P_{Ar} , P_{O_2} , are the argon and oxygen partial pressures.

	Cu^1	IZO		Cu^2	NiO
O_{PP} (%)	0 - 100	~ 1	O_t (%)	0 - 100	
P_{Ar} (Pa)	3×10^{-2}	0.2	Ar Flow (sccm)	10 and 19	7 and 20
P_{O_2} (Pa)	3×10^{-3} - 9×10^{-2}	1.5×10^{-3}	O_2 Flow (sccm)	1 - 10	1 - 20
P_{B} (Pa)	3.4×10^{-4}	$\sim 3.4 \times 10^{-4}$	P_{B}	1×10^{-5} - 1×10^{-6}	1×10^{-5} - 1×10^{-6}
P_{D} (Pa)	0.6	0.2	P_{D}	0.6	0.8
d_{TS} (cm)	15	15	d_{TSt}	20	20
Power (W)	50	75	Power (W)	100	200

3.1.3 COMPARISON BETWEEN EVAPORATION AND SPUTTERING

Some major differences between evaporation and sputtering are briefly summarized below [12-14, 16]:

1. The deposition pressure differs noticeably. Evaporation can be done in a wide range of pressures, typically from 10^{-1} to 10^{-8} Pa whereas sputtering requires a relatively high pressure up to 10^4 Pa. In evaporation process, atoms or molecules do not collide with each other, whereas in sputtering the atoms and molecules do collide with each other prior to arrival at the growth surface;
2. The growth surface is not activated in evaporation, whereas the growth surface in sputtering is constantly under highly energetic electron bombardment;
3. The evaporated films are usually formed by large grains, whereas the sputtered films

^{**} Indium Zinc Oxide (In_2O_3 : ZnO of 9:7:10.3 weight percentage).

- are usually more dense, with smaller grains and with better adhesion to the substrates;
4. Evaporation is usually performed from a point source, whereas the sputtering is done from a parallel plate source, producing films more homogeneous in large areas;
 5. Fractionation of multi-component systems is a serious challenge in evaporation, whereas in sputtering the stoichiometry of the target can be maintained in the film;

3.2 SUPPLEMENTARY TECHNIQUES

3.2.1 CLEANING PROCESS OF SUBSTRATES

In this work different substrates were used for the study and characterization of the semiconductor oxides and in the production of devices. To study the electrical, optical, morphological and structural properties, glass of 1 mm thickness and corning were used. Silicon substrates without SiO₂ (removed by etching) were used for FTIR^{††} and RBS analysis. Standard ITO/ATO substrate was used to produce bottom-gate TFTs.

In all the substrates, with exception of Si/SiO₂ substrates, a chemical cleaning process was used in a clean room environment, to ensure the cleanest surface possible. After many small variants was selected the following procedure to clean chemically the substrates (for deposition of the semiconductors).

Chemical Cleaning Process

1. Clean with a detergent solution to remove any oily residues on the glass surface (*Deconex*);
2. Clean with pure water to remove any residues of detergent;
3. Ultrasounds in acetone (~10 minutes);
4. Ultrasounds in isopropyl alcohol (~10 minutes);
5. Clean with pure water / Boil substrates in pure water;
6. Dry with nitrogen;
7. 10 minutes at ~300 °C (for glass substrates);

3.2.2 POST-ANNEALING TREATMENTS

^{††} In FTIR double face polished substrates were used.

Post Annealing treatments were used systematically during this work, to induce dramatic structural changes in the films structure (oxidation), or just to improve the electrical contacts, since the annealing treatment in an oxidative atmosphere can be effective to reduce the contact resistance in the interface of the two materials [17, 18].

The furnace used to perform the annealing treatments was a programmable 21100 Tube Furnace Thermolyne (Barnstead). This furnace allows programming the desirable annealing rate, fixing a number of steps and time in each step. These features allow the systematic repetition, avoiding differences in the process.

The range of temperatures used varied. For the oxidation of metallic Cu the temperature was fixed between 150 and 450 °C. In the case of nickel oxidation temperatures up to 600 °C were used. A post-annealing treatment for thin-film devices was performed from 150 to 200 °C.

A hot plate Heidolph MR Hei-End and an Ambios XP-200 profilometer were used in the study of the oxidation kinetics of metallic films. The film thicknesses were measured before and after several oxidation steps.

3.2.3 SPIN-COATING PROCESS

The spin-coating process is a very common procedure employed routinely in microelectronics to deposit photoresists and specialty polymers. Unlike sputtering or electron-beam evaporation (for instance), spin coating is a very fast technique, uses very simple apparatus (spin coater or spinner), without the need of vacuum.

A typical spin coating is processed in four stages: delivery of solution into the substrate centre, spin-up, spin-off and evaporation (overlaps with all stages) (Figure 3.5). After delivering the liquid to the substrate, the spin-up step starts (ramp-up) where the centrifugal forces drive the liquid across the substrate. The exceeding liquid leaves the substrate during this step (spin-off step). After this, the evaporation takes place, helping to reduce the film thickness. A uniform layer can be obtained when the viscosity of the liquid is not dependent on shear rate^{‡‡} and the evaporation rate is independent of the position. The thickness of a spin-coated film, t , is given by [13]:

^{‡‡} This happens to Newtonian fluids since they have a constant viscosity.

$$t = \left(1 - \frac{V}{\rho_{SOL}}\right) \left(\frac{3\eta R_{ev}}{2V\omega^2}\right) \quad (3.5)$$

where ρ_{SOL} is the density of volatile solvent, V its initial volume, ω the angular velocity, η the liquid viscosity and R_{ev} the evaporation rate. From this equation it is clear that adjusting the solution properties and the deposition condition is possible to control the film thickness. This process allows thin-films with thicknesses of around 10 nm. Although the most intense use of this procedure is in photolithography techniques, enabling the deposition of photoresist layers about 2.5 to 0.5 μm thicknesses and opening large possibilities in the fabrication of multilayer devices with several shapes and geometries. A photoresist is basically a sensitive UV light polymer, that when exposed to UV light can be easily removed with an adequate revelator^{§§}. It is typically spun at 20 to 80 revolutions per second (1200 – 4800 rpm) during 30 to 60 seconds in order to spread the liquid precursor in the entire substrate [3].

In this work, spin-coating was used to deposit positive photoresist (PR) layers for photolithographic processes and also to deposit SU-8 epoxy based negative photoresist (NR) for TFT passivation. The recipes used for these materials are in Table 3.3.

Table 3.3 – Recipe used in the deposition of the positive photoresist and Su-8.

	Rotation Speed / Time	Dehydration Temperature/ Time
+	3000 rpm / 10s → 4000 rpm / 20s	115 °C / 1.10 min
photoresist		
Su-8	1340 rpm / 40s	65 °C/10 min 95 °C/ 35min

After the spin coating process, the thin-film still includes a portion of solvent that needs to be removed. Therefore to achieve the desired layer, a dehydration process is fundamental, and is usually done by heating the substrate in a hot-plate or an oven. Higher thickness films can be produced just repeating the steps showed in Figure 3.5 (or select a photoresist which properties fit the purpose). In the case presented here, the dehydration process was performed at 115 °C in a 1.10 minute time period. Despite of being a fast and low cost process, spin-coating usually require high annealing temperatures to achieve thin-films with reasonable electronic properties that are usually far from the ones obtained using vacuum deposition techniques. The protocol used in this process is presented in Table 3.3.

^{§§} In the case of a positive photoresist. The negative photoresist works in an inverse way, the protected part is removed with an adequate revelator, while the exposed to UV is fixed into the substrate. This is a simplistic presentation of the procedure related to the use of a negative photoresist. In the reality the process is much more complex than that.

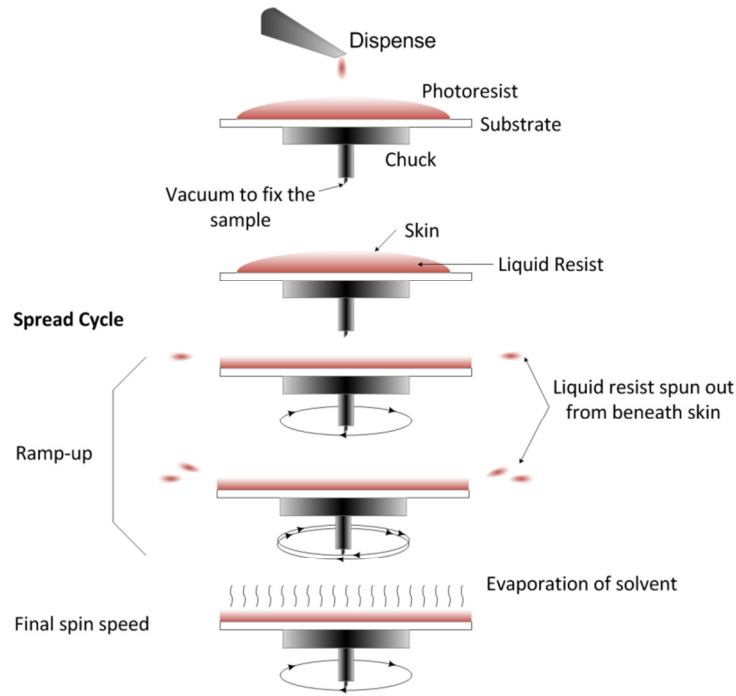


Figure 3.5 – Spin coating of photoresist. The substrate is fixed with vacuum (or mechanically).

3.2.4 PHOTOLITHOGRAPHY TECHNIQUES

In this small topic, the procedures and techniques used to produce patterns are summarized in a scheme (Figure 3.6). The adopted procedure, neglecting some details, was equivalent for the patterning of TFTs, *van der Paw* structures (for Hall effect) or contacts.

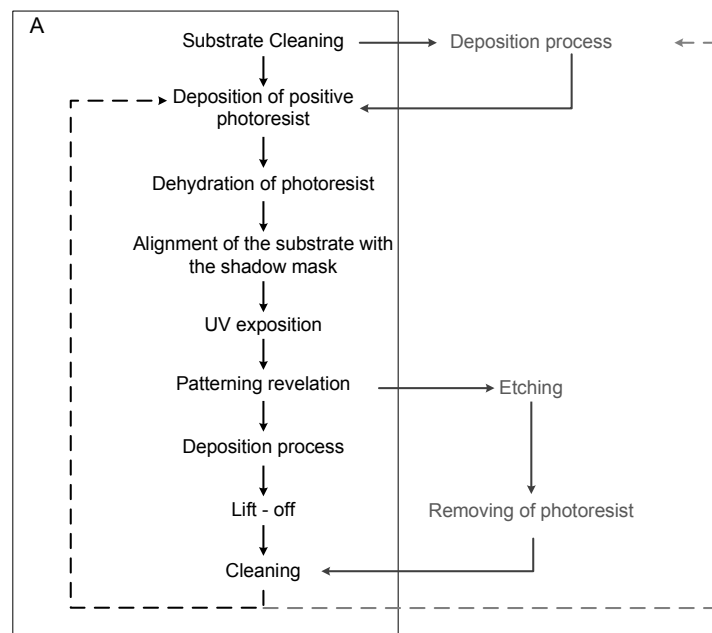


Figure 3.6 – Scheme of general processes used in photolithographic process. Some variations can be introduced depending on the application and production scale. In this work the process described by A) was the most used, although an etching process was also used, in some cases, for patterning the *van der*

Paw structures for Hall effect measurements.

3.2.4.1 PATTERNING

TFTs were produced using glass substrates coated with ITO and ATO [6], and silicon substrates with thermal SiO₂. Since the objective was the study of the active layer, the use of substrates containing a gate contact and a dielectric, reduces a lot the number of steps and consequently the time to produce a TFT. In all the devices presented here, the substrate has a common gate and dielectric. The photolithographic process was independent of the substrate used. Figure 3.7 presents the steps followed in the production of TFTs. This method relies on the properties of the photoresist used (if is PR or NR). In the case illustrated here, for the patterning of the TFTs (but also *van der Paw* structures) was used the AZ6612^{***} PR. After cleaning the substrate, the photoresist was coated, dehydrated and then aligned in a Karl SUSS MA6 (from SUSS MicroTec) mask aligner where a mask with the pattern of the TFTs was already assembled in the mask holder. Since the PR used in this process is sensitive between the wavelength (λ) of 320 – 460 nm (near UV and blue light of the visible spectrum), all the process was performed under a yellow light ($\lambda > 500$ nm) in a clean room environment to avoid damaging the PR.

After the exposition to UV radiation, performed in *soft-contact* mode (gap between mask and substrate ~ 100 μm) during 7.5 s, the substrate is removed and the pattern revealed using the revelator AZ726MIF^{†††}. The revelation process is always followed by the quality control of the pattern using an optical microscope (Laborlux 12 ME ST from Leitz) to ensure that the impressed patterns are revealed perfectly, fitting the requirements. If further chemical, physical and thermal stability on the photoresist is required, an extra hardbake can be performed in a hot-plate. In the present case, this last step was not necessary (for PR). After these steps the substrate is ready to receive the coating layer that will form the TFT channel. After the deposition a “lift – off” process is done using a solvent that dissolves the photoresist (acetone), and then cleaned with isopropyl alcohol and pure water [3]. After this step, the sample is again

^{***} This photoresist (the most used in this work) has an active compound, DiazoNaphtoQuinone-(DNQ)-sulfonate, that when exposed to a UV radiation, loses a nitrogen molecule, incorporating a water molecule, being converted into idene carboxylic acid (MicroChemicals. AZ 6000-series, 06/02/2012, http://www.microchemicals.eu/photoresist/thin_positive_photoresist.htm). The regions where the photoresist is exposed, have much higher alkaline solubility, and can be easily removed with a suitable solution.

^{†††} The revelator used to reveal the patterns defined by the photoresist AZ6612. It is a metal ion free developer, primarily composed by tetrametil ammonium hydroxide.

ready to receive a new photoresist layer to follow the procedure that will originate the contacts. In Figure 3.8 an illustration of the masks used for Hall effect and contacts are shown. There is also a picture of the mask aligner system used to perform the patterning.

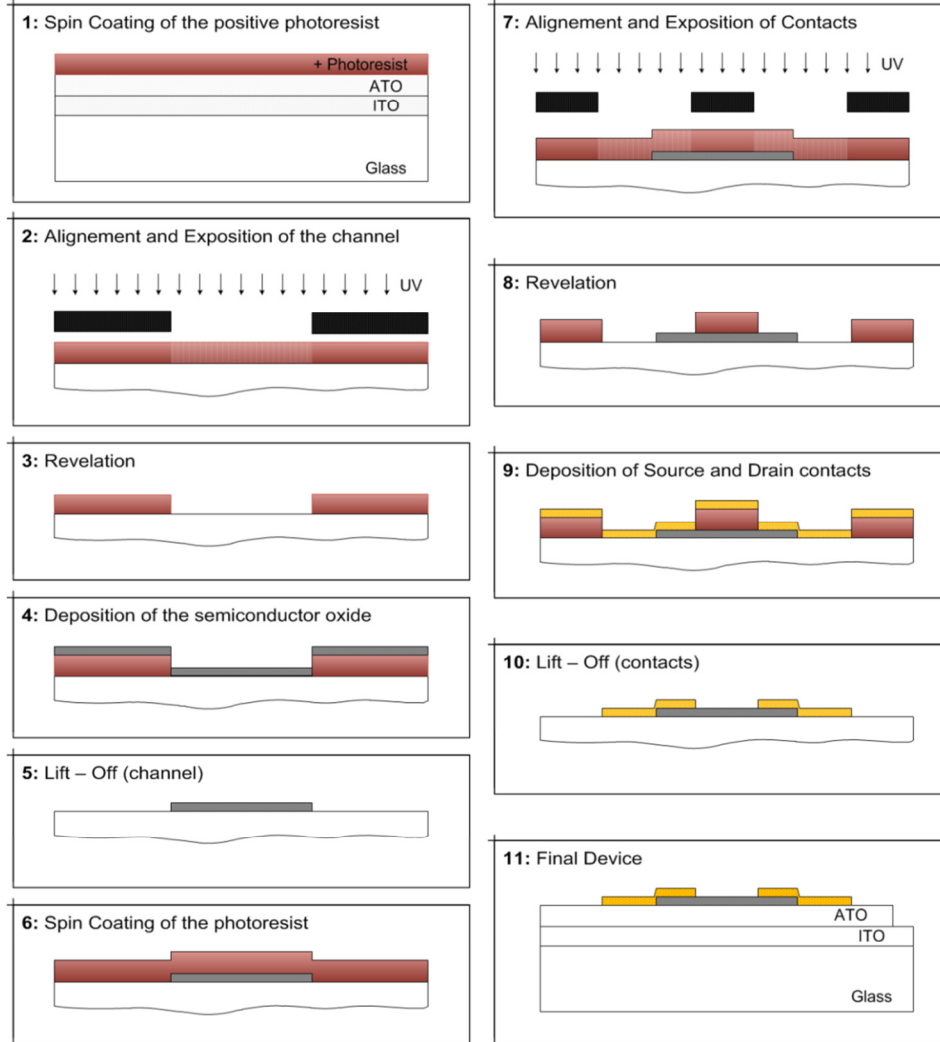


Figure 3.7 – Scheme of the photolithographic steps.

In this work wet etching^{†††} process was also used in the patterning of copper oxides samples, when the deposition process was done before the patterning. This step was performed mainly for *van der Pauw* structures used for Hall effect measurements. The principal requirement of wet etching process is that the etchant is selective regarding photoresist and the material to remove. The substrate with the structure already patterned, is immersed in an adequate solution that breaks intermolecular and/or atomic bonds of the material, dissolving it. In the specific case of CO was used a diluted solution of FeCl_3 (40° Bé):HCl (35%): H_2O (1:1).

^{†††} Another type of etching process called dry etching, is available although not used in this work. In that process the material is sputtered or dissolved using reactive ions or a vapour phase etchant.

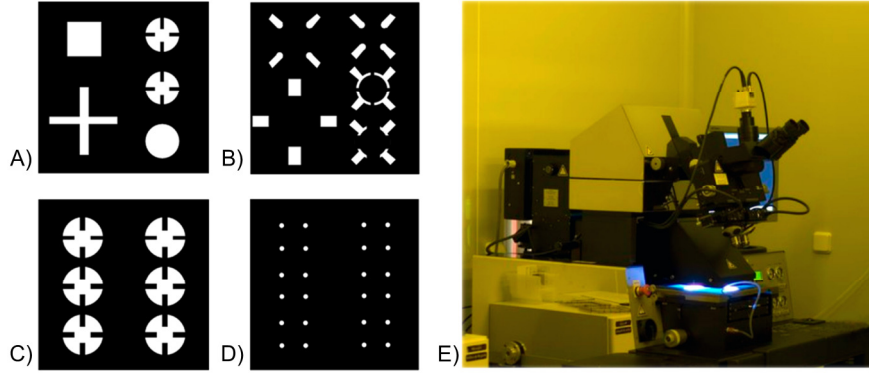


Figure 3.8 – Example of a positive mask used for patterning structures for Hall effect measurements (A to D). The mask A) and C) were used for the semiconductor and the mask B) and D) for contacts. E) Karl Suss MA6 mask aligner used for imprint the pattern using photoresist.

3.3 CHARACTERIZATION TECHNIQUES

After the production of the thin-films, they were characterized using different techniques concerning their electrical, optical, structural and morphological properties.

The electrical properties of the thin-films were estimated using a 0.5 T magnetic field Hall effect system, in the *van der Paw* geometry, allowing the estimation of the electrical resistivity, Hall coefficient (R_H), Hall mobility (μ_H) and carrier's concentration (n_0). A DC dark conductivity was also performed in function of temperature (100 to 400 K) using a coplanar configuration and a setup composed by a cryostat CS8900 (Bio-Rad) and an electrometer Keithley 617.

The optical characterization was performed using a double beam spectrophotometer, SHIMADZU UV-VIS-NIR 3100 PC, in the wavelengths range between 350 to 2500 nm. The transmittance (T) and the absorption coefficient (α) were estimated using this technique, allowing the estimation the optical bandgap of the deposited films.

The structural properties were analysed by XRD, using the Cu $K_{\alpha 1,2}$ radiations using X'Pert Pro (PANalytical) system in a 2θ range comprise between 20° and 90° . Rutherford backscattering spectrometry was also used in the film characterization^{§§§}.

The surface morphology was characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM) using an Asylum MFP3D AFM and a CrossBeam Workstation (SEM-FIB) (from Zeiss Auriga), respectively. The surface was also characterized

^{§§§} This characterization was performed at ITN (Instituto de Tecnologia Nuclear, Portugal).

using Kelvin probe equipment (KP Technology).

Concerning the electrical properties of the devices, the TFTs were characterized using a microprobe station M150 (Cascade MicroTech) attached to a semiconductor parameter analyser 4155C (Agilent). Other techniques such as profilometry, Fourier transform infrared spectroscopy (FTIR) and spectroscopic ellipsometry (SE) were also used.

3.3.1 PROFILOMETRY

The film thickness was estimated using a profilometer Ambios XP-200 (having a minimum vertical resolution of $1 \text{ \AA}$ in a $2.5 \text{ }\mu\text{m}$ range). A profilometer uses the vertical movement (ΔZ) of the tip, when it moves across the sample surface (ΔX), to determine the profile. It allows, among other things, to determine the roughness and the film thickness by comparing the ΔZ in the two regions (with film and without). Figure 3.9 shows the system used for thickness measurements and also an example of a linear and a 3D profile. The 3D profile is obtained by the scanning several linear profiles defined by a specific offset, and combined into a 3D plot.

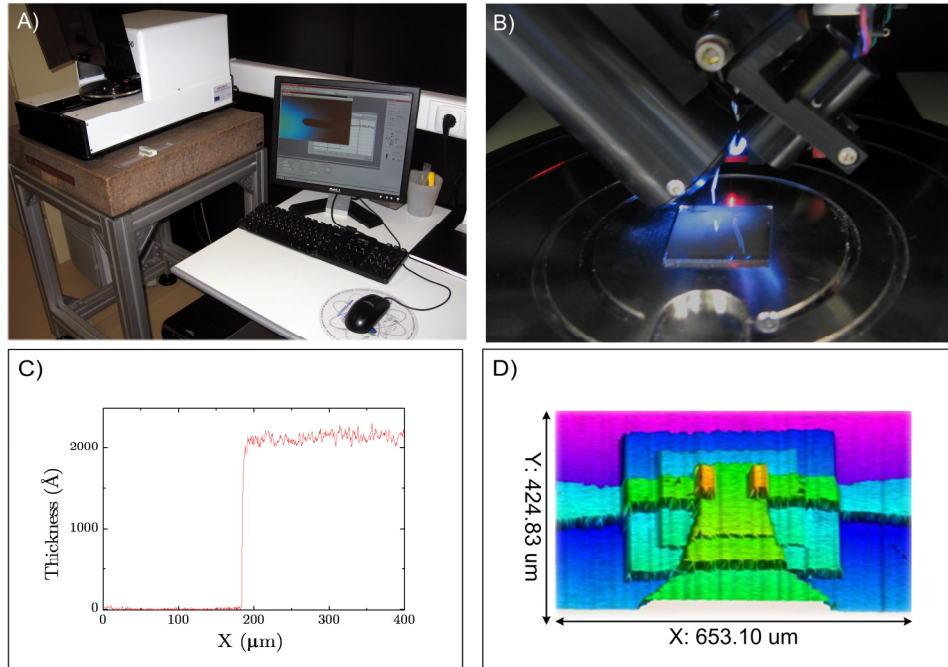


Figure 3.9 –A) and B) Profilometer Ambios XP-200, used to measure the thickness of the thin-films; C) Typical profile of a thickness measurement; D) 3D profile of a TFT.

3.3.2 ELECTRICAL CHARACTERIZATION

Some of the electrical properties of the samples were determined using a Hall effect system, Bio-Rad HL 5500, using a magnetic field of 0.5 T in a four-point-probe configuration (FPP) (Figure 3.10). This system allows the estimation of the resistivity (ρ), the Hall coefficient (used to determine the type of carriers presented in the sample), the Hall mobility (μ_H) and the carrier's concentration (n_0).

The samples were prepared in “clover leaf” shape (with approximately 10×10 mm), defined by photolithography, using Ni/Au contacts. The resistivity is one of the fundamental properties of a material, contributing to its sub-division in classes: conductor, semiconductor and insulator. The two-point-probe method is the simplest way used to measure the resistivity: a voltage is applied between two probes and the current that flows between them is measured. However, the current measured (also used in this work for DC measurements in temperature) is severely affected by the probe resistance, the spreading resistance under each probe and also the contact resistance between the semiconductor and the metal contact. For this reason, the FPP method is the most reliable and used to determine the physical properties of the films.

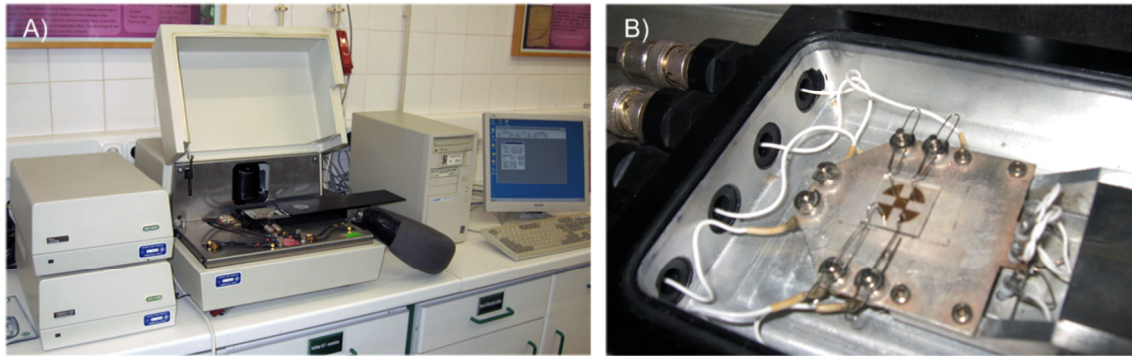


Figure 3.10 – Hall effect Bio-Rad HL 5500 system used in the electrical characterization.

3.3.2.1 VAN DER PAW METHOD

The *van der Paw* method, also using a FPP configuration, in which four small electrodes are placed on the edges of a flat and homogeneous thick film, arbitrarily shaped (in Figure 3.11 (A) is presented the shape used in the *van der Paw* method). Another usual FPP configuration consists in a four equally spaced probes, placed in a collinear way on the top of the semiconductor. In this method, two outer probes are used to apply the current (I) and the two inner probes to measure the voltage (V).

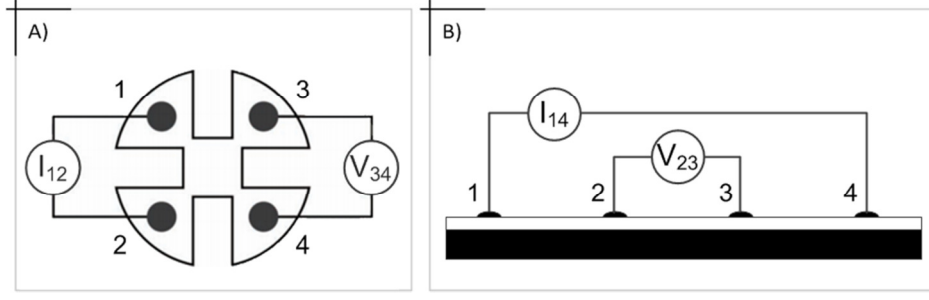


Figure 3.11 – Four-point-probes methods; A) *van der Paw* method used in this work; B) collinear;

In the *van der Paw* method, I is applied in two adjacent electrodes and V is measured in the remaining ones (Figure 3.11 – (A)), yielding four possible electrodes permutations, each with two I directions. For each sample, I is chosen to provide an acceptable signal-to-noise ratio ($V > 5$ mV) and to avoid sample heating and large potential gradients induced by excessively high I [19]. Then the sheet resistivity, ρ_s can be written by:

$$\rho_s = \frac{\pi}{2 \ln 2} \left(\frac{V_{43}}{I_{12}} + \frac{V_{23}}{I_{14}} \right) \cdot F \cdot Q \quad (3.6)$$

where F is a correction factor for geometrical asymmetry (not for material anisotropy or inhomogeneity) and it's a function of the symmetry factor (Q), defined by:

$$Q = \frac{V_{43} \cdot I_{14}}{V_{23} \cdot I_{12}} \quad (3.7)$$

The bulk resistivity (ρ) is then given by,

$$\rho = \rho_s \cdot t \quad (3.8)$$

where t is the semiconductor's thickness.

For a symmetric and homogeneous sample, is understandable that the equation (3.7) should be approximately near the unity ($Q \sim 1$). Higher values of Q are consequence of badly defined structures, non-uniform samples and also non-ohmic contacts. F and Q are correlated by the equation [19, 20]:

$$\left(\frac{Q-1}{Q+1} \right) = \frac{F}{\ln 2} \cos^{-1} [2^{1/F-1}] \quad (3.9)$$

If the asymmetry is not too large ($Q < 10$), F can be written in approximation by [19]:

$$F = 1 - 0.34657A - 0.09236A^2 \quad (3.10)$$

$$A = \left(\frac{Q-1}{Q+1} \right)^2 \quad (3.11)$$

In the measurements performed here****, ρ_s was measured with same value of constant

**** The resistivity was also measured using a HL5500PC Hall effect system and a semiconductor parameter analyzer (SPA),

current for all the possible permutations

3.3.2.2 HALL EFFECT

The Hall effect is one of the most useful physical phenomena in semiconductor physics and also a critical tool in the research of new semiconductor materials, allowing among other things the differentiation of the type of the major carriers (holes or electrons) present in the material. This effect was discovered in 1879 by Edwin Hall, observing the current flow in a gold sheet placed under a magnetic field ($\mathbf{B}$) perpendicular to the surface of the sheet. He noticed the formation of an electric field perpendicular to the direction of $\mathbf{B}$.

BRIEF EXPLANATION OF THIS EFFECT

When a charge, q , moves with a velocity $\mathbf{v}$ along a direction perpendicular to $\mathbf{B}$, it feels a magnetic force perpendicular in both directions [21-23],

$$\mathbf{F}_M = q \cdot (\mathbf{v} \times \mathbf{B}) \quad (3.12)$$

This means that when a flow of electrons (for instance) is moving in a specific direction, the electrons are deflected by the force $\mathbf{F}$, caused by $\mathbf{B}$. This effect in the sample will originate a potential difference that can be measured, V_H (Figure 3.12).

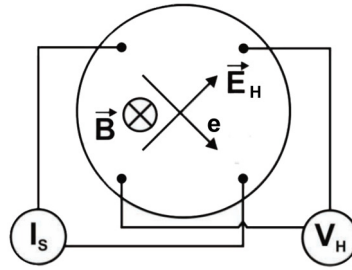


Figure 3.12 – Hall effect arrangement scheme.

This charge accumulation will increase until the electrical force resultant ($\mathbf{F}_E$) matches the applied magnetic force ($\mathbf{F}_M$). In this limited situation, the system reaches the equilibrium and the carriers will move in a linear direction without being deflected. Since $\mathbf{E}_H / \mathbf{v} \times \mathbf{B}$, the Lorentz force will be represented in the scalar form,

$$F = q \cdot (E_H - v \cdot B) = 0 \quad (3.13)$$

$$\Rightarrow E_H = v \cdot B \quad (3.14)$$

Assuming a uniform field and taking in consideration the separation between the two contacts,

w , it is possible to write the Hall voltage as,

$$V_H = E_H \cdot w = v \cdot B \cdot w \quad (3.15)$$

The total number of carriers (N) in a specific volume ($\mathbb{V} = S \cdot \Delta x$, where $S = wt$) can be related to the carriers concentration (n_0) by the relation,

$$N = n_0 \cdot \mathbb{V} \quad (3.16)$$

The total charge (ΔQ) in same volume will be,

$$\Delta Q = q \cdot N = q \cdot n_0 \cdot \mathbb{V} = q \cdot n_0 \cdot S \cdot \Delta x \quad (3.17)$$

In terms of average velocity (v), of the carriers when they travel along the volume ($\mathbb{V}$), with average time ($\Delta \tau$),

$$\Delta Q = q \cdot n_0 \cdot S \cdot v \cdot \Delta \tau \quad (3.18)$$

Considering the definition of electric current,

$$I = \frac{\Delta Q}{\Delta t} \quad (3.19)$$

it is possible to write,

$$I = q \cdot n_0 \cdot S \cdot v = q \cdot n_0 \cdot w \cdot t \cdot v \quad (3.20)$$

$$n_0 = \frac{I}{q \cdot S \cdot v} \quad (3.21)$$

The Hall voltage can also be defined as,

$$V_H = \frac{I \cdot B \cdot w}{n_0 \cdot q \cdot S} = \frac{I \cdot B}{n_0 \cdot q \cdot t} = R_H \frac{I \cdot B}{t} \quad (3.22)$$

where R_H is called Hall coefficient and is defined as:

$$R_H = \frac{1}{n_0 \cdot q} \quad (3.23)$$

Using the equation defined before (3.22), the carrier concentration in function of I , B , V_H , q and t , takes the form:

$$n_0 = \frac{I \cdot B}{q \cdot t \cdot V_H} \quad (3.24)$$

The relation between the conductivity (σ) and the mobility (μ), can then be expressed as [21, 23],

$$\sigma = n_0 \cdot q \cdot \mu \quad (3.25)$$

The mobility calculated using this method is often called Hall mobility (μ_H) and can be represented as:

$$\mu_H = R_H \cdot \sigma = \frac{R_H}{\rho} \quad (3.26)$$

The conditions to determine the carrier concentration, Hall mobility, the type of carriers and also resistivity were defined.

3.3.2.3 DC MEASUREMENTS IN TEMPERATURE

This technique was used to analyse the electrical behaviour of the films in the temperature. A computer controlled system, with a home-made software, was used to control a cryostat CS8900 (Bio-Rad) and a programmable electrometer Keithley 617 was used (Figure 3.13).

In this system the resistivity is measured in a coplanar method. This simple technique allows some considerations relatively to the fundamental properties of the semiconductors and their variation when submitted to low temperatures.

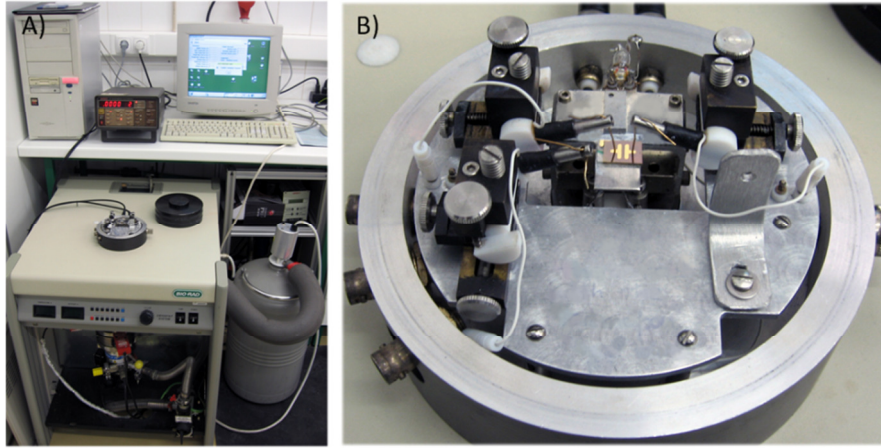


Figure 3.13 – DC dark conductivity setup with a cryostat CS8900 (Bio-Rad) and electrometer Keithley 617.

The coplanar method used here, uses a “T” shape Ni/Au contacts deposited on the top of the semiconductor (Figure 3.14) with a gap (l) of 1 mm and size (w), w of 4 mm.

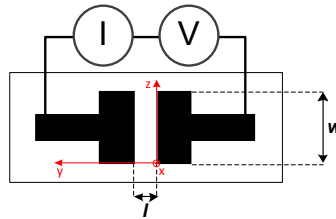


Figure 3.14 – Coplanar geometry used for DC measurements in dark and in temperature.

The general definition of current density ($\mathbf{J}$) through a generic surface is given by [23],

$$I = \int \mathbf{J} \cdot d\mathbf{S} \quad (3.27)$$

where $d\mathbf{S}$ is the surface element and the integral calculated above the entire surface. In this

case $d\mathbf{S} = d\mathbf{x} \times d\mathbf{z}$, and the current can be written in terms of the current density and the section ($w.t$),

$$I = J(w.t) \quad (3.28)$$

$$J = \frac{I}{w.t} \quad (3.29)$$

Considering the module of the electrical field E , originated by the potential applied between the two contacts, V , and admitting that the two sections of each extremity are equipotential surfaces (the intensity of the electrical field and the current are constants between them). The electrical field is then:

$$E = \frac{V}{l} \quad (3.30)$$

The module of the electrical field can also be written as,

$$E = \rho J \rightarrow \sigma = \frac{J}{E} \quad (3.31)$$

Obtaining a practical equation to use with this structure:

$$\sigma = \frac{l}{V} \frac{I}{wx} \quad (3.32)$$

The system described here, was used for conductivity measurements in vacuum in function of temperature, working in the range of temperatures between 80 K and 550 K. In this study the interval used was set around 100 and 400 K. For each value of temperature, a delay and stabilization time was defined to ensure the perfect control of temperature and also a better statistic of the current measured. With the data, it is possible to calculate and plot the conductivity versus T , allowing other considerations related to the electronic structure of the materials.

3.3.3 OPTICAL CHARACTERIZATION

The films were characterized optically by UV-VIS-NIR spectroscopy, FTIR and by Spectroscopic Elipsometry (SE).

3.3.3.1 UV-VIS-NIR SPECTROSCOPY

The UV-VIS-NIR spectroscopy was done using a double beam, Shimadzu UV-VIS-NIR 3101 PC (Figure 3.15). This system works with wavelengths between 190 and 3200 nm, comparing the intensity of two light beams. One of the beams is allowed to pass through a

reference sample (containing only the substrate), the other passes through the sample containing the substrate with the film to measure. The intensities of the light beams are then measured and compared, allowing the estimation of transmittance and absorbance. The reflectance can also be measured using another experimental set up.

With the optical measurements, it is possible to calculate the absorption coefficient (α), of the material and extrapolate the optical bandgap (E_G), its refractive index (n_r) and also make other considerations about other properties such as the film thickness (using interference fringes).

The energy transmitted or absorbed by a material, depends on their atomic or molecular structure, but also the thickness (t) of the absorbent medium.

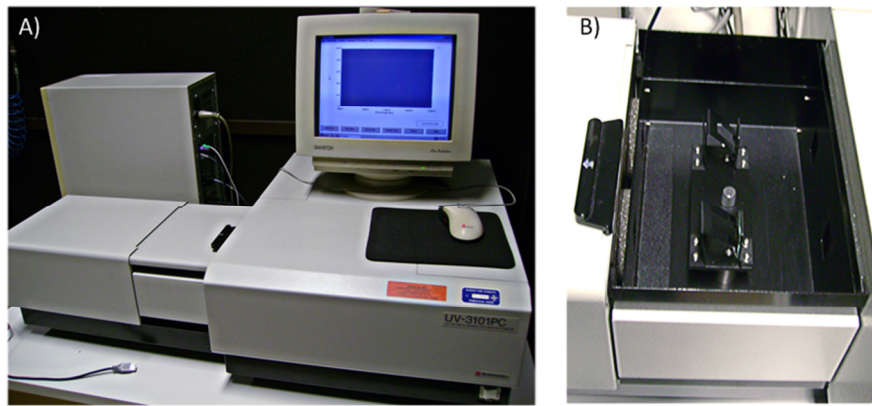


Figure 3.15 –Spectrophotometer SHIMADZU UV-VIS-NIR 3101 PC (A). Sample holders (B).

When the light wave travels along the material, its intensity is attenuated exponentially according to the Beer-Lambert law [24, 25],

$$I(y) = I_0 e^{-\alpha y} \quad (3.33)$$

where I_0 is the incident radiation and α the absorption coefficient. The absorption coefficient can be related to the transmittance (T) and to the reflectance (R) by the equation,

$$\alpha = \frac{1}{t} \ln \frac{1}{(T + R)} \quad (3.34)$$

In the fundamental absorption process, the photon causes the transition of electrons from the valence band to the conduction band. In this process the photon energy ($h\nu$) should be equal or superior to E_G . This is the limit of absorption corresponding to a frequency $\nu_0 = E_G/h$. If the transition is between a maximum of the valence band to a minimum of the conduction band which implies a conservation of the moment ($\mathbf{k}$), (selection rule $\vec{k}_f = \vec{k}_i$) the transition is called direct, and $E_{\text{Final}} = E_{\text{Initial}} + h\nu$ [23] (Figure 3.16).

In an indirect transition, the electron is also ejected from the top of the valence band to the bottom of the conduction band (Figure 3.16 (B)), but to respect the selection rule $\vec{k}_f = \vec{k}_i$, the transition will imply a simultaneously absorption of a photon and a phonon. The photon will give the necessary amount of energy needed for the transition while the phonon will offer the moment. In a general way, the optical coefficient can be written by the Tauc equation [26]:

$$\alpha^{1/n}(h\nu) = B(h\nu - E_g), \quad (3.35)$$

where h is the *Planck* constant (4.4×10^{-15} eV s) and B a proportionality constant. n is a parameter dependent on the electronic transition and can take the values of $\frac{1}{2}$ (direct allowed transition), $\frac{3}{2}$ (direct forbidden), 2 (indirect allowed) and 3 (indirect forbidden). With the equation (3.34) and (3.35) is then possible to extrapolate values for E_g [23].

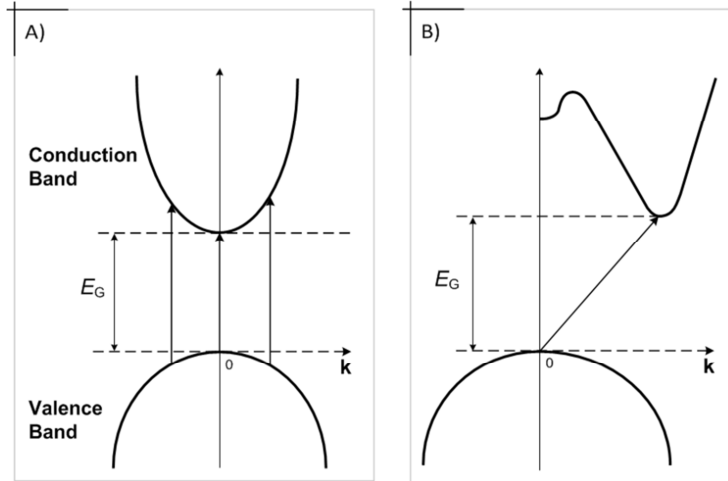


Figure 3.16 – Fundamental absorption process in a semiconductor; A) Direct transition; B) Indirect transition.

3.3.3.2 FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

Infrared spectroscopy technique is a widely used technique for material analysis allowing the study/identification of different compounds (solids, liquids or gases) using their own characteristic vibration modes. An infrared spectrum contains different absorption peaks corresponding to the vibration frequencies of the atomic bonds on the material. Each material has a unique combination of atoms and consequently no two compounds have the exact same infrared spectrum (fingerprint). Therefore, is an important tool for the identification (qualitative analysis) of a particular material. The intensity of the peaks in the spectrum can also give a direct indication of the amount of material presented in the sample.

An IR spectrometer, operates in the mid-IR ($4000 - 400 \text{ cm}^{-1}$), region where the most molecules change their fundamental vibration levels. The equipment uses the Fourier transform, to convert the raw data collected by an interferometer, to the final spectrum.

In the present work, for IR analysis the Nicolet 67000 FTIR (from Thermo Electron Corporation) was used.

3.3.3.3 SPECTROSCOPIC ELLIPSOMETRY

Spectroscopic Ellipsometry (Figure 3.17) is a very powerful non-destructive optical technique used for analysis and metrology. It is based on the measurement of the variation of the polarization state of the light (phase and amplitude) after reflexion on a plane surface. From the signal modulation^{†††} and its adjustment to a specific mathematical model is possible to estimate several properties of the analysed material, for example: thickness, morphology, roughness, chemical composition or even optical gap (among others) [27].

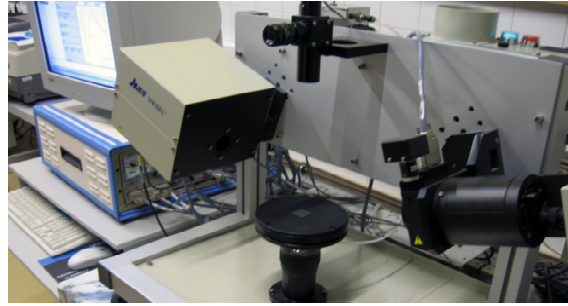


Figure 3.17 – Ellipsometry set-up used in the measurements.

Tauc-Lorentz (TL) is one of the model used in the modulation of the experimental results [28] and was used in this work. It has been currently employed for several kinds of amorphous, polycrystalline, and crystalline/amorphous mixed-phase materials [29, 30]. The imaginary part of dielectric function $\varepsilon_i(E)$ is established through the multiplication of classical Lorentz oscillator by the expression of the Tauc joint density of states [28]:

$$\varepsilon = \varepsilon_r + \varepsilon_i \quad (3.36)$$

$$\varepsilon_i(E) = 2n_r(E)k_i(E) \quad (3.37)$$

$$= \begin{cases} \frac{1}{E} \frac{A \cdot E_0 \cdot C(E - E_G)^2}{(E^2 - E_0^2)^2 + C^2 \cdot E^2}, & E > E_G \\ 0, & E \leq E_G \end{cases} \quad (3.38)$$

where E_G , is the optical band gap, E_0 the peak transition energy, C the broadening term and A

^{†††} The signal components are I_θ , I_s and I_c being all the possible parameters generated from them.

is the peak amplitude. All these constants are fitting parameters in units of energy. The real part of the dielectric function, is obtained by Kramers-Kronig integration of

$$\varepsilon_r(E) = n_r^2(E) - k_i^2(E) \quad (3.39)$$

$$= \varepsilon_r(\infty) + \frac{2}{\pi} \cdot P. \int_{E_G}^{\infty} \frac{\xi \cdot \varepsilon_i(\xi)}{\xi^2 - E^2} d\xi \quad (3.40)$$

where P stands for the Cauchy principal part of the integral. More detailed information about this can be found in Jellison and Modine work [28]. Multiple Tauc-Lorentz model, which is the sum of several single TL terms, generally corresponds to multiple transitions. Although, it should be noticed that TL model only includes interband transitions. Other effects such as defect, intraband and Urbach tail absorptions are explicitly ignored [29].

For metallic materials (for instance copper and nickel) the Drude formula was used in the layer model:

$$\varepsilon = \varepsilon_{\infty} + \frac{\omega_p^2}{-\omega^2 + i\Gamma_D\omega} \quad (3.41)$$

The quality of the fitting is measured by a function χ^2 , where a good fit is indicated by $\chi^2 \sim 1$.

The Bruggemann-Effective Medium Approximation (B-EMA) it is implemented by the software to describe the effective dielectric response in terms of the microstructural parameters such as the Tauc Lorentz [12]. More details about this powerful technique can be found in [27, 31].

3.3.4 STRUCTURAL CHARACTERIZATION

3.3.4.1 X-RAYS DIFFRACTION (XRD)

The X-rays diffraction (XRD) is a non-destructive and versatile technique that reveals information about the crystallographic structure and chemical composition. Figure 3.18 presents an image of the system used in the XRD characterization.

When a monochromatic beam (with a wavelength ranging the interatomic distances) is incident on the surface of a crystal, the photons can be absorbed or diffracted by the atoms. The diffraction effect is, in this case, what is interesting to observe because it gives information about the structural of the crystal. When the photons are diffracted, a difference in their wave phase occurs, interfering in a destructive way for the majority of the directions. However, for a

particular direction, the waves suffer constructive interference, originating a diffracted beam that is dependent of the crystalline structure of the target.

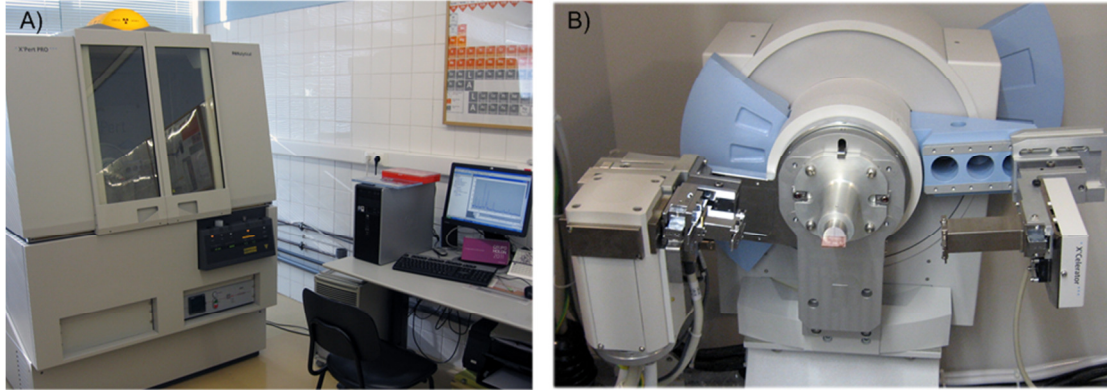


Figure 3.18 – XRD equipment, X'Pert Pro (PANalytical), used in the structural studies.

Considering a monochromatic beam of wavelength (λ) incident with an angle θ to a crystalline plane defined by the Miller index (hkl), the interference will be constructive for distances that are multiples of λ (Figure 3.19). This relation originates the well-known Bragg law postulating that for defined incident λ and d_{hkl} exist a set of incident θ angles, which can produce diffracted beam. This is defined by [32],

$$n\lambda = 2d_{hkl} \sin \theta \quad (3.42)$$

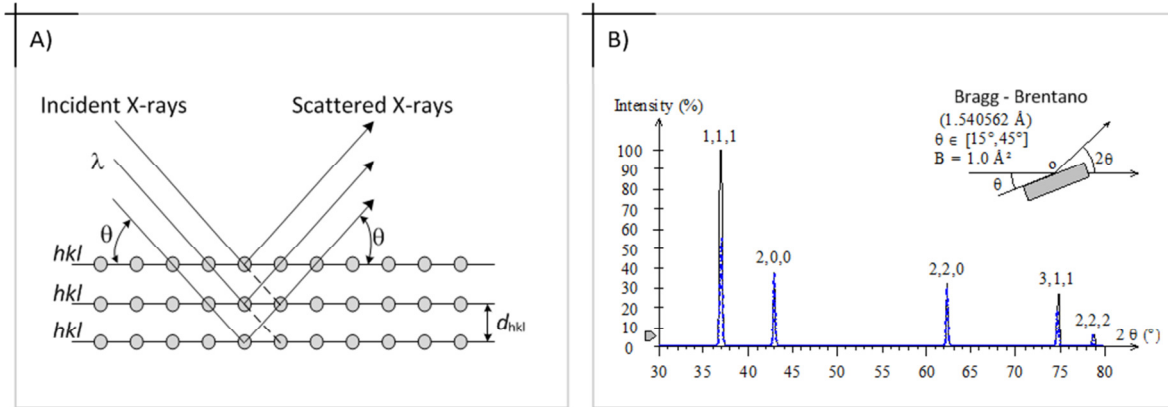


Figure 3.19 – A) Incident X-Rays are diffracted by the layers of atoms in a crystalline material; B) XRD diffractogram expected for a typical Cu_2O sample.

A crystalline lattice is defined by different crystallographic planes with different interplanar distances depending on the type of structure. For instance, for a cubic and a monoclinic structure (the two structures observed in this thesis) d_{hkl} is defined by [33, 34]:

$$\text{Cubic:} \quad \frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (3.43)$$

$$\text{Monoclinic:} \quad \frac{1}{d_{hkl}^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right) \quad (3.44)$$

Where a , b and c are the lattice parameters, and β an angle needed to define the monoclinic structure.

The combination between the Bragg law (3.42) and the equations (3.43) and (3.44) will allow the determination of the lattice parameters for all cubic and monoclinic structures. In the case of the monoclinic structure, this will result in a system with 4 equations and consequently a diffractogram with at least 4 well defined peaks is needed.

The intensity of the peaks also carries information about the atoms arrangements. The intensity of a beam, diffracted by a crystal is proportional to the square of the structure factor (F_{hkl}), defined by [32]:

$$F_{hkl} = \sum_n^N f_n e^{2\pi i(hu_n + kv_n + lw_n)} \quad (3.45)$$

where n is an index that addresses each atom inside a unitary cell (containing N atoms) of coordinates (hu_n, kv_n, lw_n) . f_n represents the atomic scattering factor that describes the scattering efficiency of the n^{th} atom that depends on the incidence angle and the atomic number of the scattering atom.

The crystals dimensions, grains or crystalline phases, are related to the width of the diffraction peak. The grain size (D) is estimated using the full width at half maximum (FWHM) of the diffraction peak by the use of the Scherrer formula [34],

$$D = \frac{K\lambda}{\beta_B \cos \theta_B} \quad (3.46)$$

where K is the shape factor, β_B is the FWHM, θ_B the Bragg angle and λ . The dimensionless shape factor has a typical value of 0.9 for particles of unknown size, but varies accordingly to the crystallite shape of the particles (0.89 to 0.94 for spherical and cubic particles, respectively).

Comparing the observed intensities with the standard intensities for the for each plan, and using the reflection number n , it is possible to calculate a parameter called texture coefficient to determine the preferable orientation present in the film, using the equation found in [35]:

$$P(h_i k_i l_i) = \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \left[\frac{1}{n} \sum_{i=0}^n \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \right]^{-1} \quad (3.47)$$

where I_0 represents the standard intensity, I is the observed intensity of $(h_i k_i l_i)$ plane and n is

the reflection number. Table 3.4 presents a summary of situations possible for the interpretation of the values $P(h_i k_i l_i)$.

In summary, combining the information obtained along the diffraction directions ($\theta - 2\theta$), is possible to gather information relatively to the type of the structure, lattice parameters, internal stresses and dimensions of the crystallites.

Table 3.4 – Texture coefficient analysis.

$P(h_i k_i l_i) > 1$	Determines the preferential orientation and are related to the abundance of grains in a given $(h_i k_i l_i)$ direction
$P(h_i k_i l_i) \approx 1$	If this is truth for all the $(h_i k_i l_i)$ planes considered at XRD patterns, the films are randomly oriented
$0 < P(h_i k_i l_i) < 1$	Indicates the lack of grains oriented in that direction

3.3.4.2 RUTHERFORD BACKSCATTERING SPECTROMETRY (RBS)

The Rutherford backscattering spectrometry^{††††} (RBS) is one of the techniques used in this work and widely used in material science to determine the structure and composition of materials by measuring the backscattering particles of a monoenergetic beam of high energy ions (usually H^+ or He^+ of energies around 0.5 – 4 MeV), after the collision with sample atoms. This technique allows the determination of the masses of the elements presented in a sample, their depth distribution over distances from 10 nm to a few microns from the surface, their areal density, and the crystalline structure in a non-destructive manner^{§§§§} [36, 37].

BASIC DESCRIPTION

During the collision with sample, the incident ions will lose their energy in a rate that is dependent on the masses ratio between the incident ions and the sample atoms. The masses relation will allow the identification of the sample atoms and the correspondent chemical element. The penetration of the ions beam into the sample (x) is also another factor that will influence the energy loss in this process, since the energy loss is proportional to the distance travelled by the ions through the sample. The analysis of a RBS spectrum is based on 3 basic concepts, allowing the determination of the constituent elements and their concentration as a

^{††††} This characterization was done in the Nuclear Technology Institute (ITN), Portugal.

^{§§§§} The high energy beam of light weight ions, used by this technique can lead to a very low concentration of defects in the sample.

function of the depth: the kinematic factor, the scattering cross section and the rate of energy loss, given by the so-called stopping power (S).

The kinematic factor (K) allows the identification of the elements available in the sample, assigning the detected signal to a specific energy. K relates the energy before the scattering, $E(0)$, and after, $E(x)$. Thin surface layers of a known elementary composition can be used to calibrate the energy scale of the detector through their kinematic factors. This collision can be described in a reasonable way by the classical mechanics, being valid for the following conditions: 1) the particle in the beam has an initial energy, $E(0)$ higher than the bonding energy of the atoms in the sample (~ 10 eV); 2) nuclear reactions and lattice resonances should not happen. This means restrictions in the maximum energy used in the beam. In the case of a H^+ and He^+ beams, nuclear effects start around 1 MeV and 2 – 3 MeV, respectively [37].

Applying the conservation of momentum and energy, for an elastic collision between a particle 1 (the projectile with mass M_1 , initial energy E_0 and final Energy E_1) and a particle 2 (with mass M_2 and final energy E_2), and solving the system of equations is possible to find a relation (K) between the backscattered particle E_1 and its initial energy E_0 [38]:

$$E_1 = KE_0 \quad (3.48)$$

$$K = \frac{M_1^2}{(M_1 + M_2)^2} \left\{ \cos \theta \pm \left[\left(\frac{M_2}{M_1} \right)^2 - \sin^2 \theta \right]^{1/2} \right\}^2 \quad (3.49)$$

For $M_1 < M_2$ only the positive sign is applied in the equation (3.49). If $M_1 > M_2$ two solutions are possible. With the determination of E_1 (for a fixed E_0 , M_1 and θ) is possible to identify M_2 , since the scattering was originated at the surface of the sample.

As mentioned before, if the atoms are located deep in the sample, the ions lose energy along their inward and outward paths, estimated by the use of the S ($S(E) = -dE/dx$), allowing a correlation of energy variations in depth. This parameter depends on the composition and density of the target, the energy, mass and atomic number of the incident ion [38].

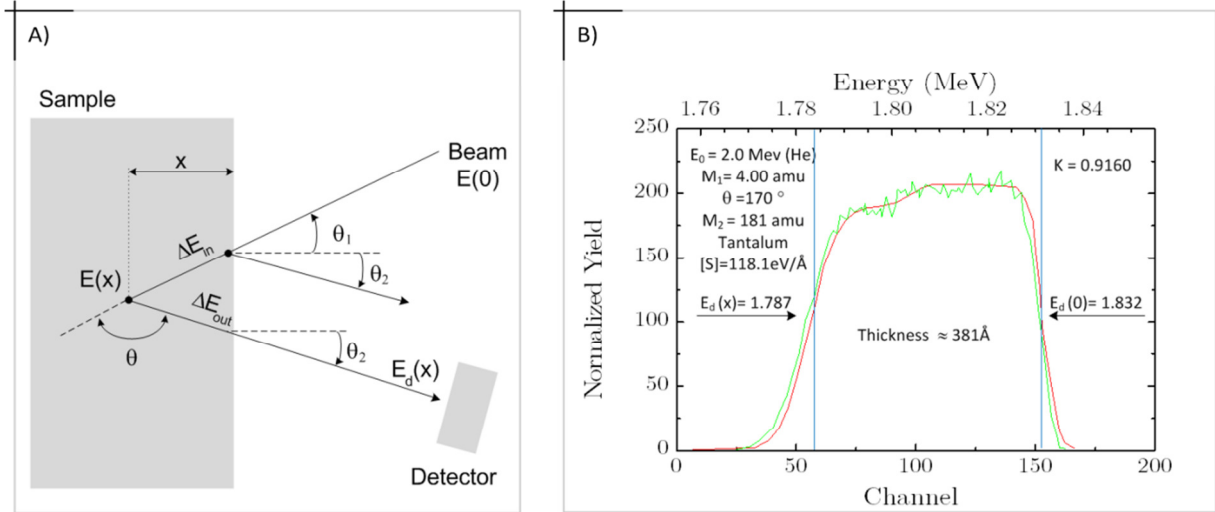


Figure 3.20 – A) Schematic of a RBS experiment, with the main parameters described for a specific geometry; B) Normalized yield to estimate M_2 from the kinematic factor (for an incident ^4He of energy 2.0 MeV)(adapted from [37]).

If the collision occurs in the surface, the detected particles will have energy $E_d(0) = KE_0$ and the mass identification is straightforward. However, if the collision occurs in a distance x from the surface, the energy of the particles that effectively collides with the atom is inferior to the initial energy ($E'_0(x) = E_0 - \Delta E_{in}$). The particle loses energy in the interactions with other atoms in its movement inside the film. After the collision, another loss of energy occurs when the backscattered particle travels to the detector ($E_1(x) = E'_1(x) - \Delta E_{out}$). The loss of energy when the particle travels through the sample ΔE_{in} and from the sample ΔE_{out} are estimated using the angles θ_1 (angle of the particle with energy E_0) and θ_2 (angle of backscattered particle with energy E_1). The total energy lost in the travel (from 0, to x),

$$\Delta E_{in} = \int_{x/\cos\theta_1}^0 \frac{\partial E}{\partial x} S(E_0(x)) dx \quad \Delta E_{out} = \int_0^{x/\cos\theta_2} S(E_1(x)) dx \quad (3.50)$$

In general, S is not constant, but dependent of the energy. However for a thin-film ($\sim$ few hundreds nanometres) can be approximately constant (surface approximation). In this situation, for a specific thickness x , the relation between the energy detected due to an ion scattered at the surface, $E_d(0)$, and due to an ion scattered at distance x , $E_d(x)$ can be expressed as ****:

$$E_d(0) - E_d(x) = KE_0 - E_1 = K\Delta E_{in} + \Delta E_{out} = \left[KS_{in}(E_0) + \frac{S_{out}(KE_0)}{\cos(\theta)} \right] x = [S]x \quad (3.51)$$

$$E_d(0) - E_d(x) = [S]x \quad (3.52)$$

**** Defining the referential at the particle 1, $\theta_1 = 0$ and $\theta_2 = 180 - \theta$.

The quantities S_{in} , S_{out} are the stopping powers for the ion travel in the inward and outward path. Stopping power data are available in literature in the form of tables and semi empirical expressions used to determine the film thickness [38].

It is possible to estimate the stoichiometry between elements (for example Cu, O) considering the yield intensities of corresponding peaks (the area of the peaks), and relate them with the RBS cross-section, that is charted (Table 3.5) for each scattering angle (in the specific case 140° and 165°), using the expression [39]:

$$\frac{N_{Cu}}{N_O} = \frac{A_{Cu}}{A_O} \left(\frac{\sigma_R(E, \theta)_O}{\sigma_R(E, \theta)_{Cu}} \right) \left(\frac{(\sigma/\sigma_R)_O}{(\sigma/\sigma_R)_{Cu}} \right) \quad (3.53)$$

Where N_{Cu}/N_O represents the stoichiometry ration, A_{Cu} and A_O are the area of the peaks of both Cu and O, σ_R is the Rutherford backscattering cross section, and σ/σ_R is the non-Rutherford cross section correction (usually neglected ~ 1) [39].

Table 3.5 – Rutherford scattering cross sections (barns) of the elements for 1 MeV ^4He [38].

Element	Scattering Angle ($^\circ$)	
	165°	140°
O	0.3028	0.3842
Cu	4.475	5.553
Ni	4.166	5.171

3.4 SURFACE AND MORPHOLOGIC CHARACTERIZATION

In this thesis two main techniques for surface and morphologic characterization were used: atomic force microscopy (AFM) and scanning electron microscopy (SEM), described below. Kelvin probe (KP) technique was also used measure surface potential and to determine the material work function.

3.4.1 ATOMIC FORCE MICROSCOPY (AFM)

The atomic force microscopy (AFM) of the samples was done using an Asylum MFP3D AFM system showed in Figure 3.21 (A). The images were acquired in AC mode with a silicon nitride (Si_3N_4) tip. This microscopy uses essentially the analysis of the forces between the sharp tip of the cantilever (usually made of Si or Si_3N_4) and the scanning sample. AFM provides very high resolution (atomic resolution) 3D surface profiles and unlike SEM without the need of

surface treatments and vacuum. In Figure 3.21 (B) the working principle of an AFM is shown. When the tip is moved into the proximity of the sample surface, forces which nature depends on the distance between the tip and the surface sample, leads to a deflection of the cantilever (according to the Hooke's law)[40].

The deflection is typically measured by a laser spot reflected from the top surface of the cantilever into an array of photodiodes^{††††}. The AFM can operate in two main modes: static (DC) or dynamic (AC or tapping mode). The DC mode is used in the contact mode, where the tip and the sample are in “contact”, meaning that the interaction force applied in the cantilever is kept constant by the use of a feedback circuit [40].

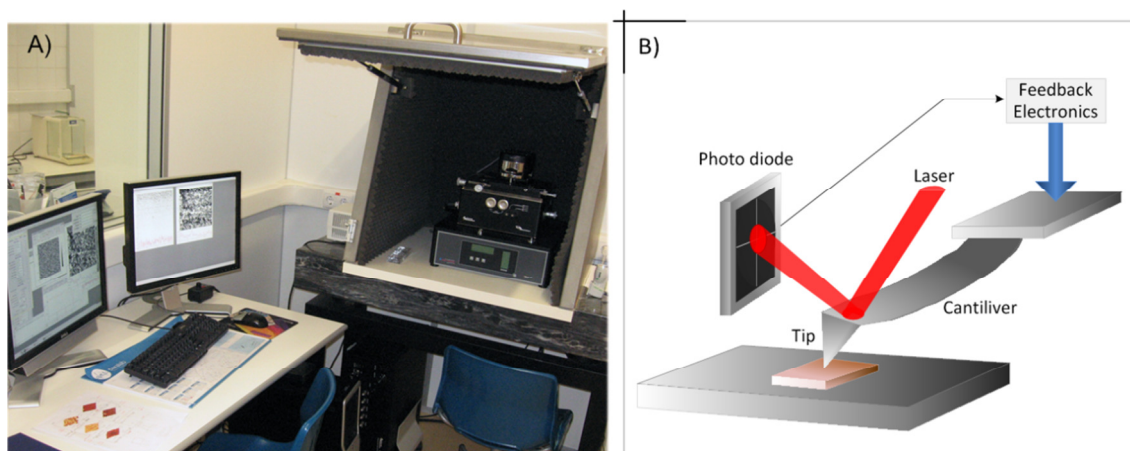


Figure 3.21 – A) Asylum MFP3D AFM system used in this thesis; B) AFM working principle.

In the AC mode, used in this work, the cantilever vibrates using a piezoelectric actuator, in its resonance frequency (corresponding to the maximum amplitude of an oscillation). When the tip is approximated to the surface, its resonance is modified by the surface interaction, changing its amplitude and phase. This “non-contact” mode is usually used to measure long-range interaction forces (such as, e.g., van der Waals, electrostatic, or magnetic dipole forces) increasing the tip-surface separation to 10 – 100 nm. It is also the preferable mode to use in soft samples since the maximum amplitude of oscillation can be controlled, avoiding changes in the sample surface [40].

AFM is usually used to obtain different 2D and 3D images, but also more information related to the surface profile, roughness and grains size. Other properties can be extrapolated selecting appropriate cantilevers. The roughness is usually represented in terms of the root-

^{††††} Other methods can be used including optical interferometry, piezoresistive or capacitive cantilevers. Although, this two last methods are not as sensitive as it is laser deflection or interferometry.

mean-square (RMS) deviation of the surface (S_q):

$$S_q = \sqrt{\frac{1}{MN} \sum_{j=1}^M \sum_{i=1}^N \eta^2(x_i, x_j)} \quad (3.54)$$

where M is the number of points per profile (scan line), N is the number of profiles and η is the amplitude at (x, y) point.

3.4.2 SCANNING ELECTRON MICROSCOPY (SEM)

The SEM analysis was done using a CrossBeam workstation (SEM-FIB) (from Zeiss Auriga), with a SEM column Schottky field emitter (resolution of 1.0 nm for 15 kV, 1.9 nm for 1 kV) with an acceleration voltage between 0.1 and 30 kV (Figure 3.22 (A)).

In a typical SEM, an electron beam is thermionically emitted (see e-beam thermal evaporation) from a filament (cathode) fitted on an electron gun. The filament is usually made of tungsten, since it combines two very important properties with its low cost: the highest melting point and lowest vapour pressure of all metals. The beam of electrons is accelerated typically with energies ranging 0.1 – 40 keV, and focused with condenser lenses to a spot about 0.4 to 5 nm diameter. To perform the scan the beam is deflected by scanning coils or deflector plates, in the electron column.

When the primary electrons (PE) collide with the sample, they lose energy by repeated random scattering and absorption in a region of the sample called interaction volume. This collision process originates high energy electrons that are reflected from the target (backscattered), emission of secondary electrons (SE) (inelastic scattering) and emission of electromagnetic radiation (X-rays) [36]. These phenomena can be analysed using different detectors represented in Figure 3.22 (B). However, the most conventional SEM images, is formed only by the detection of SE that leaves the sample with energy ≤ 50 eV. In this particular case, the SE yield depends on the material and the topography of the specimen. It can be deflected and accelerated towards the detector with weak electric fields which do not disturb the PE beam. The SE have only mean escape depths of ≈ 1 nm from metals, and so the SE emission is influenced by very thin surface layers. The backscattered electrons can also be detected, allowing a contrast between zones with different chemical composition, but also de construction of an image (EBSD, electron backscatter diffraction) that contains

crystallographic information of the sample. The system can also have an X-rays spectrometer to collect the X-rays emitted by the sample. This technique is also referred as EDS (energy-dispersive X-ray spectroscopy) and used do elemental analysis or chemical characterization.

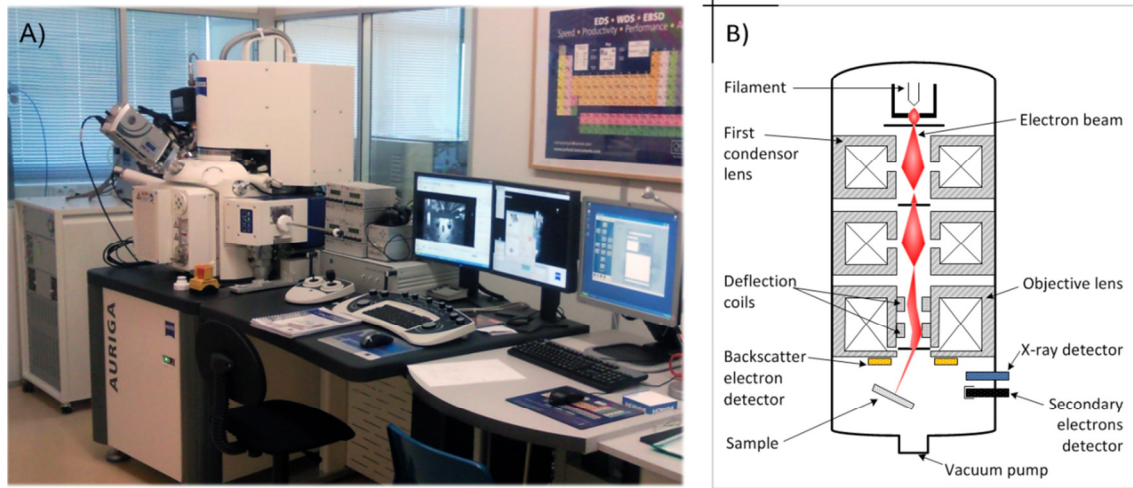


Figure 3.22 – A) CrossBeam workstation (SEM-FIB) from Zeiss Auriga used in this work; B) Schematic diagram of a SEM.

3.4.3 KELVIN PROBE

The samples were analysed using the Kelvin probe (KP) technique to estimate the work function (Φ) defined as the energy difference necessary to transport an electron between the Fermi level and the ionization level (vacuum level or infinity).

The traditional KP method consists in a simple capacitor formed by a flat circular electrode (called the reference electrode) suspended above and parallel to a stationary electrode (the specimen). The work function is traditionally measured by the vibration of the reference electrode above the sample and adjusting the “backing potential” (V_B) until a zero or null output is resulted (Figure 3.23 (C)).

In general terms, the work function of a material with Fermi energy (E_F) and vacuum energy (E_{VAC}), is defined by:

$$\Phi = E_{VAC} - E_F \quad (3.55)$$

Figure 3.23 (A) represents the case of two materials with work functions Φ_1 and Φ_2 ($\Phi_1 > \Phi_2$). When electrical contact is established, the Fermi levels E_{F1} and E_{F2} will align (Figure 3.23 (C), 2), resulting in an electric field $\mathbf{E}$ and a flow of charge between the material 1 and 2. This flow will originate a gradient potential (V_B).

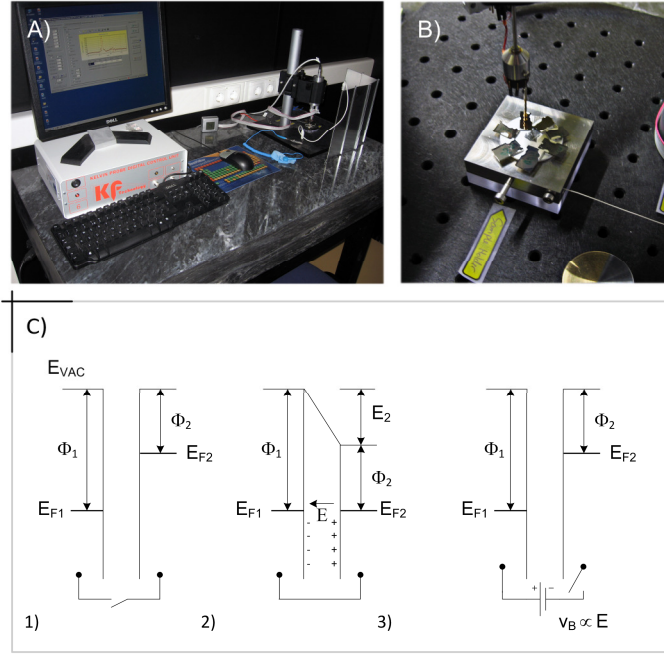


Figure 3.23 – A) and B) Kelvin probe system used for work function measurements. C) Simple band diagram with denoted vacuum energy (E_{VAC}), Fermi Level (E_F), work function (Φ), (1) – Representing two materials with $\Phi_1 > \Phi_2$, (2) when an electric contact is established between them (3), Inclusion of the “variable backing potential” V_B .

This principle will be used to measure the gold sheet surface potential (E_{Au}) that will act as a reference (the charted work function for Au is 5.1 eV). The surface potential of the sample is then measured and with the data collected is possible to estimate the work function using the relation:

$$\Phi_S = \Phi_{Au} - E_{Au} + E_S \quad (3.56)$$

3.5 SEMICONDUCTOR PARAMETER ANALYSER (TFTs)

The TFTs were electrically characterized using a measurement platform M150 (Cascade MicroTech) connected to a semiconductor parameter analyser 4155C (Agilent).

As mentioned in chapter II, the transfer and output characteristics of TFT are the most fundamental characteristics of a TFT, allowing to extract several parameters such as: μ_{FE} , V_{ON} , V_T , S and *On-Off* ratio. From the shape of the curves, other effects can be observed suggesting particular physical effects operating on the device, such as contact resistances, charge trapping, etc. From the understanding of the expected curve for a specific semiconductor, we can also use this technique as an indirect tool to determine the nature of the semiconductors carriers. Due to the systematically ambiguous signal obtained from the Hall effect measurements in the

present study, the importance of a TFT and its characterization assumed a heightened importance.

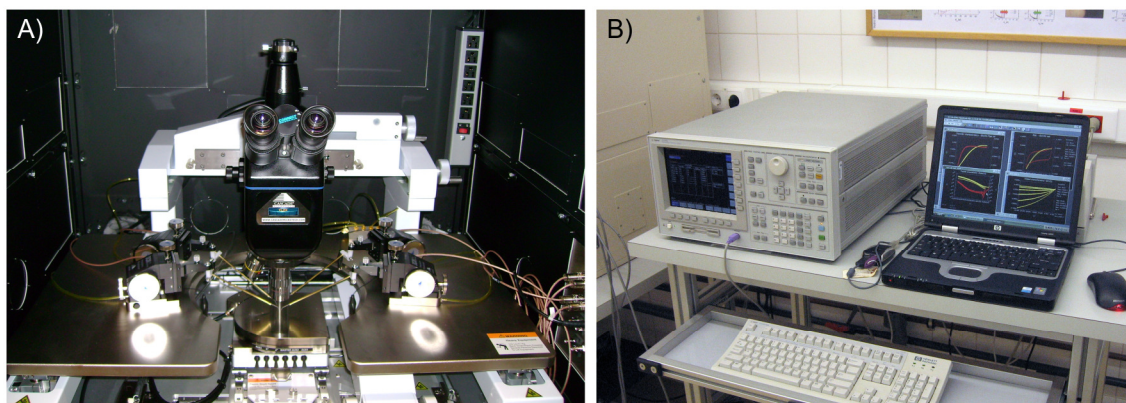


Figure 3.24 – (A) Platform M150 (Cascade MicroTech); (B) semiconductor parameter analyser 4155C (Agilent).

All the samples were measured using the same experimental protocol to avoid erroneous conclusions in the performance of the TFTs [41]. An example of the importance of a common protocol is the comparison of two transfer characteristics of two identical, but non-ideal, devices. In the first, the transference curve is taken in the beginning of the characterization, in the second device it is taken after several initial measurements. When the two transfer curves are compared, they can present totally different properties, even though they are processed under the same deposition conditions.

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Chapter IV

Copper oxides by thermal oxidation

CONTENTS

In this chapter, is discussed the results of Cu_xO films produced by thermal oxidation at different temperatures of copper thin-films. The films were characterized regarding the possible application in thin-film devices.

4 Copper thermal oxidation

4.1 Experimental details

4.2 Structural characterization

4.3 Electrical characterization

4.4 Optical characterization

4.5 Surface characterization

4.6 Oxidation kinetics

4.7 Conclusions

4.8 References

4 COPPER OXIDES BY THERMAL OXIDATION

Copper oxide (Cu_2O and CuO) films were produced from thin-films of metallic copper deposited by e-beam thermal evaporation technique and post-annealed at different temperatures (150 – 450 °C) in the air. All the samples produced were characterized concerning their electrical, optical, structural and surface properties. The best conditions were employed in the fabrication of TFTs.

4.1 EXPERIMENTAL DETAILS

Metallic copper films were deposited by e-beam thermal evaporation from 99.999% pure (Cerac) Cu pellets. After deposition, the films were annealed in 1 hour at different temperatures ranging 150 – 450 °C. Different types of substrates were employed depending on the pretended applications. To study their optical, electrical, morphological and structural properties, 1 mm thick glass was used as a substrate. Polished double face silicon substrates were used for FTIR measurements. Films with different thicknesses were deposited to study the impact of this parameter on the properties of the formed oxides, and study their oxidation kinetics. The experimental conditions and details related to the technique employed in the deposition of the films (e-beam thermal evaporation) were presented in Chapter II.

4.2 STRUCTURAL CHARACTERIZATION

4.2.1 X-RAYS DIFFRACTION (XRD)

The structure of the films was analysed using XRD to investigate the formation of the copper phases, Cu(I) and Cu(II), in terms of the oxidation temperature. The crystallite size, texture coefficient and lattice parameters were also estimated. The flat sample stage Bragg-Brentano configuration was utilized in the measurements, with a beam mask of 15 mm, divergence slit of $\frac{1}{2}^\circ$ and anti-scatter slit of 1° , obtained in the $20 - 90^\circ 2\theta$ range (Figure 4.1). The first perception observed in the XRD patterns is the polycrystallinity of the films. The diffraction peaks obtained for the as-deposited films matches with the standard cubic Cu phase (ICDD, Ref.045-03937) corresponding to the planes $(111)^\#$ and $(002)^\#$, being the most intense

peak correspondent to the direction [111].

The annealing at temperatures below 150 °C is not very effective in the oxidation of copper film. At 150 °C the conversion from Cu to Cu₂O (ICDD, Ref. 005-0667) is already visible with the appearance of a peak correspondent to the plane (111)[♦]. The Cu₂O phase will be denoted by ♦. This conversion is explained by the reaction: $2 \text{Cu} + \frac{1}{2} \text{O}_2 \rightarrow \text{Cu}_2\text{O}$.

The films produced at 200 °C showed a single phase of Cu₂O where the main plan (111)[♦] is visible. Other planes with lower intensities are also observed: (011)[♦], (002)[♦] and (022)[♦].

Increasing the temperature to 250 °C, the conversion from Cu₂O to the monoclinic CuO (ICDD File: 45-0937 and 48-1548) starts, following the reaction: $2 \text{Cu}_2\text{O} + \text{O}_2 \rightarrow 4 \text{CuO}$. The diffractograms reveal two intense peaks identified with the (11 $\bar{1}$)[◇] and (111)[◇] reflections of the CuO phase (denoted by ◇) and the (111)[♦] reflection of Cu₂O phase. At temperatures higher than 300 °C the conversion from Cu₂O to CuO is complete. With the increase of the oxidation temperature no phase changes are observed. The increase of the temperature influences the crystallization of the films, observed by an increase of the peaks intensity and a decrease of their full-width at half-maximum (FWHM). These results are in agreement with others published previously [1-4].

The XRD data for more intense peaks are summarized in Table 4.1, showing changes in the structural parameters depending on the oxidation temperatures. The size of the crystallites (D) were calculated using the Debye-Sherrer's formula, described in Chapter III, Section 3.3.4, equation (3.46). To retrieve reliable information from the Sherrer's formula analysis of the results should be done carefully. Some factors are of major importance in the calculation the crystallite size: the shape factor used, the statistic of the peaks (that will influence the FWHM), and an appropriate deconvolution of the peaks α_1 and α_2 . The evolution of the crystallite size with the temperature is not straight forward, since the phase conversion is assisted by temperature and different crystallographic planes are available. For this reason the comparison was done like it is presented in Figure 4.2, considering for the same phase, the same associated plane. In Figure 4.2, a decrease in D with the conversion of Cu to Cu₂O is noticed, and then increasing with the conversion of Cu₂O to CuO. Crystallization is a temperature dependent process having an important impact in the D value. More detailed information can be found in the previous published works [3, 4].

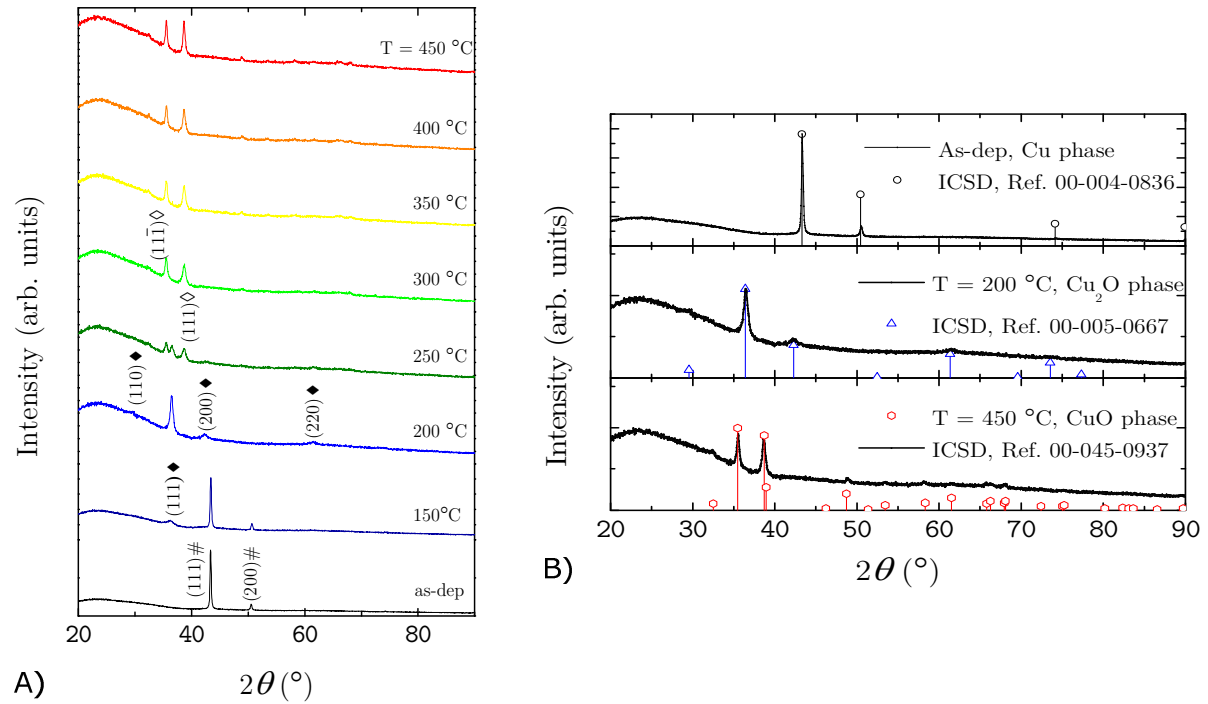


Figure 4.1 – a) Comparison of XRD patterns of the copper oxide films as a function of annealing temperature (symbol representations of the planes: (#) metallic Cu films, (♦) Cu₂O films and (◇) CuO films. b) Comparison of the Cu, Cu₂O and CuO phase obtained with standard ICSD database.

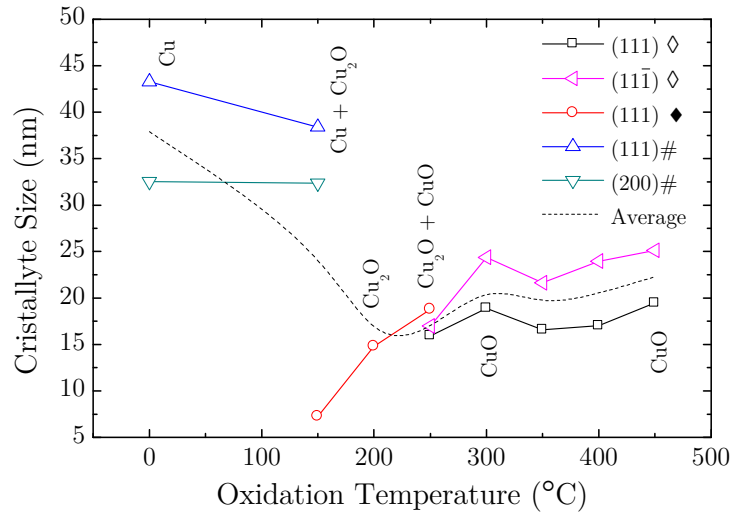


Figure 4.2 – Evolution of the crystallite size with the oxidation temperature.

The FWHM of the diffraction peaks increases as the size of the crystallite decreases [5]. Using the Bragg law and the equation for the distance between adjacent planes in the set ($h k l$), is possible to determine the lattice parameters (a , b , c) for the phases observed. In the case of cubic structures, Cu and Cu₂O, the calculation of the lattice parameter is straightforward, using equation (3.43) presented in Chapter III, Section 3.3.4. For the monoclinic CuO, to perform an estimation of these parameters it is necessary to take other peaks (with low

intensities) into account such as (110), (11 $\bar{1}$), (111), (20 $\bar{2}$), (202) and solve a system of 4 variables using equation (3.44). The lattice parameters were calculated by the average of the values determined for the temperatures between 300 °C and 450 °C. Table 4.2 presents the lattice parameters estimated for the different copper phases.

Table 4.1 – XRD data of copper oxide films as a function of annealing temperature for the more intense peaks (symbol representations: (#) metallic Cu, (♦) Cu₂O films and (◇) CuO films). The FWHM was used in radians, but for convenience it is presented in degrees.

T _{Oxid.} (°C)	Phase	2 θ (°)	(<i>h k l</i>)	<i>d</i> (Å)	FWHM (°)	<i>I</i> _{Max} / <i>I</i>	<i>D</i> (nm)	<i>P</i> (<i>h_i k_i l_i</i>)
As-dep.	Cu	43.3225	(111)#	2.0869	0.1976	100	43	1.62
		50.4904	(200)#	1.8061	0.2699	9.84	33	0.38
150	Cu	43.3597	(111)#	2.4786	0.2226	100	38	0.14
		50.6148	(200)#	2.0852	0.2715	12.44	32	2.21
	Cu ₂ O	36.2128	(111)♦	1.8020	1.1539	6.23	7	-
200	Cu ₂ O	36.4512	(111)♦	2.4629	0.5657	100	15	1.56
		42.283	(200)♦	2.1357	1.7718	9.91	5	0.25
250	CuO	35.4869	(11 $\bar{1}$)◇	1.5084	0.4910	94.3	17	1.00
	Cu ₂ O	36.5218	(111)♦	2.5276	0.4454	89.15	19	0.94
	CuO	38.6514	(111)◇	2.4583	0.5289	100	16	1.06
300	CuO	35.5105	(11 $\bar{1}$)◇	2.3276	0.3422	85.46	24	0.93
	CuO	38.6391	(111)◇	2.5260	0.4455	100	19	1.07
350	CuO	35.518	(11 $\bar{1}$)◇	2.3283	0.3853	97.95	22	0.99
		38.6558	(111)◇	2.5255	0.5079	100	17	1.01
400	CuO	35.5241	(11 $\bar{1}$)◇	2.3274	0.348	94.05	24	0.97
		38.6533	(111)◇	2.5250	0.4951	100	17	1.03
450	CuO	35.5101	(11 $\bar{1}$)◇	2.3275	0.332	84.46	25	0.92
		38.6385	(111)◇	2.5260	0.4327	100	19	1.08

Table 4.2 – Lattice parameters for the deposited Cu, Cu₂O and CuO.

Phase	Lattice Parameter	
Cu	a = 3.614 Å	
Cu ₂ O	a = 4.269 Å	
CuO	a = 4.730 Å	
	b = 3.436 Å	$\beta = 99.32^\circ$
	c = 5.064 Å	

Comparing the intensities with the standard intensities for each plan, and using the reflection number *n* is possible to calculate the texture coefficient to determine the preferable orientation in the film (Chapter III, Section 3.3.4, equation 3.47). When the *P*(*h_i k_i l_i*) values for the intense peaks were investigated, it was determined that the texture coefficient were bigger than 1 for the Cu phase (111)[#]. When the oxidation temperature increases to 150 °C, the

remaining un-oxidized Cu film appears to have a preferential orientation along the direction $[200]^\#$. This means an abundance of the crystallites in the direction of $[111]^\#$, and with increasing of temperature they start to be oriented along the $[200]^\#$. When the Cu_2O is completely formed at 200 °C the orientation is preferential to the plane $(111)^\diamond$. Increasing even more the temperature (> 250 °C) the crystallites appear to be oriented along the planes $(11\bar{1})$ and (111) , but none of the planes have a preferential orientation.

Despite previous considerations, it is important to remember that X-rays have an effective depth penetration (with 95% of information) around 25 μm [5]. So in the study of bulk materials, the thickness can be completely neglected. In the case of thin-films, the distance travelled by the X-rays in their path through the material is very dependent of θ . For example for a film of 200 nm thickness in a Bragg angle of 36° , the X-rays have to travel around 340 nm to reaches the glass interface. For a $\theta = 51^\circ$ the distance would be 257 nm. These differences can affect the intensity of the peaks and also the determination of the texture coefficient.

4.2.2 RUTHERFORD BACKSCATTERING (RBS)

The samples were analysed using Rutherford backscattering (RBS) in a 3.1 MV *van de Graaff* accelerator using a 2.0 MeV He^+ beam and barrier detectors, located at 140° . The angle of incidence, defined as the angle between the beam and the normal of the sample, was fixed constant at 0° . The current in the sample was kept below 3 nA and the charge accumulated in the spectra was 4 μC . The backside of the samples was also measured in order to clarify the glass composition, with shorter 2 μC spectra at $\theta = 0^\circ$.

RBS measurements were done on all samples and the spectrums are presented in Figure 4.3 (A). Each RBS spectrum was analysed with the IBA DataFurnace NDF software [23]. With the increase of the oxidizing temperature it is clear the formation of an oxidized Cu_xO surface layer. In fact the as-deposited films showed mainly metallic Cu, at 150 °C. In this condition, it is visible tinny step, associated to a rich oxygen layer (near the Cu_2O stoichiometry) in the top of a Cu layer. Similar situation happens with the sample oxidized at 250 °C where two different regions of poor and rich oxygen content are present. The result is shown in the inset of Figure 4.3 (A). At 250 °C the layer with more oxygen content (fitted near CuO

stoichiometry) was formed on top of a layer of Cu_2O .

Increasing the temperature, for 300 to 450 °C, the Cu layer is fully oxidized and a stoichiometry close to CuO is noticed. These results are consistent with the observations done in XRD.

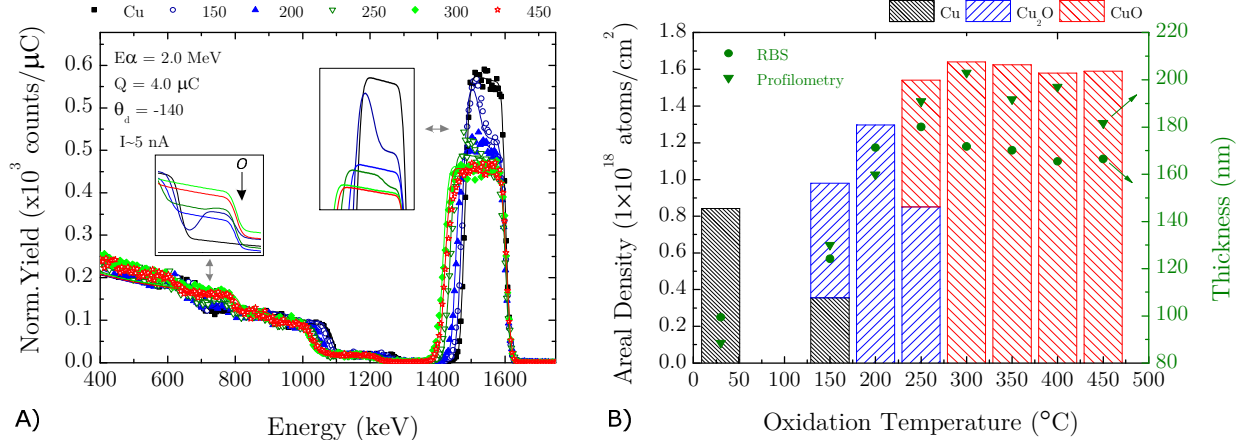


Figure 4.3 – A) RBS spectrums for the as-deposited and annealed samples; B) Areal density obtained fitting the experimental results.

The thickness was also estimated taking in consideration the standard bulk values of density of the Cu, Cu_2O and CuO (Chapter II). The values of the thicknesses obtained using RBS are consistent with the values measured by profilometry (Figure 4.3 (B)). The differences observed are an indication that the density of the films deviates from the bulk values. In Table 4.3 is summarized the values of areal density, thickness and the concentration of copper and oxygen estimated by RBS.

Table 4.3 – RBS analysis for the samples as-deposited with ~90 nm thickness. The symbols ♦, ◇ and # are used to distinguish the Cu_2O , CuO and Cu phases.

T (°C)	Areal density (atoms/cm ²)	Thickness (nm)	Cu (at.%)	O (at.%)
RT	842 [#]	99.4	100	0
150	623 [♦]	82.2	70	30
	356 [#]	42.0	100	0
200	1298 [♦]	171.2	66	33
250	850 [◇]	89.0	55	45
	690 [♦]	91.3	58	42
300	1640 [◇]	171.7	55	45
350	1625 [◇]	170.2	55	45
400	1580 [◇]	165.45	55	45
450	1590 [◇]	166.49	55	45

4.3 ELECTRICAL CHARACTERIZATION

4.3.1 HALL EFFECT

The electrical properties were estimated with Hall effect measurements in *van der Paw* configuration. Using this technique was possible to measure the electrical resistivity (ρ), Hall coefficient (R_H), Hall mobility (μ_H) and the carrier concentration (n_0). The type of conductivity was confirmed from the sign of the Hall coefficient. These results obtained for copper films produced by thermal oxidation and post-annealed are illustrated in Figure 4.4, and summarized in Table 4.4. The plot shows three regions relatively distinguished by their electrical properties. A high conductivity region (I), correspondent to the as-deposited copper film sample and the partial oxidized copper sample annealed at 150 °C. These samples showed n-type conductivity what is consistent with their metallic nature. In the region (II), the samples have similar values of resistivity, carriers concentration and mobility, corresponding to the films with single cuprous oxide (Cu_2O) phase samples (oxidized at 200 °C), Cu_2O – CuO mixture (oxidized at 250 °C) and single CuO phase (oxidized at 300 °C).

Annealing the samples at even higher temperature in air decreases their resistivity and increases their carrier concentration. Although this variation in the electrical properties of the films, no conversion of phase was observed, only changes in their crystallinity.

Reliable Hall effect measurements in this type of p-type semiconductor oxides are very difficult to achieve, due to the very low mobility of the films (< 1) which can compromise seriously the results. This is a problem faced for many researchers in the characterization of p-type semiconductor oxides [6, 7] which difficult the research of these materials. To minimize this situation, each film was measured several times with large acquiring times to achieve a better statistic. In the other hand, opposite signal values were not considered in the average of the values, since they refer to different types of carriers (electrons or holes).

Using the values obtained (presented in Table 4.4) is possible to estimate the amount of oxygen absorbed with temperature in the films. Ideally each Cu (Cu: $[\text{Ar}] 4s^1 3d^{10}$) atom contributes with one electron to the conduction. Using the copper density (around 8.94 g/cm³), assuming a free electron model, where the electrons-electrons and electron-nucleus interactions are completely neglected, is possible to estimate the carrier concentration in each cm³ of a pure

Cu film, giving a value of $8.95 \times (1 \times 6.0225 \times 10^{23}) / 63.54 \approx 8.48 \times 10^{22}$ electrons, what shows a good agreement with the experimental result obtained ($8.68 \times 10^{22} \text{ cm}^{-3}$).

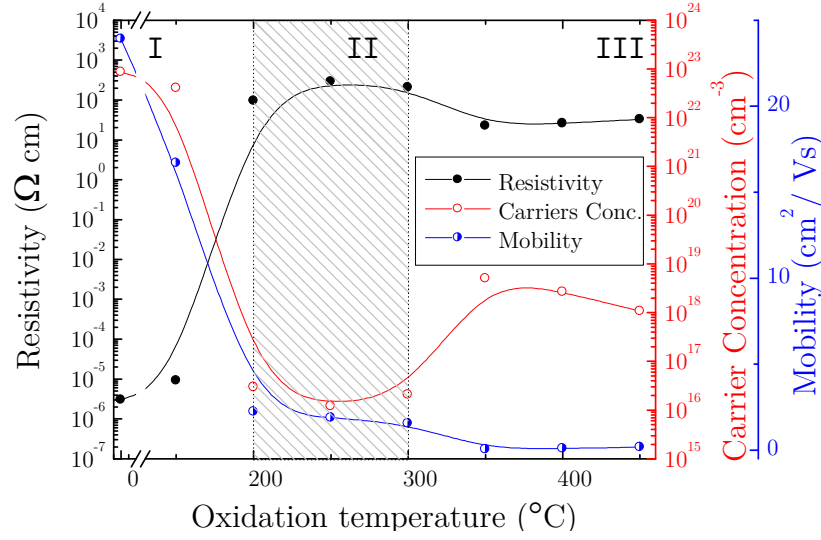


Figure 4.4 – Variation of the bulk resistivity (ρ), carrier concentration (n_0) and Hall mobility (μ_H) with oxidation temperature.

In case of Cu_2O , using the same approach would be expected from the stoichiometry insulator behaviour; this means that no electrons could be easily delocalized. However, as explained in Chapter II, the p-type nature can be related to slight differences in the Cu_2O stoichiometry that will be associated to Cu^{1+} vacancies. Assuming a basic chemistry, and the results obtained experimentally, it is possible to estimate the deviation of stoichiometry (without the consideration of the temperature effect), that was found to be around 1×10^{-6} carriers shared by a single unit cell. This means that Cu_2O is in fact Cu_{2-x}O , with $x = 1 \times 10^{-6}$. This is a very simplistic interpretation that does not consider all effects involved.

In general in Cu_2O (O: $1s^2 2s^2 2p^4$) and in p-type materials, the conduction arises from the presence of holes in the valence band (V_B) due to doping (creation of extrinsic defects) and/or annealing (in case of the existence of intrinsic defects). As shown before, the interest in Cu_2O is related to its non-stoichiometric composition which is formed (at least preferentially) through removal of copper atoms from the lattice. The resulting material is expected to be p-type,



where the hole, h^+ , can be either delocalized or localized. Interstitial oxygen is another possible mechanism used to explain the observed p-type behaviour of Cu_2O , as presented in Chapter II.

However, Cu vacancy is believed to be dominant mechanism for the origin of the p-type characteristics of Cu_2O [8].

Table 4.4– Electrical properties of Cu_xO thin-films produced with different oxidation temperatures (*phases identified by XRD assuming no stoichiometric deviations. The p-type results are emphasized using grey shading).

T (°C)	t (nm)	ρ ($\Omega \text{ Cm}$)	R_H	μ_H ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	n_0 (cm^{-3})	Phase*
RT	88.6	3.01×10^{-6}	-8.12×10^{-4}	23.9	8.68×10^{22}	Cu
150	130.0	9.20×10^{-6}	-1.18×10^{-3}	16.7	4.06×10^{22}	Cu/ Cu_2O
200	159.8	9.46×10^1	1.33×10^3	2.24	2.96×10^{16}	Cu_2O
250	190.8	2.87×10^2	2.73×10^3	1.892	1.20×10^{16}	$\text{Cu}_2\text{O}/\text{CuO}$
300	200.6	2.03×10^2	1.56×10^3	1.5512	2.08×10^{16}	CuO
350	195.4	2.24×10^1	6.51	0.0558	5.00×10^{18}	CuO
400	197.0	2.58×10^1	1.18×10^1	0.0903	2.67×10^{18}	CuO
450	185.6	3.27×10^1	3.11×10^1	0.179	1.07×10^{18}	CuO

In case of the CuO phase, with a partially filled $3d^9$, it should behave as a conductor. However, as explained in Chapter II the conventional band theory fails in the prediction of its physical properties. In the particular case of thermal oxidation, is visible an increase on the carrier concentration along the oxidation temperature.

The samples produced at 300 °C always shown less n_0 and higher ρ . For higher temperatures, it is observed an increase of n_0 coincident with a decrease of ρ . Unlike sputtering, where the ion bombardment can create copper defects, here if there is an increase on n_0 it is expected to be related to an excess of oxygen in the CO that will in another way, originate copper vacancies, according to their low enthalpy of formation (discussed in Chapter II). This oxygen excess in the film (oxygen interstials) will originate copper vacancies, explaining the high conductivity of the films produced at high temperatures.

4.3.2 DC CONDUCTIVITY VERSUS TEMPERATURE

The electrical characterization was completed with the study of the evolution of conductivity (in dark and vacuum) with the temperature ranging 100 – 400 K. The study was performed for fully oxidized samples (200 – 450 °C).

In this experiment the current (I) was measured as a function of the temperature (T) with an applied constant voltage of $V = 1 \text{ V}$. The conductivity was obtained by the relation

$\sigma = \frac{l}{wx} \frac{I}{V}$ found in Chapter III, Section 3.3.2.3. The typical behaviour expected for a semiconductor described by equation (4.2), it is observed in Figure 4.5 (A). With the increase of the temperature, the scattering of charges increases, decreasing drastically the conductivity in case of the metals. In an intrinsic semiconductor, the raise of temperature increases the scattering diminishing the mobility. The extra temperature will inject many extra carriers from the valence band to the conduction band. The carrier concentration will then grow exponentially with temperature, overcoming the effect of the scattering, and increasing in general the conductivity what is the opposite that happens with metals [9]:

$$\sigma = n|e|\mu_e + p|e|\mu_h = e^{-E_G/2kT}|e|(\mu_e + \mu_h) \quad (4.2)$$

This type of measurement at low and cryogenic temperatures are relatively simple and can give lots of information of several physical aspects related to the electronic structure and conduction mechanism of the material, revealing several effects that can be hidden at high temperatures (such as ambient temperature). It is possible to estimate activation energies of carrier ionization, hopping from site to site, the existence of donor and acceptor levels in the bandgap and phonons energy. However these measurements depend strongly on the composition as well as on the structure of the prepared film. Sample preparation conditions and the technique employed also have a significant role to influence the sample's properties [10, 11]. The measured data of σ - T are found to follow the relation [12, 13],

$$\sigma = \sigma_{0i} e^{-\frac{E_{\sigma i}}{k_B T}} \quad (4.3)$$

another form of the Arrhenius equation where σ_{0i} is the pre-exponential factor, and $E_{\sigma i}$ is the activation energy in a specific temperature range (denoted by the letter i). This activation energy of conduction is then estimated fitting $\ln(\sigma)$ versus $1/T$ as shown in Figure 4.5 (B).

The concept of activation energy is usually defined as the minimum amount of energy required to initiate a specific process. In this case $E_{\sigma i}$ can be understood as the energy barrier that a carrier has to cross to become mobile (ionization energy). Mobile carriers have to cross a barrier when jumping from one lattice site to another (mobility barrier).

For the samples studied, the conductivity appears to not follow a completely straight line along $1/T$ as it is shown in Figure 4.5 (B). The experimental data showed what appears to be two conduction paths with activation energies $E_{\sigma 0}$ and $E_{\sigma 1}$. For the Cu_2O phase ($T = 200^\circ\text{C}$) the activation energies were found to be $E_{\sigma 1} = 0.12$ eV (low temperatures) and $E_{\sigma 0} = 0.22$ eV

(high temperatures). In case of CuO ($T = 450^\circ\text{C}$) is possible to estimate activation energies of $E_{\sigma 1} = 0.11\text{ eV}$ (low temperatures) and $E_{\sigma 0} = 0.15\text{ eV}$ (high temperatures) (Table 4.5.).

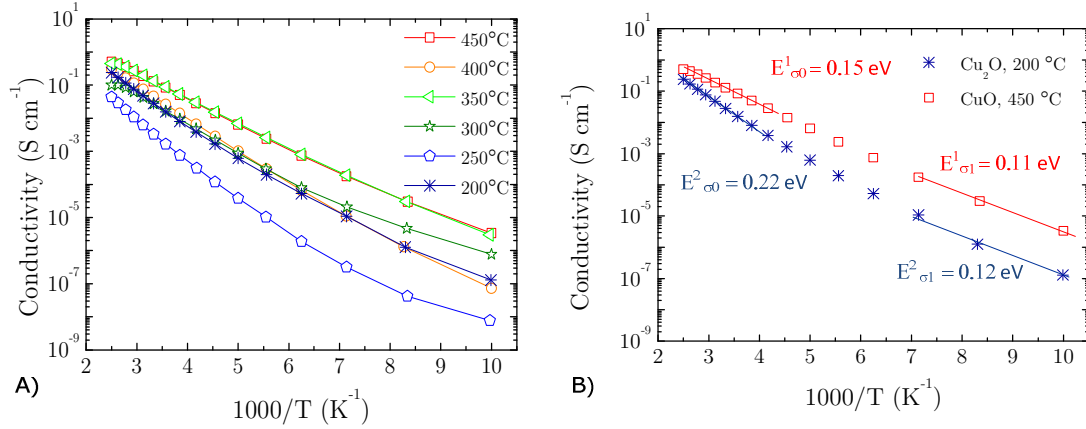


Figure 4.5 – A) Copper oxides conductivity as a function of 1000/T. B) Temperature dependent dark conductivity for the Cu₂O (oxidized at 200 °C) and CuO (oxidized at 450 °C).

Table 4.5 –Activation energy calculated using the Arrhenius equation compared with reported values. (E_A).

	T (°C)	$E_{\sigma 0}$ (eV)	$E_{\sigma 1}$ (eV)	E_A (eV) [14-16]
Cu ₂ O	200	0.22	0.12	0.14-0.22
Cu ₂ O & CuO	250	0.27	0.09	-
	300	0.18	0.09	-
	350	0.15	0.12	-
CuO	400	0.20	0.14	0.13-0.15
	450	0.15	0.11	-

The conductivity activation energies reported here, are much larger than kT (10 – 35 meV) that could indicate that the thermionic emission of charged carriers is the dominant transport mechanism in these samples [13]. This was also noticed in Cu₂O samples prepared by RF sputtering that will be presented in a further chapter. The different slopes can be attributed to the existence of an acceptor level [17]. Assuming the Fermi level energy around the middle of the energy gap, between an acceptor level (E_A) and the top of the valence band (V_B), is possible to estimate E_A from equation $2 \Delta E \approx 2 (E_F - E_V) = 2E_{\sigma 0} \sim 0.43\text{ eV}$ (at the high temperatures interval). This is in concordance with the energy of acceptor levels reported to the Cu₂O by other authors [10, 11, 18-21]. In case of CuO and assuming the same criteria, one can find values of between 0.30 eV to 0.40 eV to the acceptor level.

4.4 OPTICAL CHARACTERIZATION

4.4.1 UV-VIS-NIR SPECTROSCOPY

The transmittance of the films was analysed in wavelength range of 300 – 2500 nm. The fundamental absorption coefficient (α) was estimated and used to determine the energy of the optical bandgap (E_G) by the Tauc method (Chapter III, Section 3.3.3.1).

The oxidation temperature changes the appearance of the films from the “orange-red” colour of copper, to the yellow colour of Cu_2O and finally to the brown colour of CuO . This is consistent with an oxide growth in the surface. For thin-films (due to the low absorption) these differences observed in the colour associated to the phase changes are not so intense.

The Cu_2O has a direct forbidden bang gap (already discussed in Chapter II), however it was reported the inefficiency of the assumption of the $\alpha^{2/3}$ behaviour in the energy interval range between 2.09 to 2.64 eV, making inadequate to estimate the energy gap using a linear fit in this region [10]. Since many reports have been published considering a direct allowed transition (α^2), this transition will also be considered during this work to allow a simple comparison between the different samples produced in different conditions and also with the values reported in literature. Plots of the absorption coefficient considering all the possible transitions are presented in Appendix C. In Figure 4.6 it is visible the transmittance and direct allowed transition (α^2) for the set of films with as-deposited thickness around 90 nm.

In the plot two different regions around 2.5 – 3 eV and 3.0 – 3.5 eV are observed. However, a more linear behaviour near the bandgap is obtained for thicker films (with as deposited thickness ~ 170 nm), allowing a more precise estimation of the optical bandgap (Figure 4.6 (C) and (D)). Table 4.6 summarizes the optical data for the films and their respective thickness.

The as-deposited film showed poor transmittance ($< 1\%$), which is understandable due to the high absorption of the metallic Cu. The transmittance is increased with the oxidation temperature (following an increase in their thickness consequence of the $\text{Cu} \rightarrow \text{Cu}_2\text{O} \rightarrow \text{CuO}$ conversion, as explained before), associated to a change in the optical gap. Was expected the highest transmittance value for Cu_2O because of its optical bandgap ranging 2.1 to 2.6 eV. This was observed in our experiments for different thickness samples, and is presented in Figure 4.6.

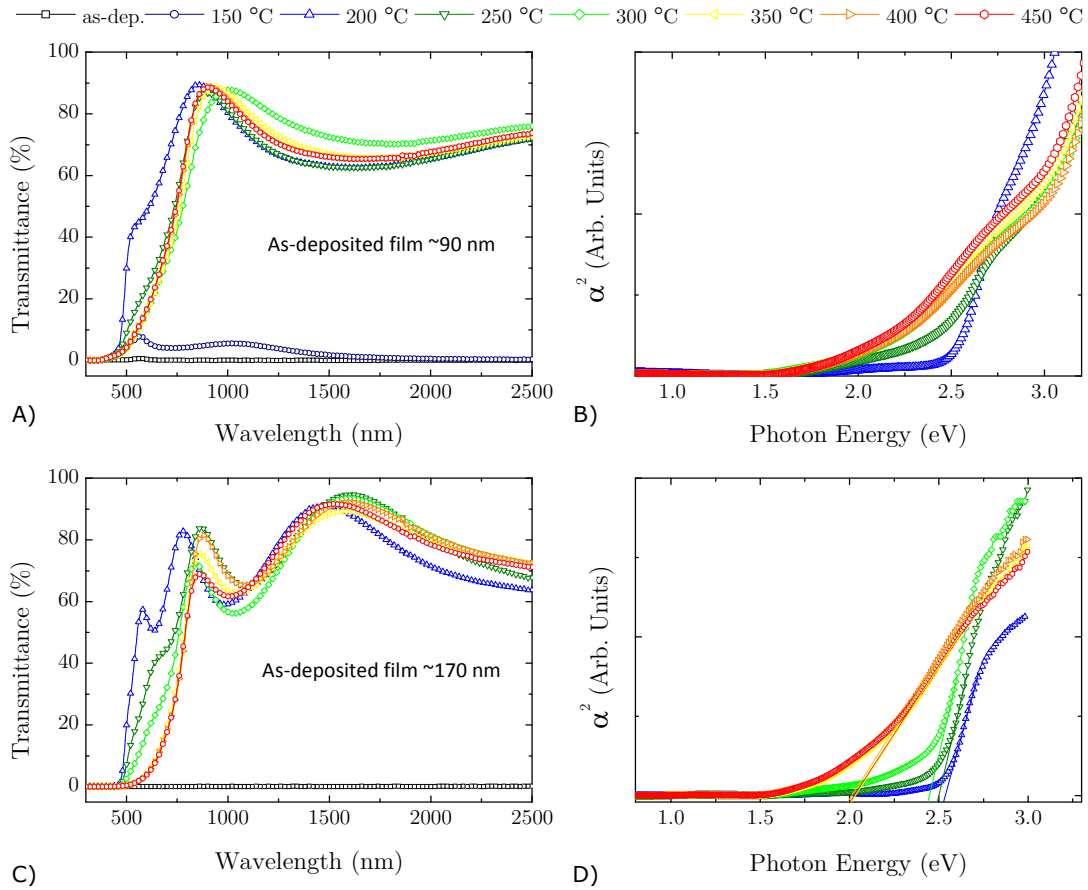


Figure 4.6 – Transmittance (A and C) and direct allowed transition (B and D) of the copper oxides films with as-deposited thickness of ~90 nm (A and B) and ~170 nm (C and D). The measurements were performed in air at RT.

The Figure 4.6 (B) shows the influence of the thickness in the optical properties dependent of the oxidation temperature that can be mainly explained due to the conversion of first Cu to Cu_2O (150 °C) and then the conversion of Cu_2O to CuO . With the increase of the thickness, should be more probable to find a mixture of $\text{Cu}_2\text{O}/\text{CuO}$ at intermediate temperatures (250 – 300 °C), that will reduce the transmittance of the samples. With the increase the temperature (for a same thickness), in a limit situation, CuO will be the major phase present. This phase has the lower optical bandgap (ranging 1.9 – 2.1 eV) what will consequently decrease the transmittance.

For the samples oxidized at higher temperatures ($T \geq 300$ °C), correspondent to the CuO phase, a difference in the transmittance values appears to exist which can be related to the increase of the film thickness. This is also exemplified if a “normalization” of the thickness (to 100 nm) is done considering equation (2.29) (Chapter III), presented as $\langle T^{N100} \rangle$ in Table 4.6. No trends were also observed in the values of the optical gap in this range of temperatures, also

confirmed by the squared absorption coefficient curves.

Table 4.6 – Optical gap data for the set of films deposited with as-deposited thickness around 90, 130 and 170 nm; (Symbols: T_{Oxid} is the oxidation temperature; ${}^{\Xi}E_G$ is the optical bandgap for the transition $\Xi = 2, 1/2$ and $2/3$; $\langle T^{\text{N}100} \rangle$ is the average transmittance (in the range of $\lambda = 400$ to 750 nm) normalized to a thickness of 100 nm)

$T_{\text{Oxid.}}$ (°C)	~90 nm			~130 nm			~170 nm			$\langle T^{\text{N}100} \rangle$ (%)
	2E_G	${}^{1/2}E_G$	${}^{2/3}E_G$	2E_G	${}^{1/2}E_G$	${}^{2/3}E_G$	2E_G	${}^{1/2}E_G$	${}^{2/3}E_G$	
	(eV)			(eV)			(eV)			
200	2.52	2.17	2.29	2.52	2.21	2.31	2.52	2.22	2.31	57
250	2.41	1.51	2.05	2.47	2.02	2.17	2.50	2.09	2.24	45
300	2.07	1.16	1.24	2.19	0.93	1.24	2.43	1.09	1.35	40
350	2.06	1.19	1.33	2.01	1.13	1.32	2.01	1.27	1.35	39
400	2.06	1.28	1.36	2.02	1.20	1.31	2.02	1.31	1.35	41
450	2.06	1.29	1.36	2.03	1.11	1.13	1.99	1.26	1.35	39

Different depositions were done to try to understand the impact of the thickness on the optical properties of the films (Figure 4.7). It is observed in Figure 4.7 (B) that, independently of the thickness, a fast decrease of the optical gap occurs for the conversion of Cu_2O into CuO . But once again, no significant change was observed for further conditions.

It is possible to do a rough estimation of the optical bandgap using the knowledge of the absorption coefficient and the first derivative. The same principle was used by Ariel *et al.* [22] for HgCdTe , assuming the existence of two main absorption regions characterized by a magnitude E in relation to E_G . The first region, defined for photon energies less than E_G , has exponential absorption behaviour and is known as the Urbach absorption range. The second range is defined for values of E higher than E_G , having a square-root dependence known by Kane absorption range.

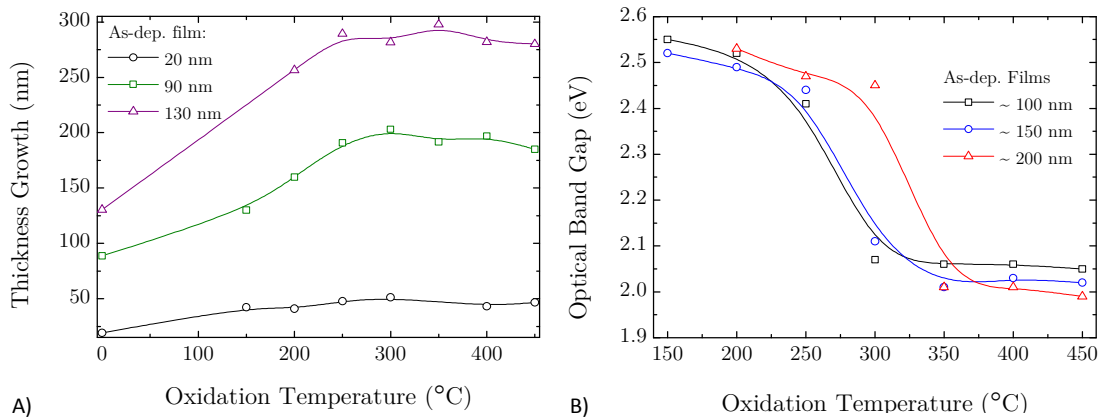


Figure 4.7 – (A) Evolution of the thickness with oxidation temperature; (B) Variation of the direct optical bandgap with the oxidation temperature for as-deposited Cu films with thicknesses around 100, 150 and 200 nm.

This model can be defined as,

$$\alpha \sim e^{\left(\frac{E-E_G}{E_t}\right)} \rightarrow E < E_G \quad (4.4)$$

$$\alpha \sim \sqrt{E - E_G} \rightarrow E > E_G \quad (4.5)$$

where E_t is a coefficient of the order of the thermal energy kT . Thus the derivative of α in respect to the photon energy can be expressed as:

$$d\alpha/dE \sim e^{\left(\frac{E-E_G}{E_t}\right)} \rightarrow E < E_G \quad (4.6)$$

$$d\alpha/dE \sim 1/\sqrt{E - E_G} \rightarrow E > E_G \quad (4.7)$$

Plotting these two derivatives, it is possible to see a sharp peak near the transition between the two types of absorption which occurs at $E \sim E_G$ (Figure 4.8 (B)). Then E_G can be estimated from the location of the peak $d\alpha/dE$. In Figure 4.8 (A) the results are displayed for both Cu_2O and CuO . For Cu_2O it is possible to see that the peak around 2.6 eV preceded and followed by a valley at ~ 2.8 eV and 2.3 eV, respectively. These points are correspondent to an inflection in the absorption coefficient curve. This means that at around 2.3 – 2.4 eV (region correspondent to the Urbach Tail) the material starts to absorb in a high rate the incident energy, being a maximum absorption at the maximum of the derivative (~ 2.6 eV).

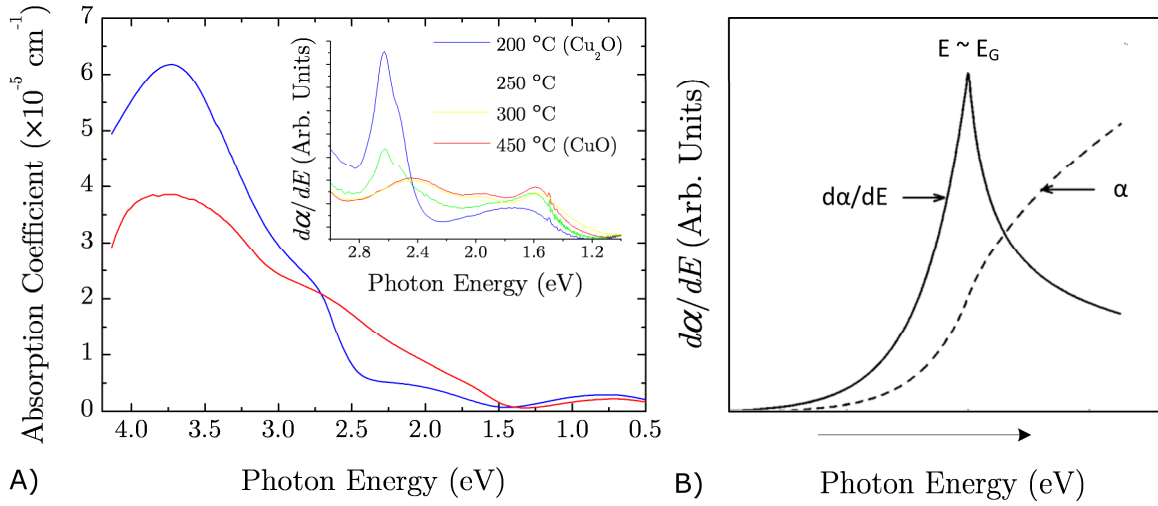


Figure 4.8 – A) Absorption coefficient of Cu_2O and CuO at room temperature, for the as-dep. film with ~ 90 nm thickness; B) Example of the Urbach absorption range (photon energies lower than E_G) and Kane absorption range (photon energies higher than E_G).

For higher energies its absorption rate continuously fall until reaches the photon energy of 2.8 eV. One can expect that the maximum of the derivative is associated to maximum absorption of the incident radiation, matching with the optical bandgap. This value estimated

for the Cu_2O is in agreement with the optical bandgap calculated using the Tauc plot model for the direct allowed transition (2.52 eV).

In case of CuO , and observing the absorption coefficient curve, the inflection point is not so evident in this case, and consequently will be traduced in wide peaks and not so accurate values. The peaks are located in the expected range of temperatures ~ 1.6 eV and 2.4 eV. The first one (2.4 eV) is in the near-infrared region where the interference tails are stronger, complicating the quality of the estimation. The peak associated to 1.6 eV is in the region correspondent to the CuO bandgap.

4.4.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

The results of FTIR measurements are summarized in Figure 4.9. The spectra of the films annealed at 150 °C and 200 °C, are characterized by a strong band with a minimum transmittance around 617 cm^{-1} , corresponding to a vibration mode of 76 meV. It starts to appear in the spectra of the films annealed at 150 °C and is also observed in films annealed at 250 °C. Balamurugan *et al.* [23] and Bellakhal *et al.* [24] identified the same absorption band assigned to the phonon spectrum of Cu_2O . Wide absorption bands are found for wavenumbers between 424 cm^{-1} and 463 cm^{-1} , corresponding to phonon energies of 53 to 57 meV, respectively. This is in agreement with the results obtained by Johan M. Rafie *et al.* [25], observing two absorption regions correspondent to 420 to 500 cm^{-1} (43.4 and 63.9 meV). However in the present case they could be misunderstood due to the noise of the measurement. The absorption band around 1064 cm^{-1} can also be attributed to a biphononic origin that was reported to be found at 1125 cm^{-1} by Burlakov *et al.* [26] corresponding to a phonon energy of ~ 140 meV. This is also a region of the Si-O-Si stretching vibration modes (1064 - 1125 cm^{-1}) [27-29]. Despite the SiO_2 was removed by an etching solution it is not possible to guarantee that after annealing no SiO_2 remains in the film.

An absorption band near $\sim 535\text{ cm}^{-1}$ (66 meV) starts to be visible when the films are annealed at 300 °C. That location is around the reported by several authors for the phonon correspondent to the CuO phase [16, 23-25]. The most important result is the conversion of Cu_2O into CuO after annealing at 300 °C, with the disappearing of the peak around 617 - 620 cm^{-1} .

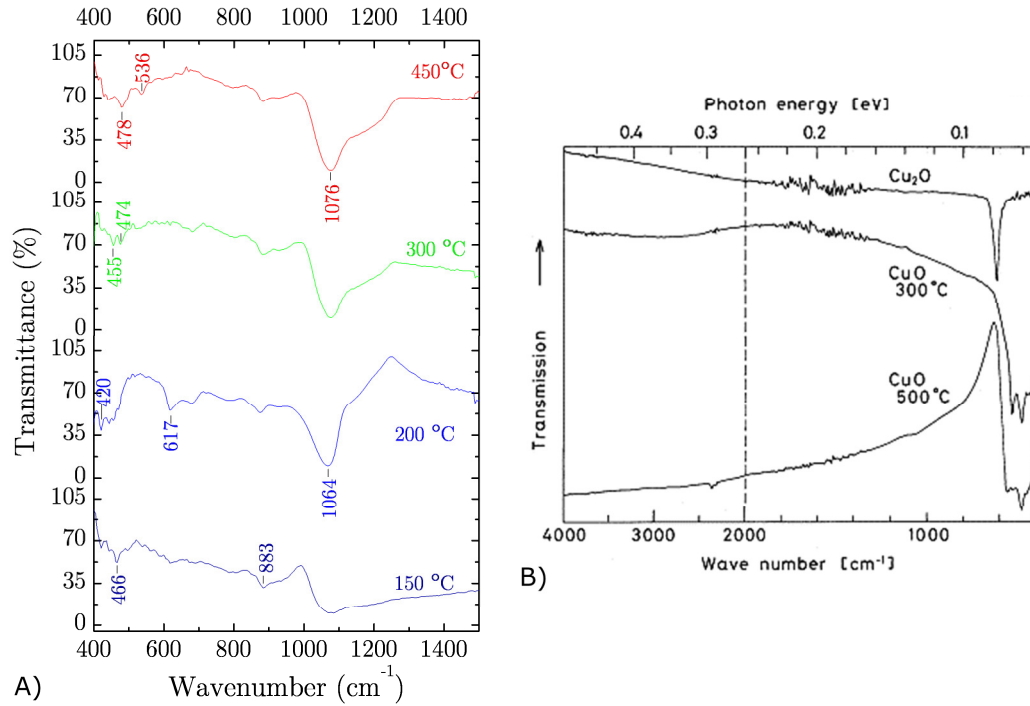


Figure 4.9 – A) FTIR spectra of copper oxides films annealed at different temperatures (150- 450 °C); B) Results obtained by Maruyama *et al.*[30] observing the phonon energy for Cu₂O ~617 cm⁻¹ and ~500 cm⁻¹ for CuO.

4.4.3 SPECTROSCOPIC ELLIPSOMETRY

The spectroscopic ellipsometry (SE) was used to complement the information obtained by the previous techniques. As described in Chapter III, Section 3.3.3. the Tauc-Lorentz (TL) model [31] was used and applied to describe the polycrystalline and polycrystalline/amorphous layers [32, 33]. The Drude model was used for the metallic layers.

The layer model shown in Figure 4.10, was built with the knowledge acquired from the results obtained by the other techniques. The measurements were repeated in different copper samples (with different thicknesses) and adjusted to the model to see its validity. The modulation started with single and high crystalline CuO samples, to avoid the possibility of un-homogeneous character along the thickness.

Cupric (produced at 450 °C) it is the most thermodynamically stable copper oxide, and at enough high temperatures is easier to assume that no cuprous oxide will be present in the sample. This specific temperature was modulated using the layer model presented in Figure 4.10 (E). In fact, the samples annealed at 450 °C showed so high crystallinity that could be adjusted to a single layer model described by Tauc Lorentz with 3 oscillators. For this specific

model the quality of the fitting was found around $\chi^2 \sim 1.4$. However, for the CuO samples produced at lower temperatures (300 – 400 °C) the model failed. To study the properties of the CuO phase with the oxidation temperature, a new model was demanded. This was achieved assuming the existence of an amorphous CuO phase near the glass surface (modelled by TL1, Figure 4.10 (E)). This assumption produced better results for all the CuO phases. Figure 4.11 presents the adjustment of the theoretical model to the experimental data for all the layer models used (Figure 4.10).

A)

	Void (%)	Cu Drude (%)
1:	Cu Drude	
2:	Cu Drude	
3:	Glass	
	Void	

B)

	Void (%)	Cu ₂ O TL3 (%)
1:	Cu ₂ O TL3	
2:	Cu ₂ O TL3	
3:	Cu Drude	
	Glass	
	Void	

C)

	Void (%)	Cu ₂ O TL 3 (%)
1:	Cu ₂ O TL 3	
2:	Cu ₂ O TL 3	
3:	Cu ₂ O TL	
	Glass	
	Void	

D)

	Void (%)	CuO TL 3 (%)
1:	CuO TL 3	
2:	CuO TL 3	
3:	Cu ₂ O TL3	
4:	Cu ₂ O TL	
	Glass	
	Void	

E)

	Void (%)	CuO TL 3 (%)
1:	CuO TL 3	
2:	CuO TL 3	
3:	CuO TL	
	Glass	
	Void	

Figure 4.10 – Layer models used to fit the experimental data for Cu (A), Cu/Cu₂O (B), Cu₂O (C), Cu₂O/CuO (D) and CuO phase (E).

In case of Cu₂O the annealed samples at 200 °C were chosen to modulate all the sub-layers of Cu₂O used (Figure 4.10 (B), (C) and (D)), since no CuO phase was clearly observed with other techniques for this temperature. In XRD was only observed a single Cu₂O phase. However is not possible to guarantee with this technique the un-existence of a very thin layer of CuO or Cu₂O/CuO mixture or even a crystalline/amorphous mixture. For this reason the Cu₂O was the most complicated of the copper phases to be modelled and was important to have the TL3 used to describe the CuO phase already “calibrated”. With this procedure the number of parameters to be modelled was reduced, simplifying the process and assisting the convergence. Once a compatible model is achieved, it is “stressed” with films of different thicknesses to guarantee its validity, In Table 4.7 some of the results obtained from the model are presented.

In an oxidation process the composition of the film along Z may be not homogeneous due to the diffusion process. However it was shown here that can be approximated by a several layers (t_1, t_2, t_3, t_4) model. The thickness t_1 is related to the roughness of the film and can be compared to the RMS roughness obtained by AFM. The RMS roughness is a measurement of

the variation of an amplitude Z along the surface sample (X - Y). This variation of the amplitude should be in the same order of magnitude of the value t_i , for a uniform film along (Z).

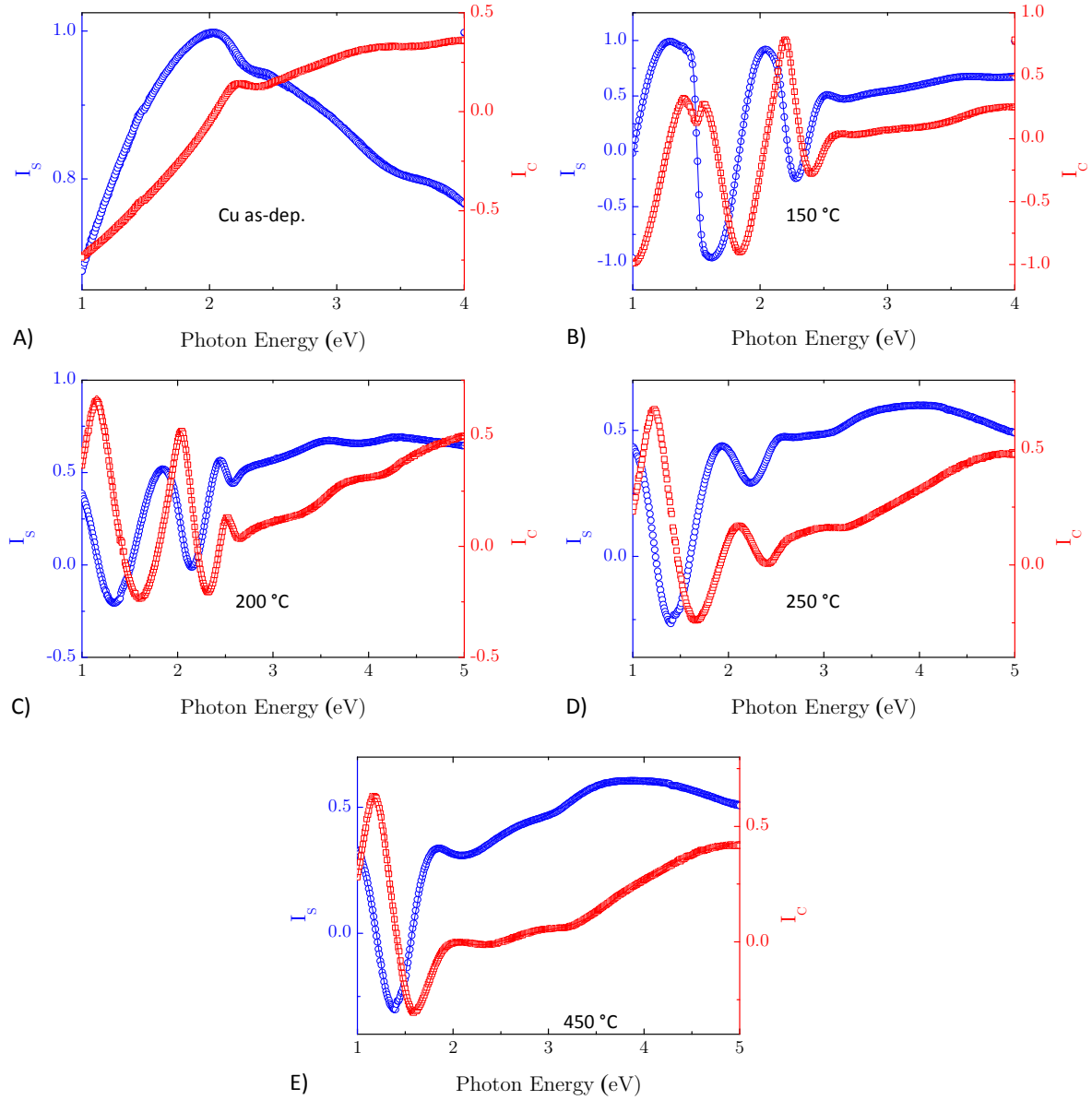


Figure 4.11 – The I_s and I_c functions are fitted using the presented models for the as-deposited and oxidized samples.

Figure 4.17 (B) shows a comparison between the RMS roughnesses obtained by AFM for an as-dep. ~ 90 nm, to the t_i roughness for the ~ 130 nm thickness. Despite of the different thicknesses of the compared films, it is possible to observe that the behaviour of the roughness versus oxidation temperature is very similar to each other, showing the agreement of the SE model to the values obtained by AFM. This was expected due to the low differences between the two set of samples, that guarantees a similar oxidation kinetics in the range of

temperatures used (this will also be presented in Section 6). The highest differences between the two techniques were observed in the region of 200 – 250 °C. This is a transition region where the conversion of Cu_2O to CuO occurs and the presented model may be not perfectly adequate. This was also one of the complicated regions to modulate. Figure 4.13 presents the refractive index (n_r) and extinction coefficient (k_i) obtained for all the Cu_2O and CuO phases.

Table 4.7 – Simulation parameters obtained for the Cu_2O and CuO using the model C and D, respectively (for as-dep. Cu film of 130 nm).

T (°C)	t_1 (nm)	t_2 (nm)	t_3 (nm)	t_4 (nm)	E_G (eV) Cryst. (eV)	Amorp. (eV)	χ^2	t_{total} (nm)
Cu	0.220±0.02	80.30±2.91	49.3±0.26	--	--	--	0.078	~127
150	14.88±0.20	188.23±1.19	20.42±1.92	--	1.79	--	2.15	~224
200	22.80±0.09	181.47±0.65	20.83±0.36	--	2.33	0.20	0.930	~225
250	6.40±0.50	91.43±2.36	87.33±4.80	27.44±4.74	1.35/2.33	0.60	0.729	
300	11.30±0.34	79.4±0.59	158.5±1.68	--	1.40	0.68	0.477	~249
350	8.64±0.15	208.6±0.81	54.3±5.28	--	1.35	0.78	0.319	~272
400	10.90±0.17	216.0±1.00	10.8±1.26	--	1.39	0.59	0.308	~238
450	7.54±0.14	209.1±0.68	8.20±0.63	--	1.35	0.60	0.372	~225

Figure 4.12 exhibits a plot of the evolution of each layer with the oxidation temperature for the as-deposited films with a thickness of ~130 nm. These results show that the films are apparently constituted by different regions, and with help of the other techniques (RBS and XRD) it was possible to understand each one of them. In Figure 4.12 some of these results are displayed.

In particular the samples obtained in the transition region (150 °C), the layer t_3 is constituted of metallic copper. The layer t_2 with a modelled optical gap of 1.79 eV is consistent with a copper rich region of Cu_xO (equivalent to Cu_2O). In the other transition region (250 °C) the modulation gave for the crystalline layer an optical bandgap of ~1.35eV (consistent with the CuO bandgap) in top of another layer of bandgap ~2.33 eV (coherent with the Cu_2O bandgap). These results are in agreement with the others obtained by RBS and XRD, showing a CuO layer (or oxygen rich CO) in top of a Cu_2O layer (oxygen poor CO). In other regions (200, 300 – 450 °C) the consistence of the optical bandgap with the results expected for Cu_2O and CuO is also noticed, ranging 1.96 – 2.33 eV and 1.35 -1.45 eV, respectively.

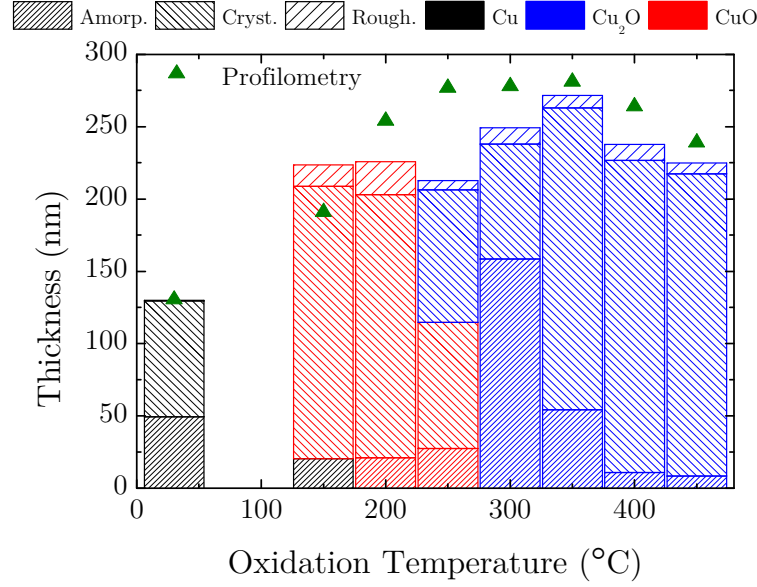


Figure 4.12 – Thickness measured by SE with different layers corresponding to crystalline (t_2), amorphous (t_3), roughness (t_1). Comparison between thicknesses obtained by profilometry and SE.

One of the major advantages of this technique is the possibility to characterize a multilayer sample, extrapolating with an adequate model information for each one of the individual layers. Figure 4.13 presents some optical properties obtained using SE for the crystalline Cu_2O and CuO : the refractive index (n_r), the extinction coefficient (k_i) and the dielectric function (real and imaginary). It is known that n_r describes de refraction and k_i the absorption. The real and the imaginary parts of the dielectric constants (ε_r and ε_i) can be related to the n_r and k_i by the expression:

$$\varepsilon_i(E) = 2n_r(E)k_i(E) \quad (4.8)$$

$$\varepsilon_r(E) = n_r^2(E) - k_i^2(E) \quad (4.9)$$

$$\tilde{\varepsilon} = \varepsilon_r + i\varepsilon_i \quad (4.10)$$

where $\tilde{\varepsilon}$ is the complex dielectric constant. It is possible to compare the results obtained with the standard refractive index* (n_r) measurements of Cu_2O and CuO , around 3.04 ($k_i = 0.14$) and 2.63 ($k_i = 0.52$), respectively [34].

* Standard refractive index are measured using a yellow doublet sodium D line, with $\lambda = 589 \text{ nm}$ (2.11 eV).

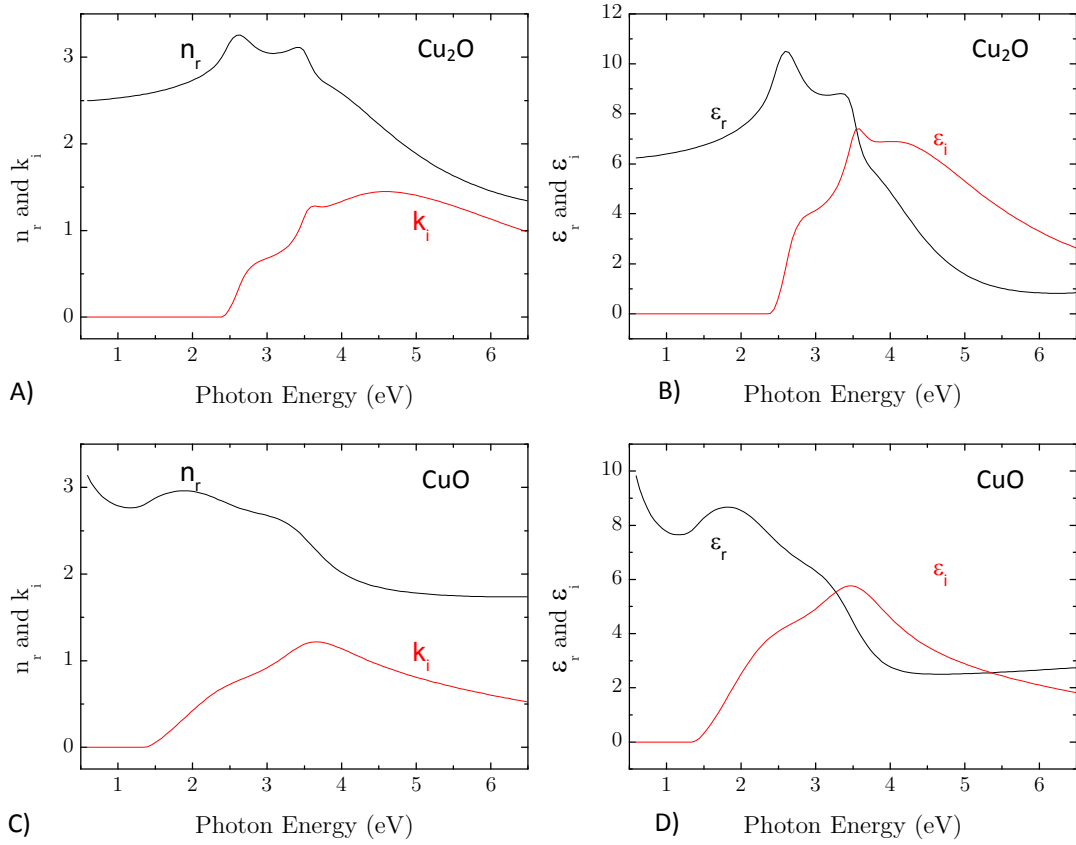


Figure 4.13 – Refractive index (n_r and k_i) and dielectric function (ϵ) of the major crystalline part of both Cu_2O and CuO (the r and i are assigned to the real and the imaginary part).

4.5 SURFACE CHARACTERIZATION

Kelvin probe (KP), AFM and SEM techniques were used to study the morphological/surface properties of the films. The AFM microstructures were also used to estimate the roughness and the size of the agglomerates. The surface potential measured by KP has served to estimate the work function of the films, important “parameter” in the design of devices.

4.5.1 KELVIN PROBE

The samples were analysed by KP explained in Chapter III, Section 3.4.3 to estimate the work function (Φ). This property is very important in the design of devices, particularly in engineering the contacts, since depending on Φ they can have an ohmic or Schottky behaviour.

The results of the measurements are in agreement with the data published in literature

[35-40] for Cu, Cu₂O and CuO and are displayed in Table 4.8.

Table 4.8 – Surface properties of copper and copper oxides (W_F is the surface potential, Φ and δ_Φ are the work function and the standard error estimated in this work, $\Phi^{Lit.}$ the work function estimated by other authors).

T (°C)	Phase	W_F (eV)	Φ (eV)	δ_Φ (meV)	$\Phi^{Lit.}$ (eV) [35-40]
As-dep.	Cu	-39.0016	4.65	3.04	4.65 - 4.70
150	Cu/Cu ₂ O	-136.0648	4.39	2.82	
200	Cu ₂ O	228.5685	4.76	2.67	4.84 – 5.2
250	Cu ₂ O/CuO	273.0567	4.80	3.60	
300		272.7337	4.80	1.41	
350	CuO	830.4707	5.25	1.75	4.8 – 5.2
400		908.3877	5.33	1.57	
450		386.3935	4.80	7.02	

Using the parameters estimated before and with the work function values presented in Table 4.8, it is possible to make a draft of a simple band scheme expected for the bands of Cu₂O and CuO (Figure 4.14) deposited here. For this purpose will be used the optical bandgap estimated by the Tauc-Lorentz model (SE) (Cu₂O ~2.37 eV and CuO ~1.35 eV).

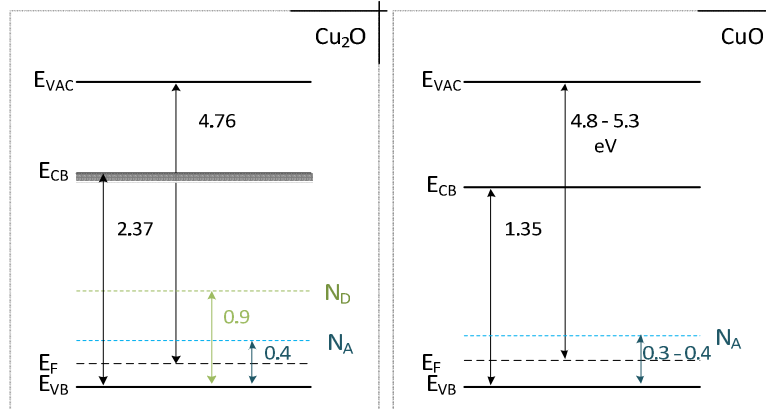


Figure 4.14 – Schematic of a simple band model of Cu₂O and CuO designed with the parameters calculated before. E_{VAC} , E_{CB} , E_{VB} , E_F , N_D and N_A are energy levels correspondent to the vacuum, lowest conduction band, highest valence band, Fermi level, donor level and acceptor level, respectively.

4.5.2 ATOMIC FORCE MICROSCOPY (AFM)

The typical AFM microstructures obtained from the surface analysis of the as-deposited and post-annealed films are shown in Figure 4.15 and in Figure 4.16. In the pictures, occasional agglomerates of grains are observed in the film surface, with sizes up to 60 nm. All the depositions were done with growth rates below 2 Å s⁻¹ to avoid surface stress and defects. However, these agglomerates (clearly presented in further SEM images) appear to persist in the

film surface even with the use of low deposition rates. Homogeneity and smoothness of surfaces are important for multilayer devices; lack of them can compromise their performance. In Figure 4.17 the profile for a 2 μm AFM scan is presented, where is possible to see the evolution of the grain agglomerates.

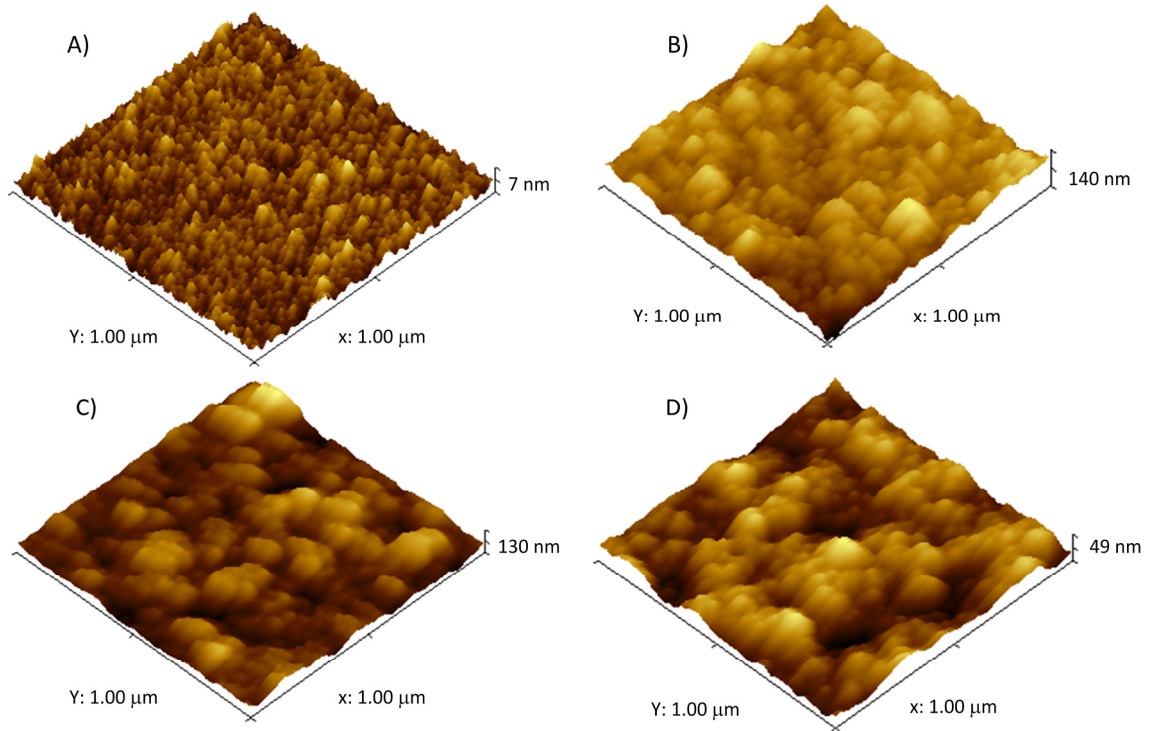


Figure 4.15 – AFM microstructures for the as-deposited copper oxide films (A), and for the films oxidized at 150 °C (B), 200 (C) and 250 °C (D).

The as-deposited copper film is comprised of uniformly distributed and well packed grains ranging $\sim 10 - 20$ nm in size, with a RMS roughness of 1.47 nm. For films annealed at 150 °C, the surface shows randomly distributed cluster of grains, which have presumably increased the RMS roughness to 11.4 nm. The size of the grains vary between ~ 10 and 30 nm with a few agglomerates on top of smaller grains, with dimensions around 60 nm. Few formations like valleys appear throughout the surface of the films as shown in Figure 4.15 (A). These structures seem to contain smaller grains underneath, apparently in a layer structure. Similar images were obtained for the CO deposited by RF sputtering. These results are similar to the ones obtained by other authors [2, 3].

The RMS roughness is found to increase to a maximum of 14.4 nm on annealing at 200 °C, decreasing gradually to 8.7 nm when the oxidation temperature increases (≤ 450 °C). The valleys appear to be replaced by morphology similar to an orange peel, when the oxidation

temperature rises 250 °C. Large grain agglomerates with sizes up to 90 nm are also observed.

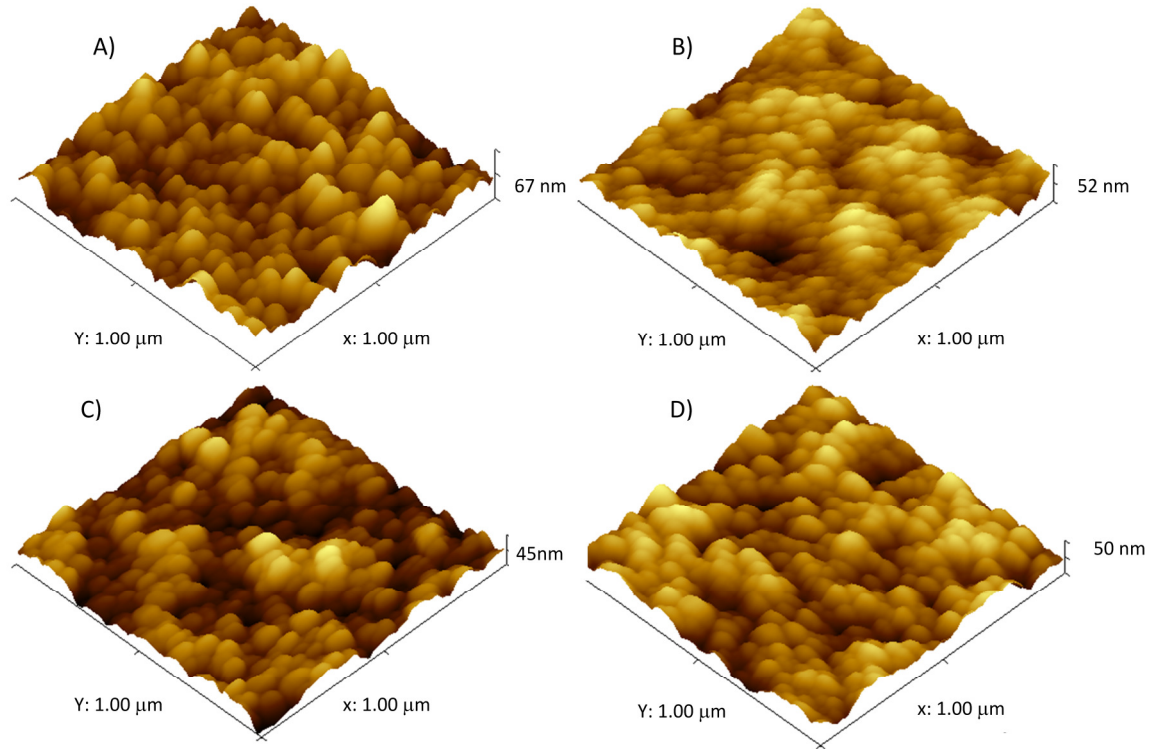


Figure 4.16 – AFM microstructures for the films oxidized at 300 °C (A), 350 °C (B), 400 °C (C) and 450 °C (D).

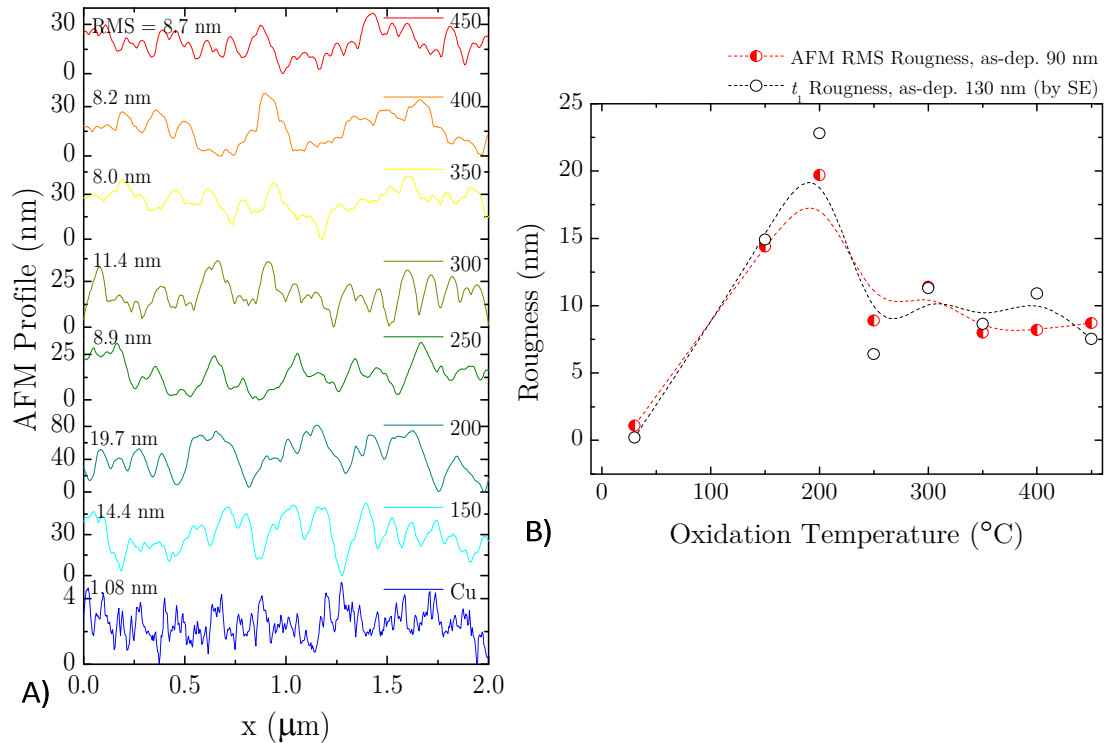


Figure 4.17 – A) AFM profiles for each oxidation temperature; B) Comparison of the roughness obtained by AFM and SE (represented by t_1) for similar as-deposited films.

4.5.3 SCANNING ELECTRON MICROSCOPY (SEM)

SEM allowed the observation of the films in a larger scale (comparatively to AFM) clarifying some aspects not understood in AFM. As showed in the set of pictures presented, it is clear a change in the morphology of Cu films, as a consequence of the temperature and phase transformation. It is seen that in fact the samples oxidized at 150 °C and 200°C presented a very rough surface (consequence of the Cu_2O phase). It is also visible that during the crystallization is favourable the formation of big agglomerates, observed in Figure 4.18 (200 °C). This was also observed on previous results of copper oxidation [4].

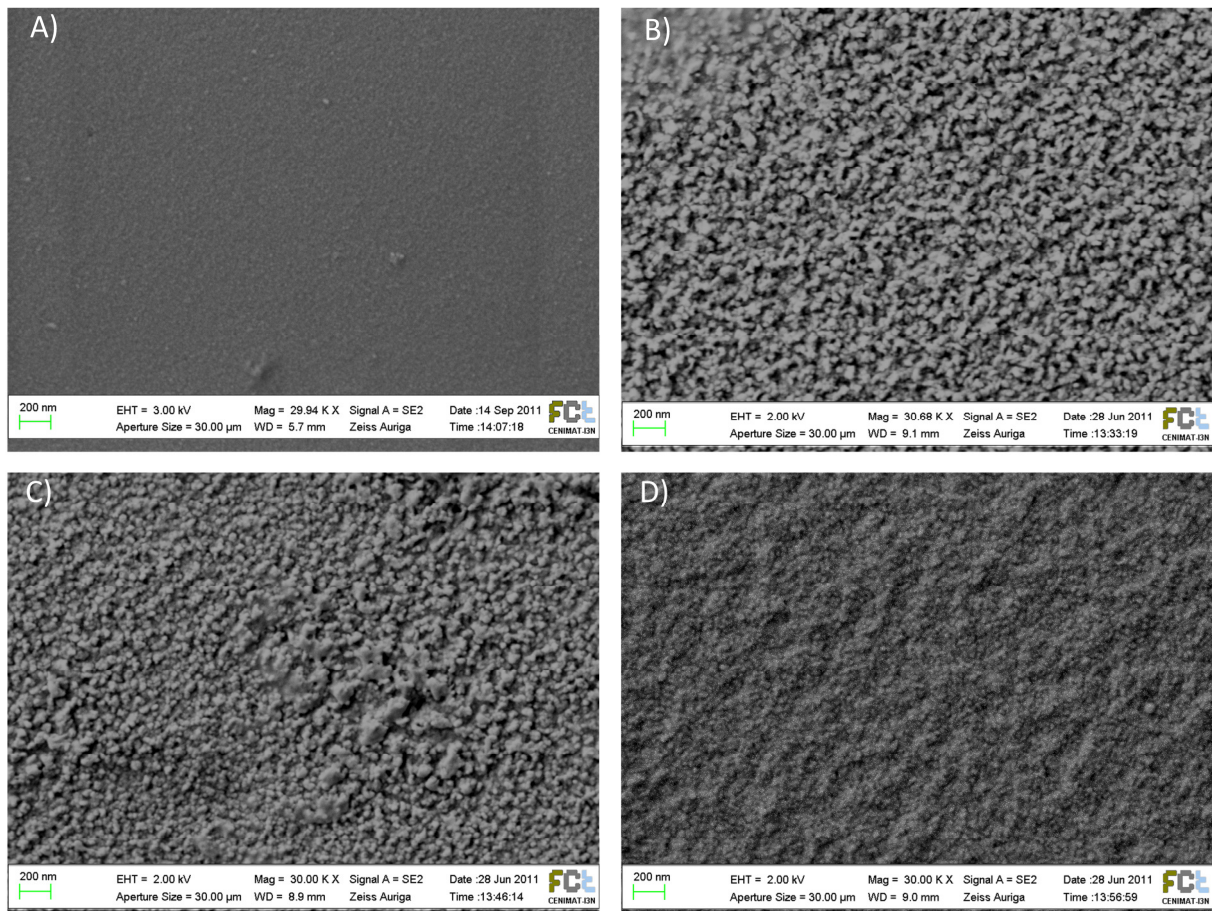


Figure 4.18 – SEM images of the as-dep. film (A) and oxidized films at 150 °C (B), 200 °C (C) and 250 °C (D).

Increasing the oxidation temperature (>250 °C), the surface presents a consistent distribution of grains, forming the “orange peel” morphology. At 450 °C the surface is more uniform, the grains appears to merge with each other, growing in size as shown in the picture (Figure 4.19). The “orange peel” morphology is less evident at this temperature, due to the large size of grains. This is consistent with the AFM analysis and SE, showing that RMS

roughness decreases with the increase of temperature (for $T > 200$ °C).

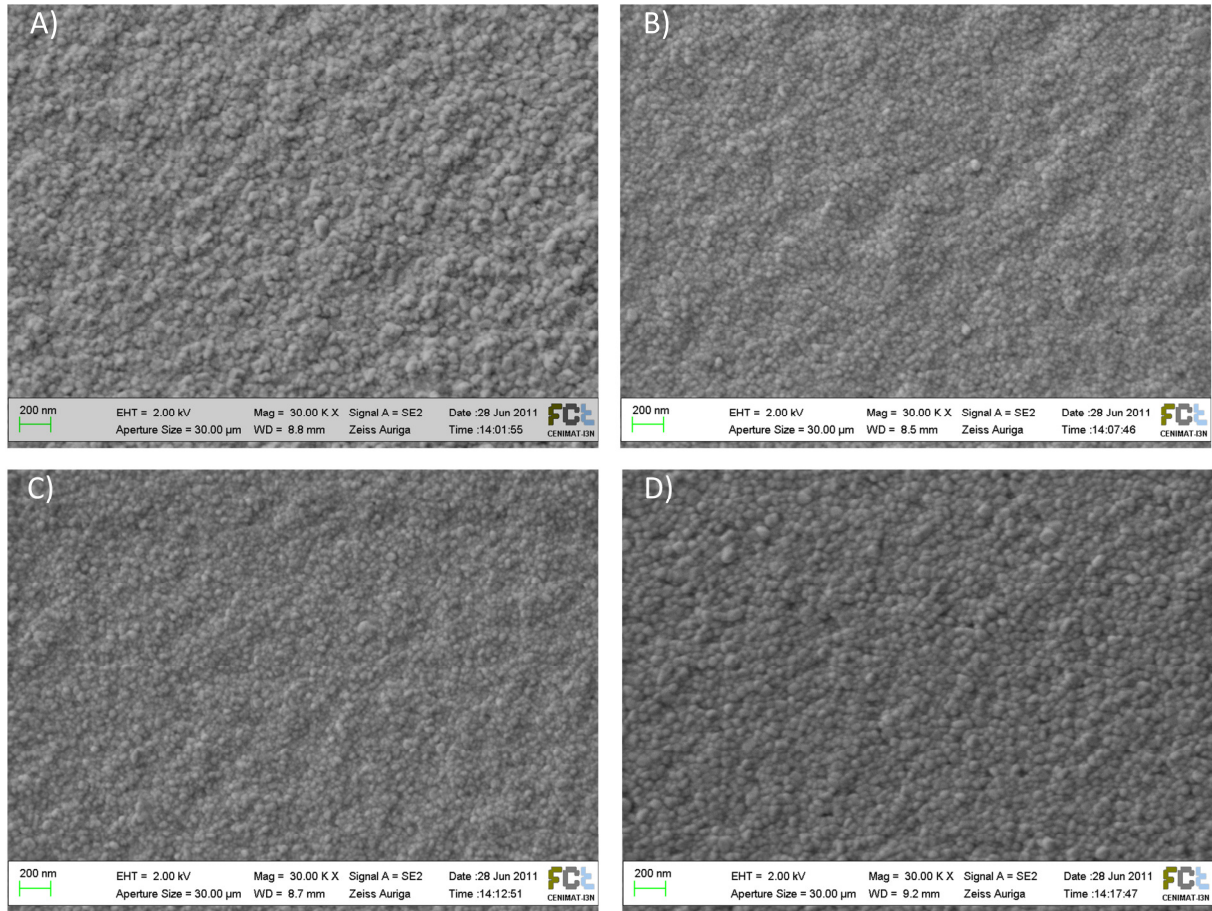


Figure 4.19 – SEM images of the films oxidized at 300 °C (A), 350 °C (B), 400 °C (C) and 450 °C (D).

4.6 OXIDATION KINETICS

The goal of this thesis was not exactly the study the kinetics of the copper oxidation, nevertheless a simple experiment was done to try to understand its dynamics in range of temperatures 200 – 300 °C[†].

From the beginning of this work, the impact of temperature oxidation on the films thickness was observed, noticing that a cooper film of initial thickness t_i will growth after oxidation to approximately $2 \times t_i$.

The oxidation is characterized by dramatic changes in the film structure and on their physical properties. The thickness increases as a consequence of the oxygen diffusion in the copper structure (Chapter II, Section 2.3), leading to the formation of an oxide layer on the

[†] Range of temperatures used in the production of TFTs.

surface of the film. In a non-volatile oxidation process, the increase of the thickness can be correlated to the changes in their structure, particularly in the unit cell volume associated to the different phases formed.

Using the initial thickness of the copper thin-film, it is possible to perform a rough estimation of the thickness when the film is fully oxidized. Taking in consideration only the lattice parameters for Cu, Cu₂O and CuO, and using the simple relations between their unit cells volumes and the volume of initial metallic film (Table 4.2 from Section 4.1.2.1 presents the structural parameters of the copper oxides). In Figure 4.20 a comparison between the increase of the thickness and the unit cell volumes is done for the as-deposited film of ~90 nm.

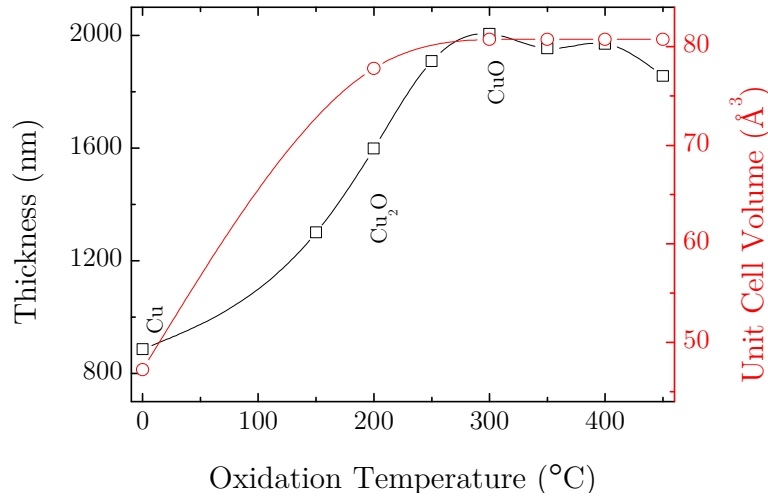


Figure 4.20 – Correlation of the thickness growth associated to the oxidation of a copper film of ~ 90 nm with the Cu, Cu₂O and CuO unit cell volumes.

Assuming that the as-deposited copper film is homogeneous and has an initial volume, $V_{initial} = S \times t_i$ (which t_i is the thickness and S the area occupied by the film, $S \approx 2.5 \times 2.5$ cm), the change in volume should be projected as a change in thickness, since the area of the deposited film is constant and copper oxidizes in a non-volatile oxidation. It is possible to obtain an expression that gives the estimation on thickness, dependent of the phase formed and the initial copper thickness:

$$\frac{V_{UCell}^{Cu_2O}}{V_{UCell}^{Cu}} \propto \frac{V_{film}^{Cu_2O}}{V_{film}^{Cu}} \rightarrow V_{film}^{Cu_2O} = A \frac{V_{UCell}^{Cu_2O}}{V_{UCell}^{Cu}} S \times t_i \quad (4.11)$$

where, A is a constant that is related to the packaging efficiency of Cu and Cu₂O and $V_{film}^{Cu_2O}$ and V_{film}^{Cu} are the volumes estimated for the films of Cu₂O and Cu, respectively. The same relation of volumes done for Cu₂O was also done for CuO. Using for simplification $A = 1$, this

expression gives an approximation of the thickness for the two CO phases. For instance, assuming a Cu film with ~ 420 nm, annealed at 300°C , the CuO phase will be formed having an expected thickness around 728 nm, what is near the real value of ~ 680 nm.

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At 200°C , the oxidation process is very rapid in the beginning, but after a few minutes the oxidation rate drops to minor values. Two reasons can explain this behaviour: copper is already fully oxidized and/or the oxide layer is thick enough to act as a protective layer. As described in Chapter II, the oxidation kinetics of Cu has already been subject of several studies at medium high temperatures ($> 300^\circ\text{C}$), being the parabolic rate law the most frequently observed.

Pilling and Bedworth, in their study of the oxidation of metals, divided metals in two classes (relatively to their oxidation kinetics), according to the relation between the volume occupied by the oxide and the metal [41]. In the first class, the oxide layer formed will protect the remaining material preventing the oxidation. In the second class (owing the necessary porous nature of the oxide) the oxide has an ineffective protective action, and the oxidation will proceed. They pointed out that when the oxide protects the metal, as soon as a complete oxide layer is formed, the rate of diffusion of oxygen through the oxide will control the rate of oxidation. The rate of diffusion is considered to be inversely proportional to the thickness of the oxide layer following [41-44]:

$$\frac{dx}{dt} = \frac{A}{x} \quad (4.12)$$

$$x_{oxide}^2 = A t + B. \quad (4.13)$$

where x is the thickness of oxide formed at time t , A and B are constants. The constant A can also be defined as $A = 2 k_p$, where k_p is the called parabolic rate constant [42, 44]:

$$k_p = k_p^0 P_{O_2}^{\frac{1}{4}} e^{-E_p/kT} \quad (4.14)$$

At low temperatures ($\leq 300 - 400^\circ\text{C}$), Mott and Cabrera [42] have theoretically proposed the inverse logarithmic and the cubic rate laws. However, experimental data at low temperature is quite rare due to the difficulty of precise measurements [43]. Initially oxidation is extremely rapid, but after a few minutes or hours it drops to very low or negligible values, following to the equation:

$$x = k_0 \ln(k_1 t + 1), \quad (4.15)$$

where k_0 and k_1 are constants.

In the present work the oxidation kinetics of copper oxide thin-films was investigated by oxidising systematically three metallic thin-films of copper of different thickness (340, 780 and 1500 nm) at different exposition periods (200 °C and 300 °C). The thickness was measured at each step and the results are presented in Figure 4.21. Cu_2O is formed effectively at 200 °C and for a long period of time it was possible to assure that there is no conversion to CuO (at least visible). At 300 °C the formation of CuO it is expected, although as discussed in Section 1.2.1 and according to the Ellingham diagram, if metallic copper exists (even when temperatures are favourable to form CuO) a Cu_2O layer will always exist below the CuO . Therefore, the oxidation temperature and time are important factors that influence the oxidation process and consequently the CO phases produced.

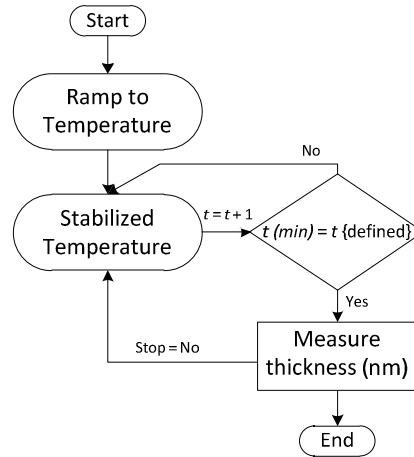


Figure 4.21 – Procedure used to observe the copper oxidation kinetics.

The range of temperatures used (200 – 300 °C) are also particularly interesting in device production, since is the interval used for post-annealing treatments of the TFTs. The logarithmic and parabolic adjustment of the experimental data was tried. It was possible to find convergence for each one of the rules (parabolic and logarithmic), with correlation factor $> 97\%$. It is possible to verify by the plot in Figure 4.22 (A), that the growth of the oxide layer follows a logarithmic behaviour. A thin oxide layer is formed, constituting a barrier for oxygen diffusion, protecting the metal below. As a result an initial formation oxide is followed by practically zero growth of the oxide.

This kind of growth is governed by a logarithmic rule and is also valid if the oxidation

occurs completely (since no more film is available to oxidize). For the as-deposited film with thickness around 1500 nm, the oxide layer achieves a thickness big enough to act as a protective layer, preventing the oxidation of the copper located below (in the range of time considered in the experiment).

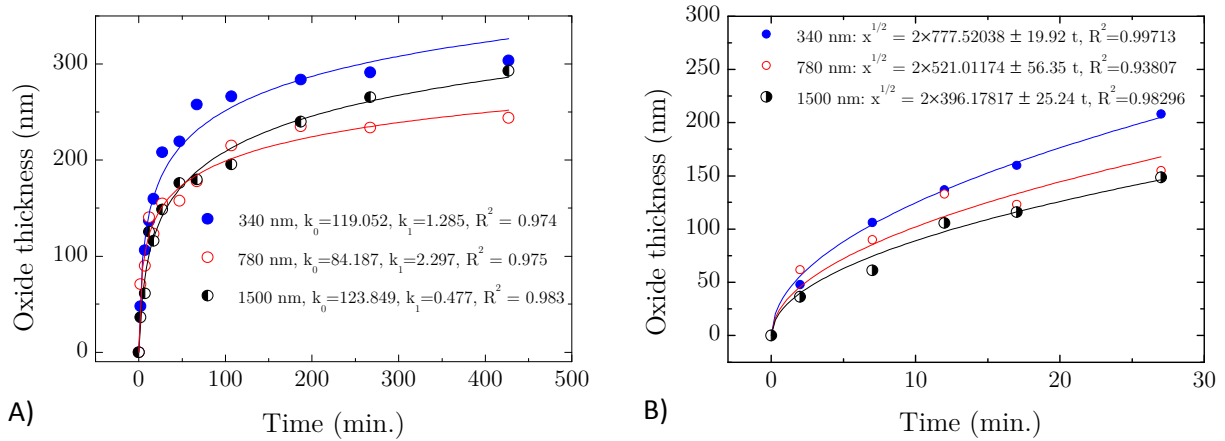


Figure 4.22 – Adjustment of the experimental data obtained for the oxidation at 200 °C to a logarithmic (A) and parabolic (B) rule. As-deposited films with thicknesses around 340, 780 and 1500 nm, respectively.

The k_0 values of the logarithmic rule are found to be between ~84 to 124 nm. In Figure 4.22 (B) it is possible to see that a parabolic rule can also be fitted to the early stages of oxidation, when the protective behaviour of the oxide layer is not so effective, and the diffusion rate controls the oxidation kinetics.

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At higher temperatures (300 °C) the oxidation occurs very rapidly, and in case of films with lower thicknesses is not possible to perform an adjustment in all the range, since the oxidation is complete (Figure 4.23 (A)).

For the higher thickness film, it is possible to obtain k_0 values of 342.8 nm. In Figure 4.23 (B) a very rapid growth is also shown in the early stages of the oxidation process, which may also be described by the parabolic rule defined in equation (4.13). Using the experimental data for the experiment $T = 200$ and $T = 300$ °C and the equation (4.14) it is possible to perform a rough estimation of the activation energy of oxidation, obtaining values of 0.50, 0.73 and 0.71 eV (47, 70 and 68 kJ mol⁻¹) for the films with as-deposited thickness of 340, 780 and 1500 nm, respectively. These results are in agreement with others found in literature between 39 kJ/mol and 223 kJ/mol [45-47].

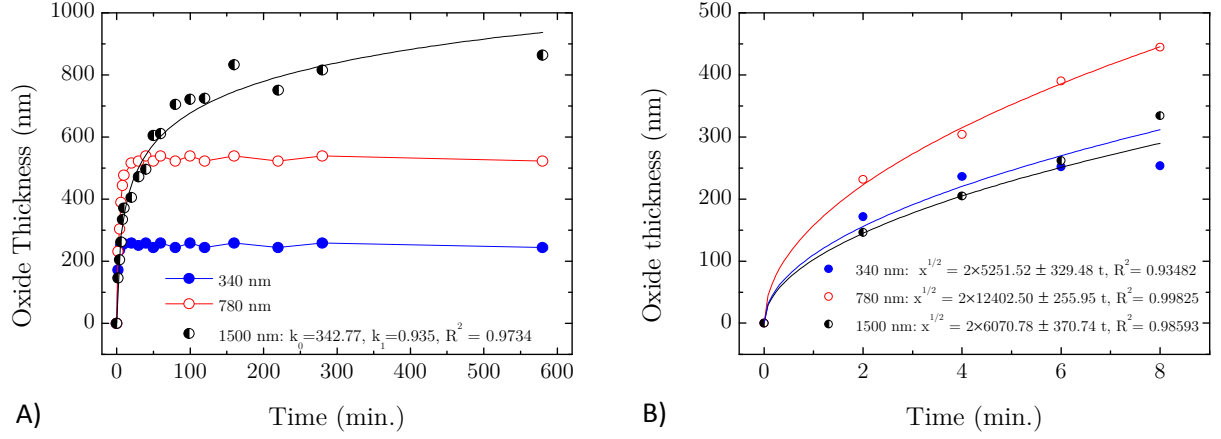


Figure 4.23 - Adjustment of the experimental data obtained for the oxidation at 300 °C to a logarithmic (A) and parabolic (B) rule. As-deposited films with thicknesses around 340, 780 and 1500 nm, respectively.

4.7 CONCLUSIONS

In this work was presented a simple method to produce p-type thin-films of Cu_2O and CuO from thermal oxidation of metallic copper. The oxidation kinetics was also observed and the data were adjusted to a parabolic and logarithmic rule. The activation energies of oxidation were also estimated using an Arrhenius equation in the range of 47 to 70 kJ/mol.

Using XRD and RBS it was possible to identify copper oxides with poor-oxygen content correspondent to the Cu_2O phase in lower temperature region (≤ 250 °C) and rich-oxygen content films, explained by the conversion of Cu_2O to CuO , at higher temperature region (≥ 250 °C). This was also confirmed by the absorption peaks of FTIR correspondent to the vibration modes of Cu_2O and CuO .

The films oxidized at 200, 250 and 300 °C showed the highest mobility values of 2.2, 1.9 and 1.6 $\text{cm}^2 \text{V}^{-1}\text{s}^{-1}$, respectively. For higher temperatures the mobility drops to negligible values around 0.1 $\text{cm}^2 \text{V}^{-1}\text{s}^{-1}$.

In terms of their optical properties, the Cu_2O phase always presents higher transparency ($\sim 57\%$ for a thin-film with a normalized thickness of 100 nm) with a direct optical gap of $E_G \approx 2.52$ eV and a direct forbidden gap of ~ 2.30 eV. The CuO , showed a direct allowed optical bandgap around 2.1 eV and an indirect allowed bandgap ranging 1.0 to 1.31 eV. SE also confirmed the optical bandgap of the films with values of 2.33 eV for the Cu_2O phase (film oxidised at 200 °C) and 1.35 to 1.40 eV for the CuO phase. This technique was applied

successfully to determine among other things the refractive index. The oxidation model by layers is consistent with the oxidation process in copper, being always observed a film of amorphous character near the interface with the glass.

FTIR was also used to try to identify the vibration modes correspondent to the Cu_2O and CuO phases. The existence of the 617 cm^{-1} absorption band is clear, correspondent to a vibration mode of 80 meV attributed to Cu_2O . However, in case of the films produced with CuO phase was difficult to identify clearly the vibrations modes, maybe due to the overlap of the minimums attributed to SiO_2 . At $450\text{ }^\circ\text{C}$ a minimum at 536 cm^{-1} correspondent to the CuO phase was visible.

The surface potential was also measured using the Kelvin probe method, allowing an estimation of the work function of the films around 4.76 eV for Cu_2O and ranging 4.80 – 5.33 for CuO . No clear trend was observed in the estimated work function with the oxidation temperature.

The morphology of the films was analysed using AFM and SEM microscopies. It was observed that the films correspondent to Cu_2O phase have the roughest surface with the maximum value of RMS around 14.4 nm. With the increase of the oxidation temperature the RMS decreases, reaching an average value about 8.3 nm for CuO .

This technique was applied in the production of p-type TFTs of Cu_2O and CuO channel successfully, the first in the world to be produced using this technique, which is presented in Chapter XVIII [48].

4.8 REFERENCES

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Chapter V

Copper oxides by RF sputtering

CONTENTS

In this section it's presented some results on Cu_2O and CuO deposited by RF Magnetron Sputtering in two different systems using different powers: 50 W (Part I) and 100 W (Part II).

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 - 5.2 Structural characterization:
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5 COPPER OXIDES BY RF SPUTTERING

Part I

5.1 EXPERIMENTAL DETAILS

Copper oxides films were also produce by RF magnetron sputtering in a reactive atmosphere. The films where studied concerning the influence of oxygen content in their properties. Controlling the oxygen pressures (flow) in the chamber it is possible to control the CO phases produced (Cu_2O and CuO). The films were investigated concerning their electrical, optical, structural and surface/morphological properties. The major objective of this section was the study of the films allowing the selection of the best conditions for the development of p-type TFTs.

Thin-films of copper oxides where obtained by RF sputtering in glass and silicon substrates, using a metallic Cu target of purity 99.997%. The distance between the sample and the magnetron was fixed constant at $d_{\text{TS}} = 15$ cm, and the atmosphere in the chamber was controlled, varying the amount of oxygen, $O_{\text{PP}} = P_{\text{O}_2}/(P_{\text{O}_2} + P_{\text{Ar}})$.

In terms of some deposition parameters, the growth rate (R) is expected to be inversely proportionality to d_{TS} and directly proportional to the power ($\mathbb{P}$). It is desirable to keep ion energies as low as possible otherwise plasma etching tends to compete unfavourably with the deposition. It is also expected that high power can lead to high concentration of defects. For this reason, the relation between power and growth ratio should be balanced. In the case presented in this subsection (Part I), the adopted power was kept at 50 W allowing a reasonable R .

It is notorious the influence of oxygen content in the growth-rate of the films (Figure 5.1), what predicts changes in their properties. The deposition pressure (P_{D}) as discussed in the Chapter II, Section 2.1.2, plays an important role in the R of the films, influencing the effectiveness of the deposition. In a general, high pressures are good to maintain the plasma and small pressures are suitable to maintain a good deposition rate and reduce random

scattering. However, if P_D is very low a concurrent etching process can take place, reducing R with consequences in the film structure and morphology. A low P_D can promote the number of defects in the film.

Table 5.1 – Principal RF magnetron sputtering parameters used in the first part of the work. The depositions were done at room temperature, $d_{TS} = 15$ cm, P_D was varied from 1 Pa^(#1), 6.0×10^{-1} Pa^(#2) and 2.0×10^{-1} Pa^(#3).

O_{PP} (%)	0	9	25	50	75	100
P_B (Pa)			3.0×10^{-2}			
P_{O_2} (Pa)	0	3.0×10^{-3}	1.0×10^{-2}	3.0×10^{-2}	9.0×10^{-2}	9.0×10^{-2}
P_{Ar} (Pa)			3.0×10^{-2}			--
P (W)			50			
$R^{(#1)}$ (Å/s)	--	1.34	0.333	0.183	0.204	0.113
$R^{(#2)}$ (Å/s)	1.61	1.51	0.387	0.227	0.151	0.204
$R^{(#3)}$ (Å/s)	--	1.20	0.237	0.131	0.106	0.221

Observing the data presented in the table or in Figure 5.1, is conclusive that the deposition condition with higher R in this system is associated to a $P_D = 6 \times 10^{-1}$ Pa.

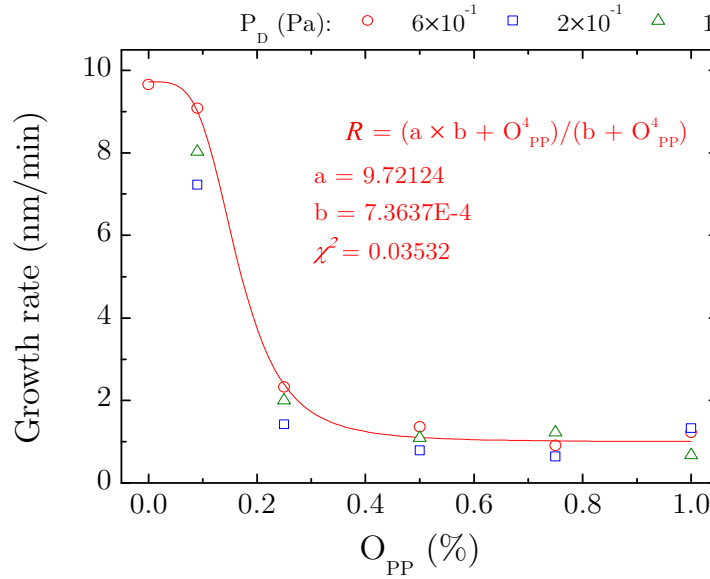


Figure 5.1 – Growth rate (R) versus O_{PP} for different deposition pressures (a and b are constants).

Regarding the relation between the mean-free path (λ_m) and P_D , also presented in the Chapter III Section 3.1.2, low values of λ_m are associated to high values of P_D . A pressure $P_D = 1$ Pa, it is associated to a $\lambda_m \approx 0.8$ cm. Decreasing P_D to 6×10^{-1} Pa, the λ_m will increase to ~ 1.3 cm. A further decrease on P_D and to 2×10^{-1} Pa will lead to a λ_m of 3.8 cm. Small λ_m means that sputtered particles will have several collisions before reaching the substrate. This high number

of collisions can be regarded as a positive effect, because will allow several elastic and (more important) inelastic collisions enabling the excitation of the neutral species, increasing the degree of ionization. In other hand, small λ_m leads to a decrease of the R .

A lower pressure implies high λ_m . The particles will have fewer collisions, accelerating in the called “dark-space” and colliding with high kinetic energy against the surface of the substrate. This process will eject particles from the substrate, influencing the structural uniformity of the films, creating defects. This process is also important in the fabrication of the devices influencing the properties of the semiconductor. Moreover this effect can lead to the degradation of the dielectric layer in the TFT, increasing the leakage current.

5.2 STRUCTURAL CHARACTERIZATION:

5.2.1 X-RAYS DIFFRACTION (XRD)

The films deposited by RF sputtering were analysed to study the formation of Cu_2O and CuO phases with O_{PP} . For this study the deposition pressure, the distance to the target and the power were fixed at 6.0×10^{-1} Pa, 15 cm and 50 W respectively. The time was controlled to obtain films with a specified thickness. For the characterization of these films the thickness was fixed around 200 nm.

The XRD patterns obtained from the as-deposited CO films are presented in their original form in Figure 5.2. However, in all the estimations the background radiation and $\text{CuK}\alpha_2$ deconvolution have been considered.

It is perceptible from the Figure 5.2 a strongly dependence of the crystalline phase on the variation of O_{PP} , in agreement to the results reported by other authors [1]. The films deposited with 0% O_{PP} are confirmed to be metallic cubic Cu phase (denoted by the symbol #) with a strong orientation along the plane $(111)^\#$, matching with the standard ICDD data. Increasing the O_{PP} to 9%, it is observed a structural change corresponding to the formation of a cubic Cu_2O phase, denoted by $\blacklozenge$, with a strongest orientation in the direction $[111]^\blacklozenge$. Further increases in O_{PP} ($\geq 25\%$) leads to a crystallization in the monoclinic CuO phase, denoted by $\blacklozenge$, with a strongest orientation in the direction $[11\bar{1}]^\blacklozenge$. It is noteworthy that the intensity of

strongest plan $(11\bar{1})^\diamond$, and other diffraction peaks associated to other plans, decreases with the increase of O_{PP} . This situation is suggesting a presumably amorphization process, which is substantiated by the result obtained for the films deposited with 100% O_{PP} (the same was verified in the experiments using 100 W, Part II of this chapter). The effect of a high O_{PP} in the formation of CuO also follows the reaction $\text{Cu}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow 2 \text{CuO}$ presented before. It is possible to reverse the oxidation and produce again Cu_2O , using high temperatures and low oxygen pressures.

The study of the structural changes in the Cu_2O after the annealing at 200 °C was also done, since post - annealing is always a step needed in the fabrication of TFTs. For this temperature no phase transformation is expected. From previous results, it was observed that it will occur for higher temperatures (> 200 °C) [2, 3].

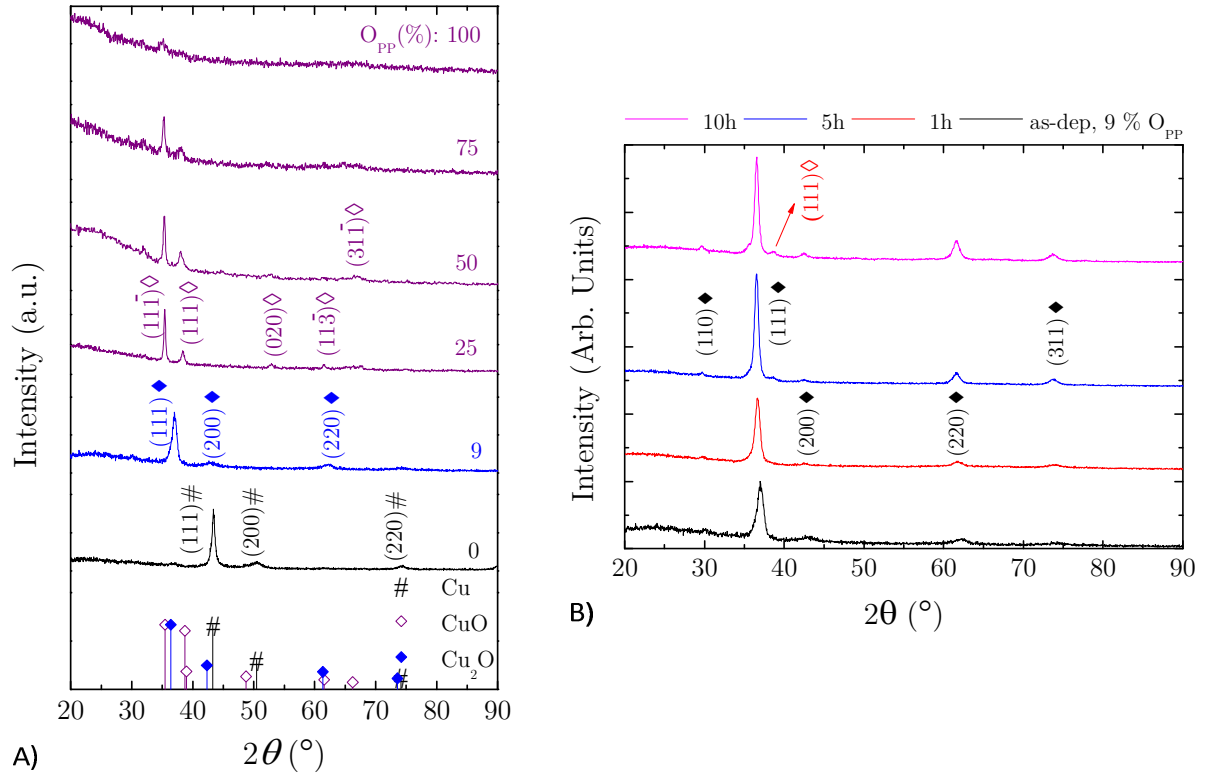


Figure 5.2 - A) XRD patterns of the as-deposited Cu_xO films as a function of O_{PP} (Symbol representations: # - Metallic Cu phase; ♦ - Cu_2O phase; ♦ - CuO phase); B) XRD patterns obtained for the film produced with 9% O_{PP} , annealed at 200 °C in air for 1, 5 and 10 hours (Cu_2O condition).

The as-deposited Cu_2O films deposited with 9% O_{PP} (one of the optimum conditions used for the fabrication of TFT) was annealed at 200 °C in air 1, 5 and 10 hours. It is conclusive that the post-annealing was not effective inducing significant phase changes. However, was

observed an increasing of the intensity of the peak in the direction $[111]^\diamond$ with the increase of time (1, 5 and 10 hours), confirming the improvement of the film crystallinity, that can be associated to the changes observed in their electrical properties (presented in the next section). An interesting remark is that the film annealed for 10 hours shows a relatively negligible peak at 2θ value of $\sim 38.79^\circ$, which matches with CuO phase.

The crystallite size (D) was estimated for the high intense peaks using the Scherrer's equation (3.46), which is quantified in Table 5.2 with other parameters extracted from XRD data. The D decreases from 12.7 nm (metallic Cu film deposited with 0% O_{PP}) to 8.3 nm (Cu₂O films deposited with 9% O_{PP}) for the plane (111). The value of D obtained for CuO with the plane $(11\bar{1})^\diamond$, decreases gradually from 23.4 nm, to 22.2 nm and 18.0 nm, for O_{PP} of 25%, 50% and 75%, respectively.

The effect of exposition time of the post-annealing step is substantial in D , increasing from 8.3 nm (for the as-deposited film) to a maximum of 15.7 nm (for the film annealed for 10 hours). In Figure 5.3 is shown the evolution of D with $O_{PP}(\%)$ and annealing time.

The lattice parameter (a) of cubic phase (Cu and Cu₂O) was estimated using the equation (3.43). For the CuO phase, a system of four variables was solved using the equation (3.44). An estimative of the lattice parameters are summarized in Table 5.2. In the case of the CuO, the use of weaker peaks of phases correspondent to the planes $(020)^\diamond$, $(11\bar{3})^\diamond$ and $(31\bar{1})^\diamond$ was necessary.

The texture coefficient, $P(h_i k_i l_i)$, was also calculated for the peaks with more statistics, showing the preferential orientation for each one of the conditions. In the case of the Cu (0% O_{PP}), the grains appears to be more orientated according to the plane $(111)^\#$, since $P(111) > 1$. Increasing the amount of oxygen to 9%, the Cu₂O phase seems to adopt a preferentially orientation along $[111]^\diamond$. For higher content of oxygen, the preferential orientation follows the plane $(11\bar{1})^\diamond$. Once again, the discussion done in the Chapter IV about the texture coefficient in thin-films is valid here.

Table 5.2 - XRD data for copper oxide films produced by RF- Magnetron Sputtering as a function of O_{PP} (Symbol representations: # Metallic Cu phase, $\diamond$ - Cu₂O phase and $\diamond$ - CuO)

O_{PP}	Phase	2θ ($^\circ$)	$(h\ k\ l)$	d (Å)	FWHM ($^\circ$)	D (nm)	I_{Max}/I	$P(h_i\ k_i\ l_i)$
0%	Cu	43.40	$(111)^\#$	2.08	0.674	12.7	100	1.57

		50.56	(200) [#]	1.80	--	--	15	0.57
		74.4	(220) [#]	1.27	--	--	9	0.86
9%	Cu ₂ O	36.96	(111) [♦]	2.43	0.994	8.3	100	1.42
		42.64	(200) [♦]	2.12	--	--	20	0.82
		62.28	(220) [♦]	1.49	--	--	14	0.76
25%	CuO	35.40	(11 $\bar{1}$) [◇]	2.53	0.356	23.4	100	1.50
		38.48	(111) [◇]	2.34	--	--	36	0.50
		52.96	(020) [◇]	1.73	--	--	17	--
		61.60	(11 $\bar{3}$) [◇]	1.50	--	--	17	--
50%	CuO	35.32	(11 $\bar{1}$) [◇]	2.54	0.375	22.2	100	1.37
		38.00	(111) [◇]	2.37	--	--	50	0.63
		52.40	(020) [◇]	1.74	--	--	22	--
		66.52	(31 $\bar{1}$) [◇]	1.40	--	--	20	--
75%	CuO	35.28	(11 $\bar{1}$) [◇]	2.54	0.463	18.0	100	1.32
		38.08	(111) [◇]	2.36	--	--	55	0.68
100%	CuO	35.16	(11 $\bar{1}$) [◇]	2.55	--	--	100	1

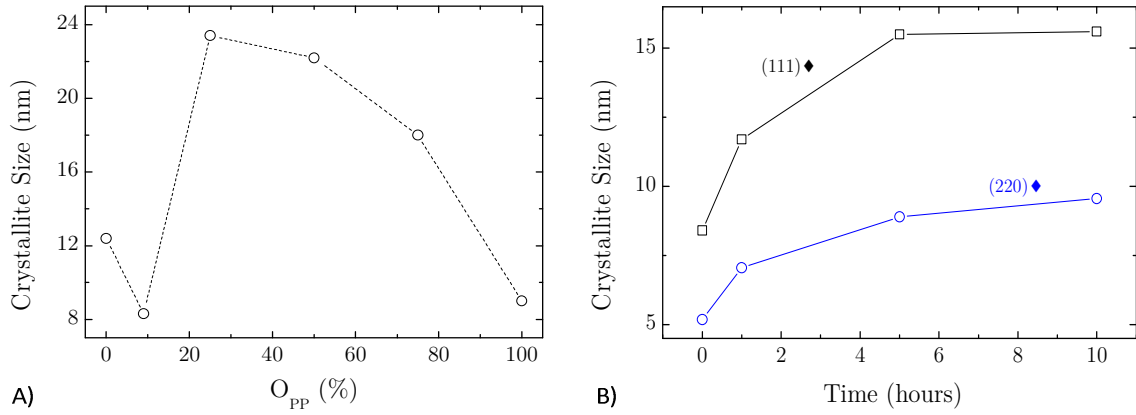


Figure 5.3 – Grain size evolution with the $O_{PP}(\%)$ (A) and with annealing temperature (B) for the sample deposited with 9% O_{PP} .

The lattice parameters (a , b , c , β) were estimated and are presented in Table 5.3. For the cubic Cu phase, $a \approx 3.607$ Å is near the value obtained for the Cu samples produced by e-beam (3.614 Å). In the case of Cu₂O and CuO, the values are also similar. However the low crystallinity of the films has consequences in the parameters accuracy.

Table 5.3 – Lattice parameters for the RF-magnetron sputtered Cu, Cu₂O and CuO.

Phase	Lattice Parameter	
Cu	$a = 3.607$ Å	
Cu ₂ O	$a = 4.200$ Å	
	$a = 4.686$ Å	
CuO	$b = 3.474$ Å	$\beta = 98.44^\circ$
	$c = 5.158$ Å	

5.2.1.1 STRUCTURAL INFLUENCE OF P_D

The deposition pressure (P_D) plays an important role as a film processing parameter, having a considerable impact in the growth-rate of the films, consequently influencing their physical properties. The Figure 5.4 shows the influence of P_D in the structural properties of the deposited films (condition of 9% O_{PP}). With $P_D \sim 1$ Pa and 6×10^{-1} Pa the film shows an intense peak corresponding to the plane $(111)^\diamond$ (the symbol $^\diamond$ identifies the Cu_2O phase). With the increase of the vacuum, the plane $(200)^\diamond$ is the most intense to be observed. In this case, seems to be evident, that the deposition pressure is indeed effective in the change of the structural properties of the Cu_2O films.

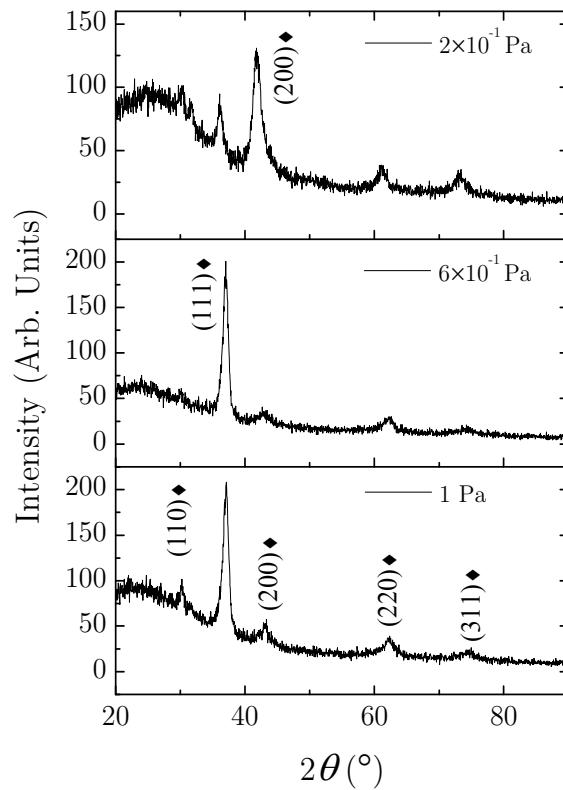


Figure 5.4 – Influence of the deposition pressure on structural properties of copper-oxide films.

In Table 5.4 is present the resume of the XRD data for films produced with different P_D . The Lattice parameters increased with the decrease of the P_D , ranging values of 4.192 Å, 4.205 Å and 4.319 Å for 1 Pa, 6×10^{-1} Pa and 2×10^{-1} Pa, respectively.

Table 5.4 – Resume of the XRD properties for the more intense peaks observed in the films produced with same 9% O_{PP} at different P_D . In all the films only the Cu_2O phase was observed.

P_D (Pa)	2θ (°)	(hkl)	d (Å)	FWHM (°)	D (nm)	I/I_0	$P(h_i k_i l_i)$
1	37.12	(111) [♦]	2.42	0.92	9.1	100.0	1.56
	43.32	(200) [♦]	2.09	0.72	11.9	15.2	0.67
	62.36	(220) [♦]	1.49	1.4	6.6	13.8	0.56
6×10^{-1}	37	(111) [♦]	2.43	0.92	9.1	100.0	1.80
	42.79	(200) [♦]	2.11	1.04	8.2	10.6	0.54
	62.22	(220) [♦]	1.49	1.08	8.6	10.3	0.66
2×10^{-1}	36.08	(111) [♦]	2.487	0.84	9.9	53	0.38
	41.8	(200) [♦]	2.159	1.24	6.9	100.0	2.01
	61.12	(220) [♦]	1.515	1.36	6.8	24.0	0.61

5.3 ELECTRICAL CHARACTERIZATION

Experiments were performed to determine the type of conductivity of the samples using the Hall and the Seebeck coefficients. The electrical characterization was complemented with the study of the conductivity (in the dark and vacuum) with the temperature (100 – 400 K). Using this technique was possible to determine the activation energy and perform some conclusions related to the conduction mechanism and band structure of the sputtered CO.

5.3.1 HALL EFFECT

It is known that the electrical properties are strongly dependent on the composition and crystalline structure of the films. As described before, Cu films were produced with no oxygen, Cu_2O films were produced with 9% O_{PP} and CuO phase for higher contents of oxygen (O_{PP} to $\geq 25\%$). It is expected that this change in the crystalline structure affects the type of conductivity. The metallic Cu film obtained from 0% O_{PP} showed an obvious n-type conductivity, which is changed to p-type for the increase in O_{PP} to 9% (Cu_2O phase). The p-type conductivity is retained until O_{PP} reaches 50% reverting the signal to n-type for higher amounts. However, the signal obtained from the Seebeck measurements (Table 5.5) suggests that the films produced with higher oxygen content ($O_{PP} \geq 50\%$) have also p-type conductivity.

These ambiguous results obtained for the type of conductivity of the CuO films can be related with the low hall mobility, which difficult the measurements. This is a very common situation in the research and development of p-type semiconductors and was reported by other

authors [4, 5].

Table 5.5 – Resume of the Seebeck measurements for the change in the oxygen content*. S is the signal of the Seebeck coefficient.

O_{PP} (%)	μ (V K ⁻¹)	S Signal
9	8000	+
25	11000	+
50	800	+
75	370	+
100	--	+

The electrical properties are presented in Figure 5.5 as a function of O_{PP} . The Cu₂O film (9% O_{PP}) exhibits the higher bulk resistivity (ρ) of $2.7 \times 10^3 \Omega \text{ cm}$, which has been gradually decreased with the increase on O_{PP} , in the case of CuO films. This behaviour is associated with phase change (Cu – Cu₂O – CuO) observed by other authors [1]. In the figure, it is observed a decrease in resistivity (and the increase of carrier concentration) with the increase of oxygen amount (for the CuO phase). The hypothesis is that an increase of O_{PP} will lead to an increase of defects (perhaps caused by oxygen interstitials that will also lead to copper vacancies), affecting the crystallization as evidenced by XRD patterns. In fact, after the post-annealing the system appears to converge for stage thermodynamically favourable. This statement can be sustained with the stability of the resistivity observed for the annealed samples (CuO phase) and also by the diffractograms presented before that supports an increase of the crystallinity with the temperature.

A high mobility (μ) of $3.93 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ obtained for metallic Cu films is significantly decreased to $0.65 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the films with Cu₂O phase and even lower for the CuO phase. The increase of O_{PP} tends to increase the carrier concentration of the annealed films, compromising the mobility. These changes in electrical properties are associated to the changes in the film crystallinity and on the grain size. The increase in crystallinity for the film deposited with 9% O_{PP} is shown in Figure 5.4. The electrical properties obtained for both as-deposited and post-annealed films are summarized in Table 5.6. The post-annealing besides triggering the increase of the crystallinity, as shown before, it is also associated to the enhancement of the electrical mobility (associated to an increase of the grain size that will be

* Performed by Dr. Nomura at Materials and Structures Laboratory, Tokyo Institute of Technology.

discussed in the further sections). Big grains will originate less grains boundaries in the film and consequently less potential barriers to diminish the drift velocity of the carriers and consequently the mobility. Some interesting study that illustrate the effect of the grains size in the mobility for a practical application (poly-Si TFTs) was done by Gupta and Tyag [6].

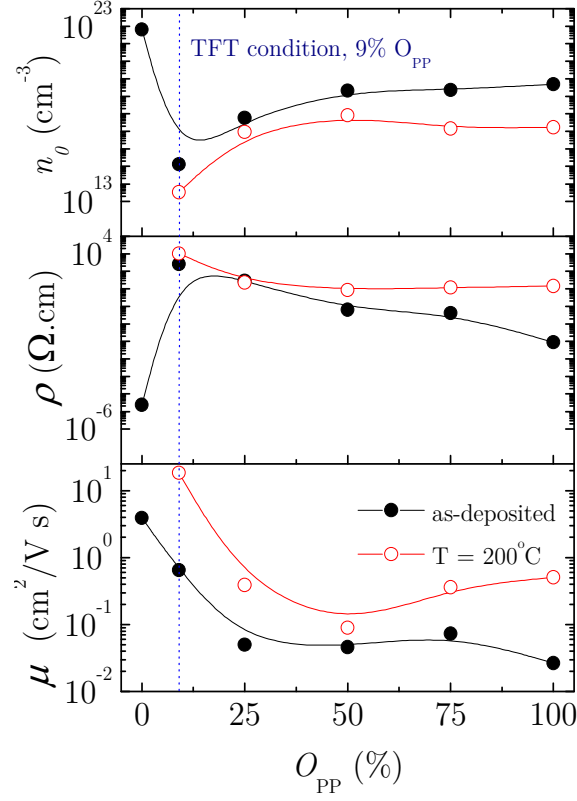


Figure 5.5 - Variation in bulk resistivity of CO films as a function of O_{PP} for the as-deposited and annealed films ($T = 200\text{ }^{\circ}\text{C}$, 10 hours). Dashed line represents the oxidation temperature used for the production of the p-type TFT.

Table 5.6 - Electrical data extracted from the as-deposited and annealed films as a function of O_{PP} (the grey zone refers to the p-type region, obtained by Hall effect measurements).

O_{PP} (%)	ρ ($\Omega\text{ cm}$)		μ ($\text{cm}^2\text{ V}^{-1}\text{ s}^{-1}$)		n_0 (cm^{-3})	
	as-dep.	ann.	as-dep.	ann.	as-dep.	ann.
0	2.39×10^{-5}	--	3.93	--	6.65×10^{22}	--
9	2.70×10^3	1.03×10^4	0.65	18.47	3.74×10^{15}	3.30×10^{13}
25	2.93×10^2	1.28×10^2	0.05	0.39	5.86×10^{17}	9.39×10^{16}
50	6.39	8.69×10^1	0.05	0.09	2.13×10^{19}	8.18×10^{17}
75	4.21	1.20×10^2	0.07	0.36	2.10×10^{19}	1.44×10^{17}
100	9.09×10^{-2}	1.46×10^2	0.03	0.51	2.68×10^{21}	1.72×10^{17}

5.3.2 DC CONDUCTIVITY VERSUS TEMPERATURE

The dependence of DC conductivity (σ) was observed in the temperature (T) ranging between 250 and 350 K for all the film conditions and between 100 and 400 K for the films correspondent to a pure Cu_2O and CuO phases. The results showed a similar behaviour observed before for the samples produced by thermal oxidation (Chapter IV, Figure 4.5). Once more it is visible that the conduction is thermal assisted mechanism, following the Fermi-Dirac distribution (Figure 5.6 (A)). Using the Arrhenius equation (presented before) was possible to estimate the activation energy as a function of O_{PP} (results presented in Table 5.7). These results are also in agreement with the others obtained by thermal oxidation (Chapter IV, Table 4.5), and other already published [3, 7, 8].

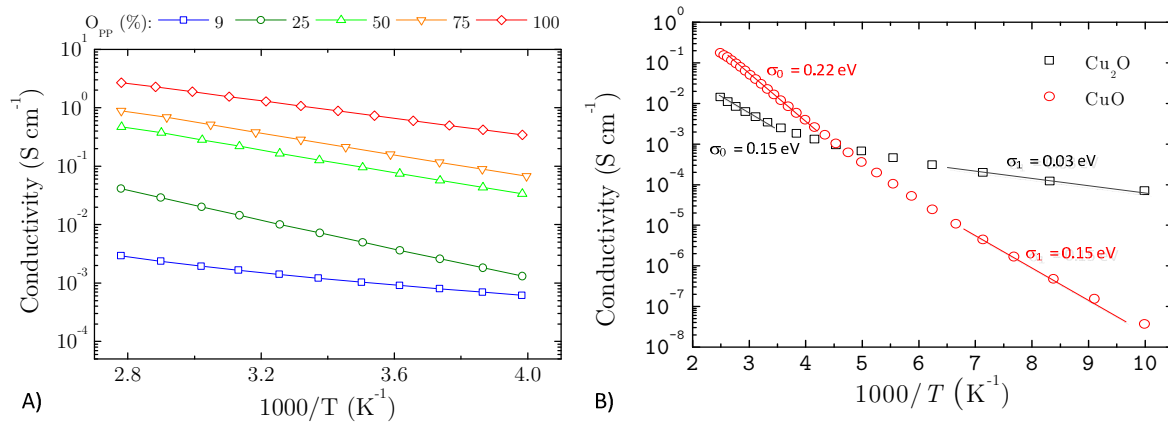


Figure 5.6 – A) Temperature dependence for a set of films deposited with 9 to 100% O_{PP} ; B) Temperature dependent dark conductivity for Cu_xO films deposited with O_{PP} ranging between 9% and 25%.

Table 5.7 – Activation energy estimated using the Arrhenius equation.

	O_{PP} (%)	E_A (eV)	E_A (eV) [9-11]
Cu_2O	9	0.13	0.14-0.22
	25	0.25	
CuO	50	0.19	0.13-0.15
	75	0.18	
	100	0.15	

It is observed in Figure 5.6 (B) that the experimental data correspondent to the films deposited with 9% (Cu_2O) and 25% O_{PP} (CuO) are fitted by two conduction paths. In the case of Cu_2O , was already stated that the conduction mechanism seems to be controlled by an acceptor energy level (E_A) above the valence band (as also discussed in the previous chapter).

The E_A estimated from the equation $2\sigma_0 \approx 2(E_F - E_V)$ is 0.30 eV for Cu_2O [12]. In the case of CuO films estimation for the acceptor level gives a value around 0.44 eV.

5.4 OPTICAL CHARACTERIZATION

5.4.1 UV-VIS-NIR SPECTROSCOPY

The optical transmittance was measured in the range of 300 – 2500 nm and the bandgap was again estimated from the absorption coefficient. The film produced with 9% O_{PP} , Cu_2O , showed higher average transmittance in the wavelength range of 400 – 750 nm ($T^{400-750}$) of 37%, for a sample of ~ 200 nm thickness. For the CuO phase, samples deposited with higher O_{PP} ($\geq 9\%$) showed transmittances between 18 to 24% (Figure 5.7 (A)). For low thickness films ~ 50 nm the results for the conditions studied are always above 40% in the same interval.

The samples produced with 9% O_{PP} were annealed at 200 °C during 1, 5 and 10 hours. No significant changes in the transmittance were observed in the visible range as shown in Figure 5.7 (B).

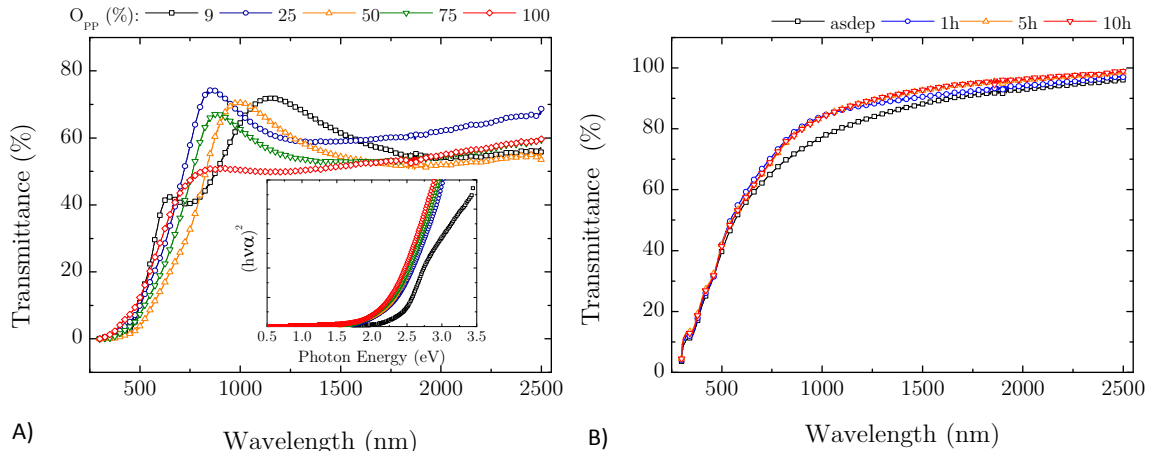


Figure 5.7 – A) Transmittance spectra of the Cu_xO 200 nm thick films produced with different O_{PP} ; B) Transmittance for the condition of 9% O_{PP} (deposited with ~ 50 nm thickness) post-annealed in different periods of time.

The direct-allowed optical gap for the films with thickness around 200 nm, was estimated ranging 2.20 – 2.29 eV for CuO and 2.42 eV for Cu_2O . These values are in agreement with previous reports [2]. However, as discussed in the previous chapter, is expected a direct forbidden bandgap for Cu_2O . Using the Tauc plot method, once again, the experimental data appears to be fitted to a direct bandgap transition (See Appendix D). In the Table 5.8 is

presented the bandgap calculated for the direct-allowed (2E_G) and forbidden ($^{3/2}E_G$) transitions and also to the indirect allowed transition ($^{1/2}E_G$).

The absorption coefficient in the physics point of view is more important than the transmittance, since takes in consideration the thickness of the film. In Figure 5.8 (A), it is presented the absorption coefficient spectra for the samples produced with different O_{PP} . The average absorption coefficient in the visible range (400 – 750 nm) it is also presented in Figure 5.8 (B).

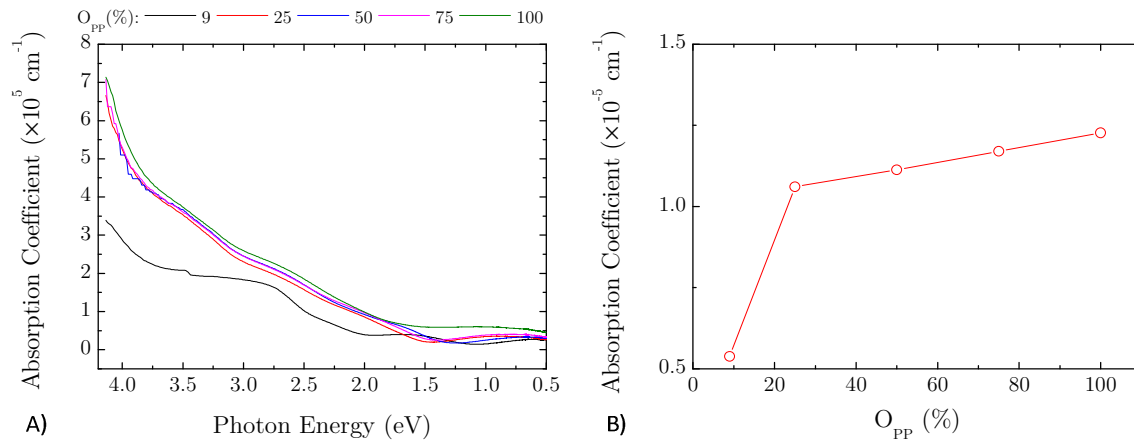


Figure 5.8 – Absorption coefficient (α) for the sputtered films deposited with 9 to 100% O_{PP} (for films with ~ 150 nm thickness); Absorption coefficient average in the visible region for the films deposited with ~ 150 nm thickness (B).

Table 5.8 – Resume of the optical properties as a function of O_{PP} for a $P_D = 6.0 \times 10^{-1}$ Pa and power of 50 W, samples with ~ 200 nm and 50 nm thickness.

O_{PP}	~ 50 nm	200 nm			
	$T^{400-750}(\%)$	$T^{400-750}(\%)$	2E_G (eV)	$^{2/3}E_G$ (eV)	$^{1/2}E_G$ (eV)
9	47	37.3	2.42	1.89	1.52
25	33.5	23.5	2.29	1.36	1.04
50	34.2	19.4	2.26	1.35	1.04
75	38.0	19.7	2.20	1.34	0.98
100	40.7	17.5	2.21	1.39	1.01

The transmittance is expected to be higher for films with major Cu_2O phase, decreasing for the films with CuO phase. It is also obvious an increase of the absorption coefficient with the increase of oxygen for the films with the CuO phase, and a consequent decrease of the transmittance of these films. This can be explained by an increase of the defect states in the bandgap caused perhaps excess of oxygen. The electrical measurement gives support to this statement, being visible an increase of the conductivity and carriers concentration for higher

percentage of O_{PP} .

5.4.2 SPECTROSCOPIC ELLIPSOMETRY

The approach used here was similar to the one used for copper by oxidation. Was used also same the Tauc Lorentz with one oscillator (TL) to simulate the amorphous layer, and three oscillators (TL3) to simulate the CO layers deposited with different oxygen partial pressures.

The layers model used to adjust the Cu_2O and CuO samples are shown in Figure 5.9. As usual, we started the simulation using the information obtained using XRD, choosing to start the sample with high crystallinity. The modulations showed always the existence of a thin layer of amorphous oxide in the interface of the film. This was also found in the case of the copper oxides by oxidation, and makes sense, since the glass does not have crystalline order. The Figure 5.10 presents the fits and experimental values for the I_s and I_c parameters, for the both Cu_2O and CuO phase, showing a perfect match. With this study it is possible to have an idea about the morphology of the films along the thickness, among other optical properties. In Table 5.9 is summarized some important factors extracted using this approach.

A)

1:	Void (%)	Cu ₂ O TL 3 (%)
2:	Cu ₂ O TL 3	
3:	Cu ₂ O TL	
	Glass	
	Void	

B)

1:	Void (%)	CuO TL 3 (%)
2:	CuO TL 3	
3:	CuO TL	
	Glass	
	Void	

Figure 5.9 – SE layer models used to adjust the experimental data obtained for copper oxides; A) to adjust the condition 9% O_{PP} (Cu_2O) ; B) to adjust the conditions 25 to 100% O_{PP} (CuO).

Using the results obtained by SE is possible to verify that CO obtained by sputtering appears to have a high homogeneity, being the convergence of the model to the experimental results much easier to achieve than in the oxidized ones (previous chapter). The lower layer (t_3) is correspondent to the thickness of the amorphous layer, the t_1 is related to the surface roughness and t_2 is related to the polycrystalline film. The optical bandgap obtained for Cu_2O was observed around 2.2 eV and for CuO between 1.15 – 1.34 eV, in agreement with the previous reported results [1, 2, 13-15].

It is observed that the films produced with lower oxygen O_{PP} showed higher surface roughness (t_1) that is consistent with the AFM measurements. As observed in the AFM images

(Figure 5.14), the CO films deposited with higher oxygen amount are more uniform and dense in comparison to the ones deposited with low O_{PP} .

Table 5.9– Simulation parameters obtained for the Cu_2O and CuO using the model A and B, respectively.

O_{PP} (%)	t_1 (nm)	t_2 (nm)	t_3 (nm)	E_G (eV) Crystalline	E_G (eV) Amorphous	χ^2	t_{total} (nm)
9	14.30±0.05	190.6±1.91	36.4±2.68	2.19	0.96	0.214	~241
25	16.24±0.24	147.6±0.52	21.9±1.83	1.34	0.63	0.218	~186
50	3.91±0.25	178.3±0.48	29.7±2.26	1.15	0.72	0.207	~197
75	8.38±0.24	149.7±0.47	43.0±2.99	1.28	0.82	0.176	~201
100	6.82±0.17	102.3±0.34	79.2±5.22	1.33	1.51	0.126	~188

The total thickness obtained using SE, is consistent with the profilometry measurements. It is visible an increase of the amorphous component from ~15% (9% O_{PP}) to ~43% (100% O_{PP}) corroborating the results obtained from XRD.

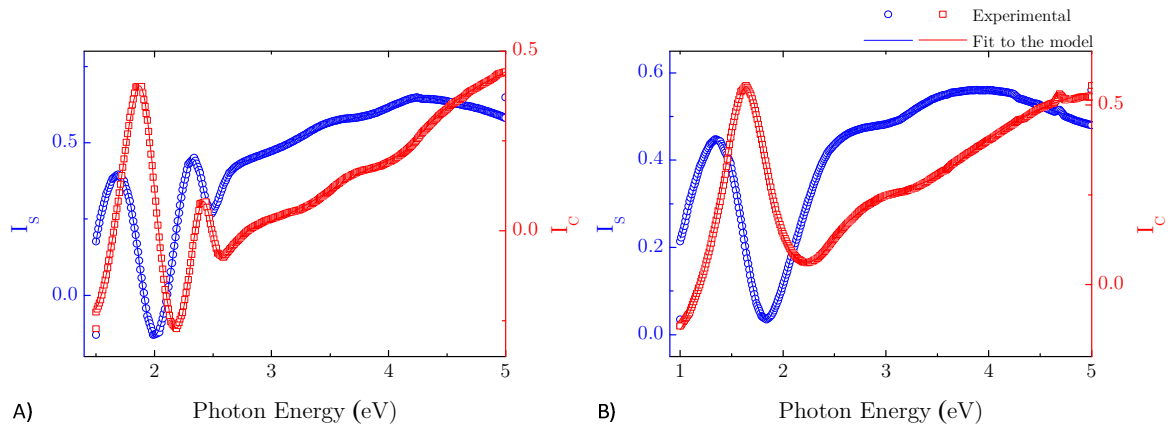


Figure 5.10 – Example of the adjustments correspondent to the models A and B, respectively for the condition 9% O_{PP} (Cu_2O) and 25% O_{PP} (CuO).

The adjustment of the experimental data to the TL models, allows the determination of some physical properties (refractive index, dielectric function, etc) for the crystalline CuO and Cu_2O phase obtained by sputtering. The diffraction index for the crystalline phase (TL3) of the films is presented in Figure 5.12. It is observed that the refraction index is higher for the film correspondent to the Cu_2O phase, and tends to increase with the oxygen content for the CuO phase. The behaviour of the curve is in agreement with the results obtained by thermal oxidation. The real and the imaginary components of the dielectric function (ϵ_r and ϵ_i) is presented in Figure 5.13.

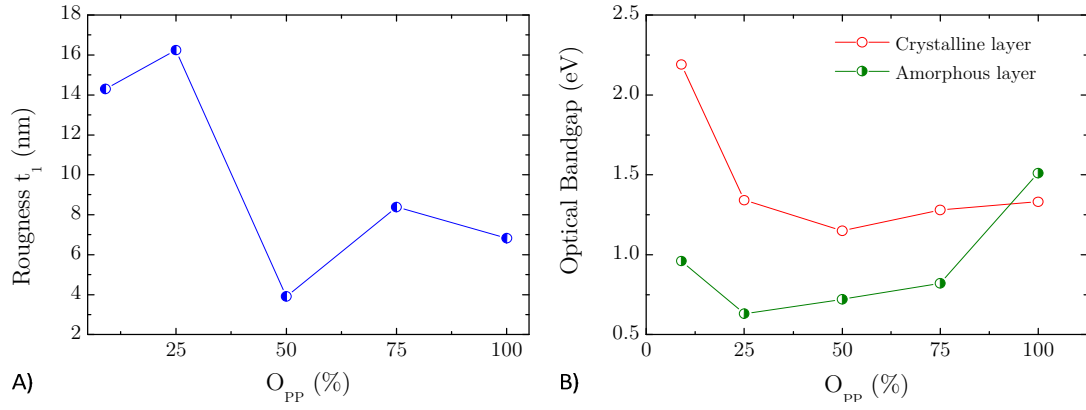


Figure 5.11 – Variation of the surface roughness (A) and the optical gap (B) with the O_{PP} .

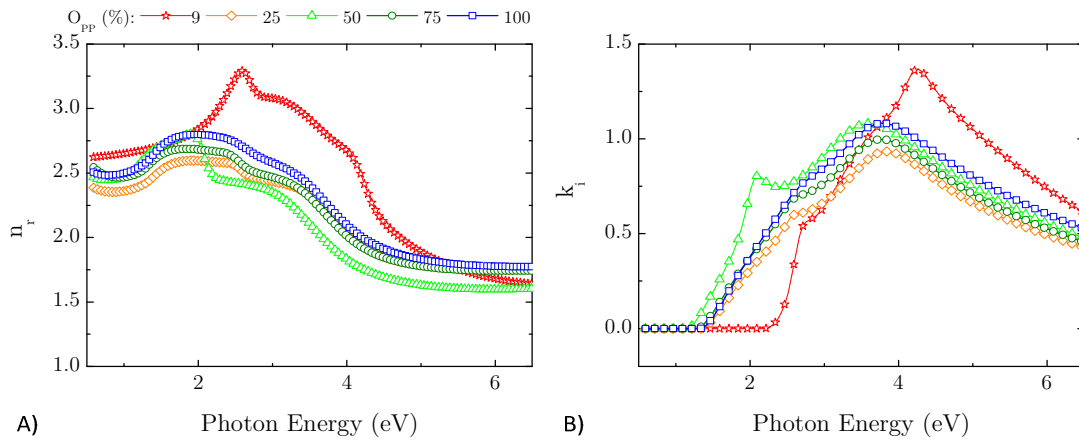


Figure 5.12 – Refraction index for the major crystalline phase in the copper oxide films deposited with 9 to 100% O_{PP} .

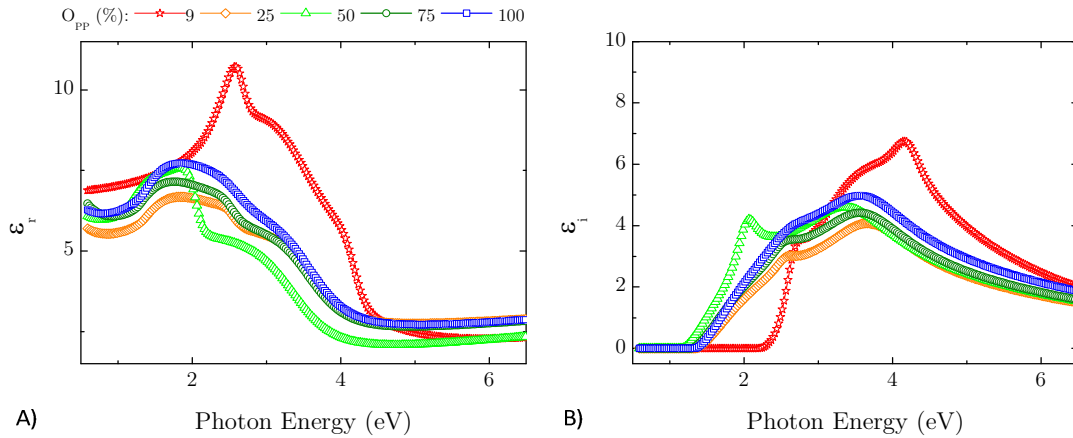


Figure 5.13 - Dielectric function, real ϵ_r (A) and imaginary ϵ_i (B), estimated for the crystalline layer for the samples deposited with different O_{PP} .

5.5 SURFACE CHARACTERIZATION

The surface of the films was analysed by Kelvin probe (KP), AFM and SEM, to study the morphological and electrical properties of the films surface. The AFM was also used to estimate the roughness and the size of the agglomerates.

5.5.1 KELVIN PROBE

The samples were analysed using KP to estimate the work function (Φ) defined before. The resume of the data is presented in Table 5.10, being evident that Φ estimated for the sputtered Cu_2O and CuO , have in general higher values than the estimated for the oxidized samples. The observed differences are obviously related to the different surface condition of the films, strongly affecting the surface work function. A presence of minimum amounts of contaminations (less than a monolayer of atoms or molecules), or the reactions that may occur at the surface (oxidation/reduction) can affect seriously the work function. In fact changes of the order of 1 eV are commonly found in metals and semiconductors, depending on the surface condition that is related to the film deposition techniques and preparation processes used. These changes can be a result of electric dipoles formation at the surface. Atmosphere is also another factor that may affect the measurement of the work function that should be done (if possible) in vacuum. Nevertheless the humidity was controlled to avoid reaction in the surface of the films [16]. The porosity of the films may facilitate the adsorption of oxygen (or other gases) into the surface (or reacting with the surface)[17]. This is another reason why this type of measurement should be done if possible in vacuum, after the deposition of the material.

Table 5.10 – Surface properties of copper and copper oxides (Φ and δ_Φ are the work function and the standard error estimated in this work, $\Phi^{\text{Lit.}}$ the work function estimated by other authors, and Φ^{Oxid} is the work function estimated for the oxidized samples).

O_{PP} (%)	Phase	Φ (eV)	δ_Φ (meV)	Φ^{Oxid} (eV)	$\Phi^{\text{Lit.}}$ (eV) [18-23]
0	Cu	4.77	1.70	4.65	4.65 - 4.70
9	Cu_2O	5.1	1.70	4.76	4.84 – 5.2
25	CuO	5.21	1.42		
50	CuO	5.18	1.57		
75	CuO	5.22	1.47	4.80 – 5.33	4.8 – 5.2
100	CuO	5.20	1.38		

5.5.2 ATOMIC FORCE MICROSCOPY (AFM)

The surface microstructures of the films deposited with 0, 9, 25 and 100% O_{PP} were analysed by AFM and the obtained microstructures are shown in Figure 5.14 and Figure 5.15. The surface of Cu film deposited with 0% O_{PP} is very smooth with a root mean square roughness (RMS) of 1.9 nm. The surface of this film is comprised of uniformly distributed and tightly packed grains with the average size of ~ 31 nm. It is also observed, further grains with a maximum size of ~ 93 nm.

When the O_{PP} is increased to 9%, the films crystallize with Cu_2O phase and the RMS roughness is increased to 4.6 nm. The surface is comprised of randomly distributed cluster of grains, which suggest that they are closely packed in different layers. The average grain size is increased to ~ 41 nm, with few grains as big as ~ 100 nm in size. The increase in grain size has also been evidenced by SEM analysis (Figure 5.16), and in the case of the films produced by thermal oxidation, being related to the formation of the Cu_2O phase.

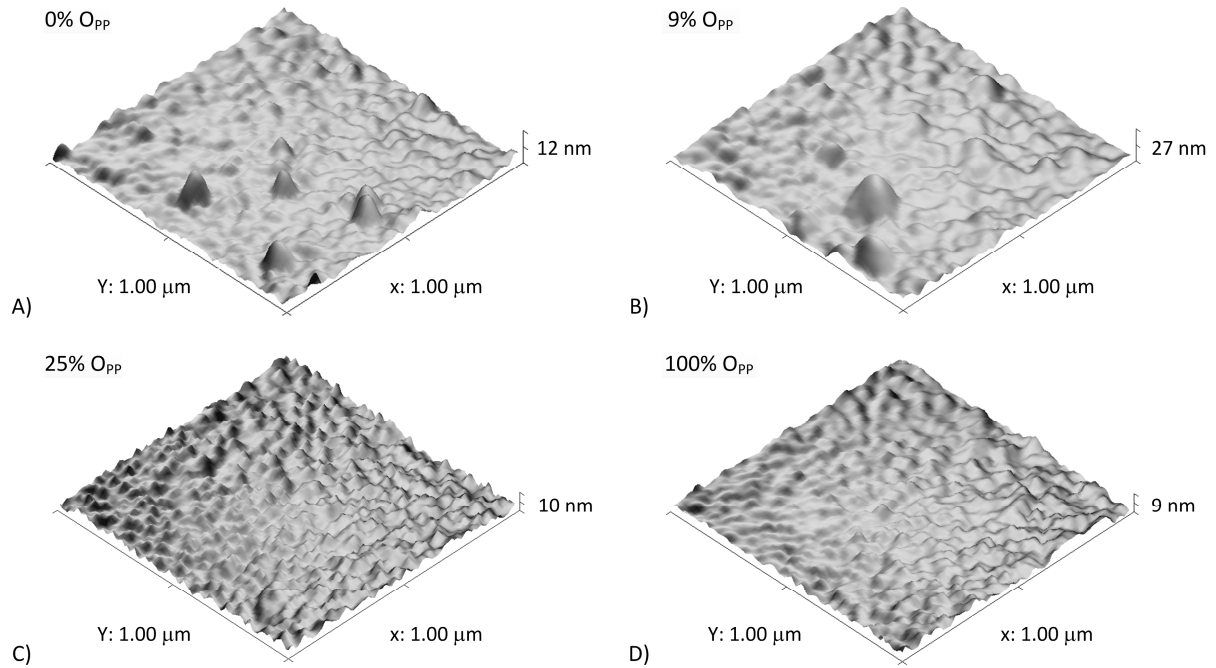


Figure 5.14 – AFM microstructures for the films deposited with 0%, 9%, 25% and 100% O_{PP} , respectively A, B, C and D.

When the O_{PP} is increased to 25% (CuO phase), the surface microstructure has been significantly changed as explained below. A significant decrease in RMS to 2.3 nm suggests an

increase in the surface smoothness, with a higher uniformity in the grain size distribution (~ 29 nm). However, a few ~ 90 nm grains are still visible.

For an O_{PP} of 100%, the films still crystallizes in CuO phase but the RMS roughness is considerably decreased to ~ 1.42 nm (Figure 5.14 (D)). The average grain size is increased a bit too ~ 34 nm, with few big grains averaging ~ 70 nm.

5.5.2.1 EFFECT OF POST-ANNEALING

The films deposited with 9% O_{PP} were annealed (10 hours), which increased the grain size of as deposited films (31 nm) to ~ 100 nm and the RMS roughness from 4.6 nm to 10.4 nm. This increasing trend of grain size with the increasing annealing time is corroborating the behaviour of the crystalline size obtained from XRD. As explained before, grains boundaries are responsible (in general) for the decrease of the mobility. So if a crystallization process occurs and it is observed an increase of the grain size (decreasing in general the number of grains boundaries that the carrier need to cross in their path through the film), it is expected an increase of the mobility (as verified in the section of the electrical characterization).

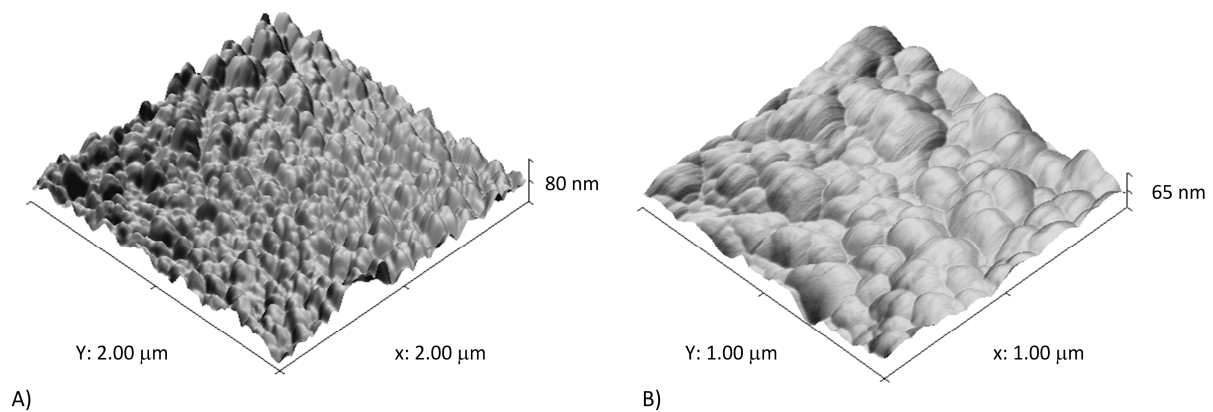


Figure 5.15 – AFM microstructures of the sample produced with 9% O_{PP} for the as-deposited condition (A) and for the annealed condition at 200 °C, during 10 hours (B).

5.5.3 SCANNING ELECTRON MICROSCOPY (SEM)

SEM microscopy helped to support and clarify some aspects not well understood using AFM. In particular the existence of possible micro-fractures not clear with AFM and visible in the Figure 5.16 (A).

The films deposited without oxygen have a smooth surface, in which is visible some

structures similar to micro-fractures. The increasing the oxygen amount to 9% O_{PP} has a significant impact in the surface morphology of the film. It is visible the existence of large grains dispersed in a uniform surface. These results are in corroboration with the AFM ones. This was also observed for the Cu_2O phase produced by metallic oxidation. Increasing even more the O_{PP} to 25%, the film crystallizes in the CuO phase, forming an “orange peel” pattern also evident at 100% of O_{PP} . This morphology was also found in the metallic oxidation for the CuO phase.

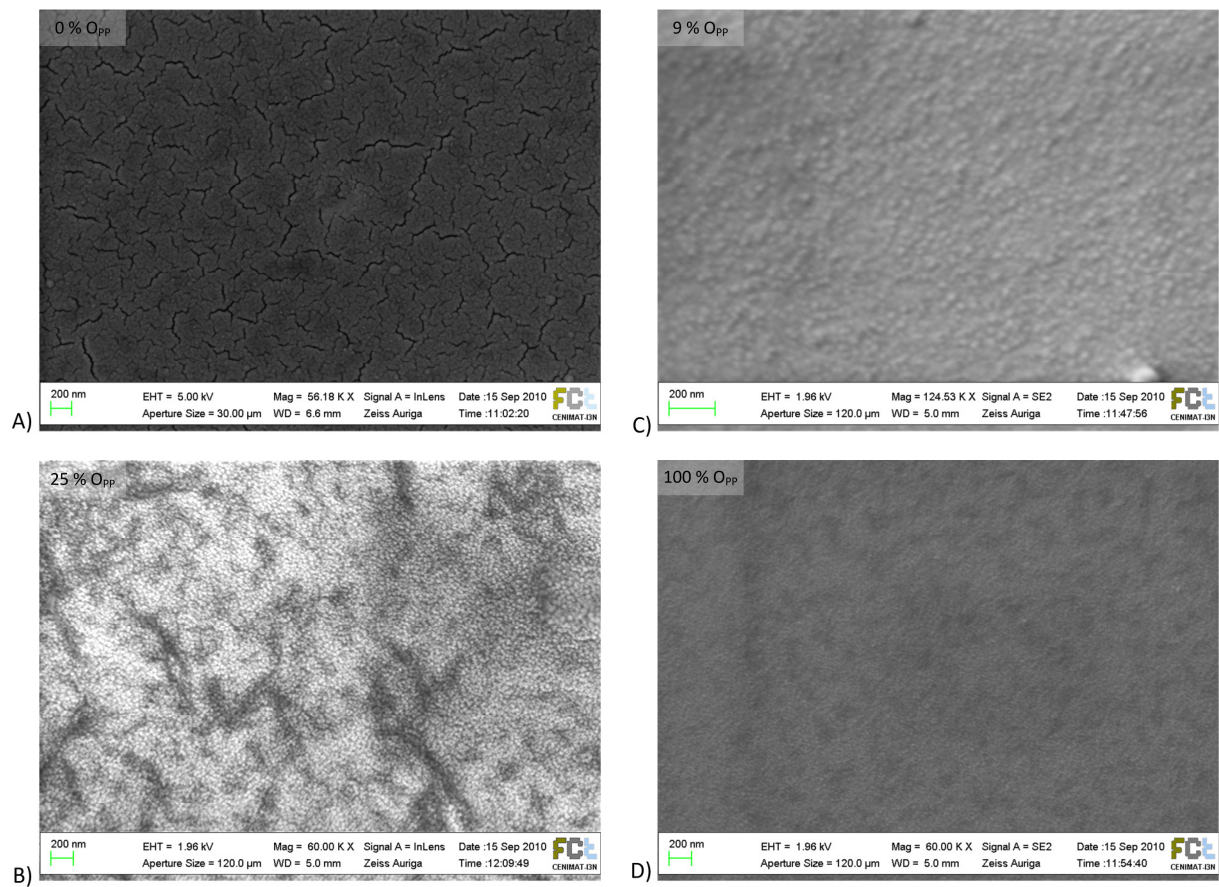


Figure 5.16 - SEM images of the sputtered films for the oxygen conditions of 0%, 9%, 25% and 100% O_{PP} .

Part II

5.6 EXPERIMENTAL DETAILS

A migration to a new RF sputtering system (AJA Corporation), impose a new and fully study on the properties of the films to optimize the conditions of TFTs production. In this section will be summarized the major and relevant data to understand the TFTs presented in the chapter VIII. The films were produced with a deposition pressure of 6×10^{-1} Pa, 100 W and with different O_{PP} (0 – 100%). Post-annealing treatments were also done to verify once again the impact of the temperature.

5.7 STRUCTURAL CHARACTERIZATION

5.7.1 X-RAYS DIFFRACTION (XRD)

The structural characterization (Figure 5.17) was needed to establish the conditions for the production of single Cu_2O and CuO layers, used in TFTs. Many considerations about the influence of oxygen in CO films were already done in the first part of this chapter.

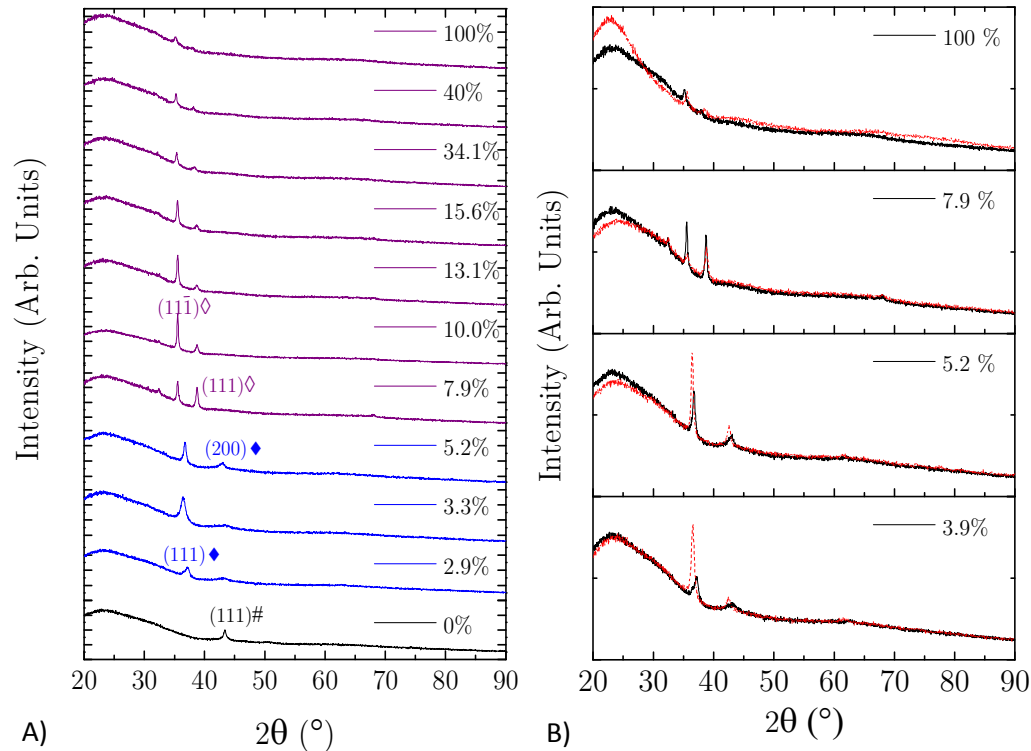


Figure 5.17 – A) Comparison of XRD of the as-dep. films produced with different O_{PP} (symbol

representations of the planes: (#) metallic Cu films, (♦) Cu_2O films and (◊) CuO films); B) Different copper phase films annealed at 200 °C.

Like in the Part I, was possible once again to define the ideal conditions for the formation of Cu_2O (again marked with ♦) and CuO phases (marked with ◊). It is visible that oxygen increase leads to a decrease of the films crystallinity (also observed before). The post-annealing temperature in air at 200 °C (temperature used in the TFT production process) was also effective in the increase of films crystallinity, but not enough to induce a phase change. This was expected since as shown in the films produced by thermal oxidation, 200 °C is not an effective temperature to assist the conversion of Cu_2O to CuO.

5.7.2 RUTHERFORD BACKSCATTERING (RBS)

The samples were also analysed using RBS in a 2.5 MV van de Graaff accelerator following the procedure explained in the Chapter III. The purpose to use RBS in the sputtered samples was to try to determine the film composition, observing the oxygen content in each film. In this study, the films were deposited in a silicon wafer, without SiO_2 (removed using an etching solution containing hydrofluoric acid, HF) to try to obtain a more defined peak for oxygen. In Figure 5.18 it is shown the RBS spectra of the sputtered CO films.

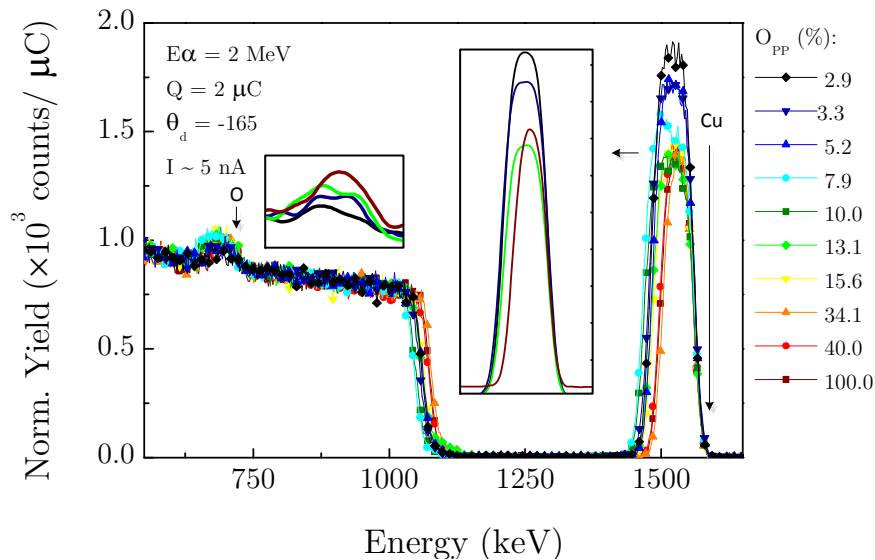


Figure 5.18 – RBS spectra for the sputtered Cu_xO films deposited with different O_{PP} .

The RBS analysis confirms the XRD results, showing a high content of oxygen in the samples produced with 2.9 to 5.2% O_{PP} near to the Cu_2O stoichiometry. With the increase of

O_{PP} it is clear the formation of CuO, with both elements (Cu and O) with similar quantities. However the statistic for the oxygen peak is always problematic for the quantification of small deviations. From the behaviour observed in Table 5.11, it is possible to assume that for higher amounts of oxygen, the deviation from stoichiometry of the CuO can be expressed in the form CuO_{1+x} . In the table is also shown the relation of N_{Cu}/N_O [†] determined using the program NDF[24] and using the relation described in the Chapter II. In this case, it is not relevant the calculation of the thickness.

Table 5.11 – RBS analysis for the sputtered Cu_xO samples, with the increase of O_{PP} (O_f is the ratio of flows and σ is the standard deviation).

O_{PP} (%)	Calculated by the relation of areas				Calculated using NDF	
	O_f (%)	Cu (%)	O (%)	σ	Cu (%)	O (%)
2.9	5	67.18	32.82	2.66	64.50	35.50
3.3	7.8	65.27	34.73	1.03	57.11	42.89
5.2	9.9	63.77	36.23	1.76	57.24	42.76
7.9	15.3	44.66	55.34	3.27	48.50	51.50
10	20	46.13	53.87	2.84	41.65	58.35
13.1	24.8	47.04	52.96	3.00	41.72	58.28
15.6	30.1	42.75	57.25	1.43	44.97	55.03
34.1	50	42.30	57.70	1.86	42.23	57.77
40	75.2	44.66	55.34	2.64	43.18	56.82
100	100	38.69	61.31	2.22	44.12	55.88

5.8 ELECTRICAL CHARACTERIZATION

5.8.1 HALL EFFECT

The electrical properties were measured to identify the best conditions for the production of a TFT. They are shown schematically in Figure 5.19 as a function of O_{PP} . It is not possible to make a direct comparison with the other results showed in the previous section (the systems and the experimental conditions are different, influencing the plasma and consequently all the deposition aspects). Nevertheless, is possible to verify that Cu_2O is formed in the experimental conditions of poor-oxygen content ($\leq 5.2\%$ O_{PP}) and in other hand CuO is formed in rich-oxygen conditions ($\geq 7.9\%$). The resistivity of these samples shows a similar behaviour of the

[†] The ration N_{Cu}/N_O represents the stoichiometric ration between copper and oxygen.

films produced with 50 W. The behaviour observed for the resistivity in the Figure 5.19 has been also reported by Parretta *et al* [1]. In general, the films produced with poor-oxygen content showed the higher resistivity values. However, the highest value is associated to CuO produced with O_{PP} 10% with a $\rho \approx 1.83 \times 10^4 \Omega \text{ cm}$. In the case of the Cu_2O phase, deposited with low O_{PP} (2.9 – 5.2%), have resistivity ranging 14.6 to $1.62 \times 10^2 \Omega \text{ cm}$. For very high amounts of oxygen ($\geq 34\%$) the copper films showed only the CuO phase, having the lowest resistivity values, ranging from 2.51×10^{-1} to $6.47 \times 10^{-2} \Omega \text{ cm}$. Typically CuO has a lower resistivity than Cu_2O due to the high carrier concentration [1, 14]. These values are in the expected range for the two copper phases produced by RF-sputtering and thermal oxidation.

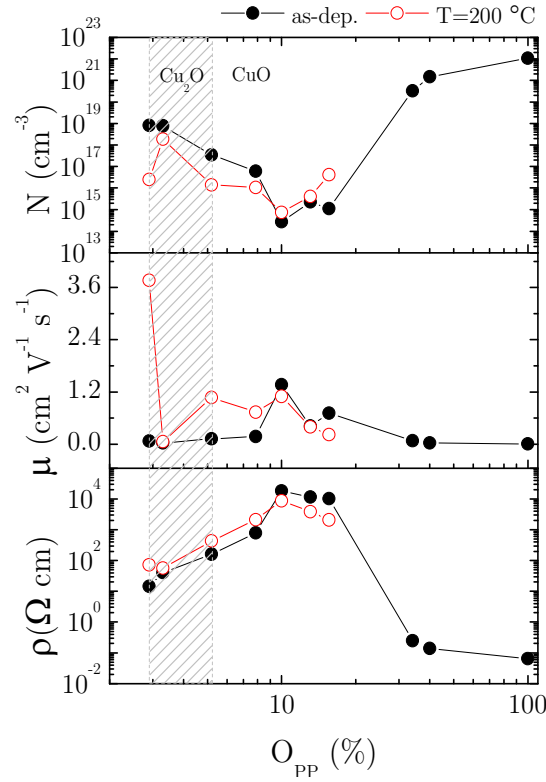


Figure 5.19 – Variation in the resistivity of CO films as a function of O_{PP} for the as-deposited and annealed films ($T = 200 \text{ }^\circ\text{C}$, 10 hours). Dashed line represents the oxidation temperature used for the production of the p-type TFT.

The increase of defects associated to the oxygen bombardment and also the amorphization can explain the variations in the resistivity observed in CuO. These excess of defects can justify the increase in the carrier concentration with O_{PP} for the CuO phase. In terms of the mobility, the highest values were found for the intermediate conditions (produced with 10 to 15% of O_{PP}). The post-annealing treatment at $200 \text{ }^\circ\text{C}$ was effective to improve the values of the motility for almost all conditions produced with low O_{PP} . The resume of the

electrical properties for the as-deposited films are presented in Table 5.12.

Table 5.12 – Resume of the electrical properties (as-deposited) obtained for the sputtered Cu_xO (Part II) (O_f is the ratio of flows used in this system, grey colour is referred to the Cu_2O phase).

O_{PP} (%)	O_f (%)	ρ ($\Omega \text{ cm}$)	μ ($\text{cm}^2 \text{ V}^{-1} \cdot \text{s}^{-1}$)	N (cm^{-3})
2.9	5.0	1.46×10^1	7.50×10^{-2}	8.23×10^{18}
3.3	7.8	4.03×10^1	3.00×10^{-2}	7.68×10^{18}
5.2	9.9	1.62×10^2	1.24×10^{-1}	3.46×10^{17}
7.9	15.3	7.84×10^2	1.75×10^{-1}	6.04×10^{16}
10.0	20.0	1.83×10^4	1.37	2.71×10^{14}
13.1	24.8	1.16×10^4	4.15×10^{-1}	2.30×10^{15}
15.6	30.1	1.02×10^4	7.17×10^{-1}	1.13×10^{15}
34.1	50.0	2.51×10^{-1}	8.10×10^{-2}	3.22×10^{20}
40.0	75.2	1.40×10^{-1}	3.07×10^{-2}	1.47×10^{21}
100.0	100.0	6.47×10^{-2}	9.76×10^{-3}	1.05×10^{22}

5.9 OPTICAL CHARACTERIZATION

5.9.1 UV-VIS-NIR SPECTROSCOPY

The films were characterized by UV-VIS-NIR to verify their optical properties: transmittance, absorption coefficient and optical gap. In Figure 5.20 it is shown the average transmittance of the films (with 100 nm) produced with different oxygen contents (Figure 5.20 (A)). The full spectrum in the wavelength between 250 and 2500 nm is also presented for all the conditions in the Figure 5.20 (B). It is clear that the highest transmittance, associated to the higher E_G , it is attributed to Cu_2O phase, with an average transmittance (for a 100 nm film) around 55% and an optical bandgap of 2.50 – 2.51 eV (2E_G). The sample produced with the lower O_{PP} (2.9%) showed the minimum value of transmittance in all the wavelength range. Regarding the data obtained by XRD it is possible to justify this low transmittance with the presence of a mixture of metallic Cu and Cu_2O phase. It is also visible in the RBS analysis a higher amount of Cu.

Increasing the O_{PP} to 3.3% and 5.2% it is favourable the crystallization in the Cu_2O phase (with the higher optical gap). For higher values of O_{PP} ($> 15.6\%$) it is possible to verify a stabilization of the $T^{400-750}$ around 37%.

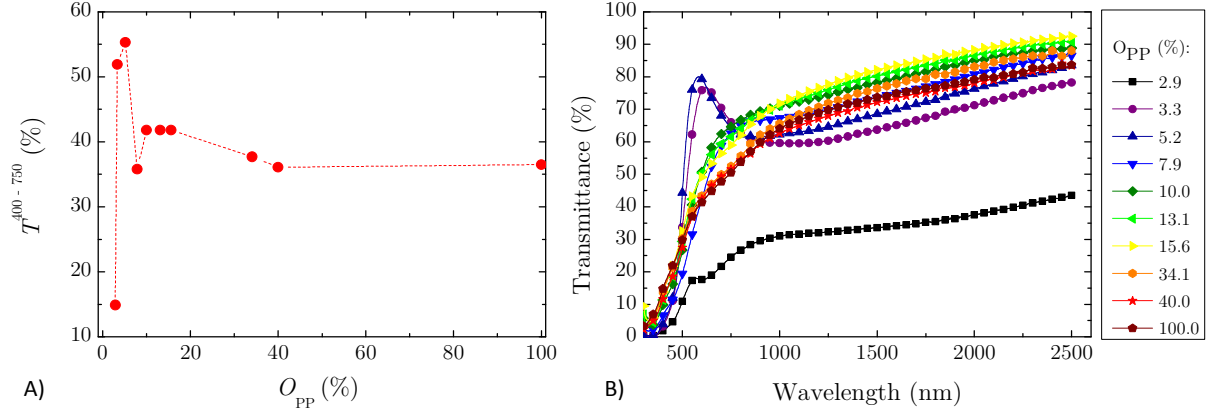


Figure 5.20 – Optical Properties of the Cu_xO films deposited in the new AJA system.

The optical bandgap was, once again, calculated according to the expected transitions (direct allowed, indirect allowed and direct forbidden). The results are presented in Table 5.13 and are in agreement with the results published by different authors [1, 2, 7, 14, 15, 25-27].

Table 5.13 – Resume of the optical properties as a function of O_{PP} for a $P_D = 6.0 \times 10^{-1}$ Pa and power of 50W, samples with ~ 100 nm thickness.

O_{PP}	$T^{400-750}(\%)$	$\alpha^2 E_G$ (eV)	$\alpha^{2/3} E_G$ (eV)	$\alpha^{1/2} E_G$ (eV)
2.9	14.9	2.01	1.63	1.35
3.3	51.9	2.50	2.08	1.92
5.2	55.3	2.51	2.24	2.11
7.9	35.8	2.26	1.62	1.53
10.0	41.8	2.36	1.65	1.43
13.1	41.8	2.38	1.68	1.41
15.6	41.8	2.33	1.63	1.32
34.1	37.7	2.30	1.49	1.10
40.0	36.1	2.38	1.51	1.17
100.0	36.5	2.01	1.37	0.94

5.10 GENERAL CONCLUSIONS

Copper oxide thin-films were deposited on glass substrates by reactive RF magnetron sputtering and were studied as a function of oxygen partial pressure (O_{PP}).

In the first part of this study, was shown that is possible to produce different copper phases tuning the oxygen content in the chamber. With 9% O_{PP} is possible to produce Cu_2O phase. Increase even more the O_{PP} will lead to the formation of a CuO phase ($O_{PP} \leq 50\%$). This is analogous with the oxidation process where the increase of temperature allows more diffusion

of oxygen into the Cu crystal originating Cu₂O (low temperatures → low oxygen diffusion) and CuO (at higher temperatures → higher oxygen diffusion). The structural parameters were calculated and the crystallite size estimated between 8.3 to 23.4 nm.

In terms of their electrical properties, the films deposited with O_{PP} of 9, 25 and 50% showed p-type conductivity with ρ around 2.70×10^3 , 2.93×10^2 and $6.39 \Omega \text{ cm}$, respectively. The resistivity and mobility decreased with the increase of O_{PP} , related to the phase change from metallic Cu to Cu₂O and CuO, and also influenced by change in crystallinity and oxygen excess. The films produced with higher O_{PP} showed lower resistivity, with ρ ranging between 4.21×10^{-2} - $9.09 \times 10^{-2} \Omega \text{ cm}$. This may be related to an amorphization process verified in the films with higher O_{PP} , but also with the creation of defects originated by oxygen bombardment (copper vacancies). The post-annealing has increased the crystallinity and the roughness of the films deposited with 9% O_{PP} (Cu₂O). The Hall mobility (μ_H) of these films was increased from 0.65 to $18.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with annealing temperature.

In the results presented in the Part II of this chapter, was possible to achieve similar conclusions observed in the Part I. Controlling the oxygen amount in the chamber was possible to “tune” the Cu₂O and the CuO phase. High amounts of oxygen leads to almost amorphous films with impact in their electrical and optical properties. Temperature is effective to increase the crystallinity of the films in all the deposition conditions. The electrical characteristics are also dependent on the O_{PP} . Specifically the resistivity increases with the oxygen content reaching a maximum of $18.3 \times 10^3 \Omega$ around 10% O_{PP} and then decreases reaching a minimum of conductivity around $6.4 \times 10^{-2} \Omega \text{ cm}$. This study also leads to the production of a working TFT presented in the Chapter XVIII.

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Chapter VI

Nickel oxides by thermal oxidation

CONTENTS

In this section, will be presented some of the results obtained for NiO films produced by thermal oxidation of nickel thin-films. All the films were characterized concerning their possible application in TFTs.

- 6 Nickel oxides by thermal oxidation
 - 6.1 Experimental details
 - 6.2 Structural characterization
 - 6.3 Electrical characterization
 - 6.4 Optical characterization
 - 6.5 Surface characterization
 - 6.6 Atomic force microscopy (AFM)
 - 6.7 Scanning electron microscopy (SEM)
 - 6.8 Conclusion
 - 6.9 References

6 NICKEL OXIDES BY THERMAL OXIDATION

6.1 EXPERIMENTAL DETAILS

Metallic nickel films were deposited by thermal evaporation (e-beam) of Ni pellets with 99.997% purity (Cerac). After the deposition, the films were annealed 1 hour at different temperatures in the range of 300 – 600 °C. Corning and glass substrates of 1 mm were used for electrical, optical, morphological and structural measurements. Glass/ITO/ATO substrates for TFTs and double face polished silicon substrates for FTIR.

The oxidation process, like what happens in annealed copper films, produces dramatically changes in the nickel structure and on their physical properties. The thickness increases as consequence of temperature, leading to the formation of NiO on surface of the film.

Table 6.1 – Resume of deposition parameters used in the e-beam evaporation system (ρ_d and Z are the material density and acoustic impedance, respectively. R is the growth rate).

Deposition Parameters	Ni
P_B (Pa)	$\sim 10^{-4}$
T_0 (°C)	17 – 22
ρ_d (g cm ⁻³)	8.91
Z ($\times 10^5$ g.cm ⁻² s ⁻¹)	26.68
P_{Final} (mbar)	$\sim 10^{-3}$
I_{Filament} (A)	0.06 – 0.08
R (Å s ⁻¹)	1 - 2

It is possible to understand the growth of the thickness (like in the case of copper), taking in to consideration the structure of the formed oxide, the packaging effect or the density of the material. Regarding the structural parameters presented in the Chapter II, and the equation (6.1) it is possible to estimate the expected increase on thickness. Once again, assuming that relation between the unit cell for Ni and NiO, is proportional to a relation of the volumes of these respective films and considering their density, is possible to find the relation that allows an estimation of the film thickness:

$$t_{\text{NiO}}^{\text{film}} = \frac{\rho^{\text{Ni}} V_{\text{UCell}}^{\text{NiO}}}{\rho^{\text{NiO}} V_{\text{UCell}}^{\text{Ni}}} t_{\text{Ni}}^{\text{film}} \quad (6.1)$$

where t_A^{film} , ρ^A and V_{UCell}^A are the thickness, the density and the unit cell volume of the specie A (A = Ni and NiO). This relation gives an explanation of the increase of the thickness with the

formation of the NiO phase presented in Figure 6.1.

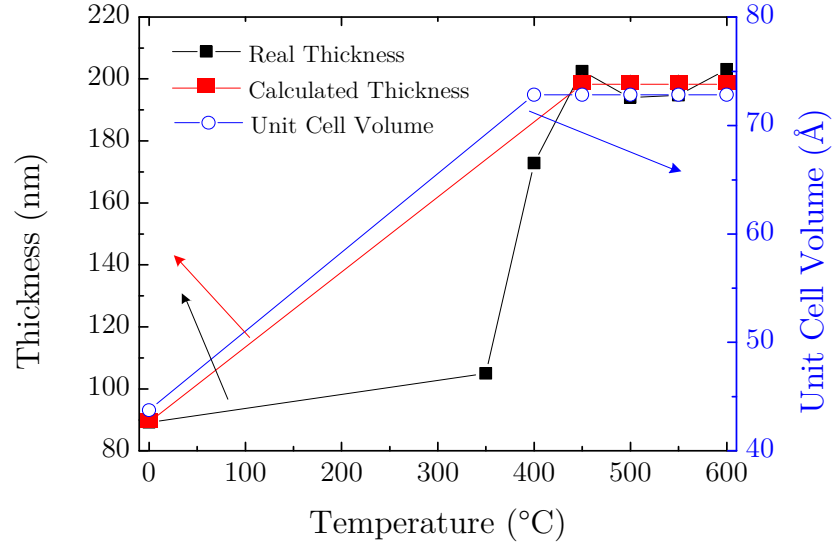


Figure 6.1 – Correlation of the thickness growth with the Ni and NiO unit cell volume.

6.2 STRUCTURAL CHARACTERIZATION

6.2.1 XRD

The films structure was analysed using XRD to investigate the formation of the nickel phases with the oxidation temperature. The grain size, texture coefficient and lattice parameters were also calculated. The nickel films were annealed at different temperatures (< 600 °C) after the deposition, to study the effect of the oxidation temperature in their physical properties.

The X-ray diffraction experiments were performed to study the structure of the nickel oxidized sample, and to confirm the production of the NiO phase expected by the Ellingham diagram.

The measurements were performed using a Bruker-AXS D8 Discover diffractometer* in grazing incidence geometry using Cu $K\alpha_{1,2}$ ($\lambda = 1.5406 \text{ \AA}$) collimated with a Göbel mirror with a divergent slit of 0.6 mm. An incidence angle of 1.5° and a 2θ ranging from 20° to 90° using a 0.12° seller slit with a step size of 0.04 and an acquisition time of 3 s were used. It's is perceptible from the XRD patterns that the films are polycrystalline (Figure 6.2). The as-

* These measurements were done in the Nuclear Technology Institute (ITN), Portugal.

deposited film exhibits a single nickel phase, with preferential orientation according to $(111)^\diamond$, with a texture coefficient $P \approx 1.39$. Reflection peaks with the directions of $(200)^\diamond$ and $(220)^\diamond$ are also visible, but less intense.

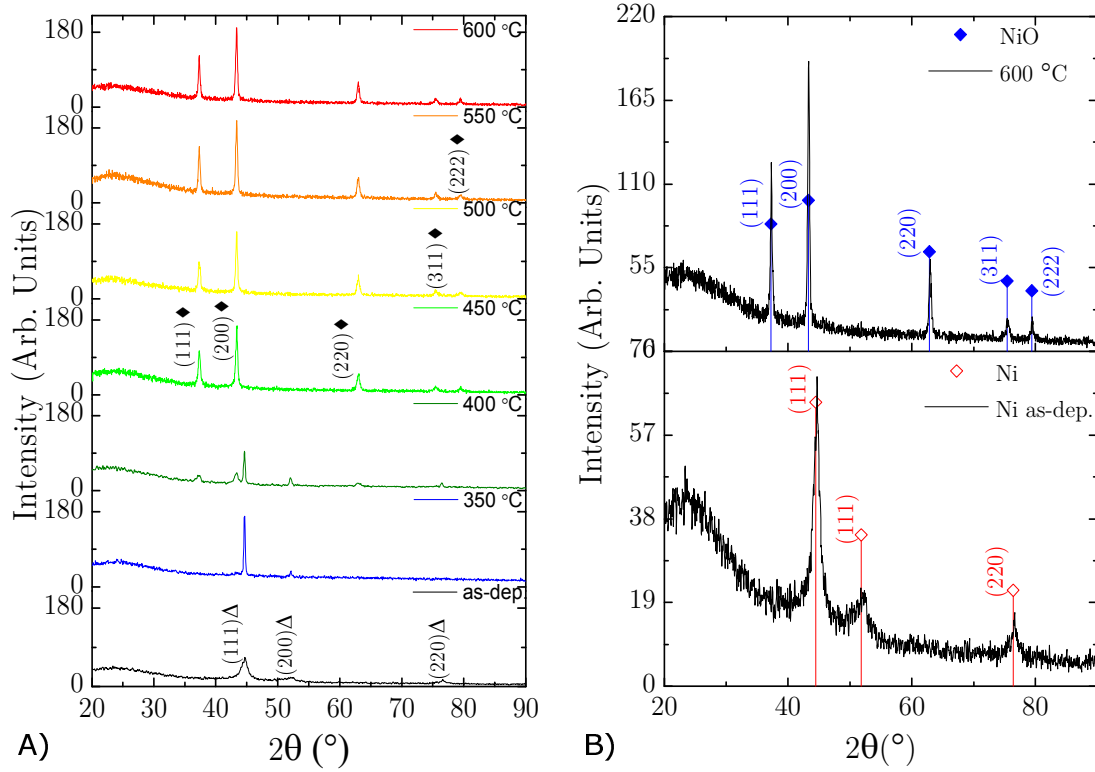


Figure 6.2 – A) XRD patterns of nickel oxides produced by thermal oxidation process (for the as-deposited film with initial thickness around 90 nm). B) Comparison of the Ni (as-deposited) and the NiO (oxidized at 600 °C) patterns with the standard ICDD data).

With the increase of the oxidation temperature, a NiO phase starts to be visible, and a mixture of Ni and NiO phases is observed at 400 °C. At this temperature it is observed three peaks associated to the NiO phase, related to the $(111)^\diamond$, $(200)^\diamond$ and $(220)^\diamond$ planes. However, the most intense peak is also associated to the nickel $(111)^\diamond$ plane. This region is very dependent of the sample thickness and exposition time. Thinner samples may be oxidized completely exhibiting a single phase of NiO at 400 °C.

When the temperature is raised (for this particular thickness) to 450 °C, it is only present the single phase of NiO associated to the planes referred before. For higher temperatures (up to 600 °C), only small changes were detected. The texture coefficient (with the limitations already discussed for thin films) shows a preferable orientation in the direction $[200]^\diamond$. The crystallite size D of the films was calculated from the Debye-Sherrer's formula, and are presented with the other structural properties in Table 6.2.

An estimation of the lattice parameters (a , b , c) for the phases observed was done using the Bragg law. In the case of Ni and NiO, the phases observed have cubic FCC structures. The calculation of lattice parameters is straight forward using the equation presented before (Chapter III, Section 3.34). For the Ni phase a was estimated to be around 3.51 Å and NiO ~4.17 Å, in agreement with what was expected by the reference diffraction files (ICDD, Ref. 047-1049 and 004-0850).

Table 6.2 – XRD data of nickel oxide films as a function of annealing temperature for peaks with higher intensity (symbol representations: ($\diamond$) metallic Ni, ($\blacklozenge$) NiO films.

T (°C)	Phase	2θ (°)	$(h\ k\ l)$	d (Å)	FWHM (°)	I_{Max}/I	D (nm)	$P(h_i\ k_i\ l_i)$
As-dep.	Ni	44.68	(111) $\diamond$	2.03	1.20	100	7	1.39
		52.36	(200) $\diamond$	1.75	1.36	18	6	0.61
		76.68	(220) $\diamond$	1.24	0.48	19	17	-
400	Ni	44.68	(111) $\diamond$	2.03	0.24	100	33	1.78
		52.12	(200) $\diamond$	1.75	0.32	24	25	1.01
		76.48	(220) $\diamond$	1.24	0.40	13	20	-
	NiO	37.16	(111) $\blacklozenge$	2.42	0.64	20	12	0.59
		43.36	(200) $\blacklozenge$	2.09	0.64	31	12	0.61
		62.84	(220) $\blacklozenge$	1.48	0.80	10	10	-
450	NiO	37.32	(111) $\blacklozenge$	2.41	0.32	56	25	1.03
		43.40	(200) $\blacklozenge$	2.08	0.36	100	22	1.12
		63.00	(220) $\blacklozenge$	1.47	0.48	27	17	0.85
		75.48	(311) $\blacklozenge$	1.26	0.48	8	17	-
		79.56	(222) $\blacklozenge$	1.20	0.56	6	14	-
500	NiO	37.32	(111) $\blacklozenge$	2.41	0.40	46	20	0.89
		43.40	(200) $\blacklozenge$	2.08	0.32	100	25	1.17
		63.00	(220) $\blacklozenge$	1.47	0.56	28	14	0.94
		75.48	(311) $\blacklozenge$	1.26	0.48	10	17	-
		79.36	(222) $\blacklozenge$	1.21	0.88	5	9	-
550	NiO	37.32	(111) $\blacklozenge$	2.41	0.40	61	20	1.09
		43.4	(200) $\blacklozenge$	2.08	0.36	100	22	1.17
		62.96	(220) $\blacklozenge$	1.48	0.56	26	14	0.94
		75.52	(311) $\blacklozenge$	1.26	0.48	8	17	-
		79.64	(222) $\blacklozenge$	1.20	0.40	6	20	-
600	NiO	37.32	(111) $\blacklozenge$	2.41	0.32	58	25	1.05
		43.32	(200) $\blacklozenge$	2.09	0.32	100	25	1.11
		63.00	(220) $\blacklozenge$	1.47	0.40	26	20	0.83
		75.36	(311) $\blacklozenge$	1.26	0.56	7	14	-
		79.48	(222) $\blacklozenge$	1.20	0.24	8	33	-

The increase of the oxidation temperature leads to a growth in the crystallite size as

displayed in Figure 6.3. The behaviour is similar for all the planes plotted. The sample oxidized at $T = 400\text{ }^{\circ}\text{C}$, shows the larger grains maybe related to the non-uniformity of the films induced by the co-existence of two different phases (Ni and NiO) and an increase of crystallization associated specially to the Ni phase. This increase of the crystallization was clearly observed in the *in situ* experiment presented in Figure 6.4 (A).

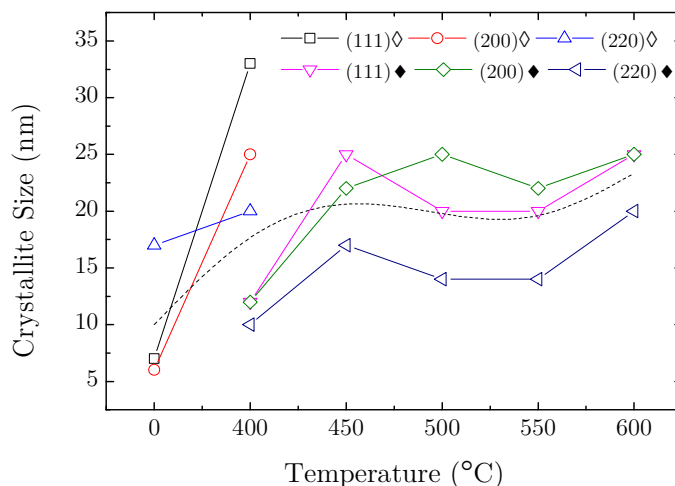


Figure 6.3 – A) XRD patterns for a nickel film oxidized at different temperatures.

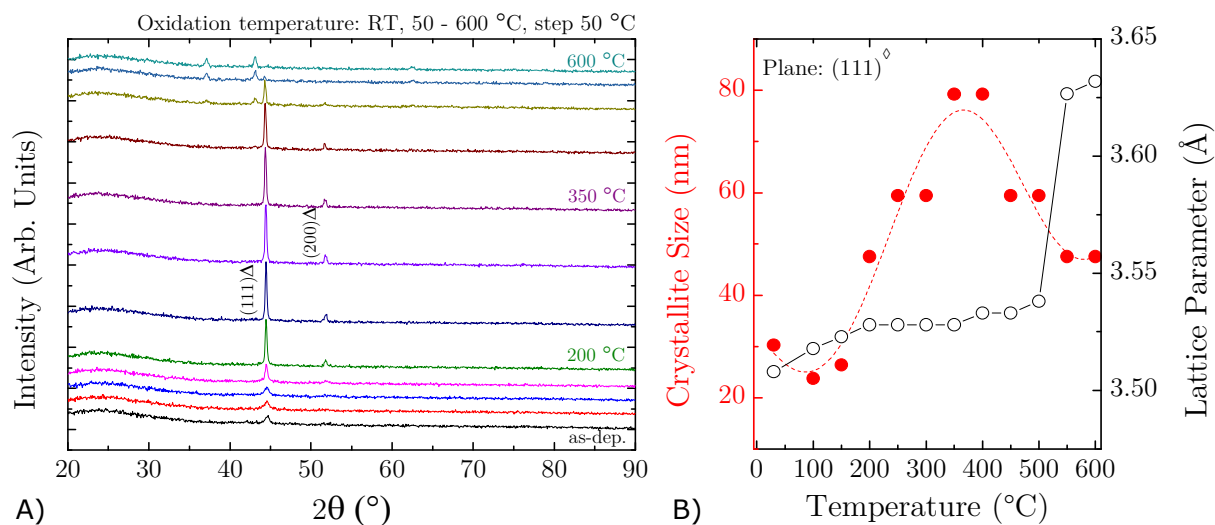


Figure 6.4 – A) XRD patterns obtained for a $\sim 100\text{ nm}$ thick nickel film oxidised *in situ*. B) Evolution of Nickel $(111)^{\diamond}$ grain size with the temperature (oxidation *in-situ*).

The *in situ* analysis was done to trace the path of the structural changes in the nickel with the oxidation temperature Figure 6.4. This analysis was performed using a PANalytical's X'Pert PRO diffractometer[†] in the Bragg-Brentano configuration with a beam

[†] Characterization performed in CENIMAT-I3N, FCT/UNL.

mask of 5 mm, divergence slit of $\frac{1}{4}^\circ$, anti-scatter slit of $\frac{1}{2}^\circ$. Scans of 6 min were performed with a step of 0.033° , from $2\theta = 20^\circ$ to $\theta=65^\circ$. The sample was measured at RT (30 °C) and then the temperature was increased gradually from 50 °C to 600 °C, with a step of 50 °C.

In this experiment a nickel film of ~ 100 nm was oxidized “*in situ*” (in air) with temperatures from 30 °C to 600 °C and measured simultaneously. This analysis revealed (as explained before in the kinetic oxidation of metals) that the time of oxidation plays a very important role in the conversion of Ni to NiO. Furthermore, it is observed an increase of the crystallinity of the Ni films even before the conversion for NiO starts to be visible. The same behaviour was observed for the copper samples (results not presented here). In Figure 6.4 (B) is only presented the evolution of the grain size for the crystallographic plan (111) with the oxidation temperature.

6.2.2 RUTHERFORD BACKSCATTERING (RBS)

The Ni /NiO samples (as-deposited, 350 °C and 600 °C) were analysed by RBS using the same protocol described before.

The as-deposited film is composed of pure nickel containing no oxygen in its composition (see the inset Figure 6.5). To confirm where the elements are located at film surface, different spectrums are obtained with different angles. Particles (in this case He^+) that collide with the elements of the surface will reach the detector with the same energy (Chapter III, Section 3.3.4.2) independent of the angle. Then no shift of energy is expected for the elements that are located on the film surface.

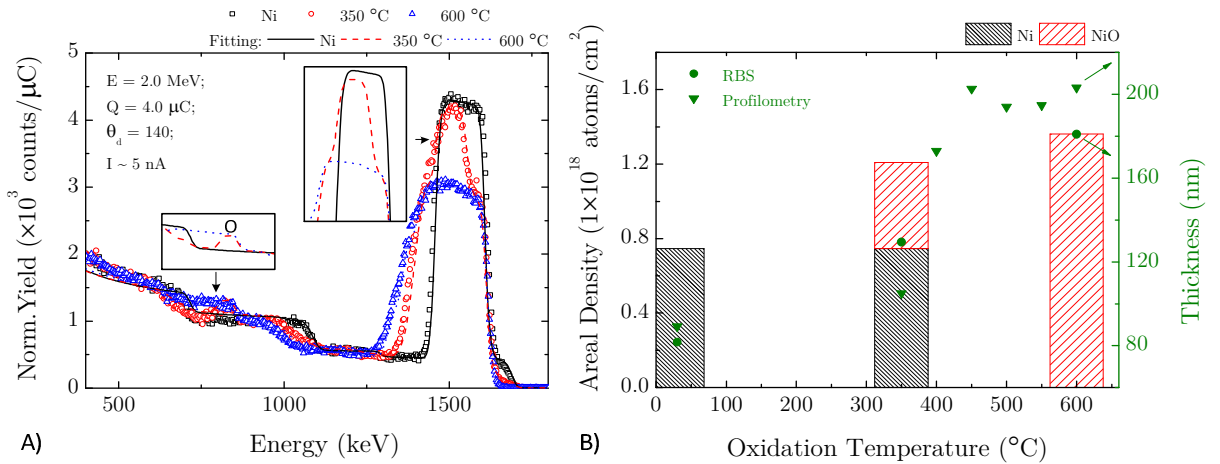


Figure 6.5 – A) RBS spectra for the as-deposited and annealed samples; B) Areal Density obtained

fitting the previous spectra.

In the particular case of Ni was also visible a small level in the Ni curve, that is not related to the film composition, but associated to a rare earth existent in the substrate.

With the increase of the oxidation temperature to 350 °C it is visible an enlargement of the spectrum when compared with the as-deposited one, indicating an increase in the film thickness (also observed in the Figure 6.5 (B)). It is also visible that in the region of high energies the curve has two levels, one correspondent to a nickel oxide layer and a second correspondent to the un-oxidized Ni. This is substantiated by the appearance at low energies of a small peak corresponding to oxygen. A measure done with two angles verifies that the oxygen is also available in the surface of the film. With the increase of the annealing temperature to 600 °C is visible that the oxygen peak is extended in the film thickness. This indicates the fully oxidation of the Nickel film.

The thickness of the films was also estimated using this technique. Figure 6.5 (B) displays the evolution of the thickness (estimated by RBS and Profilometry) with the oxidation temperature. For the estimation of this parameter by RBS, was used the standard bulk values of the Ni and NiO density. The differences observed are an indication that the density of the films deviates from the bulk values. This was also observed in the case of CO films produced by thermal oxidation, and may be originated due to an excess of oxygen, consequence of the diffusion process that assists the oxidation. In the surface of the film is always expected a less dense film.

6.3 ELECTRICAL CHARACTERIZATION

The nickel oxide films were characterized by Hall effect and dark DC conductivity, to try to determine the evolution with the temperature of their electrical properties. The electrical characterization followed the procedure adopted for CO films.

6.3.1 HALL EFFECT

The electrical properties were measured in the *van der Paw* configuration, allowing the estimation of the electrical resistivity (ρ), Hall coefficient (R_H), Hall mobility (μ_H) and carrier

concentration (n_0). In Figure 6.6 is presented the typical behaviour of the nickel oxide films versus oxidation temperature. These results are also summarized in Table 6.3. In a similar way to what was detected for CO by oxidation, the plot shows 2 regions relatively distinguish by their electrical properties. The region (I) correspondent to a high conductivity region, that includes the as-deposited nickel samples and a partial-oxidized nickel samples (≤ 400 °C). The region (II) correspondent to the NiO phase, samples with a similar electrical properties (high resistivity, carriers concentration, mobility) annealed at 450, 500, 550 and 600°C,

The oxidation process depends obviously of the sample thickness. Small differences in the thicknesses and a low (enough) temperature can lead to a partially or fully oxidized film. This was observed with the samples deposited with 350 - 400 °C were small differences in the thickness originated partially or fully oxidized films. This means, that in some cases the NiO layer is in large enough to act as a protective barrier preventing the oxidation of the Ni layers located in beneath.

A post-annealing step at 200 °C, after the deposition of Ni/Au contacts, appears to be effective in the reduction of the contact resistance, being observed a significantly impact in the electrical properties. In the case of copper oxides, the change was attributed to structural changes in the films since the Cu_2O is formed at temperatures ~ 200 °C. In the case of Ni or NiO no change (conversion) of phase is expected to occur at so low temperatures, only the enhancing of crystallization supported by the XRD results previously discussed. The differences in the electrical properties of the samples before and after annealing (200 °C, 1 hour) presented in Figure 6.6 can be related to the improvement of the electrical contacts. The crystallization is not expected to change much in case of the NiO samples oxidized at these temperatures.

Reliable Hall effect measurements to determine the mobility and carrier concentration of this type of oxides, as explained for Cu_xO films, are difficult to achieve. Even measuring several times, the results showed inconsistencies being impossible to do a satisfactory statistics regarding the nature of the carriers (changing from n to p). In the case of the copper samples the scattering on the results were assumed to be due to the low mobility of the films, and for higher mobility the results were more “stable”. However, in this case low mobility appears to not be the reason. The reversion of the mobility sign was been already reported to be dependent on the temperature [1].

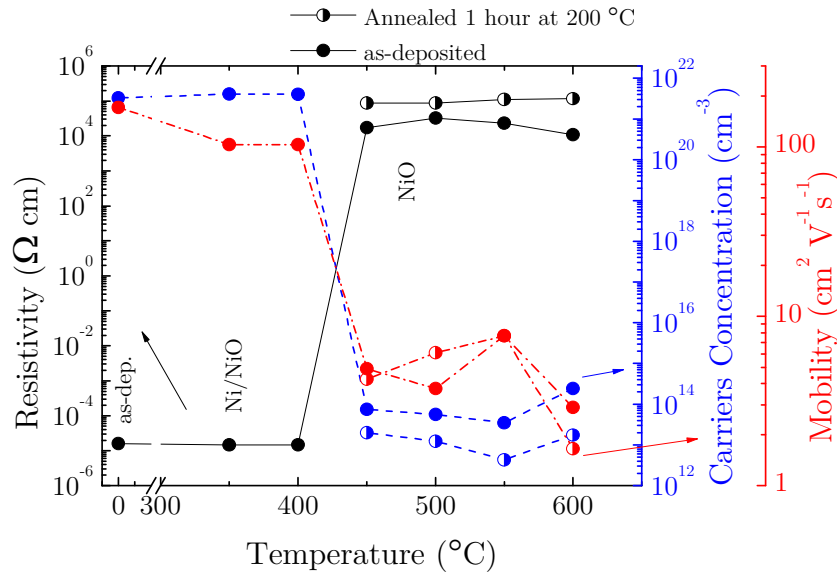


Figure 6.6 – Variation of the bulk resistivity (ρ), carrier concentration (n_0) and Hall mobility (μ) with oxidation temperature.

NiO is a paramagnetic material and the Hall effect is strongly influenced by the interaction between the magnetization induced in the material and the external magnetic field that may affect movement of the charge carriers. This characteristic may be the cause of the ambiguous results obtained for NiO. It was proposed by Maranzana *et al.* [2] and reviewed by Van Daal and Bosman [3] that the Hall coefficient for the paramagnetic phase of NiO is composed of two components: the “normal component” (found normally in nonmagnetic band semiconductors) and the “magnetic component”. The magnetic component has the sign opposite to that of the normal component and can overcompensate it, leading to a reverse of the sign. This is applied for the conduction by holes (in the case of NiO) or by electrons [2, 3]. In the antiferromagnetic NiO, it is assumed that below the Néel temperature the Hall effect has the normal sign. The magnetic component starts to be noticeable at temperatures above 400 K. The measurements were performed at 300 K. Apparently the magnetic component of the mobility is not be the cause of the inconsistencies observed during the measurements. The oxidation is a diffusion process being possible to have nickel with different oxidation states in a single film, what may change the conclusions observed for a single stoichiometric pure NiO film. To clarify this point, would be interesting in a future approach, to investigate the Hall coefficient and also the other electrical parameters more influenced by this type of effect

(mobility and carrier concentration) with the temperature[‡].

Another explanation more simple, is related to the high resistivity of the samples, that combined with the low magnetic field (0.5 T) originates very low Hall voltages that are difficult to measure. Perhaps a Hall effect with a large magnetic field will solve this problem and reduce the number of hypothesis.

Table 6.3 – Resume of the electrical properties for the NiO samples deposited with ~90 nm thickness.

T (°C)	As-dep. ρ ($\Omega\cdot\text{cm}$)	200 °C	As-dep. μ_H ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	200 °C	As-dep. n (cm^3)	200 °C
RT	1.60×10^{-5}	--	171.0	--	3.30×10^{21}	--
350	1.45×10^{-5}	--	103.0	--	4.11×10^{21}	--
400	1.49×10^{-5}	--	103.0	--	4.04×10^{21}	--
450	1.73×10^4	8.68×10^4	4.9	4.25	7.42×10^{13}	1.99×10^{13}
500	3.27×10^4	8.79×10^4	3.8	6.09	5.58×10^{13}	1.23×10^{13}
550	2.34×10^4	1.11×10^5	7.7	7.67	3.49×10^{13}	4.33×10^{12}
600	1.08×10^4	1.16×10^5	2.9	1.65	2.42×10^{14}	1.74×10^{13}

6.3.2 DC CONDUCTIVITY VERSUS TEMPERATURE

The DC dark conductivity versus temperature was used to study the nickel oxide films produced by metallic oxidation. The typical behaviour of a semiconductor was analysed and the activation energy calculated. Some hypothesis about the conduction mechanism and band structure of the oxides were analysed.

The conductivity (in the dark and vacuum) was measured in the range of temperatures 100 – 373 K. The study was performed on four samples fully oxidized (450– 600 °C) (Figure 6.7 (A)), being observed a similar behaviour of the conductivity.

The semiconductor like behaviour (already explained for Cu_2O and CuO films) was also observed for the NiO samples. Like in the CO case, two different regions are observed in Figure 6.7 that can be explained by two different conduction regimes. The measured data of σ - T are found to follow an Arrhenius like relation presented before, $\sigma = \sigma_0 e^{-\frac{E_{\sigma l}}{k_B T}}$. It is possible to adjust this equation to the two regions obtaining activation energies denoted by $E_{\sigma 0}$ and $E_{\sigma l}$, for high (region near 370 K) and low temperatures (region near 100 K) respectively.

[‡] This was tried during this thesis (also for copper samples), however the resolution of the system does not allow to collect reliable data to enlighten a specific behaviour.

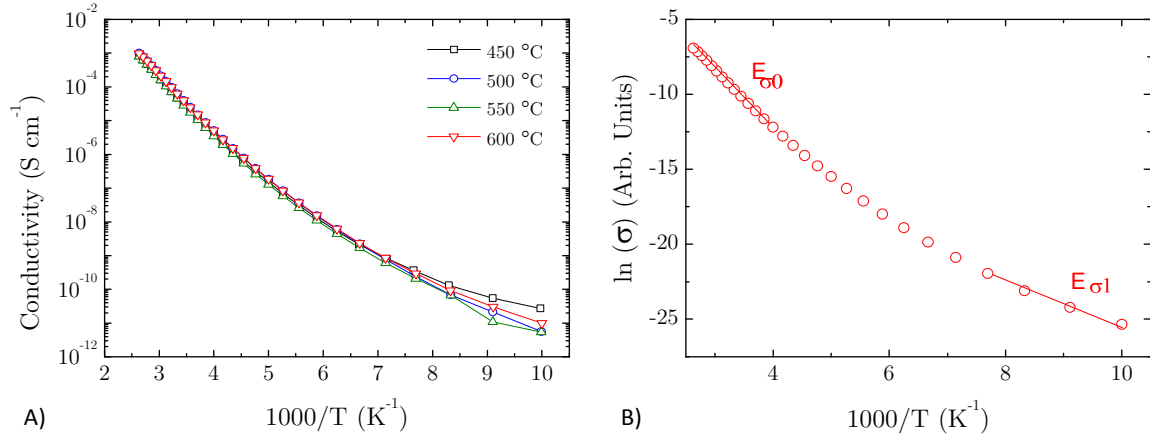


Figure 6.7 – A) Nickel oxides conductivity as a function of 1000/T. B) Temperature dependent dark conductivity for the NiO sample oxidized at 600 °C.

The activation energy is usually referred to the value determined at high temperatures. The results published for NiO have a quite disperse values from 0.08 to 0.89 eV [4-8], consequence of different deposition methods and fittings in different temperature regions. In Table 6.4 is compared the values obtained in this work with other reported in the literature by different authors. The Figure 6.8 shows the variation of $\ln(\sigma)$ with $(T_0/T)^\nu$, with $\nu = 1, 1/2$ and $1/4$. The plot shows a behaviour in agreement with $(T_0/T)^{1/4}$, suggesting that the temperature dependence of electrical resistivity is consistent with the relation [8, 9],

$$\sigma = \sigma_0 e^{-\left(\frac{T_0}{T}\right)^\nu} \quad (6.2)$$

and ν depends on kind and degree of disorder of the system and on temperature. In doped crystalline semiconductor, the common values for ν are $1/4$ and $1/5$ [8]. Figure 6.8 (B) presents the fit for all the samples using $\nu = 1/4$.

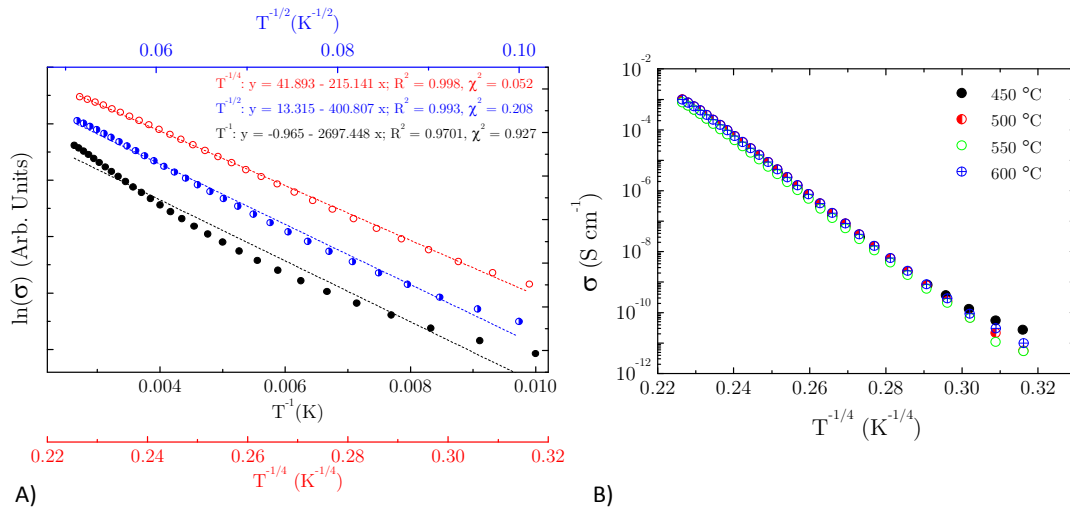


Figure 6.8 – Variation of $\ln(\sigma)$ with T^{-1} , $T^{-1/2}$ and $T^{-1/4}$ for the film produced at 600°C (A); $T^{-1/4}$ behaviour for the films produced at 450 – 600 °C (B).

Using the equation (6.2), it is possible to determine the best value of ν , adjusting the equation to the experimental data correlating the parameters that will allow the convergence of the model.

Table 6.4 –Activation energy calculated using the Arrhenius equation: low temperature (E_A^{Low}) and high temperature (E_A^{High}) regimes.

	T (°C)	$E_{\sigma 0}$ (eV)	$E_{\sigma l}$ (eV)	E_A^{High} (eV)[7, 8]	E_A^{Low} (eV)[4, 6]	Best ν	R^2
NiO	450	0.33	0.08			0.11	0.9986
	500	0.34	0.13			0.19	0.9997
	550	0.35	0.07	0.35-0.4	0.08 - 0.16*	0.18	0.9997
	600	0.32	0.11			0.17	0.9995

These results may evidence a variable range hopping mechanism of the charge carriers between randomly distributed localized electronic states in the NiO samples. However, the change in the slope can also be attributed for the anomalous Hall effect of NiO, also suggested by Vandaal and Bosman [3]. More experiments should be done in the future to try to go deeper in the magnetic properties of the NiO and the consequence of them in their electric properties.

6.4 OPTICAL CHARACTERIZATION

6.4.1 UV-VIS-NIR SPECTROSCOPY

The transmittance of the films was analysed in the range of 300 – 2500 nm. The fundamental absorption coefficient (α) was plotted to estimate the optical band-gap of these films. The average transmittance ($T^{400-750}$) and the average absorption ($\alpha^{400-750}$) were also estimated in the wavelength interval between 400 – 750 nm, to observe the influence of the oxidation temperature in such properties. In Figure 6.9 is presented the optical spectrum of a film deposited with ~90 nm thickness.

The as-deposited film showed poor transmittance ($< 1\%$) and a high absorption coefficient ($\sim 7.80 \times 10^5 \text{ cm}^{-1}$) due to the high absorption of the metallic Ni (Figure 6.9 (A)). With the increase of the temperature, and when the formation of NiO starts to occur in the metal surface, the transmittance increases. NiO has a low absorption coefficient and a high optical gap (expected to be around 3.25 – 4.3 eV), which explains the high transmittance in the visible spectrum of these films. The average value of the absorption coefficient was estimated in the visible spectrum around $\sim 1.17 \times 10^4 \text{ cm}^{-1}$. It is understandable that in the oxidation process, the

thickness of the metallic film will be reduced originating a NiO layer in the surface.

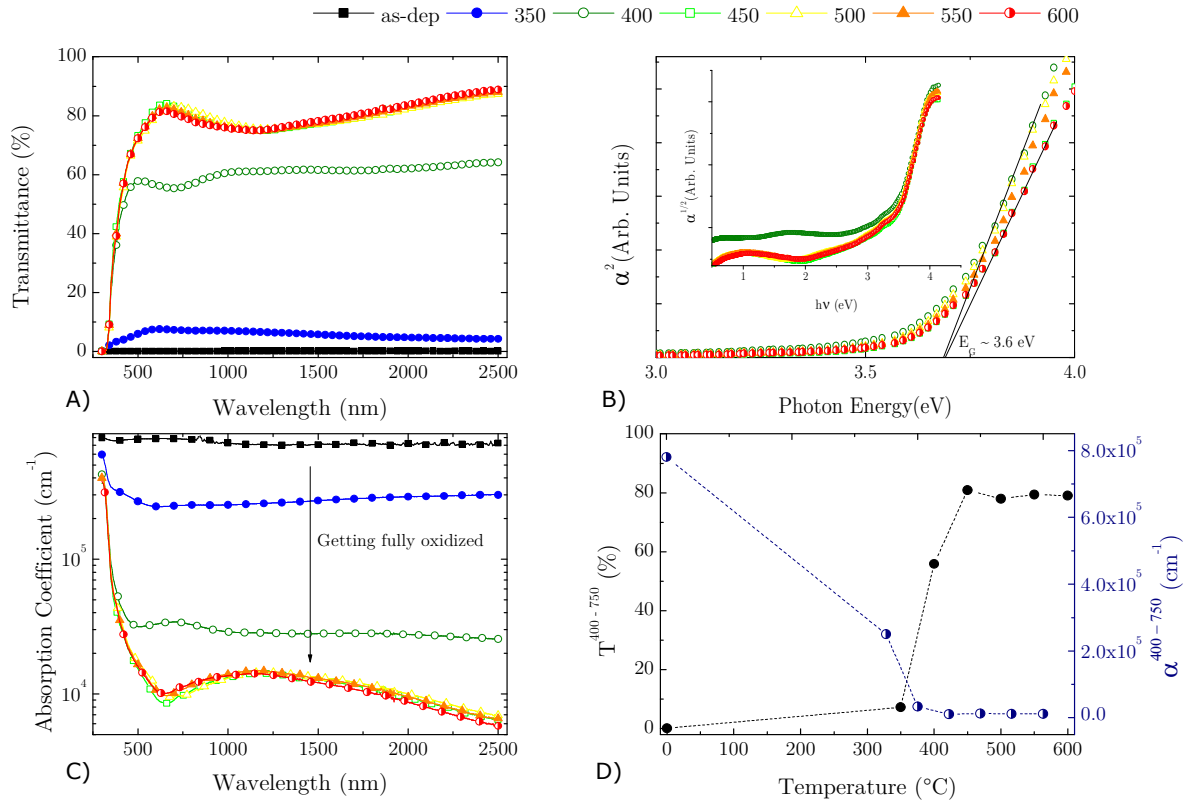


Figure 6.9 – Transmittance spectrum (A); Optical bandgap estimated using the direct allowed transition (α^2), with an inset of the indirect allowed transition (B); Absorption coefficient (C); Average transmittance ($T^{400-750}$) and absorption ($\alpha^{400-750}$) in the visible range (400 – 750 nm) (D).

With increase of the temperature to 350 °C (1 hour) the nickel phases oxidizes partially increasing its transmittance to ~7%. Just as a curiosity, using the equation (3.33) presented in the Chapter 3, Section 3.3.3, for the exponential decay of the light intensity with the thickness, and the average absorption coefficient (for Ni and NiO), it is possible to perform an estimation of the thicknesses for the Ni/NiO “sandwich”, with are respectively ~32 nm and ~70 nm.

At 400 °C the transmittance increases to ~56% (with is attributed to the existence of still a very thin layer of Ni in the surface of the glass) and stabilizing around 80% for higher temperatures (for fully oxidize samples).

The optical gap was estimated using the Tauc model, and it's observed in Figure 6.9 (B). The behaviour matches with the first allowed transition, ranging between 3.65 – 3.69 eV, consistent with the reported experimentally and theoretically [10-16]. In Table 6.5 it is presented a resume of the results obtained for this set of films, oxidized from an as-deposited nickel film of 90 nm thickness.

Table 6.5 – Optical data for the set of films deposited with a thickness around 90 nm.

$T_{\text{Oxid.}} (^{\circ}\text{C})$	$T^{400-750}(\%)$	thickness (nm)	E_G (eV)
as-dep.	0.1	90	--
350	7.2	105	--
400	55.9	173	3.65
450	80.8	203	3.68
500	78.0	194	3.67
550	79.5	195	3.69
600	79.0	203	3.67

6.4.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

The Ni – O orbitals are formed by overlapping of the 3d and 4s orbitals of the nickel atom with the 2p orbitals of the oxygen atom (Figure 6.10). According to Moravec and Jarrold [17] the neutral state ($^3\Sigma$) of $\text{NiO}^{\S}$ has a vibrational frequency 840 cm^{-1} and the first excited state ($^3\Pi$)^{**} has a vibrational frequency of 777 cm^{-1} . They also report a frequency of 660 cm^{-1} for anion state ($^2\Pi$) [17].

In Figure 6.11 is presented the results for NiO samples, for the conditions of 450 – 600 (NiO phase). It is visible that all of the samples have a similar spectrum with strong absorption bands near $669 - 682 \text{ cm}^{-1}$ ($82.9 - 84.6 \text{ meV}$), 728 cm^{-1} (90.3 meV) and $1033 - 1072 \text{ cm}^{-1}$ ($0.128 - 0.133 \text{ eV}$). It is also observed a band around 810 cm^{-1} (0.1 eV), displayed in Figure 6.11 (B).

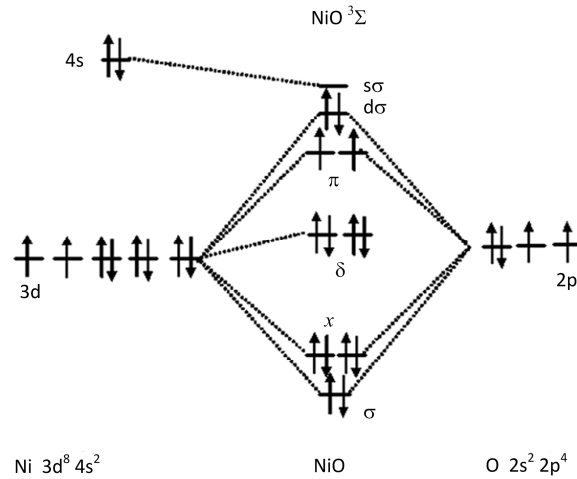


Figure 6.10 – Schematic diagram showing the molecular orbital of the $^3\Sigma$ ground state of NiO, with the mixing of the atomic orbitals of O and Ni [18].

^{\S} The ground state of NiO is described by the electronic configuration approximately as $...(8\sigma)^2(3\pi)^4(1\delta)^4(9\sigma)^2(4\pi)^2$

^{**} The first excited state has a electronic configuration approximately $...(8\sigma)^2(3\pi)^4(1\delta)^4(9\sigma)^1(4\pi)^3$

The absorption region around $669 - 682 \text{ cm}^{-1}$ can be attributed to the anion state ($^2\Pi$) [17, 18]. The bands around 728 and 736 cm^{-1} can be attributed to the state ($^4\Sigma^-$) and the band around 810 cm^{-1} to the neutral state ($^3\Pi$) [17]. Figure 6.11 (A) shows an absorption band growing with the oxidation temperature around 1033 cm^{-1} , showing that this vibrational mode is been accentuated with the increase of temperature, evidencing internal changes in their structure. This peak as already discussed in the previous chapters, can be attributed to the stretching vibration modes of Si-O-Si that are located near the vibration frequency of $1064 - 1125 \text{ cm}^{-1}$ ($0.132 - 0.140 \text{ eV}$). The vibration frequency located around 810 cm^{-1} can be also attributed to the bending vibration modes of Si-O-Si. This means apparently that the annealing step leads to the formation of a SiO_2 layer in the interface with NiO.

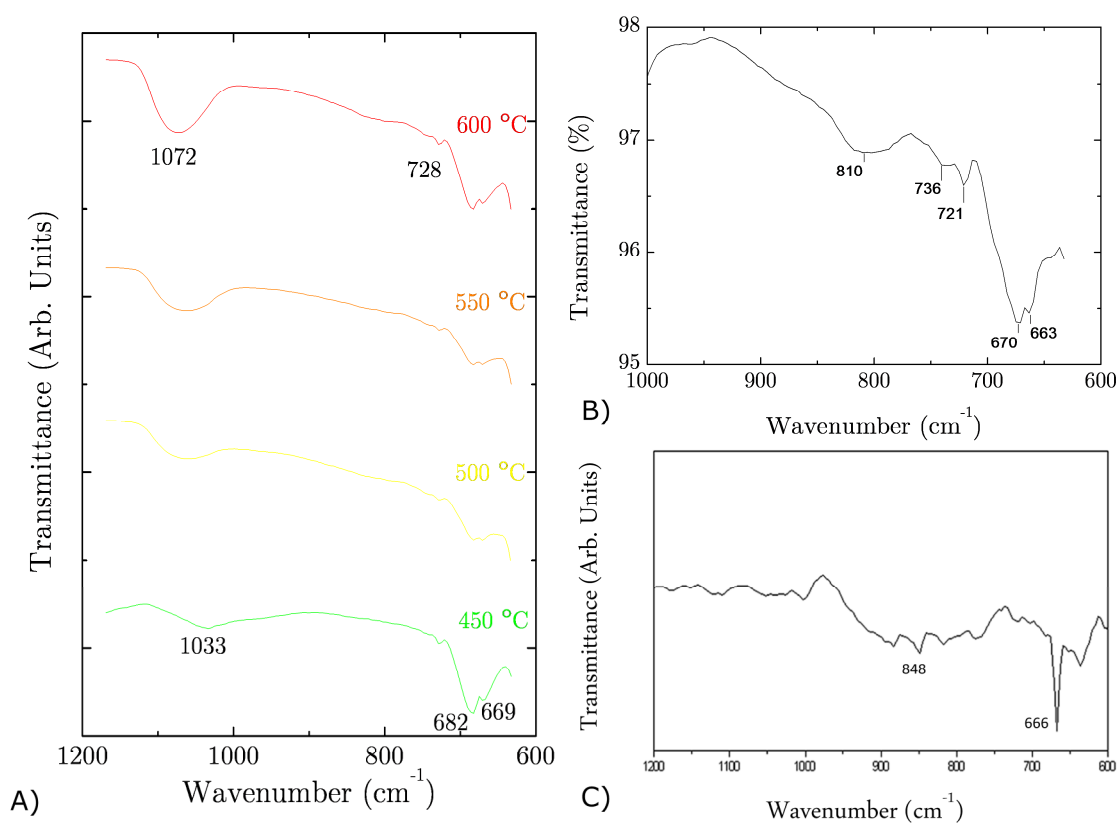


Figure 6.11 – A) FTIR spectra for NiO samples ($\sim 100 \text{ nm}$ as-dep.) oxidized at temperatures between $450 \text{ }^{\circ}\text{C}$ to $600 \text{ }^{\circ}\text{C}$; B) NiO sample ($\sim 50 \text{ nm}$ as-dep.) oxidized at $600 \text{ }^{\circ}\text{C}$; C) Results obtained by Nandy [19].

6.5 SURFACE CHARACTERIZATION

The surface of the films were analysed using the KP, AFM and SEM techniques. This study allows the understanding of the impact of the oxidation temperatures in the morphological properties of the NiO films.

6.5.1 KELVIN PROBE

KP was used to estimate the work function (Φ) following the procedure already explained in other chapters. The surface potential for fold sheet was measured to compare with the work function expected (5.1 eV) and presented in Table 6.6 for the different samples. The results are in agreement with the values reported in literature, for Ni around 5.04 - 5.35 eV and for NiO around 5.3 eV [20, 21]. In the case of the NiO phase it is observed a high consistence of the results around 5.19 - 5.23 eV, revealing a high uniformity of the films surface along the temperature, that was also visible by AFM and SEM.

Table 6.6 – Surface properties of Nickel and NiO (W_F is the surface potential, Φ is the work function, $\Phi^{Lit.}$ the work function estimated by other authors).

$T_{Oxid.}$ (°C)	Phase	W_{Au} (meV)	W_F (meV)	Φ (eV)	$\Phi^{Lit.}$ (eV) [20, 21]
As-dep.	Ni	19.67±1.59	112.94±1.45	5.19	5.04 – 5.35
350	Ni/NiO	19.67±1.59	134.78±1.84	5.22	
400	Ni/NiO	19.67±1.59	101.41±1.58	5.18	
450		28.13±1.53	143.00±1.64	5.21	
500		22.91±1.35	108.18±1.56	5.19	
550	NiO	34.78±1.64	159.51±1.59	5.22	5.3
600		34.78±1.64	162.45±1.90	5.23	

6.5.2 ATOMIC FORCE MICROSCOPY (AFM)

The typical AFM microstructures obtained from the surface of the as-deposited and post-annealed films are shown in Figure 6.12. The surface roughness of the films was also estimated. The surface of as-deposited films is comprised of uniformly distributed and well packed grains with a RMS roughness of 1 nm.

With the increase in temperature to 350 °C, the surface shows a dramatic change in appearance, showing what seems to be a more oriented distribution of grain agglomerates similar to a pyramidal shape (Figure 6.13 (B)) (with a triangular base larger as $150 \times 150 \times 200$ nm). The RMS also increases from ~1.0 nm (for the smooth and uniform packed Ni film) to 2.13 nm (for the oxidized NiO film at 350 °C). Further increase of the temperature to 400 °C, shows an increase of the dimensions of the pyramidal structures. In Figure 6.13 (A) to (C) is shown the edges of grains agglomerates using an edge detection filter based on RMS analysis.

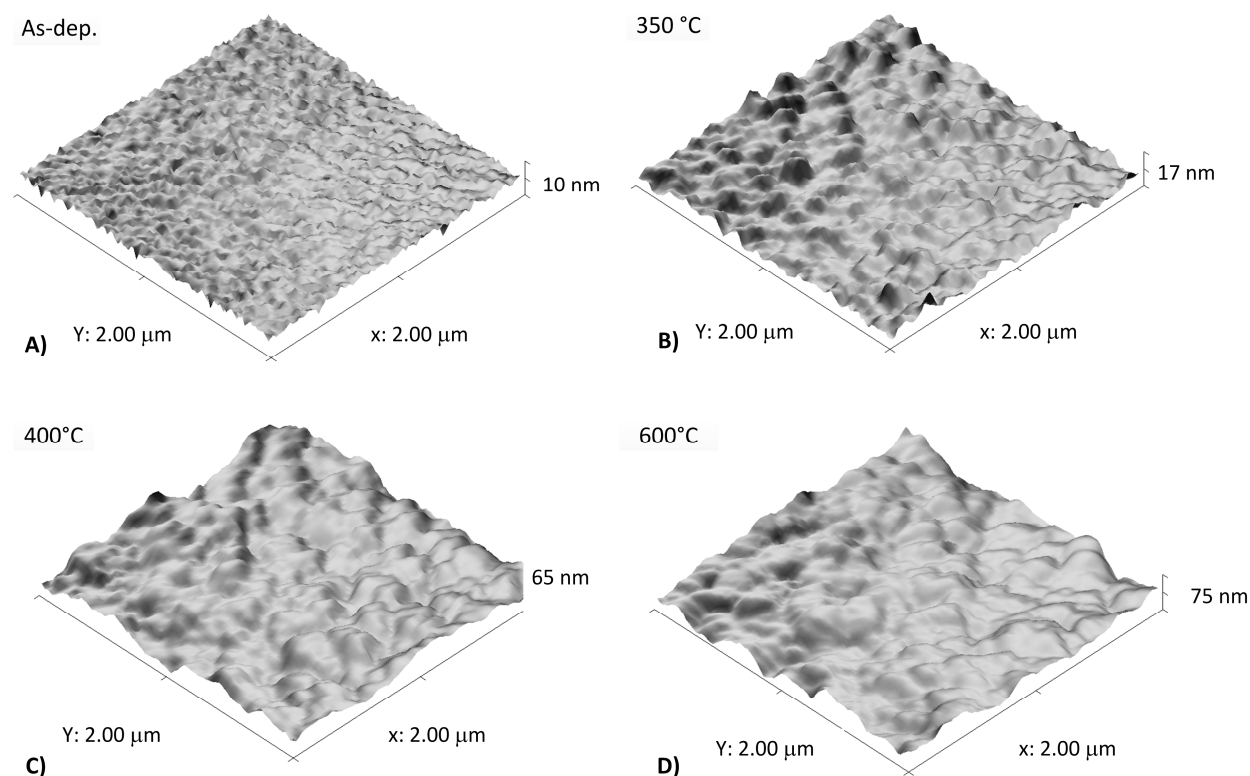


Figure 6.12 – AFM microstructures for the as-deposited nickel films (A) and for the films oxidized at 350 °C and 400 °C and 600°C, respectively B, C and D.

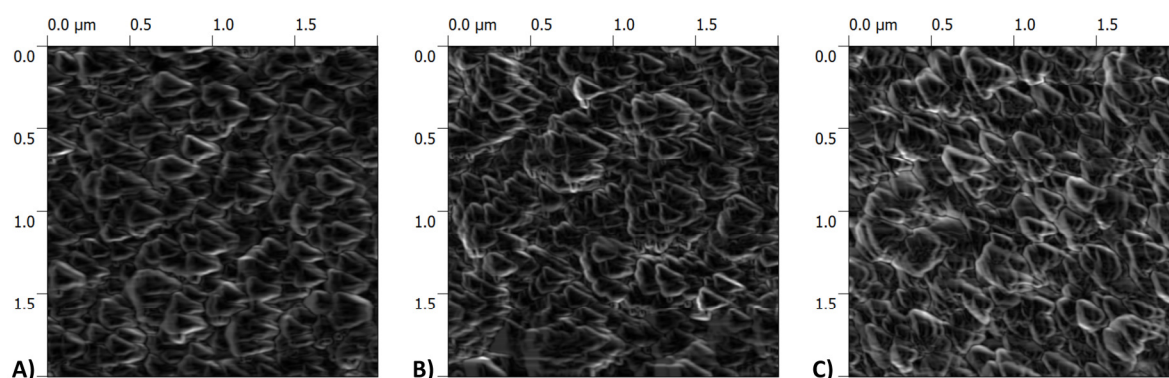


Figure 6.13 – AFM images with an edge detection filter based on RMS, for the samples annealed at 400 (A), 500 (B) and 600 °C (C).

With the increase of the oxidation temperature (≥ 400 °C) it is visible what appears to be a condensation of small agglomerates in to bigger structures dispersed by layers. In terms of RMS roughness, the surface morphology appears to become stable when NiO is formed, not being noticed dramatic changes after $T > 400$ °C. In fact, for the oxidation temperature of 400 °C and higher, the RMS roughness stabilizes around 11~12 nm. The pyramidal structural appears to grow for dimensions of the base larger as $180 \times 180 \times 260$ nm. However the surface appears to have a randomly uniform distribution that explains the stabilization of the RMS

roughness and may be related to the stability of the work function values found in the previous section.

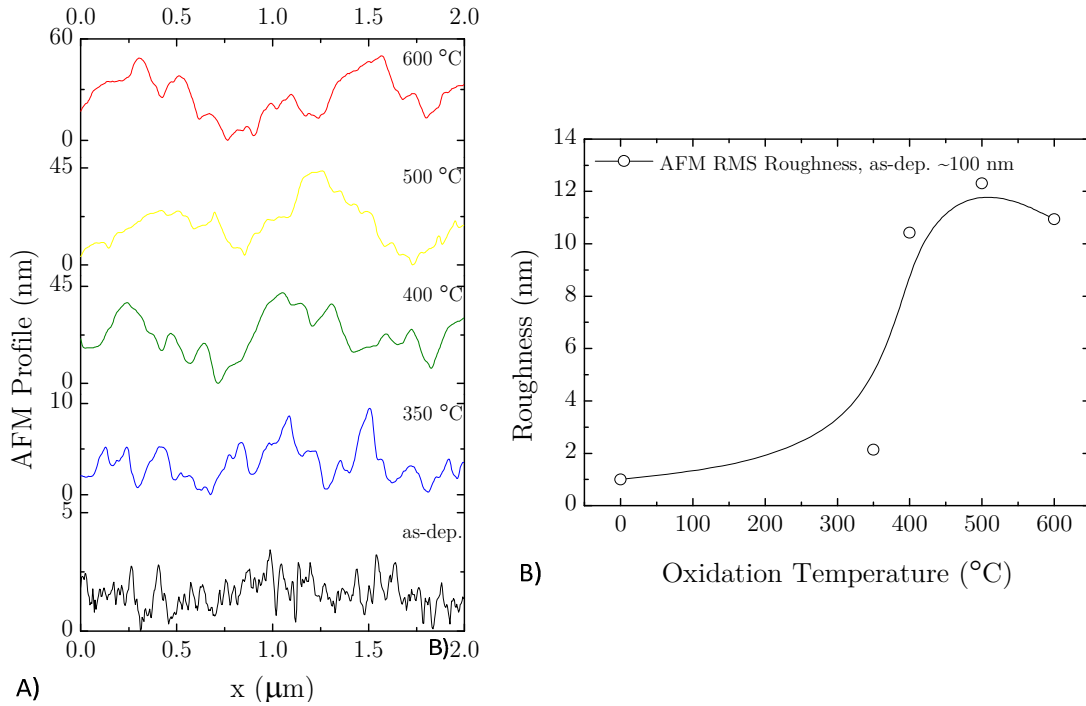


Figure 6.14 – AFM Profiles for the as-dep. Ni film, and for the oxidized at 350, 400, 500 and 600 °C temperatures (A); RMS roughness obtained by AFM (B).

Table 6.7 – Surface roughness for the as-deposited and oxidized films.

Sample	RMS (nm)
As-dep.	1.00
350	2.13
400	10.42
500	12.31
600	10.94

6.5.3 SCANNING ELECTRON MICROSCOPY (SEM)

SEM microscopy was used to see large areas of the samples surface, allowing a comparison with the images obtained by AFM. Observing the images (Figure 6.15 and Figure 6.16) is clear that the radical changes in the films surface occurs with the oxidation temperature. A structure like “orange peel” it is also observed for the films oxidized at temperatures higher than 350 °C (Figure 6.15 (B - D)). The formation of this type of structure can be associated to the thermal growth of NiO, when different reactions take place at different rates for different grain orientations [22]. SEM micrographs are taken in larger areas being

visible structures like “red blood cells” (more visible at high temperatures 500 – 600 °C, Figure 6.16 (B)). Structures like that were also described in this range of temperatures described as disc-shaped NiO platelets. These images are commonly observed in the study of the NiO phase [22, 23]. Although when someone cut these images and uses a program to treat them as 3D images^{††} (in equivalent dimensions to those of AFM) it is possible to see what looks like pyramidal structures (Figure 6.17). These structures increase their sizes with the temperatures, maybe due to a coalescence process of small agglomerates. This effect was also observed using AFM

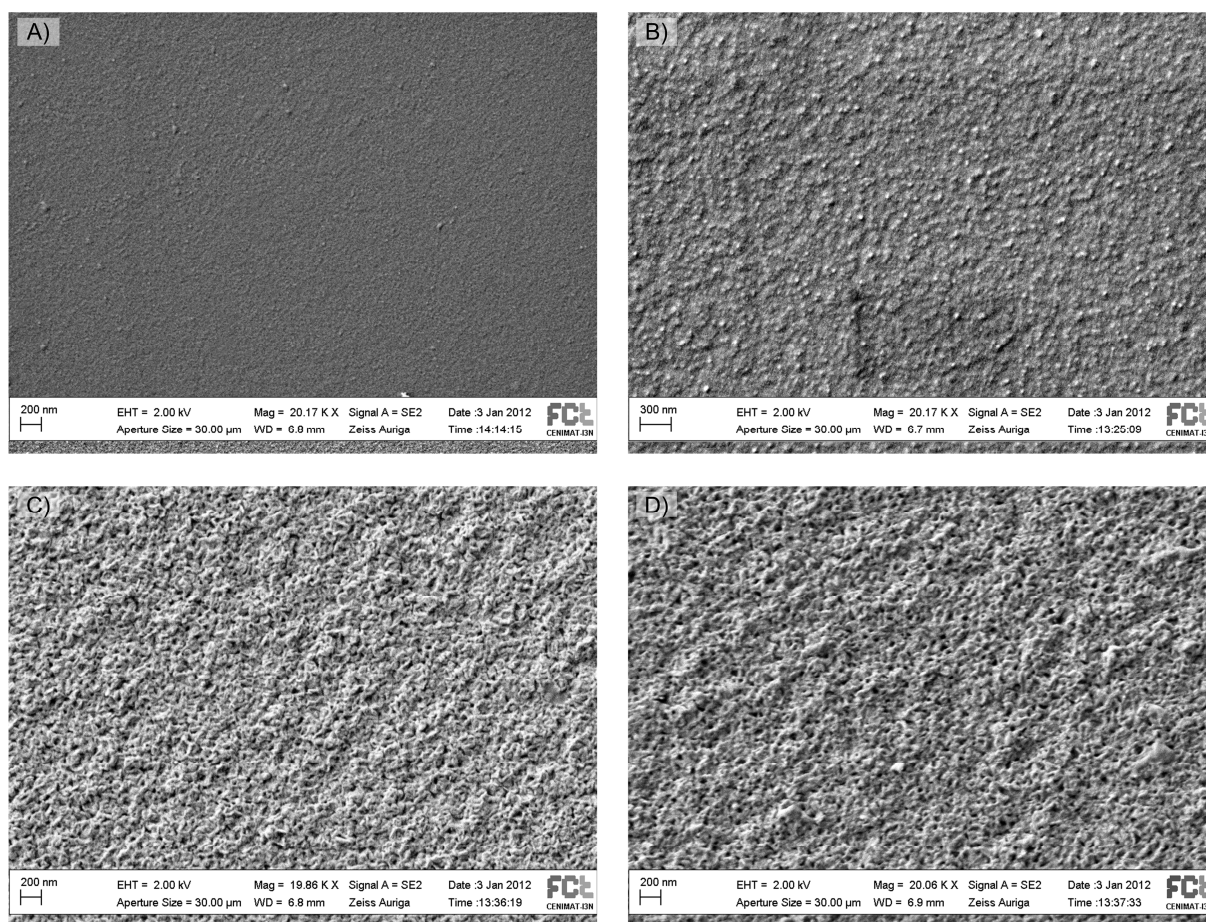


Figure 6.15 – SEM images of the as-deposited film (A) and oxidized films at temperatures: 350 °C (B), 400 °C (C) and 450 °C (D).

^{††} The program Gwyddion was used in this treatment.

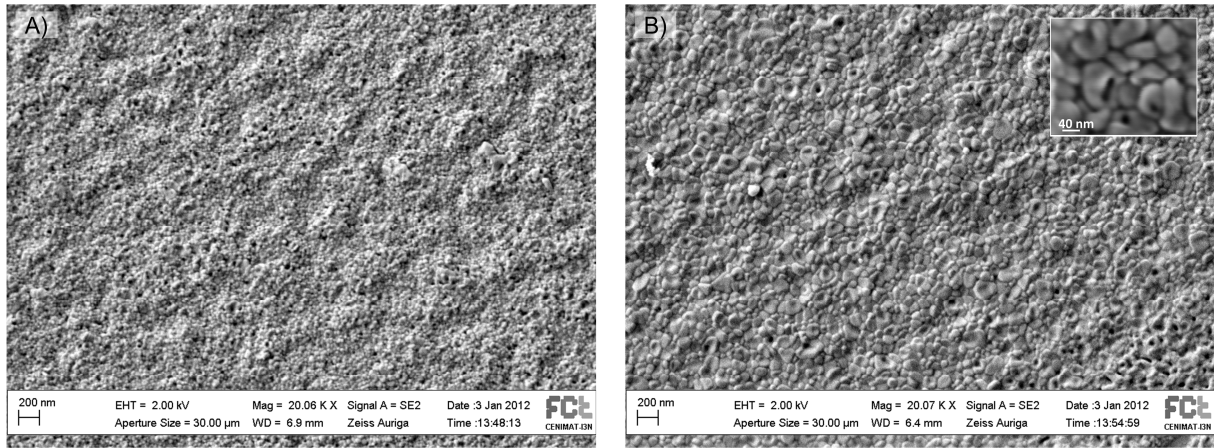


Figure 6.16 – SEM images of the oxidized films at temperature of 500 °C (A) and 600 °C (B).

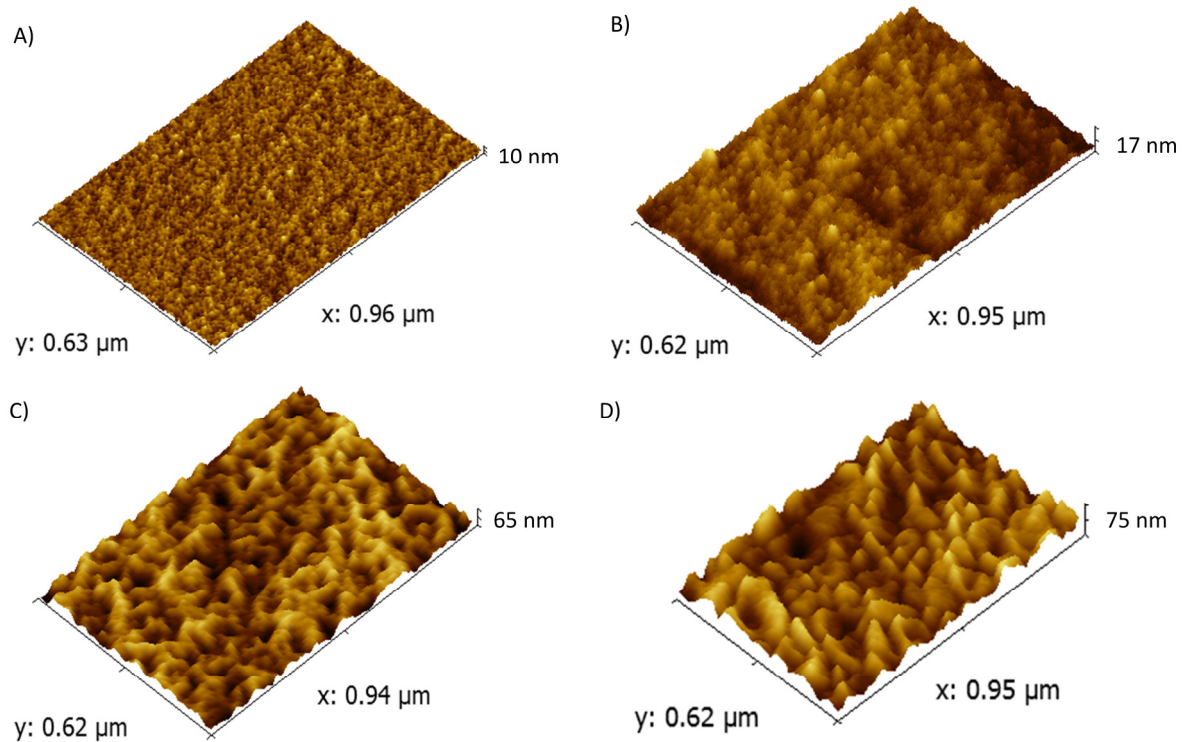


Figure 6.17 – 3D treatment of the SEM images.

6.6 CONCLUSIONS

The temperature was effective controlling the conversion of Ni to NiO phase in air. No other nickel phase was observed in this study. It is visible by XRD that temperature assists the oxidation process but also enhancing the crystallization. This was visible in the case of the metal (the film annealed at 350 °C showed a higher intense peak for Ni than the as-deposited one) but is also visible in the NiO samples. The size of the crystallites was estimated using different planes and increases with temperature. For a film with thickness around 100 nm is

visible that the effective temperature (to accomplish a full oxidation of the film) should be higher than 400 °C. The oxidation is adjusted to a layer model as observed by RBS. In the top of the film is visible the Ni (O-rich) film and in the bottom the nickel film.

In terms of their electrical properties it is visible two regions: one correspondent to the partial-oxidised films (metallic behaviour), and other correspondent to the fully oxidised films. It is visible a small decrease on the resistivity with the temperature ($T > 450$ °C), that could be related to an increase of crystallinity of the films and an also an increase on the crystallite size (observed by XRD). The film with higher mobility ($7.7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) was observed for the condition correspondent to $T = 550$ °C.

DC conductivity allowed the estimation of the activation energies ranging 0.32 – 0.35 eV (in the high range) and 0.08 – 0.13 eV (in the low range). These values are in agreement with the other published by other authors.

The optical properties of the films were also analysed, showing high transmittance in the visible spectrum up to 80%. The optical bandgap was also estimated using the direct allowed transition in the range of 3.65 – 3.69 eV. The work function was measured by KP ranging 5.19 – 5.23 eV, in agreement with reported values.

AFM and SEM spectroscopy was performed to characterize the morphology of these films, showing that temperature appears to enhance the formation of big agglomerates. This was also observed using the RMS value, showing an increase from 1 to 12 nm with the temperature.

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Chapter VII

Nickel oxide by RF sputtering

CONTENTS

In this section some results of NiO deposited by RF magnetron sputtering will be presented and discussed.

- 7 Nickel oxide by rf sputtering
 - 7.1 Experimental details
 - 7.2 Structural characterization – XRD
 - 7.3 Electrical characterization
 - 7.4 Optical characterization
 - 7.5 Surface characterization
 - 7.6 Conclusions
 - 7.7 References

7 NICKEL OXIDE BY RF SPUTTERING

Nickel oxide (NiO) films were produced by RF magnetron sputtering in a reactive atmosphere. The films were characterized to analyse the influence of the oxygen in their electrical, optical, structural and surface/morphological properties. In this specific system was used the ratio of flows between oxygen and argon as a main parameter of deposition. The results presented here are only preliminary results in the sense of many developments should be done in future in the research of this promising material. Further studies and developments will help to understand why the produced p-type NiO TFTs did not work.

7.1 EXPERIMENTAL DETAILS

Thin-films of NiO were produced by RF sputtering in glass and silicon substrates, using a ceramic NiO target of purity 99.997%. The distance between the sample and the magnetron was fixed constant at $d_{TS} = 15$ cm, and the atmosphere in the chamber was controlled, varying the flow (F_{O_2}) of oxygen, $O_f = F_{O_2}/(F_{O_2} + F_{Ar})$. The O_f was varied between 0 to 100%. The growth rate revealed to be very low at lower powers (50 ~ 100 W) for all the oxygen content atmospheres, and consequently was fixed at 200 W. In this study was also applied bias in the substrates during the deposition to see its influence in the growth rate of the films but and also in their properties. Table 7.1 presents some of the conditions used in this study. In the case of the deposition conditions of 0%, 12% and 25.5% O_f was also varied the RF power applied in the substrate from 0, 10 and 20 W. The conditions between 0 to 25.5% were used mainly in the production of TFTs.

Table 7.1 – Main RF magnetron sputtering parameters used to deposit NiO. The depositions were done at room temperature, with a d_{TS} of 15 cm. The P_D and the Power was kept constant at 0.8 Pa and 200 W respectively.

O_f (%)	0	5.2	9.9	12.0	14.6	20.0	25.5	50.0	75.0	100.0
P_{Base} (Pa)	7.0×10^{-7} - 9.0×10^{-7}									
F_{Ar} (scm)	7.0	20.0	10.0	14.0	7.0	8.0	7.0	7.0	7.0	-
F_{O_2} (scm)	-	1.1	1.1	1.9	1.2	2.0	2.4	7.0	20.0	13.0
R (nm/min)	2.4			1.6			1.43	1.28	1.23	1.24

It is regarded in Figure 7.1 that the conditions with more oxygen content, have a lower

growth rate for the reasons explained before (Chapter V). However, in this case the influence is not so dramatic like what was observed in the case of Cu by RF sputtering. For copper, was used a metallic target and the oxygen in the chamber was critical to oxidize the Cu producing Cu_2O and CuO . Depending on the amount of oxygen in the chamber was possible to tune the production of Cu, Cu_2O and CuO . In the case of the NiO oxygen will not play a so dramatic role since NiO target already has oxygen in its composition. Nevertheless, oxygen in the chamber is still important to control the stoichiometry deviations of the film. In Figure 7.1 (A) it is presented the growth rate of the films as a function of O_f . The ratio of flows is correlated with the oxygen partial pressure for this system and is represented in Figure 7.1 (B). However, all the results in this section will be presented in terms of O_f , since was the experimental parameter controlled.

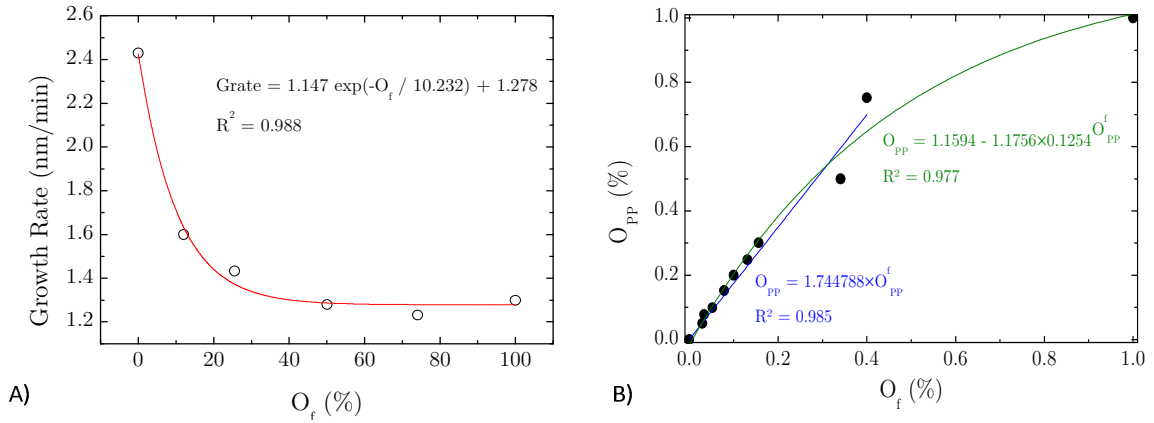


Figure 7.1 – A) Growth rate versus oxygen amount for different flow ratio; B) Relation between the O_f and the O_{PP} for the region of interest.

7.2 STRUCTURAL CHARACTERIZATION – XRD

The films produced were analysed by XRD to determine their structural properties. The measurements were performed using PANalytical's X'Pert PRO diffractometer in the Bragg-Brentano configuration from $2\theta = 20^\circ$ to $\theta = 65^\circ$, with the same procedure described in the previous chapter.

The diffractograms shows the existence of a single NiO phase, matching with the standard cubic NiO phase (ICSD, Ref. 98-006-2843, space group #225). It is visible the presence of the crystallographic planes (111), (200) and (220). Figure 7.2 shows a decrease of the samples crystallinity with the increase of oxygen content (O_f). This was also observed for

thicker films (not presented here). At higher oxygen partial pressures, the excess of oxygen may induce defects in the films, influencing the nucleation and the growth rate and degrading the crystalline quality. This was already observed by other authors for NiO samples deposited with other techniques with preferential orientation along (220) [1-3].

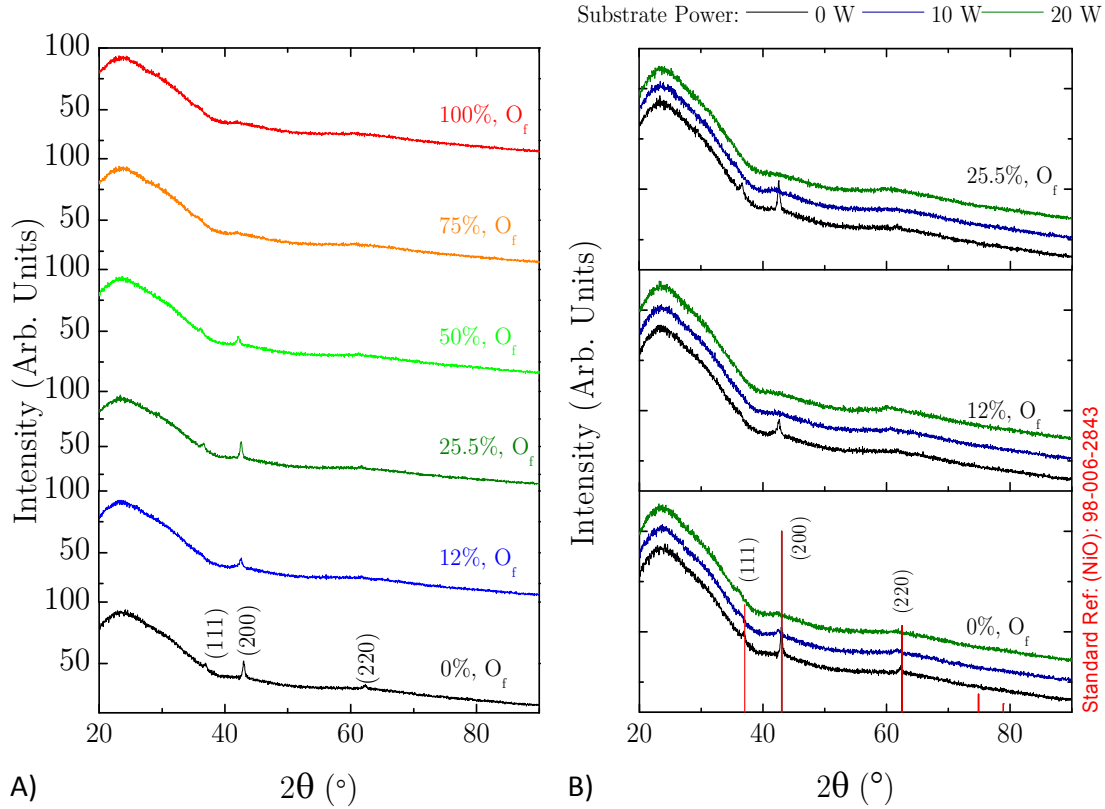


Figure 7.2 – A) XRD patterns of Nickel oxides produced by sputtering, for a film with initial thickness around 50 nm; B) Study of the application of substrate RF power in the structural properties of the films.

Reddy *et al.* [1] verified a change in the preferential orientation with the increase of oxygen content from [200] to [220] for NiO samples deposited with DC sputtering in corning substrates. They explained that the increase in the oxygen partial pressure affects: the mean free path of the atoms, their energy, momentum and mobility. These effects will change the conformity of the atoms in the substrate and can lead to a change in the preferential orientation. However in this work, no change of orientation was observed here with the increase of oxygen content, being the most intense peak observed always along [200]. Nandy *et al.* [4] also verified a preferential orientation along [200] using DC sputtering of NiO in glass substrates at 350 °C. This author also observed a continuously increase of intensity (meaning an increase of the crystallinity) associated to the peak correspondent to the plane (200) with

the increase of oxygen content in the chamber. A possible explanation is the influence of the substrate temperature in the nucleation process, increasing the atomic order and consequently the crystallinity. Further experiments should be done to evaluate this hypothesis.

The RF power applied in the substrate plays also an important role in the structural properties of the films (as shown the Figure 7.2 (B)). The introduction of a substrate RF power may give an additional energy to the ions that reaches the substrate more violently, reducing the crystallinity quality of the samples. This effect can be explained by an artificial conformity of the ions that reaches the substrate rotating with higher kinetic energy, leading to a creation of defects. The application of a substrate bias provides additional energy to the growth process but also enhances the re-sputtering from the growing film. These effects may lead to a dense and nearly void free film, rounding of the evolving grain structure, and a reduction of the deposition rate [5-7]. In Table 7.2 it is presented a resume of the structural characteristics of these films.

Table 7.2 – XRD data of copper oxide films as a function of annealing temperature for the most intense peaks (symbol representations: ($\diamond$) metallic Ni, ($\blacklozenge$) NiO films.

O_f (%)	2θ (°)	(h k l)	d (Å)	FWHM (°)	I_{Max}/I
0.0	36.85	(111)	2.44	0.840	19.3
	42.97	(200)	2.10	0.475	100.0
	62.28	(220)	1.49	1.053	17.7
12.0	42.54	(111)	2.12	1.193	100.0
25.5	36.60	(111)	2.45	0.473	86.0
	42.55	(200)	2.12	0.374	100.0
50.0	36.18	(111)	2.48	0.428	42.7
	42.10	(200)	2.14	0.652	100.0

7.3 ELECTRICAL CHARACTERIZATION

7.3.1 HALL EFFECT

Experiments were performed to determine the type of conductivity of the samples using the Hall coefficient. It is known, and was also shown in this dissertation, that the electrical properties are strongly dependent on the composition and crystalline structure of the prepared films. Figure 7.3 shows the behaviour of the resistivity, mobility and carrier concentration as a

function of O_f for the NiO films. The films produced with no oxygen have the highest resistivity around $2.67 \times 10^3 \Omega \text{ cm}$. With the increase of the oxygen flow rate the value of the resistivity decreases reaching a minimum of $2.83 \Omega \text{ cm}$. This is consistent what was observed by other authors [1, 4, 8]. The carriers concentration increases with the increase on the O_f from 10^{15} to 10^{19} . The mobility in the other hand shows the highest values for the lower oxygen content, ranging 2 to $6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This is in fact a very good result for a p-type semiconductor oxide, making these results promising for future application in TFTs. In Table 7.3 is a summary of the best values results obtained for a set of films deposited with thickness around 50 nm.

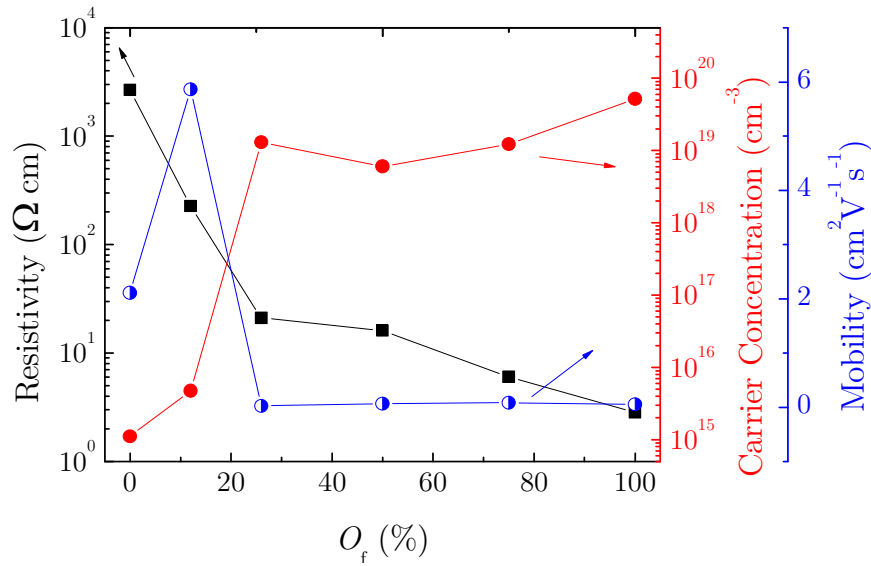


Figure 7.3 – Electrical properties of NiO films as a function of O_f .

Table 7.3 - Electrical data extracted from the as-deposited and annealed films as a function of O_f (the grey zone refers to the p-type region, obtained by Hall effect measurements*).

O_f (%)	ρ ($\Omega \text{ cm}$)	μ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	n_0 (cm^{-3})
0	2.67×10^3	2.11	1.11×10^{15}
12	2.26×10^2	5.87	4.73×10^{15}
26	2.11×10^1	0.023	1.30×10^{19}
50	1.61×10^1	0.06	6.03×10^{18}
75	6.02	0.08	1.22×10^{19}
100	2.83	0.05	5.20×10^{19}

7.3.1.1 EFFECT OF THE SUBSTRATE BIAS

* It is not possible to guarantee that all the samples with higher O_f are p-type, due to the observed fluctuations of the Hall coefficient signal.

NiO films were also deposited with different substrate bias to evaluate the impact of this parameter in the properties of the films (Figure 7.4). Was verified that the application of a low RF power between 10 to 20 W has a huge impact on the electrical properties of the films (but also in their optical properties). In fact, for all the deposition conditions when a substrate RF power of 10 W is applied, there is a decrease in the resistivity of the films, in some cases around three orders of magnitude. The same happens for a 20 W bias (with exception for the condition of 0 % O_f). However, in comparison with the samples produced with 10 W the resistivity increases slightly. This change on the electrical properties of the films can be a consequence of the collision of high energy of ions with the films during their preparation. This bombardment can affect the growth rate of films, enhancing the re-sputtering, creating interstitial defects in the film [9]. This will lead to a modification of the films properties, removing the void present (described before) and consequently decreasing the electrical resistivity [6, 9]. With a higher RF power applied in the substrate it is observed a slightly increase of resistivity more evident in the film deposited with no oxygen. This can also be explained by the creation of defects, consequence of the entrapment of argon ions in the films [9].

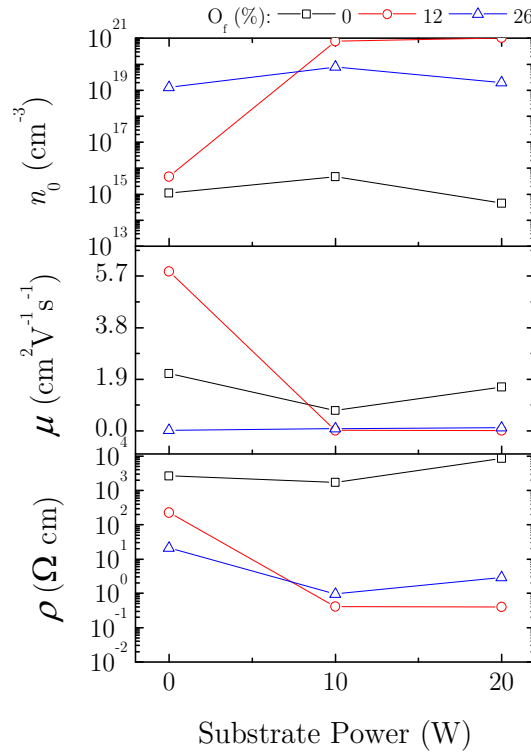


Figure 7.4 – Effect of the substrate RF power in the electrical properties of the films (resistivity, mobility and carrier concentration).

In Table 7.4 it is presented the resume of the electrical properties obtained for the films deposited with 0, 10 and 20W substrate RF power.

Table 7.4 – Electrical data extracted from the as-deposited films as a function of O_f and the substrate RF Power.

O_f (%)	Substrate Power (W)	ρ (Ω cm-1)	μ (cm ² /V-s)	n_0 (cm-3)
0	0	2.67×10^3	2.11	1.11×10^{15}
	10	1.74×10^3	0.75	4.77×10^{15}
	20	8.69×10^3	0.98	1.31×10^{15}
12	0	2.26×10^2	5.87	4.73×10^{15}
	10	4.10×10^{-1}	0.02	7.73×10^{20}
	20	3.99×10^{-1}	0.02	1.04×10^{21}
25.5	0	1.09×10^3	0.44	1.3×10^{16}
	10	9.63×10^{-1}	0.08	7.83×10^{19}
	20	2.88	0.11	1.95×10^{19}

7.4 OPTICAL CHARACTERIZATION

7.4.1 UV-VIS-NIR SPECTROSCOPY

NiO films were characterized in the range of 300 – 2500 nm and the bandgap estimated from the absorption coefficient (Figure 7.5 (A) and (B)). The NiO films showed high transmittance with average values ($T^{400-750}$, calculated from 400 nm to 750 nm) of $\sim 76\%$ for a film with 50 nm thickness deposited with 0% O_f . The optical transmittance of the films is dependent of the oxygen content, decreasing with the increase of the O_f from 76% to $\sim 50\%$ ($O_f = 100\%$) (Table 7.5).

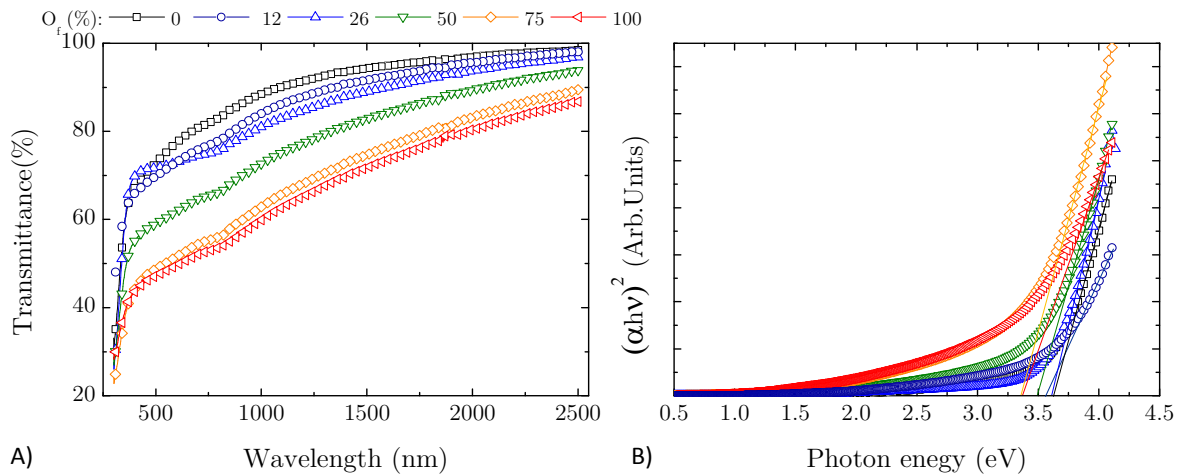


Figure 7.5 – Optical transmittance spectra of the NiO films produced with different O_f (A).

The optical band gap was estimated using the direct allowed transition (2E_G), between 3.63 to 3.23 eV. In fact other authors also verified that after certain amount of oxygen content in the chamber the deposited NiO films showed a decrease in the values of the band gap [1, 4, 10]. An possible explanation for this decrease can be related to the increase of the defect states density in the bandgap tails due to the excess of oxygen [4]. This is supported by an increase on the conductivity for the samples deposited with higher oxygen content, following a similar behaviour observed for the E_G , presented in Figure 7.6.

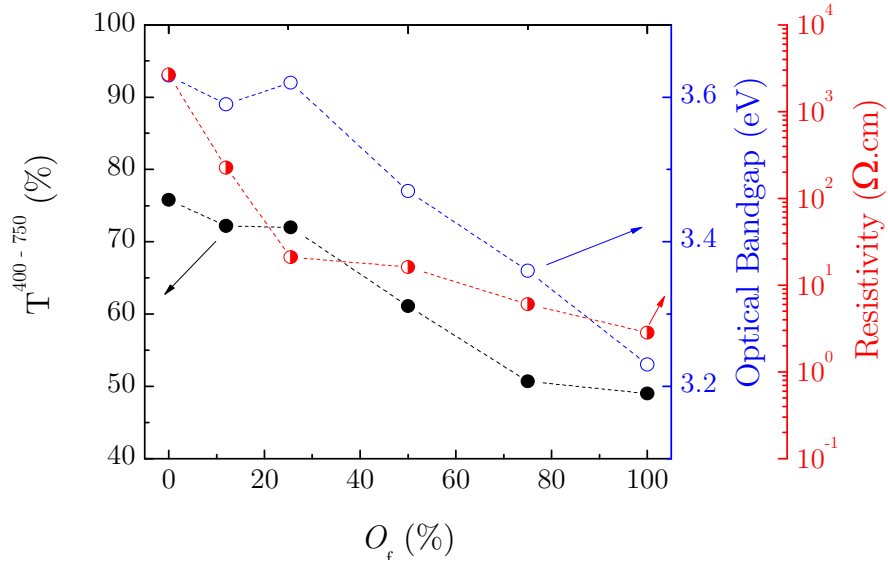


Figure 7.6 – Influence of the oxygen content on the optical and electrical properties of the films.

Table 7.5 – Resume of the optical properties as a function of O_f for a $P_D = 8.0 \times 10^{-1}$ Pa and power of 200 W (no substrate RF power applied), samples with ~ 50 nm.

O_f (%)	0	12	26	50	75	100
$T^{400-750}$ (%)	75.8	72.2	72.0	71.1	50.7	49.0
2E_G (eV)	3.63	3.59	3.62	3.47	3.36	3.23

7.4.1.1 EFFECT OF THE SUBTRACT BIAS

In the present work, was noticed that the RF power applied to subtract affects the physical properties of the films. Examples of these changes in the optical properties are shown in Figure 7.7 for three conditions deposited with and without substrate power (10 W and with 20 W). In Table 7.6 is resumed the optical properties of these films. It is conclusive that transmittance decreases for all the condition with the increase of the substrate power. This effect was observed by other authors, and a partial explanation was already given before. The power applied in the substrate gives additional energy to the ions that reaches the substrate.

This appears to improve the electrical properties, reducing the resistivity of the films. In the same way the optical gap decreases (as observed for the films with high amount of oxygen). It is also possible that bias is contributing to the introduction of oxygen impurities in the film, introducing states in the bandgap [4], or a consequence of the entrapment of argon ions in the films as explained before [9].

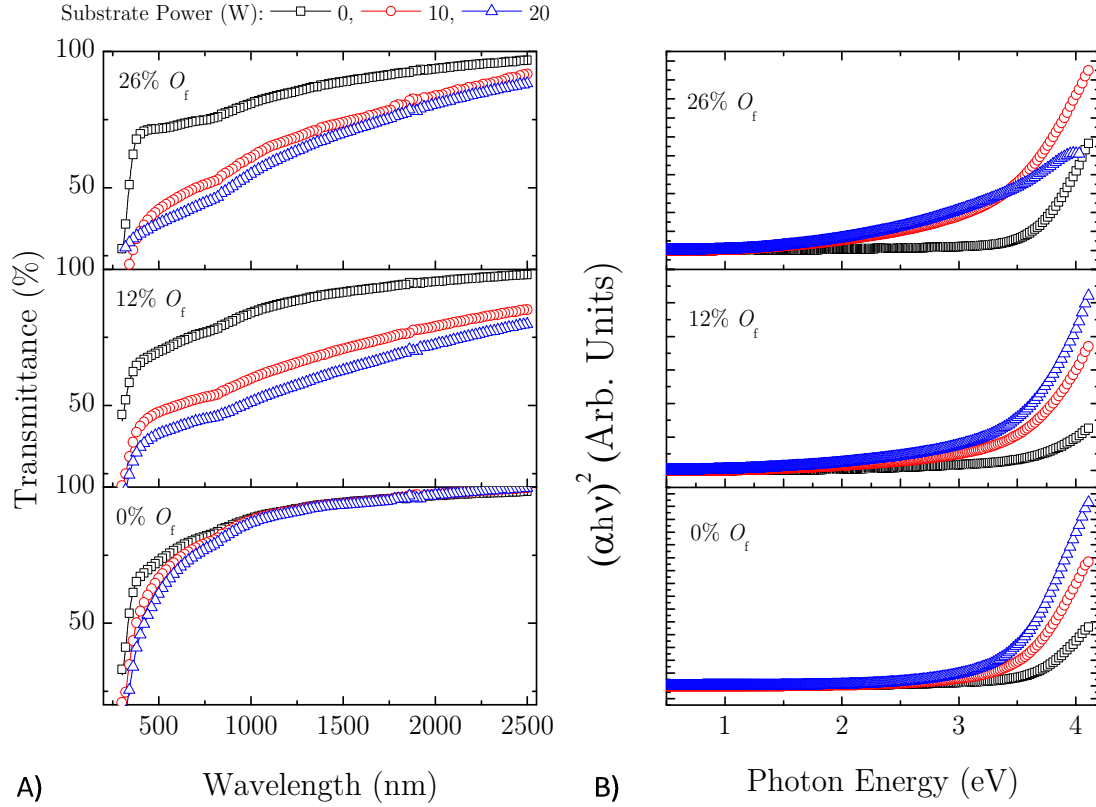


Figure 7.7 – Substrate RF power effect on the optical properties for the conditions produced with low amount of oxygen (0 – 26 % O_f).

Table 7.6 – Average transmittance and optical band gap for the films with substrate RF power of 0, 12 and 26 W.

O_f (%)	0			12			26		
Substrate Power (W)	0	10	20	0	10	20	0	10	20
2E_G (eV)	3.63	3.52	3.46	3.59	3.48	3.44	3.62	3.32	2.75
$T^{400-750}$ (%)	76	70	66	72	49	41	72	45	39

7.5 SURFACE CHARACTERIZATION

The surface of the films were analysed by Kelvin Probe (KP). In further developments of this work, AFM and SEM should be done to clarify the morphology of the films. However, the

main interest here was the study of the electrical and optical properties of NiO and in the possibility to apply it as an active layer of a TFT.

7.5.1 KELVIN PROBE

The RF sputtered NiO samples were analysed using the KP and the results are presented in Table 7.7. From the table, oxygen appears to have an impact in the work function (Φ). In general, is visible an increase of the work function (with exception of the condition of 12% O_f) with the increase of the oxygen content. As explained before, surface reactions can change the value of the work function and excess of oxygen can lead to the formation of electric dipoles in the surface, influencing the surface voltage measured. The excess of oxygen as a responsible for changes in the work function was also pointed by other authors for different metal oxides [11-13]. The use of bias (substrate power) appears to have a major impact in Φ , with an significant increase in all the tested conditions. This behaviour was also observed in the case of Tungsten [12], where the inclusion of the oxygen is the main hypothesis proposed to the increase of the work function. Similar conclusions were achieved in the case of Mo and ZrO₂ films [13], showing that the additional oxygen atoms in the interface can lead to a partial cancellation of the interface dipole due to charge transfer from both the oxide and the metal.

Table 7.7 – Surface properties of nickel and nickel oxides (Φ and δ_Φ are the work function and the standard error estimated in this work, $\Phi^{Lit.}$ the work function estimated by other authors, and Φ^{Oxid} is the work function estimated for the oxidized samples).

Substrate Power	0 W		10 W		20 W		
O_f (%)	Φ (eV)	δ_Φ (meV)	Φ (eV)	δ_Φ (meV)	Φ (eV)	δ_Φ (meV)	Φ^{Oxid} (eV) $\Phi^{Lit.}$ (eV) [14, 15]
0	4.91	1.858	5.17	1.486	5.22	1.932	5.19-5.23 5.30
12	5.22	1.857	5.29	1.467	5.36	2.487	
26	5.06	1.489	5.31	1.782	5.82	1.413	
50	5.02	1.417	--	--	--	--	
75	5.15	1.445	--	--	--	--	
100	5.12	1.511	--	--	--	--	

7.6 CONCLUSIONS

Nickel oxide was produced by RF sputtering, in different oxygen conditions, from a

ceramic target of NiO. It was conclusive the influence of oxygen in the optical properties of the films, showing that (in concordance with the results obtained for copper) the crystallinity decreases with the increase of the oxygen content. The power applied in the substrate has an impact on the film properties was also analysed. From the results, obtained, the substrate power appears to conduct to an amorphization of the films. The electrical properties was estimated showing the higher values of mobility associated to the low amounts of oxygen, with a maximum of $5.87 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the condition deposited with 12% O_i . The resistivity decreases with the increase of the oxygen content and also with the application of a substrate power. High conductive films were always observed for the condition deposited with 10 W applied in the substrate. This can be related to the enhancement of the amorphous character of the films. The application of a substrate power (similar way to the application of a Bias) can also conduct to a re-sputtering of the film, creating defects, affecting their electrical and optical properties.

The films presented very high optical transmittance, with values up to 76% (in the case of condition with low amount of oxygen) associated to an optical gap around 3.63 eV. With the increase of oxygen, it is visible a decrease in both transmittance and optical bandgap. A possible explanation is the increase of the state density tails due to the excess of oxygen and this is also associated to a decrease in the resistivity of the films and an increase in the carrier concentration. The substrate power appears to contribute also to this effect, maybe due to the introduction of the oxygen impurities in the film. It is visible that the transmittance and the optical gap of the films decrease substantially with the increase of the power. In the case of the bandgap this decrease can reach ~24% the value of the un-biased film (in the case of the condition associated to 26% O_i) from 3.62 eV to 2.75 eV. In terms of transmittance the decrease is around 46% (for the same condition). The work function was estimated for the un-biased samples (no power was applied in the substrate) in the range of 4.91 – 5.22 eV. Oxygen and substrate power appear to have an influence in the estimated values. The work function showed a strong increase with the increase of the substrate power, maybe due to the excess oxygen in the bulk and at the surface.

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Chapter VIII

Production of devices and characterization

CONTENTS

In this section, will be presented some results illustrating the possibility of the use of copper oxides for the production of p-type semiconductor oxides TFTs. The results showed that CO oxides are promising candidates for the “third wave” in transparent electronic industry, allowing processes at relatively low temperatures, using two deposition techniques wide available in industry.

- 8 Production of devices and characterization
 - 8.1 Thin-film transistors based on Cu_xO
 - 8.1.1 Effect of post-annealing temperature
 - 8.1.2 Effect of oxygen partial pressure (O_{PP})
 - 8.1.3 Thermal oxidation
 - 8.2 Conclusions
 - 8.3 References

8 PRODUCTION OF DEVICES AND CHARACTERIZATION

In this chapter will be presented a resume of the results obtained for copper oxide channel TFTs produced by RF sputtering (using two different systems) and by thermal oxidation. The reader should regard that, these results shall be seen only in a preliminary level since this is a very new area and further developments should be done in future. Nevertheless, the achievements reported here are already published and presented in high level international conferences, being among the first published results concerning the application of p-type semiconductor oxides in TFTs [1-4].

The challenging in the production of working p-type semiconductor oxides TFTs, is shown in the limited number of publications in the topic, consequence of (usually) low mobility p-type semiconductor oxides available. The “lack” of high mobility p-type oxides, is a direct consequence of the holes large effective mass (in comparison with electrons) in most materials. The usually large work function needed for p-type semiconductor oxides, also limits the choice of materials for contacts, since they required a large work function. These among other factors makes this one of the most exciting and challenging area today in the semiconductors research. This brief introduction only serves to emphasise the achievements reported here in the case of CO TFTs. P-type TFTs are not in the same level of the n-type counterparts, but they are a fundamental key in the development of transparent circuits and complex devices, contributing to the revolution of the transparent electronics (as explained in the first chapter of this thesis) with impact in areas so important today like energy generation. In case of NiO until now no clear field effect was observed in a device and no p-type semiconductor oxide TFT was published yet in literature using this material. The research in NiO is still on going, but the results obtained as a single semiconductor layer, are promising and further developments using this material in TFTs should appear in literature soon.

Bottom-gate TFTs were produced using commercial ITO/ATO glass and Si/SiO₂ substrates, using Cu₂O, CuO* thin films as semiconductor channel.

* Different conditions of NiO were applied as a channel layer of the TFT but without success. These results are in a very preliminary stage and will not be presented here.

In case of TFTs produced with ITO/ATO (with high transparency), an engineered insulator consisting of a superlattice of ATO (Al_2O_3 and TiO_2) [5] with a thickness of 220 nm deposited on a glass coated with a 200 nm thick indium tin oxide (ITO) film, was used. In case of Si/ SiO_2 substrates, 100 nm thickness SiO_2 thermally grown dielectric was used.

For the source-drain electrodes, were used two main contacts: Ni/Au and indium zinc oxide (IZO). The semiconductor and the source-drain electrodes were patterned by lift-off. The final devices were always post-annealed using a Barnstead Thermolyne F21130 tubular furnace. The electrical characterization was performed with a relative humidity of 35 – 40%, using an Agilent 4155C semiconductor parameter analyser and a Cascade Microtech M150 microprobe station. All the electric measurements were done inside a dark box at ambient atmosphere.

8.1 THIN-FILM TRANSISTORS BASED ON Cu_xO

In this subsection it is shown some results obtained for Cu_xO films deposited by RF Magnetron Sputtering. Bottom-gate TFTs were produced using 40 nm thick Cu_2O thin films as semiconductors, deposited in a glass with ITO and ATO.

For the source-drain electrodes two sets of TFTs were produced: TFT-M with a double layer of Ni/Au (50/800 nm thick) films, evaporated by e-beam using a home-made evaporation system and TFT-O with an IZO film of 250 nm produced by RF magnetron sputtering at room temperature (no intentional heating of the substrate). In Figure 8.1 it is presented a picture of two different substrates containing TFTs with different dimensions.

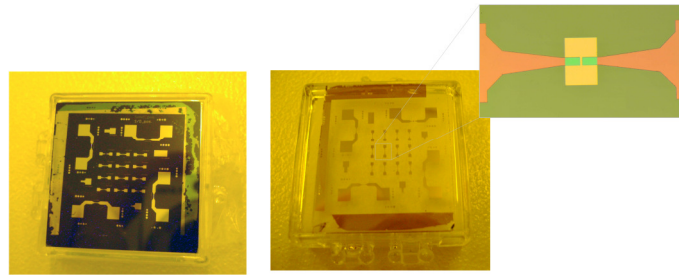


Figure 8.1 – Image of a Si/ SiO_2 (Left) and Glass/ITO/ATO (Right) wafer with TFTs with different W, L .

8.1.1 EFFECT OF POST-ANNEALING TEMPERATURE

In this section, the TFTs characteristic curves presented were obtained from the

conditions optimized for the new RF sputtering described in Chapter V, Part II. To avoid confusions relatively to the oxygen content, the samples produced in this system will be described in this chapter in terms of ratio of flows (O_f).

In the metal oxides presented here, the annealing at low temperatures ($\leq 200^\circ\text{C}$) is not effective in phase changes on the films (when they are already oxidized). However, temperature affects the crystallinity and can be associated to the change of the electrical and optical properties of the films, influencing the properties of the TFTs.

In all the experiments done, the as-deposited TFTs only exhibit insignificant field effect (regard Figure 8.2 (A)), being the post-annealing step always fundamental in the production protocol. This should be related to the reasons already explained before, with an increase of the semiconductor crystallization, a growth in the grains size and consequent enhancement of the mobility (more evident in the case of CO films).

Another aspect is related to the reduction of the contact resistance in the interface in particular between the SD contact and the semiconductor. In Figure 8.2 (B)) is presented the transfer characteristics of two TFTs deposited in the same conditions with 25 % O_f (CuO), produced with Ni/Au and IZO source and drain (SD) contacts. Both TFTs were measured with the same experimental protocol trying to overcome the possible effect of trap charging (and other similar effects) that could influence the transfer characteristics. It is visible that the TFT with IZO SD contacts have usually the best performances recorded. The work function of IZO is assumed to be between 4.7 to 5.1 eV [6] usual inferior to the nickel work function around 5.04 – 5.35 eV [7, 8]. The difference in the work functions appears to not explain the differences observed in the TFTs performances, since in a simplistic analysis was expected that Ni/Au contacts used with Cu_2O will be traduced in lower contact resistance, due to the large work function of Ni in comparison with IZO. However, the band alignment in the interface between different materials with the possible diffusion of oxygen into one of the layers or maybe interface traps can give a possible explanation to the differences in the performance observed in the devices. In the work published by Deuermeier *et al* [9] it is explained the importance of the interface band alignment and the valence band offset for the ITO - Cu_2O and how it can compromises the rectifying current-voltage characteristic of a p- Cu_2O /n-ITO junction. Further work in an optimized semiconductor Cu_2O (NiO) layer should be done to

study interfaces that are crucial in the understanding of the characteristic curves of TFTs.

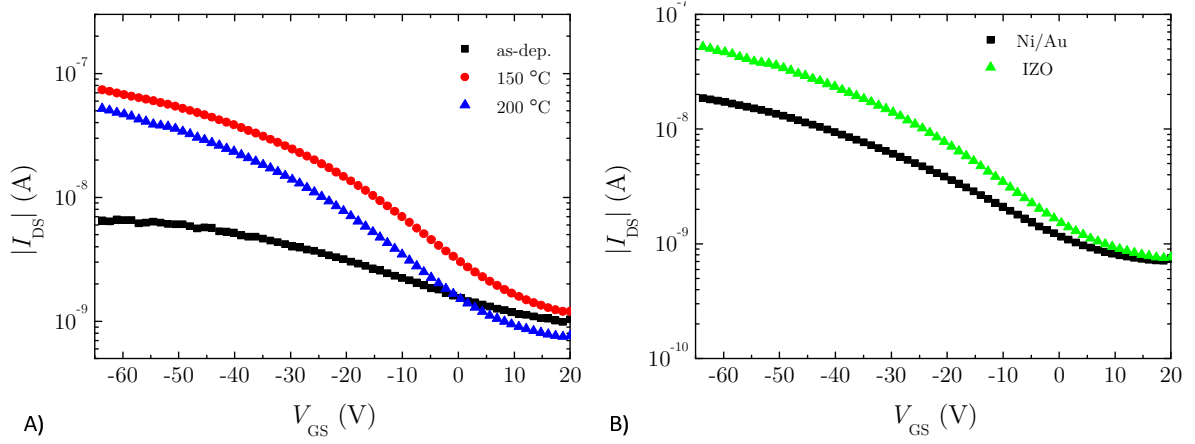


Figure 8.2 – Transfer characteristic of TFTs produced with 25 % O_f . A) Influence of the annealing temperature. B) Influence of the source and drain contacts used (samples annealed at 200 °C).

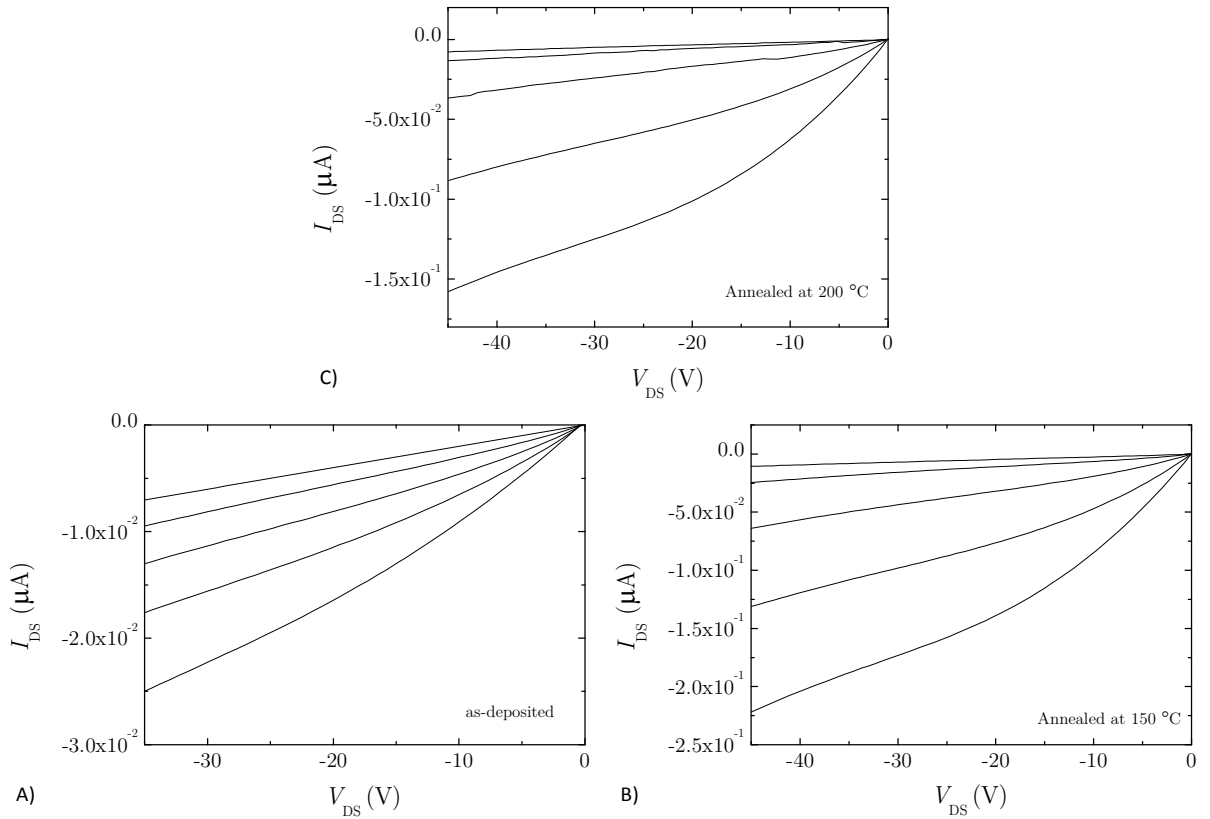


Figure 8.3 – Output characteristics, I_{DS} vs. V_{DS} ($W, L = 50, 15$, IZO contacts): as-deposited (A), annealed at 150 °C (B) and annealed at 200 °C (1 hour) (C).

8.1.2 EFFECT OF OXYGEN PARTIAL PRESSURE (O_{PP})

The TFTs were produced in all the conditions described before. The mobility is one of the main parameter to tune and presumably the responsible to the negligible field effect presented in the samples with higher O_{PP} (Figure 8.4). Even after post-annealing at 200 °C (10

hours) the TFTs have shown a low performance. The optimum growth conditions for the optimization of the mobility in case of p-type semiconductors are in general very narrow [10]. Even when a p-type layer is optimized and shows high mobility, its performance is often compromised when applied into device. Usually the mobility estimated for p-type TFTs is three orders of magnitude smaller than Hall effect mobility measured for the semiconductor layer. One of the reasons pointed for this difference is the existence of a large amount of hole trap states in the channel and/or near the channel-gate insulator interface, pinning the Fermi level of the channel. Once again it is of fundamental importance the study of the interfaces. The thickness of the films is also an important factor and should be optimized in function of the semiconductor characteristics.

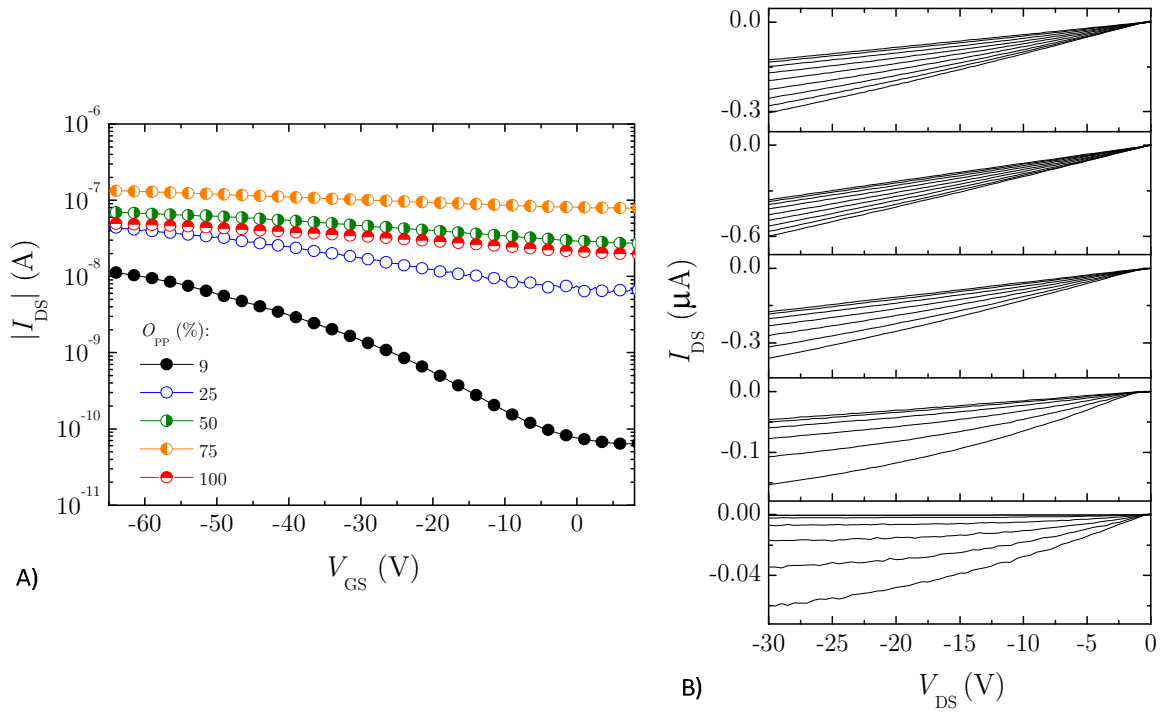


Figure 8.4 – Transfer characteristics, $|I_{DS}|$ vs. V_{GS} at $V_D = -5$ V for the Cu₂O TFT annealed in air at 200 °C (10 hours) for films produced with O_{PP} : 9, 25, 50, 75, 100 % (A). Output characteristics, I_{DS} vs. V_{DS} for the same set of films ($W, L = 50, 50$) (B).

In Figure 8.5 it is presented a TFT produced with 9% O_{PP} (the best mobility condition achieved in Chapter V) for a $W, L = 50, 15$ (μm). The devices were produced with the condition that gives the Cu₂O phase and annealed in air at 200 °C in 10 hours. The Figure 8.5 (A)) shows the transfer characteristics with for a $V_{DS} = -5$ V. V_{GS} is swept between -60 to +10 V. The *On/Off* ratio is 2×10^2 , the field-effect mobility (μ_{FE} , calculated by the transconductance

in linear regime) is around to $1.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, while the V_T is -12.0 V. The Figure 8.5 (B)) shows the output characteristics of a Cu_2O p-type TFT. The drain-to-source voltage (V_{DS}) is swept from +10 to -60 V and the gate-to-source voltage (V_{GS}) is stepped between +5 and -55 V. The device shows clear linear and saturation regions of the output characteristics and does not present significant current crowding for low V_{DS} , indicating low series resistance in source-drain contacts [4].

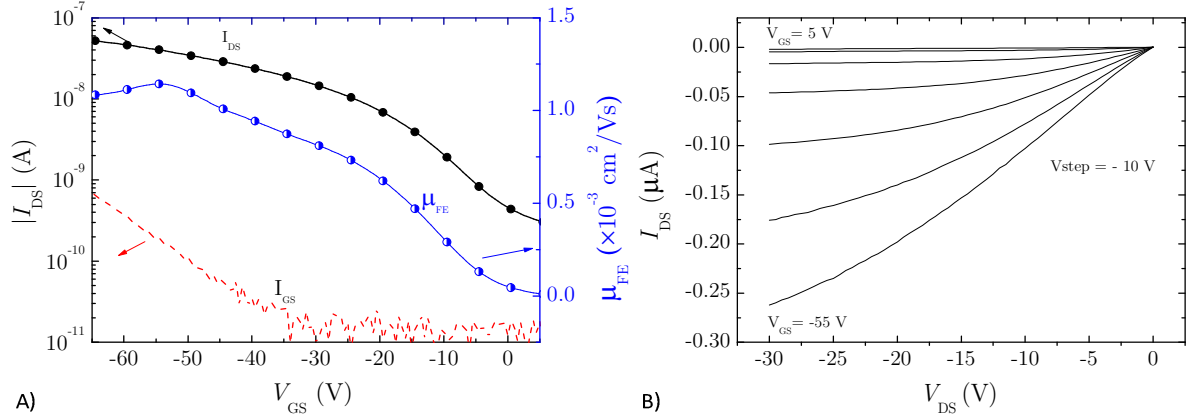


Figure 8.5 – Transfer characteristics ($|I_{\text{DS}}-V_{\text{GS}}|$) at $V_{\text{D}} = -5 \text{ V}$ (left axis) and μ_{FE} as a function of V_{GS} (right axis), for a typical Cu_2O TFT produced at room temperature and annealed in air at 200°C (A). Output characteristics ($I_{\text{DS}}-V_{\text{DS}}$) ($W, L = 25, 25$) (B)[4].

These results were reproduced using $\sim 40 \text{ nm}$ thickness TFT as shown in Figure 8.6. In Figure 8.6 (A) V_{GS} is swept between -65 to +10 V. The *On/Off* ratio was found to be around $\approx 10^3$ and the field effect mobility (μ_{FE}) around $7 \times 10^{-3} \text{ cm}^2/\text{V.s}$. In this TFT was decided to estimate the turn-on voltage (V_{On}) that was found to be $\sim 7 \text{ V}$. A more practical device performance metric, that directly characterizes the gate voltage required to fully “turn off” the transistor in a switching application [11]. In Figure 8.6 (B) it is presented the drain-to-source voltage (V_{DS}) that is swept from +5 to -75 V and the gate-to-source voltage (V_{GS}) is stepped between +5 and -30 V. No significant current crowding for low V_{DS} was visible [12].

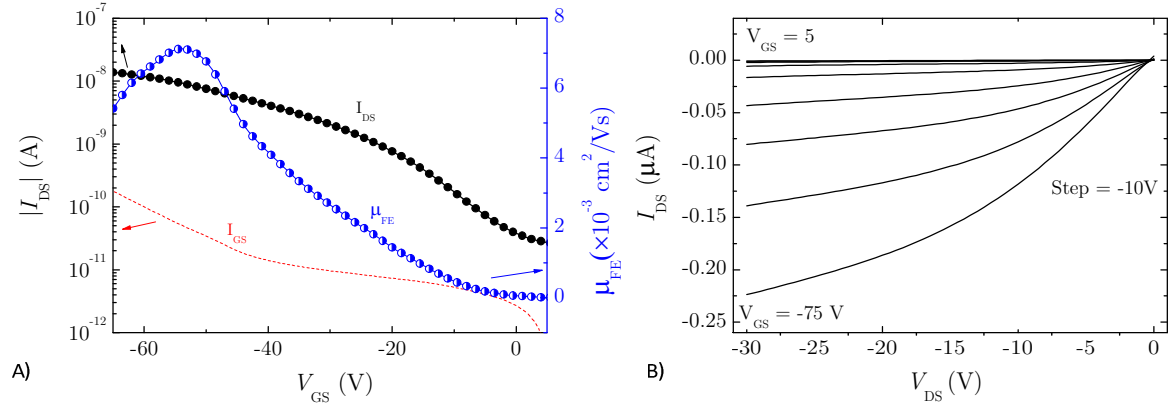


Figure 8.6 –Transfer characteristics, $|I_{DS}|$ vs. V_{GS} at $V_D = -5$ V (left axis) and μ_{FE} vs. V_{GS} (right axis), for the Cu_2O TFT annealed in air at 200 °C (A). Output characteristics, I_{DS} vs. V_{DS} ($W, L = 50, 15$) (B) [12].

8.1.3 THERMAL OXIDATION

In this section will be presented two TFTs with two different channel formed by Cu_2O and CuO , with channel thicknesses of 50 nm and 40 nm, respectively. They were produced oxidizing a metallic film of copper 200 and 250 °C (Figure 8.7 (B)) showing high transmittances compatible with the concept of transparent electronics (Figure 8.7 (A)). For an as-deposited Cu film of ~20 nm, 250 °C is enough to achieve a fully conversion to CuO (as observed in Chapter IV). The films produced in these conditions (200 and 250 °C) have the two highest Hall motilities (Chapter IV) and are the two lowest temperatures to produce the both Cu_2O and CuO phases (as presented before).

The TFTs were also post-annealed at 200 °C after the deposition of the Ni/Au multilayer contact (~50/580 nm thickness). The same procedure was previously adopted for TFTs of CO films produced by RF sputtering [4]. The post-annealing improves the observed field-effect in these TFTs, perhaps due to the diffusion between Ni/Au contact and the Cu_xO films, reducing the contact barrier (resistance). The impact of the annealing temperature in the films (as explained before), inducing the crystallization, can also be a reason. It was not expected significant structural changes in the films, since both were already oxidized in temperature (≥ 200 °C) and also due to the low exposition time ~1 hour.

The TFT produced using a Cu_2O channel (Figure 8.8), showed an *On/Off* ratio around $\approx 6 \times 10^1$, a $V_{ON} \approx 7$ V and a field effect mobility $\mu_{FE} \approx 1.56 \times 10^{-3} \text{ cm}^2/\text{V.s}$. In case of the TFT produced with a CuO channel (Figure 8.9), the device shows an *On/Off* ratio $\approx 10^2$, a $V_{ON} \approx 6$

V and a $\mu_{FE} \approx 1.16 \times 10^{-3} \text{ cm}^2/\text{Vs}$.

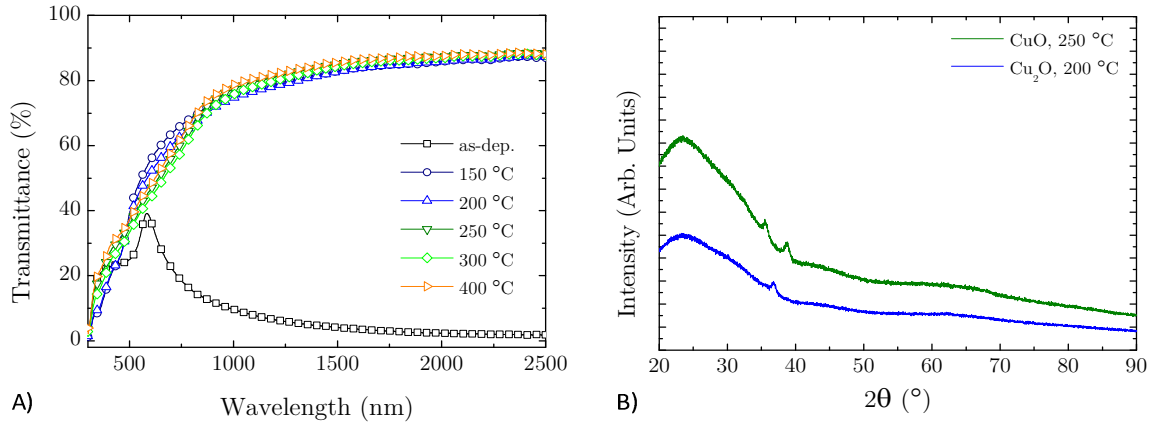


Figure 8.7 – A) Transmittance of thin films of Cu_xO (as-dep. thickness ~ 20 nm, oxidized $\sim 40 - 50$ nm). B) XRD patterns of the Cu₂O and CuO films oxidized at 200 and 250°C, respectively. (Symbol representations: $\blacklozenge$ - Cu₂O phase; $\diamond$ - CuO phase).

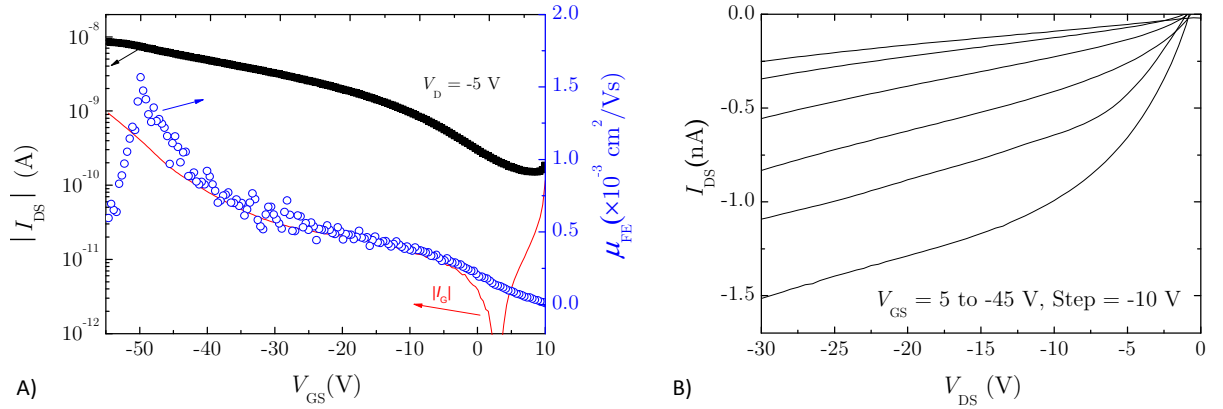


Figure 8.8 – Transfer characteristics, $|I_{DS}|$ vs. V_{GS} (left axis) and μ_{FE} vs. V_{GS} (right axis), for the Cu₂O TFT oxidized at 200 °C, with a $W, L = 15, 20$ (Å). Output characteristics, I_{DS} vs. V_{DS} (B).

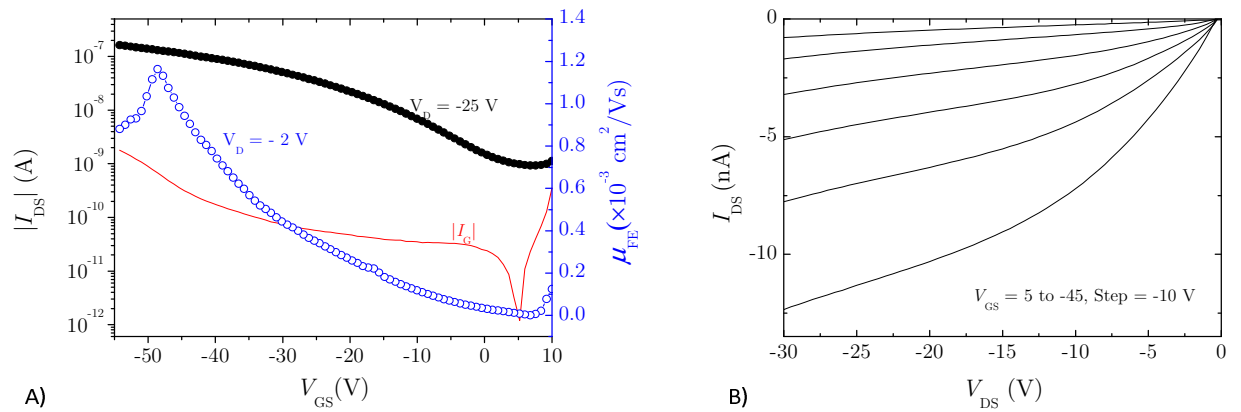


Figure 8.9 – Transfer characteristics, $|I_{DS}|$ vs. V_{GS} (left axis) and μ_{FE} vs. V_{GS} (right axis), for the CuO TFT oxidized at 250 °C, with a $W, L = 50, 15$ (Å). Output characteristics, I_{DS} vs. V_{DS} (B)[13].

These TFTs do not have performances as good as the already reported for CO, mainly produced using PLD and RF sputtering [14, 15]. However the potential of thermal oxidation

technique to produce heterojunctions was shown by Han *et al.* [16] where Cu_2O channel was produced by thermal oxidation in a copper wire transistor. Is possible to imagine the use of these techniques in nano-wire based transistors, oxidized nano-particles (of Cu_2O and CuO) to apply in inks for inkjet printing, etc. Nevertheless, it should be remarked that there is no published work until now on CO TFTs produced by thermal oxidation. In the case of CuO , only few published works exist where this oxide is used alone or mixed with Cu_2O as p-type channel. [15, 17].

8.2 CONCLUSIONS

The curves presented here demonstrated the possibility to produce p-type transparent oxide semiconductors based on Cu_2O and CuO by reactive magnetron sputtering but also by a simple thermal oxidation technique. The low temperature process used and the compatibility of the production of $\text{CuO}/\text{Cu}_2\text{O}$ semiconductors in large areas, enable easy industrial implementation, combined with low process costs.

Was demonstrated the use of thermal oxidation technique, a simple and low cost method, compatible with industrial applications, to obtain both copper oxide phases: Cu_2O and CuO . Controlling the oxidation kinetics it is possible to produce, using the same metal sheet, heterojunctions for device and sensor applications, among others.

These advantages and the reasonable electrical performance of the devices are promising; however the research is still in an early stage and should be continued. Further developments should be done for optimization of p-type oxide-based devices and for the integration of optimized p-type semiconductors in CMOS structures, which can be used in flexible, low cost and transparent electronic circuits.

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Chapter IX

Conclusions and future perspectives

CONTENTS

In this section will be resumed the principal conclusions and also present some ideas to improve the semiconductor, leading to high performance devices.

9 Conclusions and future perspectives

9.1 Final conclusions

9.2 Future perspectives

9.3 References

9 CONCLUSIONS AND FUTURE PERSPECTIVES

9.1 FINAL CONCLUSIONS

9.1.1 Cu_xO

The main conclusion that should be emphasized in this work is the possibility to produce p-type semiconductor oxides TFTs based on both copper oxide phases: Cu_2O and CuO [1-5]. This was systematically achieved using both thermal oxidation and RF sputtering.

Using thermal oxidation was possible to produce p-type thin-films of Cu_2O and CuO controlling the oxidation temperature of metallic copper films. Using XRD and RBS techniques, copper oxides with poor-oxygen content (Cu_2O) in lower temperature region ($\leq 250^\circ\text{C}$) and rich-oxygen content (CuO) in high temperature region ($> 250^\circ\text{C}$), were identified and studied.

The films oxidized at 200, 250 and 300 $^\circ\text{C}$ showed the highest mobility values of 2.2, 1.9 and 1.6 $\text{cm}^2 \text{V}^{-1}\text{s}^{-1}$, respectively. For higher temperatures the mobility drops to low and negligible values around 0.1 $\text{cm}^2 \text{V}^{-1}\text{s}^{-1}$. The Cu_2O phase have always the higher transparency, around 57% (for a 100 nm thick film) with an optical band gap about 2.5 eV (direct allowed) and a 2.3 eV (direct forbidden), and a work function around 4.8 eV. The CuO with a transparency of ~40 % (for a film with 100 nm thickness), presents a band gap around 2.1 eV (direct allowed), 1.1 eV (indirect allowed), and a work function around 5.05 eV. From SE was visible that for the polycrystalline semiconductor, the model gave a value of 2.37 eV and around 1.37 eV, for Cu_2O and CuO , respectively. The morphology of the films was also analysed, to try to understand its impact in the other electrical and optical properties. The films with Cu_2O phase have the roughest surface with the maximum value of RMS around 14.4 nm. Higher grain size, leads to less grain boundaries, and to a higher mobility, since the carrier has less barriers to cross through. This can be one of the explanations for the higher

mobility ($2.2 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$) of the films possessing Cu_2O phase. With the increase of the oxidation temperature the RMS decreases reaching an average value about 8.3 nm for the CuO phase. The same trend was observed with the mobility. The thermal oxidation of copper was successful applied in the production of p-type TFTs of Cu_2O and CuO channel, being the first successful report of the application of this technique in TFTs.

Using RF sputtering was also possible to “oxidize” the samples, tuning the amount of oxygen in the chamber. For low amounts of oxygen (low O_{PP}) RBS and XRD techniques showed a Cu-rich phase being formed nears the stoichiometry of the Cu_2O . This is also confirmed by the identification of the crystallographic planes assigned to the Cu_2O phase. For higher oxygen content, RBS shows a Cu-poor phase near the stoichiometry of the CuO . Moreover, for the highest O_{PP} a deviation from the stoichiometry appears to be visible in the form of CuO_{1+x} . DRX also showed the existence of the CuO phase for the conditions with more oxygen content; with the increase of O_{PP} the film crystallinity tends to decrease.

The post-annealing temperature at 200°C , although not effective to induce a phase change, appears to enhance the crystallinity of the films increasing the grain size of the crystallites. This is consistent with the observed in the electrical properties, being the highest value of mobility assigned to Cu_2O phase around $18.5 \text{ cm}^2 \text{ V}^{-1} \cdot \text{s}^{-1}$. This result is one of the highest values of mobility reported in the literature for both CO. Seebeck measurements also confirmed their p-type nature. The Part II of this work also confirms the general trend of the electrical properties before and after annealing, consistent with the results observed in the Part I.

9.1.2 NiO

The nickel oxides were also studied in this thesis using both PVD techniques already mentioned for copper. However, NiO sputtered films were produced from a ceramic target to overcome the problem associated to the ferromagnetic properties of metallic nickel.

NiO phase was produced by thermal oxidation using a similar procedure used for

copper. The effective oxidation temperature for the conversion of Ni to NiO appears to be around 350 to 400 °C. The thickness of the metallic film and the time of oxidation are fundamental parameters to take in consideration. XRD data allowed observe increase of the crystallinity of the films with the temperature followed by an increase of the crystallites size.

In terms of their electrical properties it is visible two regions, one correspondent to the partial-oxidised films (metallic behaviour), and other correspondent to the fully oxidised films. It is noticed a small decrease on the resistivity with the increase of temperature ($T > 450$ °C), that could be related to an enhancement of the films crystallinity and also to a growth on the crystallites size. The higher mobility ($7.7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) was observed for films correspondent to an oxidation temperature of 550 °C. DC conductivity allowed the estimation of the activation energies ranging 0.32 – 0.35 eV (in the high range) and 0.08-0.13 eV (in the low range). These values are in agreement with others published in literature.

The optical properties of the films were also analysed, showing high transmittance in the visible spectrum up to 80%. The optical gap was also estimated around 3.67 eV (direct allowed transition) and the work function around 5.21 eV. AFM and SEM spectroscopy was performed to characterize the morphology of these films, showing that temperature appears to enhance the formation of big agglomerates. This was also observed using the RMS value, showing an increase from 1 to 12 nm with the temperature.

Nickel oxide was also produced by RF sputtering from a ceramic target of NiO in different oxygen contents. The influence of oxygen and the substrate RF power have a high impact in the properties of the films. High amounts of oxygen and the introduction of a substrate power appears to conduct to an amorphization of the films.

The electrical properties were also estimated showing the higher values of mobility associated to the low amounts of oxygen, with a maximum of $5.87 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the condition deposited with 12 % O_2 . In the other hand, the resistivity appears to decrease with the increase of the oxygen content and with the application of a substrate power. This can be related to the enhancement of the amorphous character of the films due to the excess of

oxygen. These films presented very high optical transmittance, with values up to 76% (for the condition with low amount of oxygen) associated to an optical gap around 3.63 eV. With the raise of oxygen (and also with application of substrate power) it is visible a decrease in both transmittance and optical bandgap. A possible explanation to this behaviour is the increase of the density of states in the tails due to excess of oxygen. In the case of the bandgap this reduction can reach about 24% the value without substrate power (for the condition associated to a 26% O_2) from 3.62 eV to 2.75 eV. In terms of transmittance the diminution can be around 46% (for the same condition). The work function was estimated, for the samples without substrate power, in the range of 4.91 – 5.22 eV. The work function showed also an increase with the increment of the applied bias, presumably due to excess of oxygen in the bulk and at the interface.

9.1.3 TFTs

The first report of an inorganic p-type semiconductor TFT appears only in the second half of 2008. Is admirable the evolution in this research field in the past four years. This is still today a “hot topic” being the results presented here among the first reported for p-type TFTs. It was demonstrated the possibility to produce p-type transparent oxide semiconductors based on Cu_2O and CuO by reactive magnetron sputtering but also by a simple thermal oxidation technique, with *On/Off* ratios up to tree orders of magnitude. However the motilities estimated are tree orders of magnitude below the Hall mobility for the single semiconductor layer. Nevertheless, the results presented here showed the promising features of CO, to be introduced alone or doped in the so called “transparent electronics”, and in the complementary metal-oxide semiconductor technology (CMOS). Unfortunately the success of CO was not verified in the case of NiO . After many attempts, the TFTs of NiO showed negligible field-effect characteristics.

9.2 FUTURE PERSPECTIVES

In case of the CO films deposited by RF sputtering, many aspects should be considered in a future approach. The impact of the substrate temperature (alone or with bias) should be analysed, to investigate how they influence the properties of the films. Study of the interface it is also very important and critical to enhance the performance of the devices. Introduction of a buffer layer and the deposited in vacuum of the dielectric and semiconductor layers, without break the vacuum, can help also to limit the interface defects and traps, which can compromise the TFTs performance. Doping Cu_xO with other elements to introduce hole producers, perhaps introducing Br, Al, In, Li, or even doping Cu_xO with SnO, NiO, among other known p-type metal oxides.

In the case of NiO more research should be done to obtain a clearer picture about the use of this material alone in the production of TFTs. Should be interesting to investigate the Hall parameters with the temperature, to try to study the influence of the magnetic properties of NiO in its electrical properties. The same work should be also interesting for CuO, to try to clarify the existence of defects, and the conduction mechanisms in CO.

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APPENDIXES

APPENDIX A: THERMODYNAMICS OF METAL OXIDATION

When a high-temperature reaction of a metal, M , with an oxidant gas (in the case oxygen) occurs, the metal initially absorbs oxygen and then a chemical reaction takes place to form the oxide. In the specific case of the metals interested for this thesis (Cu and Ni), the resulting oxide is a solid. The oxide will nucleate and grow to form a layer on the metal surface. This layer may or may not have a protective character in the underlying metal.

A formation of an oxide can be generally described by the reaction [1]:



The high-temperature oxidation process of metals may be thought to follow simple reactions, however they can involve a large variety of factors: porosity, electrical conductivity or resistivity, dissolved salts, moisture, and pH [1].

Taking in consideration the chemical equilibrium expressed at equation (I), the mass action law can be written as:

$$K = \frac{a_{M_xO_y}^{2/y}}{a_M^{2x/y} a_{O_2}}, \quad (ii)$$

where K is the equilibrium constant (temperature dependent), a_α is the thermodynamic activity of species α .

In the majority of the cases, solids (metal and oxide) are assumed to be in their standard state. Activity depends on temperature, pressure and composition of the mixture, among other things, but at relatively high temperatures and moderate pressures, the oxidant gas can be treated as being ideal. Consequently the activity of oxygen can be approximated by its partial pressure in atmospheres. The equation (ii) simplifies to

$$K = \frac{1}{P_{O_2}}, \quad (iii)$$

which P_{O_2} is the partial pressure of oxygen.

GIBBS FREE ENERGY: ELLINGHAM DIAGRAM

Considering the equation (i), the Gibbs free energy, ΔG , can be expressed as:

$$\Delta G = \Delta G_f^0 + RT \ln K, \quad (\text{iv})$$

this equation is spontaneously from the left to the right, when the ΔG is negative. ΔG_f^0 is the standard free energy of oxide formation at absolute temperature T , and R is the gas constant. K was defined by equation (ii).

- $\Delta G < 0 \rightarrow$ favoured reaction (spontaneous);
- $\Delta G = 0 \rightarrow$ the system is in equilibrium;
- $\Delta G > 0 \rightarrow$ disfavoured reaction.

Taking in consideration the system in equilibrium ($\Delta G = 0$) and the relation (III) we can define the dissociation pressure as:

$$\Delta G_f^0 = -RT \ln K = RT \ln P_{O_2} \quad (\text{v})$$

In equilibrium both forward and reverse reaction rates are equal, being possible to define the oxygen dissociation pressure ($P_{O_2}^{diss}$):

$$P_{O_2}^{diss} = e^{\frac{\Delta G_f^0}{RT}}. \quad (\text{vi})$$

This dissociation pressure gives information relatively to the minimum oxygen pressure needed to make the reaction possible, in other words, the metal M oxidized to M_xO_y .

The Ellingham diagram (Figure i) is a Gibbs energy diagram, and summarizes the temperature dependence of ΔG_f^0 for some common oxidation reactions at standard state ($P_{O_2} = 1 \text{ atm}, \sim 100 \text{ kPa}$). This type of diagram shows the thermodynamic stability of the indicated oxides. The more negative the standard free energy of formation, the more stable the oxide is. Using the P_{O_2} scale from the Figure i and designing a straight line from the index point labelled “O” at the upper left side of the diagram, through a specific temperature point on the oxide line, intersects the P_{O_2} scale at the dissociation oxygen partial pressure $P_{O_2}^{diss}$, for that oxide at that temperature.

The oxidation will occur for any value of $P_{O_2} > P_{O_2}^{diss}$ and for $P_{O_2} < P_{O_2}^{diss}$ the oxide will be reduced to metal, at that temperature. The oxides occupying a lower position in the diagram are more stable and consequently have lower $P_{O_2}^{diss}$ values. Taking in consideration the Ellingham diagram, the dissociation pressure, for instance, in the case of Cu_2O and NiO at 400°C ($P_{O_2}^{diss}$) is about 10^{-19} and 10^{-28} atm, correspondingly.

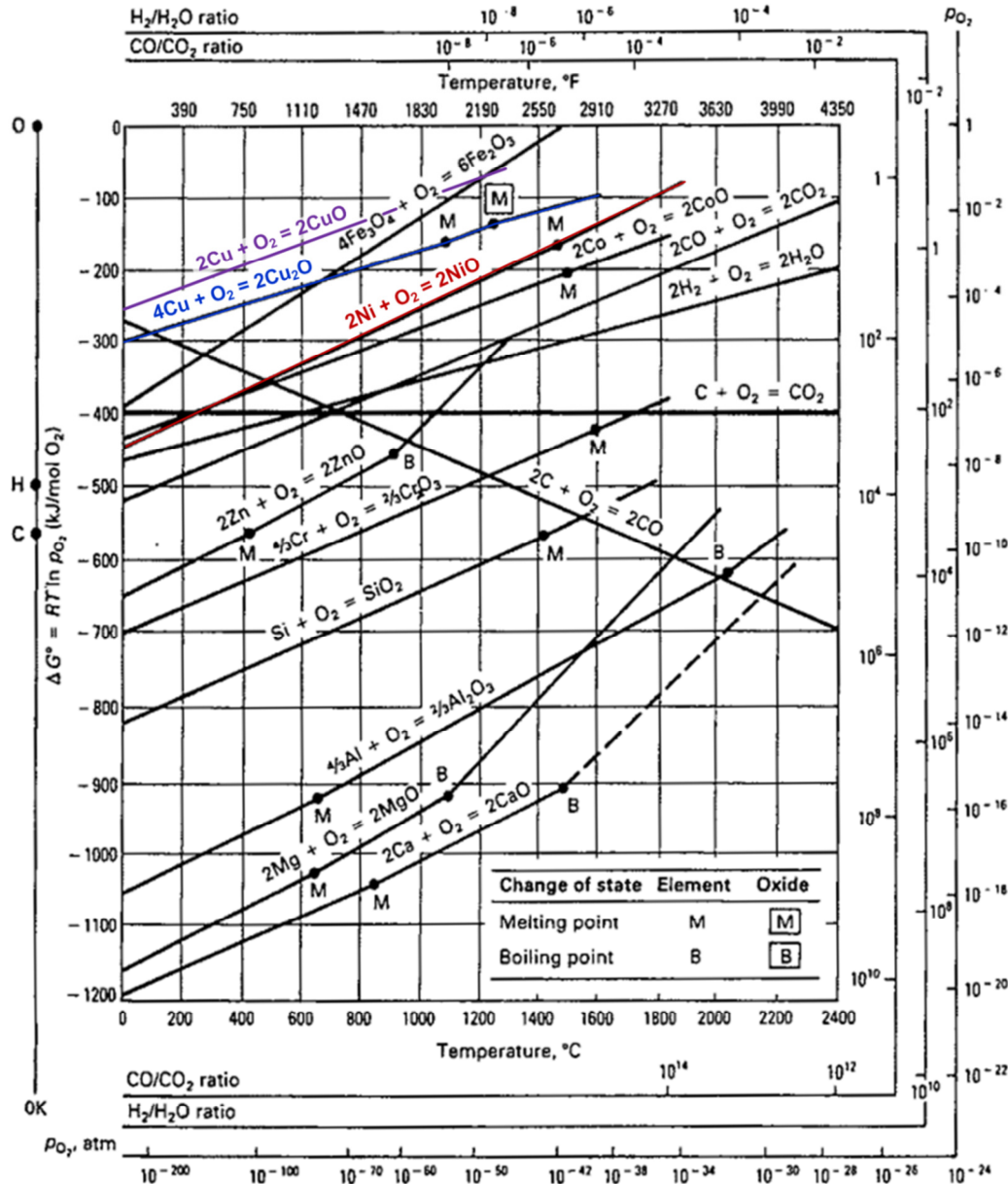


Figure i – Ellingham diagram showing the standard Gibbs energies of formation of selected oxides as a function of temperature (adapted from [1]).

As a curiosity and taking the given example, the low oxygen pressures exemplified are impracticable controlling only the O_2 directly. This means that a reduction is not expected for these oxides at $400^\circ C$ (1 atm). In practice these low amounts of oxygen are achieved using gas mixtures, being the most common the H_2O/H_2 and CO_2/CO .

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APPENDIX B: KINETICS OF METAL OXIDATION

The oxidation kinetics explains how fast the reaction will occur and makes it possible to determine the extent of metal consumption, and consequently, lifetimes. Oxidation kinetics, in other words, turns possible to describe the change in the oxide thickness (x) or the samples weight, (ΔW) – the oxidation rate. These two parameters can be directly related by the equation,

$$x = \frac{V_{\text{oxide}}}{y M_0} \Delta W \quad (\text{i})$$

where y is the stoichiometric amount of oxygen in oxide M_xO_y , M_0 is the atomic weight of oxygen and V_{oxide} is the molar volume of the oxide ($\text{cm}^3 \text{ mol}^{-1}$). In the same way it is possible to correlate the consumption of metal using a similar equation

$$X = \frac{V_m}{\gamma M_0} \Delta W \quad (\text{ii})$$

where X is the thickness of consumed metal, V_m is the molar volume of metal ($\text{cm}^3 \text{ mol}^{-1}$) and γ is the stoichiometric factor (i.e., for M_xO_y , $\gamma = y/x$).

For most metals the oxidation kinetics for oxidation rates, follow different rate laws being the most common: linear, logarithmic and parabolic. Although other laws are presented in the literature, being possible to find theoretical justifications for all [1]:

$$\text{Parabolic Law:} \quad x^2 = 2At \quad (\text{iii})$$

$$\text{Cubic Law:} \quad x^3 = 3At \quad (\text{iv})$$

$$\text{Linear law:} \quad x = At \quad (\text{v})$$

$$\text{Logarithmic} \quad x = A \ln(Bt + 1) \quad (\text{vi})$$

The metallic oxidation which forms volatile oxides, it is represented by a linear weight loss and is related to metals that do not have an ability to form oxides with protective behaviour. In the case of a metal oxidation that shows a gain in weight, their kinetics may obey to a linear, parabolic and logarithmic rule. The behaviour of these laws is illustrated in Figure i.

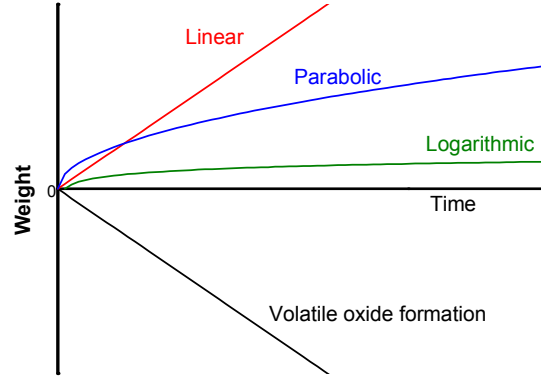


Figure i – Oxidation rate laws obeyed by metals during an oxidation process.

TAMMANN PILLING BEDWORTH (TPB) – PARABOLIC LAW

For sufficient high temperature and sufficient thick films, the oxidation of a metal, which results in weight gain and follows a parabolic like rule, it is commonly typified by an oxide film that remains intact on the metal surface, offering a uniform barrier to the diffusion of metal or ions through the film [2].

The oxide thickness, x , increases with the time, t , and will correspond to an increase of the diffusion distance and consequently a decrease of the oxidation rate. So the equation that described a process like that is expected to have an oxidation rate inversely proportional to the oxide thickness [2, 3]:

$$\frac{dx}{dt} = \frac{C_1}{x} \quad (\text{vii})$$

where C_1 is a proportionality constant. The integration of this equation with respect to x results in a parabolic relation,

$$x^2 = 2k_p t + C \quad (\text{viii})$$

where k_p ($\text{cm}^2 \text{s}^{-1}$) is the parabolic constant and C is an integration constant. Examples in this category contain the oxides studied in this thesis, copper and nickel. Another form of this equation is given by a weight gain parabolic rate equation:

$$\Delta W^2 = 2k_p t + C \quad (\text{ix})$$

which k_p in this case has the units $\text{g}^2 \text{cm}^{-4} \text{s}^{-1}$.

This kinetic law is standard for the analysis of high-temperature oxidation kinetics, controlled by the diffusion through a relatively thick layer of oxide. It is thermally

activated, increases exponentially with temperature and follows the Arrhenius equation [4, 5]:

$$k_p = k_0 e^{-\frac{E_p}{kT}} \quad (\text{x})$$

where k_0 is a constant that depends on the oxide composition and gas pressure, E_p is the activation energy for the oxide growth, k is the gas constant ($8.617\,332\,478 \times 10^{-5}$ eV K⁻¹) and T is the absolute temperature.

Copper oxides are examples of oxides that dissolve oxygen, becoming defect semiconductors. The concentration gradient of oxygen depends of the oxygen pressure and will influence the oxidation growth rate. Nevertheless, it is not the oxygen, which diffuses, but the metal [3].

LINEAR RATE LAW

The oxidation of metals, under certain conditions, follows a linear constant rate according to the equation [1-3]:

$$\frac{dx}{dt} = k_l \rightarrow x = k_l t \quad (\text{xi})$$

where x is the layer thickness and k_l is a linear rate constant. In this type of oxidation, the oxide formed on the surface is unable to offer a protection barrier against the oxygen diffusion. A linear rate law may result when a phase-boundary reaction controls the kinetics rather than a transport process. The oxidation process never slows down and the consumption of the metal will occur in a relatively short time. Examples of oxidation rates that follow this type of law are iron at 1000 °C and magnesium at 500 °C [3]. In general, in the early stages of a metal oxidation process, the oxide layer is sufficiently thin and the linear kinetics prevails. Then with the oxidation processes the linear behaviour may change for parabolic or logarithmic and the reverse can also happen (called breakaway). With the increase of the oxide thickness, it is possible to be developed micro-cracking and porosity, reducing the protectiveness of the oxide layer and changing the oxidation process to linear rate behaviour.

LOGARITHMIC RATE LAW

Many metals, perhaps all that oxidize readily, show very similar behaviour when exposed to oxygen at sufficiently low temperatures. Initially the oxidation process is extremely rapid, but after a few minutes or hours it drops to very low or negligible values.

An explanation for this type of behaviour was performed by Mott [2], conjecturing that a strong field is set up in the oxide film due to a contact potential difference between the metal and the adsorbed oxygen, enabling the traveling of metal ions through it without much help from temperature. This hypothesis is consistent with an oxidation rate inversely proportional to time [2, 3],

$$\frac{dx}{dt} = C \frac{1}{t} \quad (\text{xii})$$

where C is a constant. The integration of this equation will result in a logarithmic rate law,

$$x = C_0 \log(C_1 t + 1) \quad (\text{xiii})$$

where C_0 and C_1 are constants. This shows that a stable film will grow (at constant temperature) until it reaches a limiting thickness, and stop growing. To continue the oxidation is generally needed an increase of the temperature. In the work of Wilkins and Riedel [2] they enumerate the different reasons for that, explaining in detail some of the things that were briefly exposed here. It is also interesting to add, that in some cases of oxidation of metals, the growth rate of the oxide layer follows multiple stages of growth already mentioned (Figure ii).

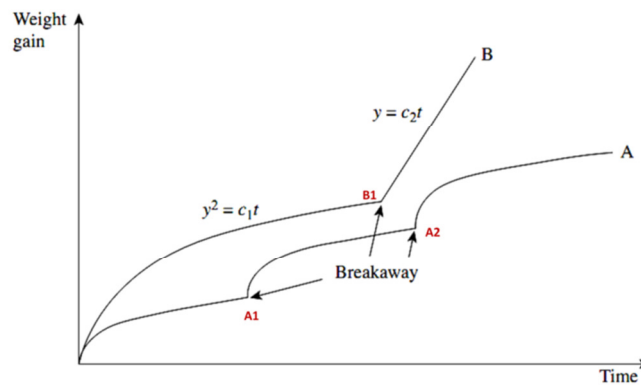


Figure ii – Typical breakaway corrosion curves

The figure shows two oxidation processes represented by A and B. In the process A two points of change (A1, A2) are observed and in the process B only one point of change (B1) is represented. These points are regions of abrupt changes in the oxidation rate, also commonly named as breakaway points.

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APPENDIX C: Optical Data Cu_xO by thermal oxidation

It is presented here as an example, the Tauc Plot model, considering the different transitions, applied in the case of copper oxides produced by thermal oxidation.

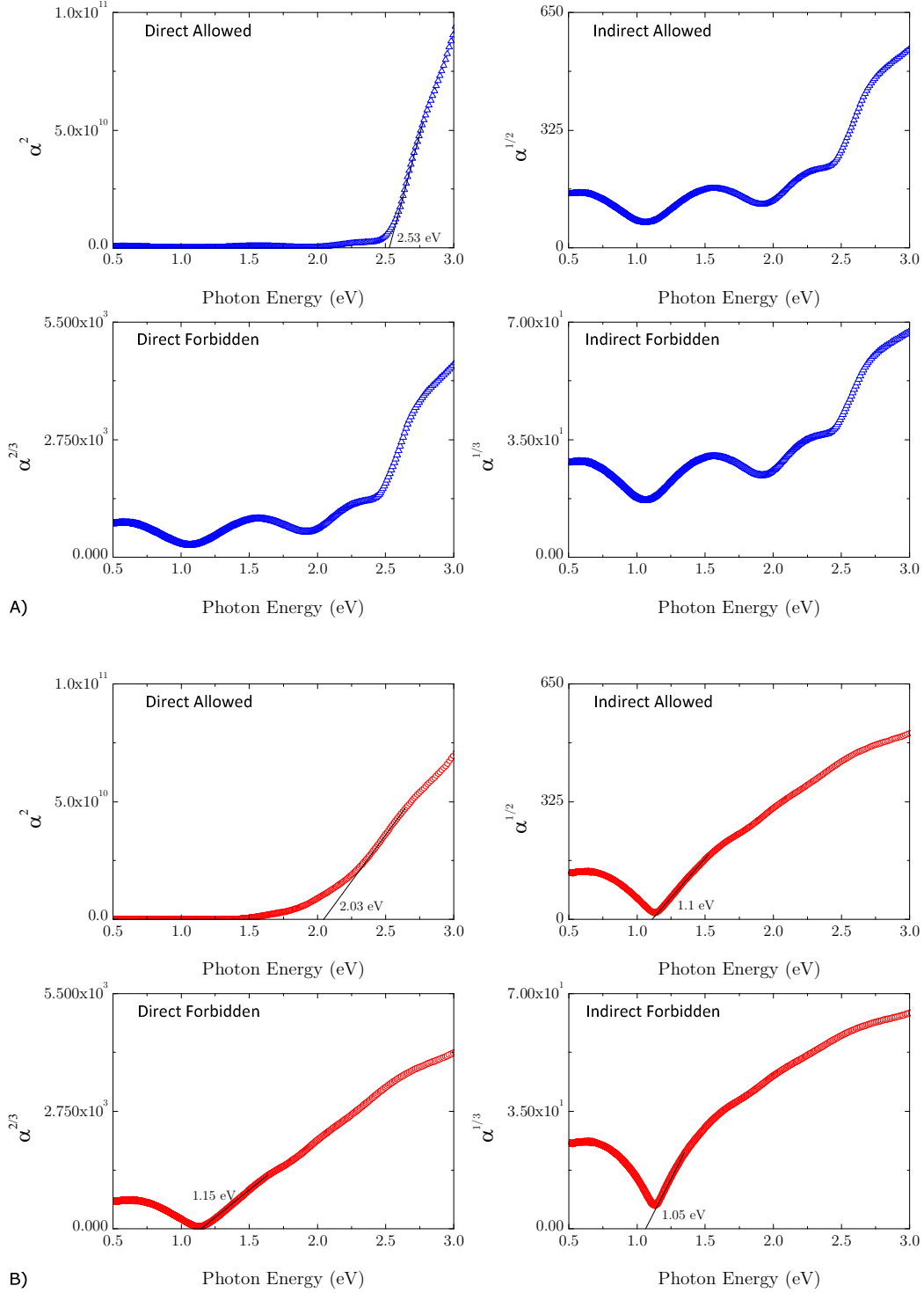


Figure i – Different Plots of the absorption coefficient for a Cu₂O sample (A) and for a CuO sample (B) considering different transitions.

APPENDIX D: OPTICAL DATA Cu_xO BY RF SPUTTERING

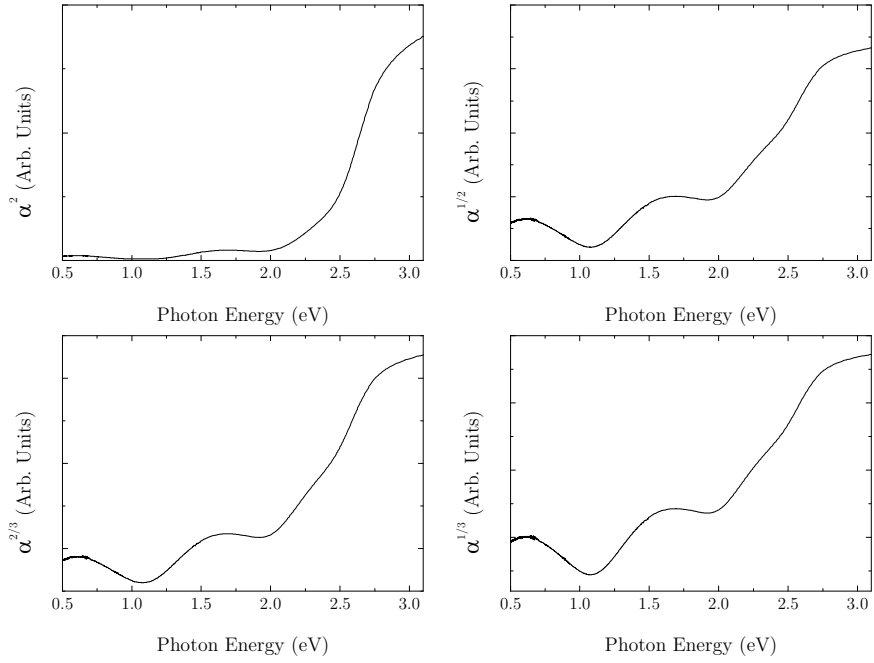


Figure 1 – Direct allowed (A) and forbidden (B) bang gaps. Indirect allowed (C) and forbidden (D) for the deposition condition correspondent to the Cu_2O phase (9 % OPP).

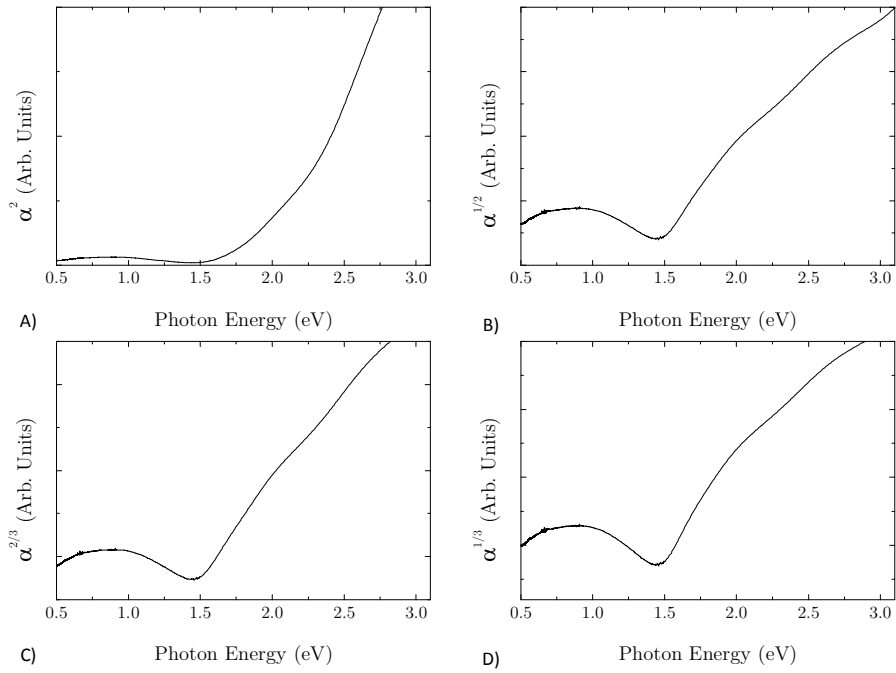


Figure 2– Direct allowed (A) and forbidden (B) bang gaps. Indirect allowed (C) and forbidden (D) for the deposition condition correspondent to the CuO phase (25% OPP).

