New Challenges of High-κ Oxide Dielectrics: *from Spin to Large-Scale Device Fabrication*

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1. Abstract

High-permittivity (κ) oxide dielectrics have been widely demanded concerning the Internet of Things (IoT) requirements, such as flexible large-area manufacturing, energy efficiency, low-cost processes, and sustainable electronics, especially in thin-film transistors (TFTs). From there emerged the necessity of printing energy-efficient (vacuum-free) eco-devices using low-temperature methods (e.g., combustion synthesis, post-treatments) in the production and processing of nanomaterials, thus reducing the human carbon footprint. However, currently the main deposition method used is typically spin-coating which requires higher temperatures and long annealing times, not compatible with the printing industry. Besides the concerns with process integration, the market highly demands high-κ dielectrics with great stability and high yield. To surpass these challenges, some crucial parameters in the ink design need to be considered to guarantee successful upscale for large-area electronics manufacturing.

2. Introduction

Since 2010, the interest in solution-processed high-κ oxide dielectrics have grown drastically to enhance the field of microelectronics, sensors and wearables.[1] These dielectrics possess an excellent thermal and chemical stability, mechanical tolerance and high permittivity, parameters that are fundamental for large-area electronics manufacturing. Also, the high-κ insulator oxide layer plays a crucial role in memories and more particularly in TFT performance since the tunneling effect is suppressed when compared to SiO_2 due to their typical high permittivity.[2], [3] This feature leads to low power consumption and easier miniaturization reaching smaller and faster circuits.[4] To be an ideal gate dielectric for application in TFTs this layer must present certain characteristics such as a large breakdown field (> 1 MV/cm), a low leakage current density (< 1nA/cm^2 at 1 MV/cm), a high dielectric constant (> 20), a high bandgap (> 5 eV) and, should be amorphous with a smooth surface (< 1nm) and a low interface defect density with the semiconductor. Considering these features solution based ZrO_2 and HfO_2 are desirable gate dielectrics as these fulfill the main requirements. However, these dielectrics typically provide a lower κ and bandgap compared to the theorical values due to the presence of organic residues and unconverted hydroxide groups with the films (M-OH instead of M-O-M formation). To guarantee a band offset higher than 1 eV with the semiconductor and avoid a thermionic emission of electrons or holes into the dielectric band, insulators such as Al_2O_3, multilayers of different insulators and multicomponent doping (e.g., Hf, Zr, La, Yt, Mg) have been used.[4]

Towards the production step of these dielectrics, generally a high process temperature (> 400 °C) is required to achieve high quality materials, which is not suitable for low-cost flexible substrates as PEN, PET or paper. To overcome this challenge different approaches have been established in relation to the solution synthesis design and postdeposition processes.

The ambient conditions, such as humidity and temperature are crucial parameters in the deposition of solution-based metal oxides in their final properties. Typically, these parameters are overlooked which can significantly affect the device performance and reproducibility. Page et al. reported the importance of relative humidity (RH) in the deposition of different dielectric oxide thin films (e.g., AlO_x, LZO).[5] By changing only the RH parameter from a dry (~22 %) to a humid (~ 71 %) environment the thickness decreased from 78 to 42 nm. Also, Kim et al. demonstrated that the humidity and temperature, clearly affect the electrical properties of solution-based AlO_x dielectric films.[6] For humidity below 30 % the films present partial cracks. Maintaining the RH at 40 % - 50 % and the temperature at 25 °C - 35 °C during the film's deposition led to low current density and high breakdown voltage of the dielectric improving TFT overall performance.

Regarding solution synthesis, a metal salt precursor based on metal nitrates is preferred over chloride or acetate precursors which require higher conversion temperatures to effectively remove organic residues and impurities (**Figure 1 (a)**).[7] Metal nitrate precursors typically require lower conversion temperatures considering the high volatility of the decomposition by-products due to the electronic interaction between the metal and the nitrate group.[8] Another promising approach is solution combustion synthesis (SCS) established by Marks et al. for the production of solution-processed metal oxide TFTs.[9] In this method, instead of using the conventional synthesis (sol-gel) a fuel is used as reducing agent (e.g., urea) and metal nitrates as oxidizing agents leading to a self-sustained redox reaction. Through combustion synthesis, an exothermic reaction occurs, resulting in a reduction of the external heating required for the film's formation, i.e., the removal of organic solvents and film densification at lower process temperatures.[10] In 2014, Bae et al. and Branquinho et al. applied this method in solution-processed oxide dielectrics reaching low temperatures up to 250 °C.[11], [12]

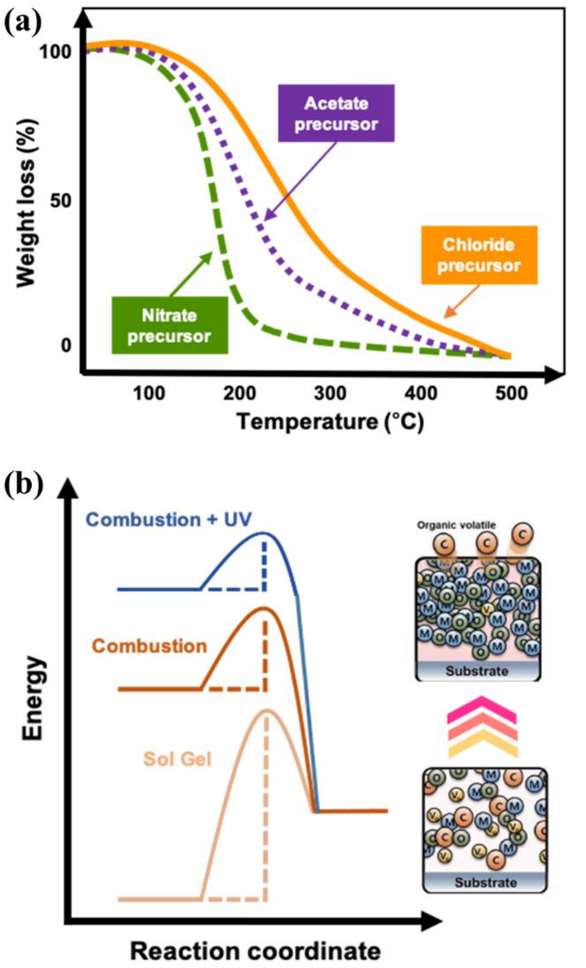

Fig. 1: (a) Schematic diagram of thermogravimetric analyses of various precursors. Adapted from [7]. Copyright 2014, IOP Publishing Ltd. (b) Illustration of the three different synthetic approaches for metal oxides: energetics of combustion synthesis-based process combined with ultraviolet (UV) treatment versus combustion and sol–gel conventional process. Adapted from [3]*. Copyright © 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.*

Since 2012, photoactivation processes have been used to improve the quality of the metal oxide thin films at low processing temperatures by decreasing the number of metal-hydroxide bonds.[13] This method uses a deep-ultraviolet (DUV) irradiation to induce the photochemical cleavage of alkoxy groups and activates metal and oxygen atoms which improves the M-O-M frameworks. Further irradiation leads to a rapid decrease of oxygen and carbon contents promoting a near-complete condensation and a transition to film densification. In 2015, Park et al. implemented this methodology to produce diverse oxide dielectrics (AlO_x, ZrO_x, HfO_x) with a suitable densification at low temperature.[14] The resulting thin film capacitors showed a clear improvement in the overall electrical performance (breakdown field, leakage current density and capacitance-frequency stability) when compared with high and low temperature annealed devices without UV treatment. By combining UV irradiation with SCS the densification of the metal oxides can be further improved at lower processing temperatures (**Figure 1 (b)**). Carlos et al, reported that merging these elements lead to the improvement of solution-based dielectric properties.[15], [16] Scheideler et al. produced a fully printed (source and drain, semiconductor, and dielectric) TFT at 250 ºC assisted by UV irradiation.[17] Nevertheless, to process these printed metal oxide layers and assure their compatibility with low-cost flexible substrates a lower thermal budget (≤ 150 ºC) is still required (**Figure 2**).

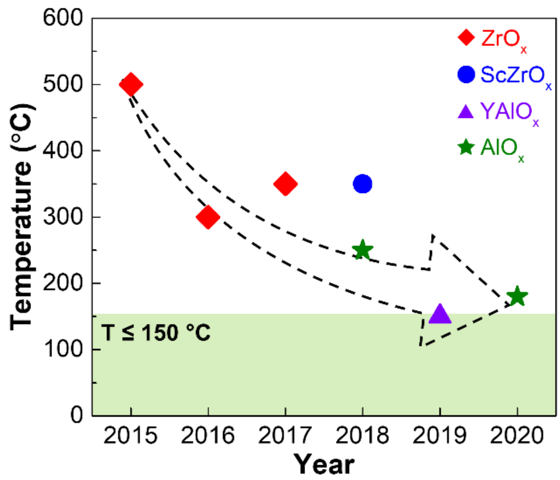

Fig. 2: Lowest processing temperature required for printed metal oxide dielectrics applied in metal oxide TFTs using different printing methods. [17]–[23]

Improving the solution-based dielectrics' overall properties is also a challenge. The permittivity and bandgap can be increased by doping the metal oxide network, but this typically require high annealing temperatures. Park et al. surpassed that issue using 5 % of Zr doped AlO_x and DUV annealing at a maximum temperature of 150 °C. The optimized Zr incorporated AlO_x (ZAO) gate dielectric, presented low leakage current density and high breakdown field. Besides that, an increase of the dielectric constant was observed with the increment of Zr doping, from 6.08 (without Zr) to 8.82 (9 %).[24] Recently, Bolat el at. printed aluminum oxide layers doped with yttrium (10 %) at low temperature (150 ºC) which led to low leakage current density and higher breakdown and permittivity of the insulator.[22] Another way to improve the dielectrics performance for application in TFTs with low thermal budget is the use of multilayers as described by several research groups.[16], [25], [26]

3. From Traditional Coating to Printing

Besides, annealing temperature and the dielectric ink design one of the main obstacles for large area fabrication is the deposition method. Typically, the most adopted technique to deposit solution-processed metal oxide thin films to produce TFTs is spin-coating due to its simplicity and reproducibility (**Figure 3**).[4] However, this technique requires substrative processes (e.g., lithography) to fully pattern the devices and most of the solution is wasted during the process. So, clearly great effort is needed to relocate from traditional coating to printing techniques being compatible with large-scale production. This transfer is not linear as many challenges must be overcome and several parameters specific to the printing industry need to be considered such as, inks compatibility with the printing components, substrate wettability and roughness, electrode features, printing speed and curing, resolution, and accuracy.

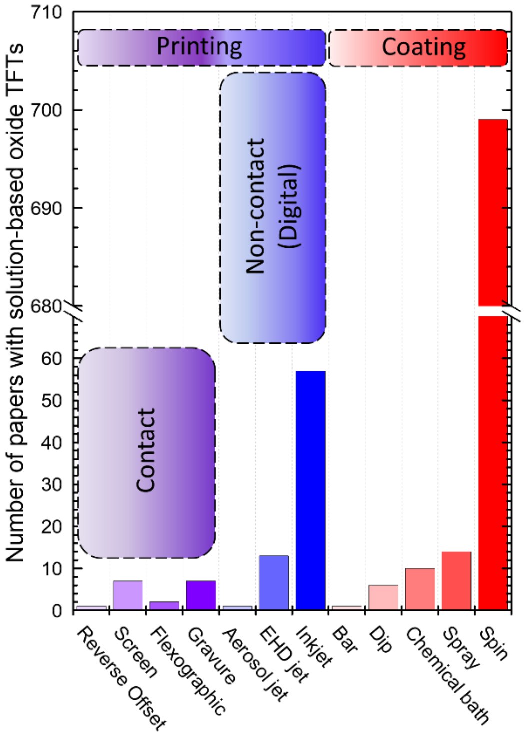

Fig. 3: The number of publications on the particular processing techniques (coating and printing) in solution-processed oxide TFTs over a decade (2009 – 2019). Adapted from [4]. *Copyright © 2021 Elsevier Ltd.*

Ink transfer compatibility: To assure the best transition to large-scale manufacturing the dielectrics inks should be stable for more than 6 months in ambient or refrigerated (5 ºC) conditions. One way to stabilize the inks is using SCS, as the fuel can act as stabilizer and also enhances stoichiometry.[10] The ink viscosity is also a highly important parameter to control for each printing technique (**Figure 4**). This can be controlled mainly by the ink concentration increment avoiding additional solvents/stabilizers and by mixing two solvents where the minor solvent (high boiling point and low surface tension) retards the evaporation at the contact edge reducing the coffee ring effect.[4] Usually, spin-coating requires low viscosity inks which facilitates the optimization of these inks for inkjet and reverse-offset printing techniques. Another factor to consider is the size of the particles comprising the inks (should have less than 1/20 size of nozzle diameter) as these can clog the inkjet printing nozzles (e.g., form aggregates) or hinder the adsorption of solvent onto the polymer stamps in contact printing techniques. Finally, the dielectric inks' toxicity must be considered in the upscaling of these materials. Ideally the inks should be mainly composed of greener solvents (e.g., ethanol, water) to meet safety requirements of the printing industry.[11], [27]

Substrate properties: Typically, flexible substrates suffer from high surface roughness when compared with rigid substrates. Also, even when the root mean square (rms) roughness is low, some spikes (i.e., high aspect ratio features) are usually present. This feature can compromise the subsequent layers of the full device as it is composed by submicron thick layers leading to short-circuited devices or higher device-to-device variability. To overcome this, substrates should be polished or coated with a specific layer to attain a smoother surface. Other important factor to consider are the thermal expansion coefficient (CTE) and the maximum temperature acceptable for each substrate to prevent their shrinking and/or degradation during the full device fabrication process. Good ink adhesion should also be assured which can be achieved with a substrate surface treatment (e.g., UV or plasma) prior to ink deposition. This improves the substrate's surface energy (prevents ink aggregation) and wettability.[28] However, this process needs to be optimized to avoid the ink's overspreading before drying. The implemented surface treatment should also be considered for the subsequent device layers to optimize layer-to-layer adhesion. Concerning sustainability, great effort has been made on the recyclability of flexible electronics substrates. Lately, Chen et al. reported a highly thermally stable polymer substrate that can be quickly disintegrated and recycled in a green solvent.[29]

Electrode features: The metal inks currently used for the printed electrodes are mainly nanoparticle-based which is a critical issue for the subsequent layers due to the high surface roughness of the conductive layer. This is quite challenging especially for thin film transistors where an ultra-thin high-κ dielectric is desirable to reach low power consumption. Nevertheless, Kusaka et al. recently reported conductive MoO_x-printed layers based on metal acetylacetone inks that were processed at low temperature (200 ºC) for source and drain (S/D) electrodes with high resolution and smooth surface.[30] This methodology can be implemented in the near future to produce smooth gate electrodes. Solution-processed transparent oxides (TCOs) are also a promising option, however further developments are still needed to reach the required conductivity with low thermal budget.

Printing speed and curing: For large-scale manufacturing, a high printing speed is desirable. This is reachable with contact printing techniques (**Figure 4**) such as gravure (up to 1000 m/min) and flexographic printing (up to 500 m/min).[4] Nevertheless, to assure the complete formation of the high-κ oxide dielectric layers lower speeds than the ones reachable by the printing industry are required when printing dielectric inks. This is possible due to inline ovens that promote ink drying (i.e., solvent evaporation) and inline high power lamps or lasers that can induce photonic curing in a short processing time (≤ 1 min) to form the final layers.[23], [31]–[33] Ink evaporation rate and ambient conditions (humidity and temperature) must also be considered during printing as the printed layers' properties can be highly affected. Finally, the production of uniform patterns over large areas to achieve a great yield (≥ 98 %) and low devices variability must also be assured. Printing thin uniform pinhole-free gate dielectric layers is quite challenging. Nevertheless, Carlos et al. recently reported a printed highly stable ultrathin (< 25 nm) high-κ dielectric using flexographic printing with a fast printing speed of 50 m/min at low processing temperatures (≤ 200 ºC).[23] This dielectric presented low leakage current density, good breakdown field, low capacitance-frequency variation and device ageing stability being successfully implemented in TFTs.

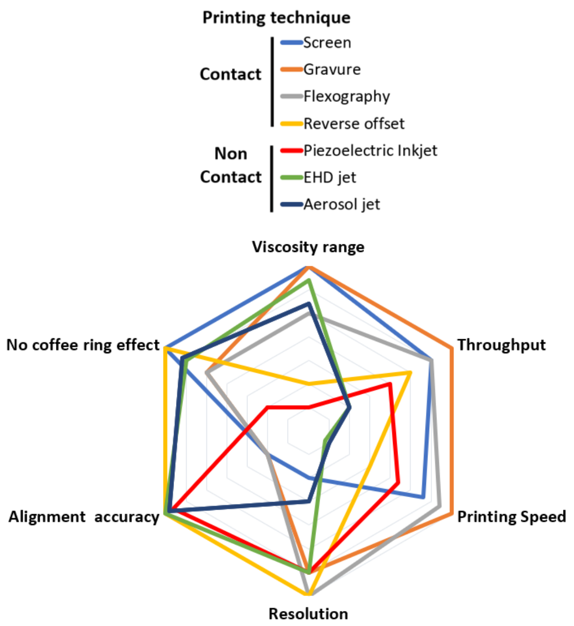

Fig. 4: Comparison of relevant features for various contact and non-contact printing techniques. Copyright © 2021 Elsevier Ltd.[4]

Resolution and Accuracy: Resolution is one of the main printing bottlenecks as the highest resolution currently achieved is 1 µm by flexographic and reverse offset printing.[4] Nanoimprint lithography allows printing of nanometric areas however, this technique requires lithographic processes increasing the associated costs. Certainly, more effort is demanded in the manufacture innovation to reach higher resolution patterns (i.e., stamps). However, it should be considered that higher resolution comes at the cost of the printing speed need which would then need to be reduced. Also, the printing alignment accuracy is of extreme importance since it ensure the alignment of the subsequent layers, always required when producing a complete device. Noncontact (digital) printing techniques (inkjet, EDH jet, aerosol jet) are in clear advantage in comparison with contact printing techniques since an alignment accuracy of ± 1 µm can be attained (**Figure 4**).[4] Nevertheless, reverse offset printing allows an identical alignment accuracy which clearly demonstrates the potential of contact printing techniques.[30]

5. Conclusions

The transfer of high-κ oxide dielectrics from coating to printing techniques requires several parameters to be studied and controlled to assure the successful upscale for large-scale manufacturing as described previously. To apply these layers in devices and more complex structures it is highly important to perform further work to reduce the curing time to process these layers in controlled ambient conditions (atmosphere, humidity, and temperature) suitable for roll-to-roll (R2R). In terms of device-to-device and sample-to-sample variation it is fundamental to reach the lowest variability possible ensuring their implementation in real products.

Printing technology is not yet fully mature but undoubtedly has enormous potential for future IoT applications leading to low-cost and more sustainable electronics. For now, to implement robust products, the printed devices must be correlated with the conventional silicon devices to attain a reliable flexible hybrid electronic structure in the market.

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