We are IntechOpen, the world's leading publisher of Open Access books
Built by scientists, for scientists

5,900
Open access books available

145,000
International authors and editors

180M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Solution Combustion Synthesis: Applications in Oxide Electronics

Rita Branquinho, Ana Santa, Emanuel Carlos,
Daniela Salgueiro, Pedro Barquinha,
Rodrigo Martins and Elvira Fortunato

Additional information is available at the end of the chapter

Abstract

Oxide-based electronics have been well established as an alternative to silicon technology; however, typical processing requires complex, high-vacuum equipment, which is a major drawback, particularly when targeting low-cost applications. The possibility to deposit the materials by low-cost techniques such as inkjet printing has drawn tremendous interest in solution processible materials for electronic applications; however, high processing temperatures still required. To overcome this issue, solution combustion synthesis has been recently pursued. Taking advantage of the exothermic nature of the reaction as a source of energy for localized heating, the precursor solutions can be converted into oxides at lower process temperatures. Theoretically, this can be applied to any metal ions to produce the desired oxide, opening unlimited possibilities to materials' composition and combinations. Solution combustion synthesis has been applied for the production of semiconductor thin films based on ZnO, In_2O_3, SnO_2 and combinations of these oxides, and also for high κ dielectrics (Al_2O_3). All of which are required for numerous electronic devices and applications such as fully oxide-based thin-film transistors (TFTs). The properties of produced thin films are highly dependent on the precursor solution characteristics; hence, the influence of several processing parameters; organic fuel, solvent and annealing temperature was studied. Although precursor solution degradation/oxide formation mechanisms are not yet fully understood, particularly for thin films, we demonstrate that high-performance devices are obtained with combustion solution-based metal oxide thin films. The results clearly show that solution combustion synthesis is becoming one of the most promising methods for low-temperature flexible electronics.

Keywords: solution processing, combustion synthesis, environmentally friendly, metal oxide materials, thin-film transistors, semiconductor oxides, dielectric oxides

1. Introduction

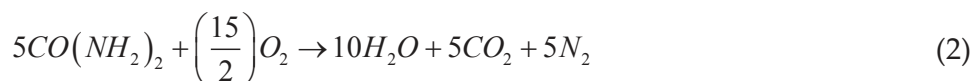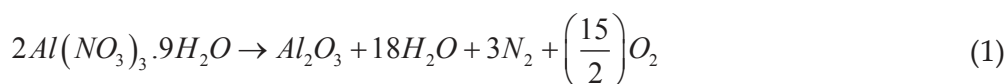## 1.1. Solution combustion synthesis

Solution combustion synthesis (SCS) is a popular method for the preparation of a wide variety of materials due to its simplicity, broad range of applicability and the possibility of easily obtaining products in the desired composition. This method has been widely used for the development of oxide powder materials; including perovskites, spinels, ferrites; for diverse applications, such as catalysis and solid oxide fuel cells [1–3] and is becoming one of the most convenient methods for the preparation of simple and multicomponent oxides for electronic applications [4].

SCS is based on a redox system that requires a solution that upon heating to moderate temperatures leads to the development of a strongly exothermic redox reaction, which generally provides the energy for the metal oxide formation. The ignition temperature of the exothermic reaction is significantly lower than the final combustion temperature which results in the material formation; thus allowing the conversion of solution precursors into oxides at lower process temperatures [1–3].
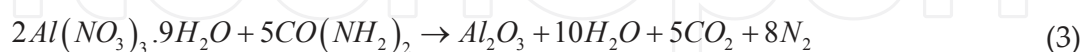
The precursor solution for combustion synthesis is typically constituted by metal nitrates, which are employed simultaneously as metal source and oxidizing agents, and an organic fuel that acts as a reducing agent. However when using metal chlorides, as a metal ion source, a combustion aid is required to provide the oxidizing nitrate ions; in this case, ammonium nitrate is typically used. The most frequently applied fuels are urea, acetylacetone and glycine, amongst others, since these can form stable complexes with metal ions to increase solubility and prevent selective precipitation of the metal ions in solution. This process produces oxide materials of good compositional homogeneity, which is especially important in the synthesis of multicomponent oxides. Historically, water is the most widely used solvent for the combustion synthesis of powder materials [1–3]. Recently, the pursuit of environmental friendly solvents for electronic applications, such as ethanol and water, is growing [5–7]; however, organic solvents, including 2-methoxyethanol and acetonitrile, are currently the most widely used for the production of oxide thin films for electronic applications purposes [5].

The resulting solution is then heated to evaporate the solvent and when ignition temperature is reached the exothermic reaction takes place. During the combustion reaction, the fuel is oxidized by the nitrate ions. The precursor materials are converted into the metal oxide, and gaseous H_2O, CO_2 and N_2 are the remaining products formed in the combustion reaction. This process can in theory be applied to any desired metal ion.

The solution combustion synthesis of a metal oxide can be represented by the combination of metal nitrate decomposition reaction and fuel oxidation reaction. As an example, respective equations for the combustion synthesis of Al_2O_3 from aluminium nitrate and using urea as fuel are given as follows [Eq. (1) and (2)] [6].

$$2Al(NO_3)_3 \cdot 9H_2O \rightarrow Al_2O_3 + 18H_2O + 3N_2 + \left(\frac{15}{2}\right)O_2 \tag{1}$$

$$5CO(NH_2)_2 + \left(\frac{15}{2}\right)O_2 \rightarrow 10H_2O + 5CO_2 + 5N_2 \tag{2}$$

The overall combustion reaction can thus be written as Eq. (3)

$$2Al(NO_3)_3 \cdot 9H_2O + 5CO(NH_2)_2 \rightarrow Al_2O_3 + 10H_2O + 5CO_2 + 8N_2 \tag{3}$$

Note that these are theoretical reaction equations that do not consider possible secondary reactions such as nitrates decomposition, urea hydrolysis, thermal decomposition and also fuel-oxidizer adducts; however, the overall reaction allows the calculation of a stoichiometric condition that can be used as a reference [3, 6].

There are many essential variables in solution combustion synthesis, including metal ion, metal precursor type and concentration, content of organic fuel, combustion aid and oxidizer/fuel proportion; which is determinant for the thermodynamics of the oxide formation [2].

A concept for determining the stoichiometric proportion of oxidizer and fuel for SCS was adopted from the Jain method [8], which is based on propellant chemistry and allows the calculation of the reducing/oxidizing valences (OV/RV) of a redox mixture. In this method, oxygen and nitrogen are considered oxidizers with the respective valence of −2 and 0. On the other hand, carbon, hydrogen and metal ions are considered as reducing elements with their final valences of +4 and +1 and the corresponding metal valence, respectively. Consequently, urea has a reducing valence of +6 (RV = 4 + 4 × 1 + 2 × 0 − 2) whilst aluminium nitrate has an oxidizing valence of −15 (OV = 3 + 2 × 0 − 3 × 6), resulting in a 15/6 (or 5/2) reducing/oxidizing valences for an optimal stoichiometric redox mixture of urea-aluminium nitrate.

The relation between the redox stoichiometry and the molar ratio of reagents can be determined by the reducing/oxidizing valences (RV/OV) of the reagents and is given by Eq. (4)

$$\Phi = \frac{RV}{OV} n \tag{4}$$

The oxygen consumption or production is controlled by the fuel/oxidizer ratio (Φ) which also depends on n; the number of moles of fuel per mole of oxidizer [1–3]. The optimal stoichiometry composition of the redox mixture is obtained for $\Phi = 1$ that corresponds to a condition in which the reaction does not require any molecular oxygen to occur. For the given example of urea-aluminium nitrate redox mixture, 5 moles of urea are required per 2 moles of aluminium nitrate to assure redox stoichiometry of the aluminium oxide formation reaction, as depicted in Eq. (3) [6].

A fuel-lean condition is obtained when $\Phi < 1$ and upon reaction molecular oxygen is produced; whereas when $\Phi > 1$ molecular oxygen is required to fully convert the fuel and the redox mixture is in a fuel-rich regime [3].

1.2. Solution-based oxide electronics

The evolution from rigid silicon-based electronics to flexible electronics requires the use of new materials with novel functionalities that allow non-conventional, low-cost and environmental friendly processing technologies [9, 10]. Metal oxide-based electronics have been well established as an alternative to silicon technology, demonstrating exceptional electronic performance as active semiconductor components, which can be tuned for the applications, where high transparency/electrical conductivity is demanded [11, 12]. The major investment of several high-profile companies: SHARP, SAMSUNG, LG, BOE has led to the commercialization of oxide-based display backplanes in a very short period of time, and the global market is expected to increase [9, 10]. The current typical processing techniques require complex high-vacuum equipment which is a major drawback, particularly when targeting low-cost applications.

Recently, the demands for low-cost flexible electronics has led to a remarkable development of solution-based production methods and solution-processed inorganic metal oxide semiconductor materials for high-performance thin-film transistors (TFTs), and such devices have demonstrated competitive results when compared with materials obtained by physical techniques [4, 13].

Several solution-based chemical synthetic routes have been exploited for the preparation of these oxides because of their simplicity, versatility, and scale-up capability; however, the application of solution combustion synthesis to the production of thin films for TFT applications was first reported in 2011 [4]. Since then, significant research efforts have been put on the development of semiconductor materials such as indium oxide and indium, zinc tin and gallium-based multicomponent oxides [13–16] and more recently of dielectric materials [5, 6, 17]. However, most of the research as focussed on the use of toxic solvents (2-methoxyethanol) and scarce materials (indium), which can be a major drawback in the upscaling of this technology. Consequently, the challenge remains to unveil the combination of solution combustion synthesis processing parameters that allow an environmentally friendly production of high-quality insulator and semiconductor thin films at low temperature and their combination in fully combustion solution-processed TFTs.

In this work, we focus on the environmentally friendly solution combustion synthesis of oxide-based materials for electronic applications, including insulator and semiconductor thin films by studying the influence of synthetic and processing parameters, such as fuel type; solvent and annealing temperature, on their electrical properties. Fully combustion solution-processed indium-free AlO_x/ZTO TFTs using ethanol as solvent were successfully produced demonstrating extremely promising performance for electronic applications.

2. Experimental details

2.1. Precursor solution preparation and characterization

The preparation of all precursor solutions was performed in a similar manner. Typically, the metal salts were dissolved in 25 mL of solvent, either 2-methoxyethanol (2-ME, $C_3H_8O_2$, Fluka, 99%), ethanol (C_2H_6O, Merck, 99.5%) or deionized water, to yield solutions with the desired metal ion concentration. Then, the fuel (urea; $CO(NH_2)_2$, Sigma, 98%) and ,if required, the combustion aid (ammonium nitrate; NH_4NO_3, Roth, 98%) were added to the prepared solutions which were maintained under constant stirring until complete dissolution. The urea to metal nitrate molar proportion was determined by the Jain method, as described in Section 1.1, to guarantee the redox stoichiometry of the reaction for each material; namely 1.6:1 for Zn^{2+} metal ions and 2.5:1 for In^{3+} and Al^{3+} metal ions. In the case of metal chloride precursors, a combustion aid is required and the molar proportion of metal ion:NH_4NO_3:urea used was 1:1:1 for tin chloride solutions.

Semiconductor ZTO precursor solutions were prepared by mixing zinc oxide and tin oxide precursor solutions in a 2:1 proportion. Zinc oxide precursor solution was prepared as described earlier in 2-methoxyethanol or ethanol to yield solutions with 0.05 M concentration. Tin oxide precursor solutions were prepared by mixing tin chloride ($SnCl_2 \cdot 2H_2O$, Sigma, 98%), urea and ammonium nitrate to yield solutions with 0.05 M concentration. Individual solutions were magnetically stirred for 12 h before ZTO solution preparation.

Dielectric aluminium oxide precursor solutions were prepared by dissolving aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, Fluka, 98%) and urea in 2-methoxyethanol, ethanol or water, to yield solutions with 0.1 M concentration. Prior to their use, all solutions where magnetically stirred for at least 15 min and filtrated through a 0.45 μm hydrophilic filter. All reagents were used without further purification.

Thermal characterization of precursor solutions was performed by thermogravimetry and differential scanning calorimetry (TG-DSC). TG-DSC analyses were performed on precursors dried for 12 h at 80°C under air atmosphere up to 550°C with a 10°C/min heating rate in an aluminium crucible using a Simultaneous Thermal Analyzer, Netzsch (TGA-DSC—STA 449 F3 Jupiter).

2.2. Thin-film deposition and characterization

Prior to deposition all substrates (silicon wafer and soda-lime glass) were cleaned in an ultrasonic bath at 60°C in acetone for 15 min, then in 2-isopropanol for 15 min. and dried under N_2; followed by a 30 min. UV/Ozone surface activation step using a PSD-UV Novascan system. Thin films were deposited by spin coating the precursor solutions at 2000 rpm for 35 s (Laurell Technologies) followed by an immediate hotplate annealing in ambient conditions; this procedure was repeated to obtain the desired thickness.

The films' structure was assessed by glancing angle X-ray diffraction (GAXRD) performed by an X'Pert PRO PANalytical powder diffractometer using with Cu Kα line radiation

(λ = 1.540598 Å) with angle of incidence of the X-ray beam fixed at 0.9°. The surface morphology was investigated by atomic force microscopy (AFM, Asylum MFP3D) and scanning electron microscopy (SEM-FIB, Zeiss Auriga Crossbeam microscope). Cross section of produced films and devices was performed by focussed ion beam (FIB). In FIB milling experiments, Ga^+ ions were accelerated to 30 kV at 5 pA and the etching depth was around 250 nm. Spectroscopic ellipsometry measurements of thin films deposited on silicon substrates were made over an energy range of 1.5–6.0 eV with an incident angle of 70° using a Jobin Yvon Uvisel system to determine film thickness.

2.3. Electronic device fabrication and characterization

Metal-insulator-semiconductor (MIS) capacitors were produced by AlO_x thin-film deposition onto p-type silicon substrates (1–10 Ω cm) as described earlier (see section 2.2). Aluminium gate electrodes (100 nm thick) with an area of 8.7 × 10^{-3} cm^2 were deposited by thermal evaporation via shadow mask. A 100-nm-thick aluminium film was also deposited on the back of the silicon wafer to improve electrical contact. Electrical characterization was performed measuring both the capacitance-voltage and capacitance-frequency characteristics in the range off 10 kHz to 1 MHz of the devices using a semiconductor characterization system (Keithley 4200SCS).

Thin-film transistors (TFTs) were produced in a staggered bottom-gate, top-contact structure by depositing AlO_x thin films onto p-type silicon substrates (1–10 Ω cm) as described earlier. The semiconductor layer was deposited by sequentially spin coating four layers of semiconductor precursor solution 0.05 M onto the AlO_x thin films and annealed in air at 350°C for 30 min after each layer deposition. For comparison, AlO_x/IGZO TFTs were also produced with sputtered IGZO thin films. IGZO thin films were fabricated in a AJA ATC-1300F sputtering system using a IGZO target with 2:1:1 composition (in In_2O_3:Ga_2O_3:ZnO molar ratio). Deposition was carried out in Ar+O_2 atmosphere at a pressure of 2.3 mTorr and r.f. power of 100 W, to obtain a 30 nm thick film. Post-processing annealing was performed in air on a hotplate at 180°C for 1 h. Finally, source and drain aluminium electrodes (100 nm thick) were deposited by e-beam evaporation via shadow mask onto annealed films, defining a channel width (W) and length (L) of 1400 µm and 10 µm, respectively (W/L = 14). Electrical characterization was performed by the measurement of current-voltage characteristics of the devices using a semiconductor parameter analyser (Agilent 4155C) attached to a microprobe station (Cascade M150) inside a dark box, at room temperature. The saturation mobility (μ_{SAT}) was determined from the following equation: [18]

$$I_D = \left(\frac{C_i W \mu_{SAT}}{2L} \right)(V_G - V_T)^2 \tag{5}$$

where C_i is the gate dielectric capacitance per unit area, W and L are the channel width and length, V_G is the gate voltage and V_T is the threshold voltage, which was determined in the saturation region by linear fitting of a $I_D^{1/2}$ vs. V_G plot.

3. Results

The core of oxide-based electronics for displays applications are thin-film transistors (TFTs). **Figure 1** shows a schematic representation of a TFT structure and respective transfer plot. TFTs are three terminal field-effect devices, whose working principle relies on the modulation of the current flowing in a semiconductor placed between two electrodes (source and drain). A dielectric layer is inserted between the semiconductor and a transversal electrode (gate), being the current modulation achieved by the capacitive injection of carriers close to the dielectric/semiconductor interface, known as field effect [12].
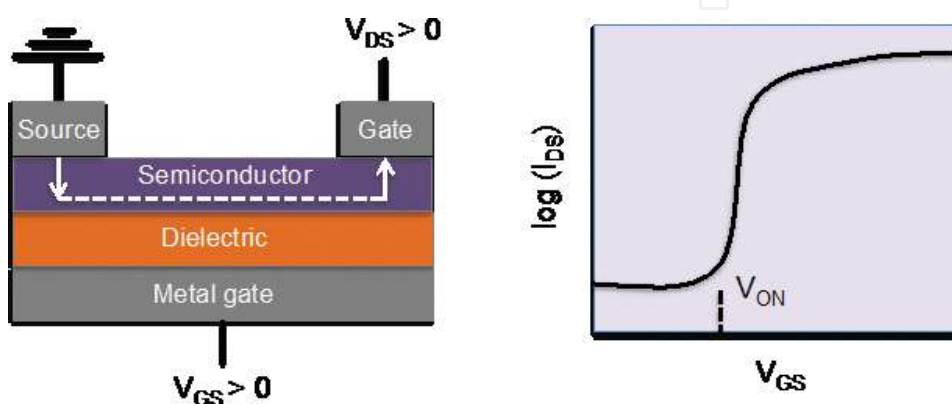
Figure 1. Schematic representation of a bottom-gate TFT structure and typical field effect electrical characteristics plot.

The semiconductor and gate insulator are equally important material components in field-effect transistors; consequently, the development of both materials by solution techniques is essential [6].
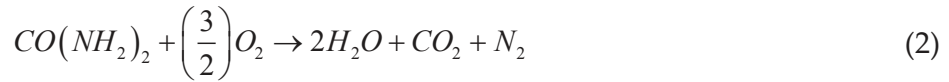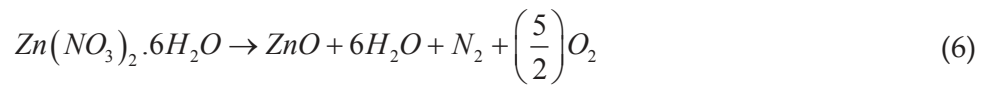
3.1. Amorphous semiconductor oxides

Amorphous oxide semiconductors (AOSs) have drawn significant attention in the field of flat panel displays during the last decade, due to their high carrier mobility when compared to amorphous silicon (a-Si). Indium-gallium-zinc oxide (IGZO) is the most explored semiconductor due to its superior field effect mobility and enhanced electrical performance [11, 12]. However, alternative semiconductor materials that rely on abundant and non-toxic elements are required due to environmental demands. Zinc-tin-oxide (ZTO) is a promising indium and gallium-free alternative and impressive results have already been obtained in TFTs applications [19, 20].

Several solution-processed ZTO-based TFTs have been reported; however, processing temperature above 400°C and a toxic organic solvent, such as acetonitrile, 2-ethoxyethanol or 2-methoxyethanol are usually required [5]. The use of non-toxic solvents has been pursued and ethanol [5] and water [7] based ZTO TFTs have already been reported.

The decomposition of urea [Eq. (2)] and zinc nitrate [Eq. (6)] is represented as follows.
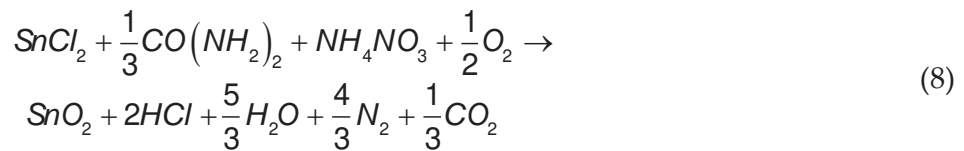
$$Zn(NO_3)_2 \cdot 6H_2O \rightarrow ZnO + 6H_2O + N_2 + \left(\frac{5}{2}\right)O_2 \tag{6}$$

$$CO(NH_2)_2 + \left(\frac{3}{2}\right)O_2 \rightarrow 2H_2O + CO_2 + N_2 \tag{2}$$

The overall ZnO formation reaction can thus be written as follows Eq. (7).

$$\begin{aligned} 3Zn(NO_3)_2 \cdot 6H_2O + 5CO(NH_2)_2 \rightarrow \\ 3ZnO + 28H_2O + 8N_2 + 5CO_2 \end{aligned} \tag{7}$$
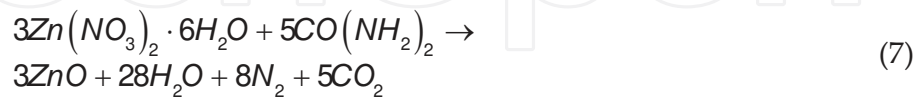
Using the Jain method, the reducing valence of urea is +6 and the oxidizing valence of zinc nitrate is −10. In order to assure the redox stoichiometry 5/3 (or 1.6), moles of urea are required per mole of zinc nitrate.

The tin oxide formation can be represented by the following equation:

$$\begin{aligned} SnCl_2 + \frac{1}{3}CO(NH_2)_2 + NH_4NO_3 + \frac{1}{2}O_2 \rightarrow \\ SnO_2 + 2HCl + \frac{5}{3}H_2O + \frac{4}{3}N_2 + \frac{1}{3}CO_2 \end{aligned} \tag{8}$$

In the combustion synthesis of tin oxide, a combustion aid, ammonium nitrate, was added to the precursor solution as commonly performed for chlorine-based metal salts. According to Jain's method, the oxidizer valence of ammonium nitrate (NH_4NO_3) is −2 and to achieve $\Phi = 1$ 0.3 mol of urea per mole of ammonium nitrate are required. In this case, a fuel-rich condition, $\Phi > 1$, was used to ensure the full oxidation of the metal precursor.

ZTO precursor solution was prepared after mixing individual of zinc and tin oxide precursor solutions of 0.05 M concentration in a 2:1 proportion, respectively. Thermal analysis of ZTO precursor solutions was performed to investigate the influence of solvent on their decomposition behaviour. TG-DSC measurements were performed on precursors dried for 12 h at 80°C. **Figure 2** shows the DSC results for ZTO precursors up to 350°C as above this temperature no further events were observed.

The combustion reaction of the organic fuel with the metal nitrates typically leads to an intense exothermic peak with corresponding abrupt mass loss. For ZTO precursors, these were observed at 125°C and 108°C for 2-ME and ethanol-based solutions, respectively. A smaller peak is observed at 275°C which can be related to secondary reactions [3, 4] that can occur during thermal decomposition of the reagents.
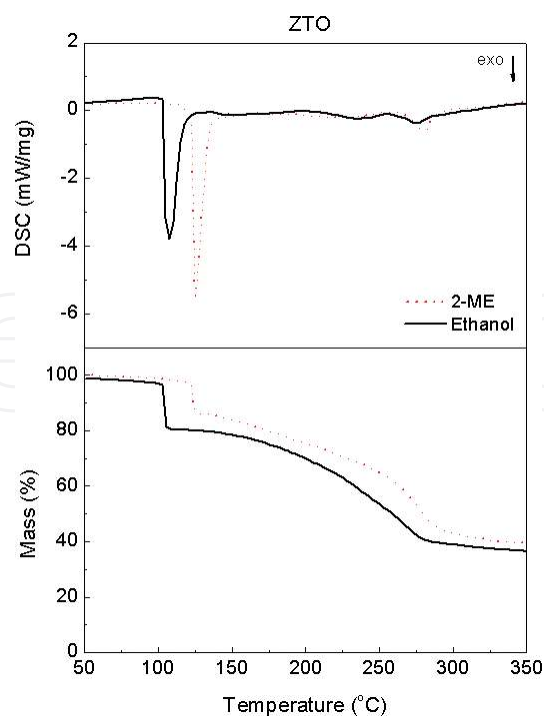
Figure 2. TG-DSC analysis of ZTO-based precursor solutions using 2-methoxyethanol (2-ME) and ethanol as solvent. Adapted from [5].

The precursor solution degradation mechanism is expected to be different in bulk and thin-film form which explains the need for higher thin-film processing temperature than the one determined by thermal analysis. Devices annealed at temperatures below 350°C did not show effective gate modulation as such, the processing temperature was fixed at this temperature although the minimum temperature required for full degradation of the precursors is 275°C.

Structural characterization of the films (**Figure 3a**) indicates that amorphous films are obtained up to 350°C for both precursor solution solvents, as no diffraction peaks were observed. Morphological surface analysis show that smooth and uniform films are obtained regardless
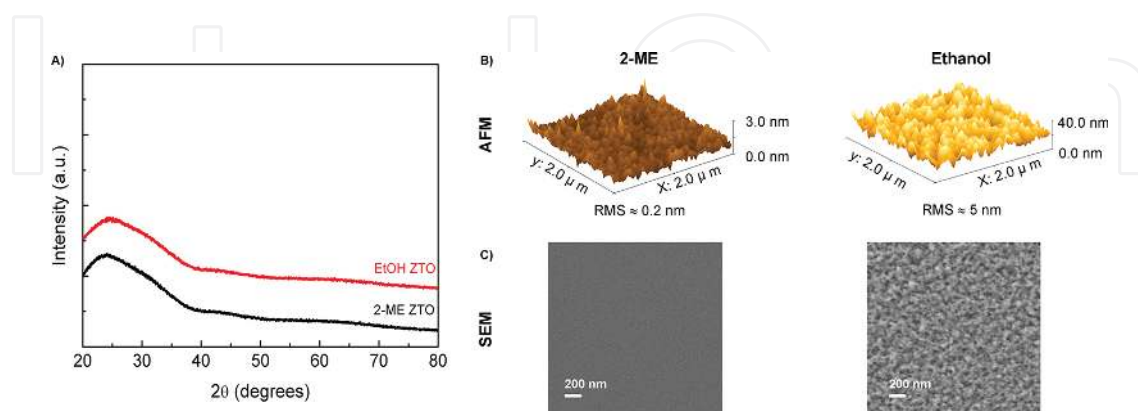
Figure 3. Structural and morphological analysis of 2-methoxyethanol (2-ME) and ethanol-based ZTO thin films produced at 350°C: a) XRD, b) AFM, c) SEM.

of solvent; however, 2-ME-based ZTO films demonstrate a lower surface roughness, 0.2 nm, when compared to ethanol-based films; 5 nm.

Combustion solution-based ZTO TFTs were produced by spin-coating precursor solutions onto commercial Si/SiO_2 substrates. Electrical characterization of TFTs was performed by measuring the transfer and output characteristics of the devices in ambient conditions in the dark. **Figure 4** shows a cross section SEM image of ZTO TFTs produced on Si/SiO_2, with Al source-drain electrodes, obtained after FIB milling and electrical characterization of 2-ME and ethanol-based ZTO TFTs.
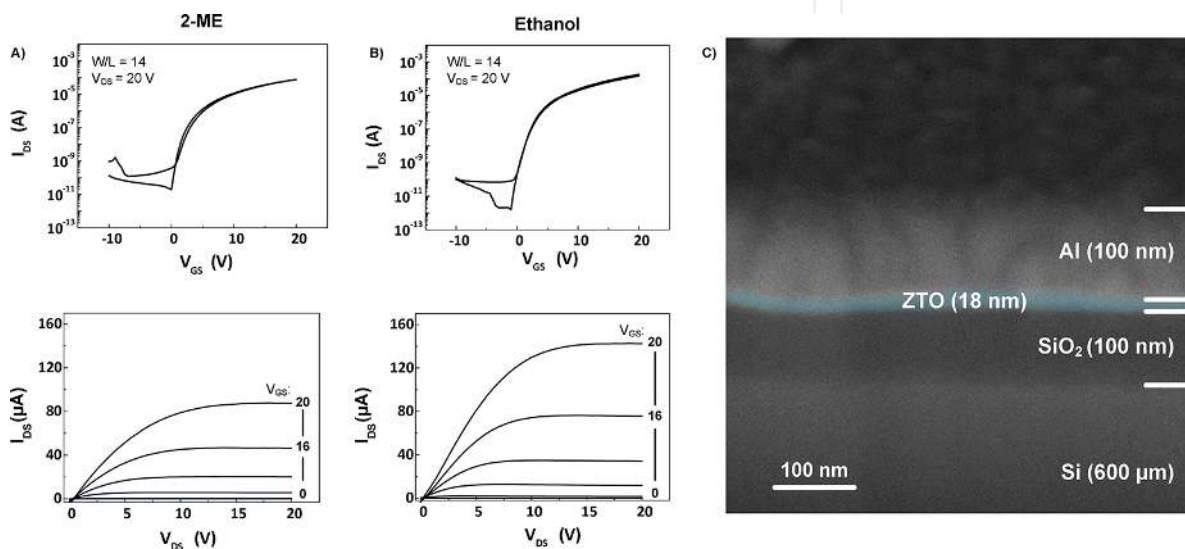
Figure 4. Electrical and morphological characterization of ZTO/SiO_2 TFTs produced at 350°C: transfer and output characteristics of a) 2-methoxyethanol (2-ME) and b) ethanol-based ZTO/SiO_2 TFTs. c) SEM-FIB cross section of a ZTO/SiO_2 TFT.

The analysis of the electrical characteristics reveals that ZTO TFTs show an I_{on}/I_{off} above 10^6, saturation mobility of 2 cm^2/V·s, low subthreshold swing and low hysteresis. Output characteristics exhibit saturation suggesting a low background carrier concentration and anticipate the absence of transconductance degradation as V_{GS} increases, revealing good dielectric/semiconductor interface properties and no significant carrier injection problems. These devices exhibit high operational stability under positive gate bias stress [21]. Combustion synthesis-based ZTO thin films thus demonstrate high potential for alternative and environmental friendly solution-based electronic applications, allowing their use as reliable switching elements in active matrices.

3.2. Dielectric oxides

Insulator materials suitable for TFT gate dielectric applications must fulfil some criteria, namely i) high bang gap, with favourable conduction band offset to avoid high gate leakage; ii) high dielectric constant (high-κ) the added capacitance can compensate interface traps, thus

improving the transistor performance and allow low operating voltage; iii) good interface properties, which can be achieved using amorphous dielectrics [11, 22, 23].

Solution-based high-κ dielectrics, such as Al_2O_3, HfO_2, ZrO_2, have demonstrated high performance and suitability for the application in metal oxide semiconductor-based TFTs [5, 6, 17, 24–28]. Amongst these, aluminium oxide is one of the most developed materials from solution synthesis since several aluminium precursors salts are readily availability at low cost. The influence of processing parameters on the solution combustion synthesis of aluminium oxide was studied.

The decomposition reactions for aluminium, urea and the overall aluminium oxide formation reaction are already represented by Eq. (1), (2) and (3), respectively. According to Jain's method and to ensure redox stoichiometry, 2.5 mol of urea per mole of aluminium nitrate were used to prepare aluminium oxide precursor solutions with 0.1 M concentration. The influence of several processing parameters such as fuel, solvent and annealing temperature on the properties of dielectric AlO_x thin films was studied.

Thermal analysis of AlO_x precursor solutions was performed to investigate the influence of solvent on their decomposition behaviour. **Figure 5** shows the DSC results for AlO_x precursors prepared with 2-methoxethanol, ethanol and water.
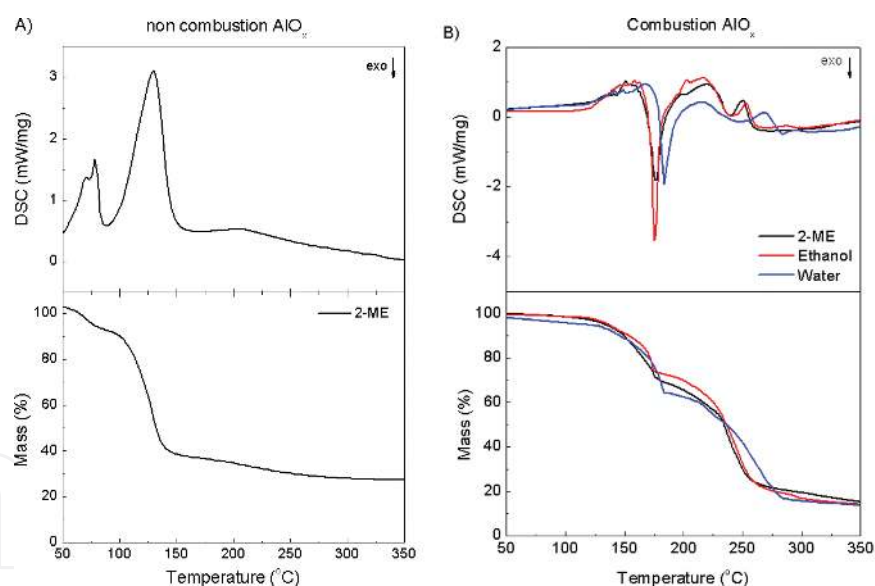

Figure 5. TG-DSC analysis of AlO_x-based precursor solutions: a) non-combustion AlO_x precursor using 2-methoxyethanol (2-ME) and b) combustion AlO_x precursor using 2-ME, ethanol and water as solvent.

Thermal behaviour of AlO_x precursor solutions is strongly affected by the presence of urea, which acts as fuel; when no fuel is added only endothermic peaks corresponding to solvent evaporation (water at 95°C and 2-methoxyethanol at 125°C) which is the main component of the solution with a corresponding 60% mass loss and subsequent organics decomposition (235°C) are observed, meaning that additional energy must be supplied to promote oxide formation. On the other hand, when urea is added in a stoichiometric proportion an intense

exothermic peak with corresponding abrupt mass loss at about 180°C is observed. This exothermic event is attributed to the combustion reaction of the organic fuel with the metal nitrates; a smaller peak at 250°C is also observed and can be related to the degradation of residual organics. Thermal behaviour of combustion AlO_x precursor solutions does not shown significant variations when using different solvents. The influence of solvent in the oxide formation reaction is apparently more significant for multicomponent oxides, such as ZTO (**Figure 2**).

Thin films of AlO_x were produced by spin-coating precursor solution onto a substrate (either soda-lime glass or Si) and annealing on a hotplate for 30 min. The influence of several processing parameters on the structural and morphological properties of dielectric AlO_x thin films obtained from 0.1 M concentration solutions was studied. XRD, SEM and AFM characterization of the AlO_x thin films was performed and **Figure 6** shows typical data obtained for AlO_x thin films produced at 350°C from 2-methoxyethanol, ethanol and water-based precursor solutions.
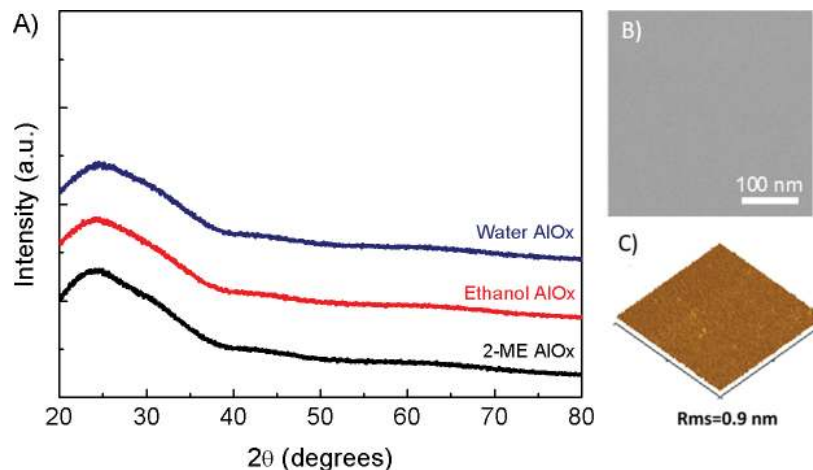

Figure 6. Structural and morphological analysis of combustion solution AlO_x thin films produced at 350°C: a) XRD, b) SEM and c) AFM of water-based films. Inset show gate current density.

Generally, structural and morphological properties of AlO_x thin films did not vary significantly regardless of processing parameters within the studied range. The variation of precursor solution's solvent does not influence the structural properties of the films, which is in agreement with that observed for DSC measurements. Morphological properties are slightly influenced by the solvent used with rms film roughness increasing from 0.3 nm when using 2ME or ethanol to 0.9 nm for water-based films. Fuel content and annealing temperature also do not affect structural and morphological properties as amorphous, highly uniform and smooth AlO_x thin films with rms roughness of below 1 nm were consistently obtained at 350°C. The properties demonstrated by these aluminium oxide thin films produced from solution synthesis are highly desirable for electronic applications as low surface roughness leads to enhanced interface properties.

The effect of processing parameters on the electrical properties of these films was studied by assessing the electrical performance of capacitors and thin-film transistors comprising the solution-based AlO_x films.

Solution-based AlO_x capacitors were produced by spin-coating AlO_x precursor solutions onto commercial Si substrates followed by aluminium gate contact deposition by thermal evaporation. The effect of processing parameters on the electrical performance of these devices was studied and **Figure 7** shows capacitance-voltage measurements for different fuel, using either urea, citric acid or no fuel; and annealing temperature, 350, 250 and 200°C. The effect of precursor solution solvent variation has already been reported elsewhere [6].
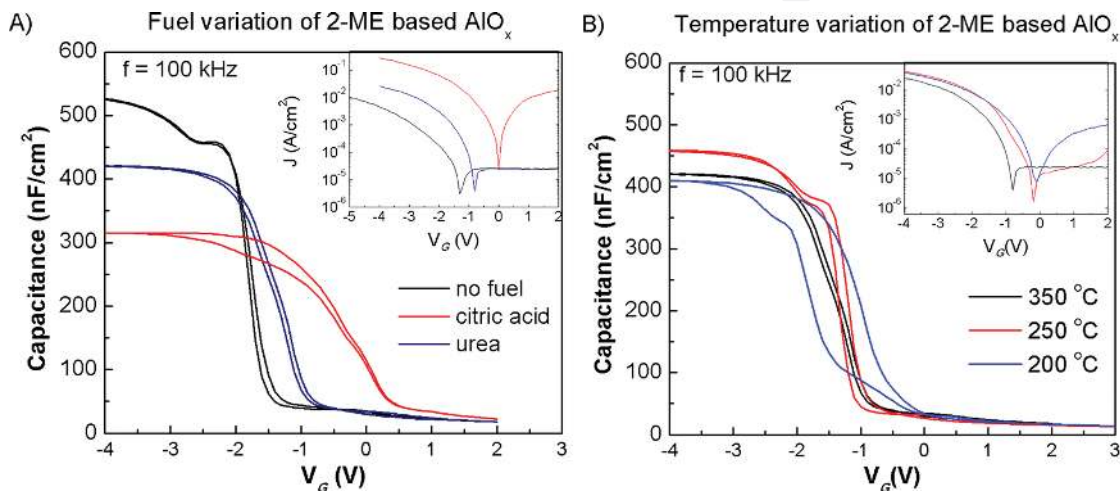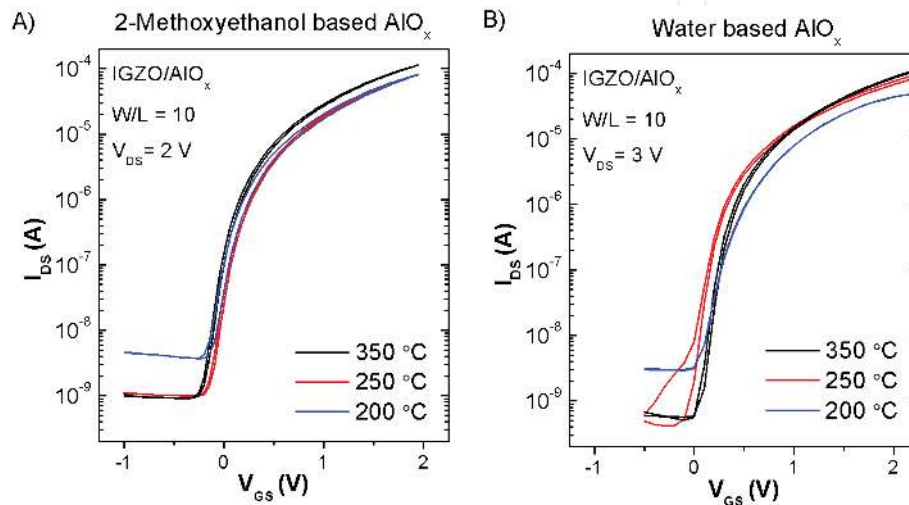

Figure 7. Electrical characterization of AlO_x capacitors produced with different parameters: a) fuel variation in 2-ME; b) temperature variation for 2-methoxyethanol-based films. Inset show gate current density.

The electrical characteristics of AlO_x capacitors produced with no fuel show a non-uniform capacitance variation at −3 to −2 V indicating the presence of organic residues within the film such as nitrate groups; these ions favour water adsorption leading to higher capacitance due to the high dielectric constant of water, as previously observed [6, 29]. To improve film properties, when a non-combustion synthesis route is applied, either higher temperature or UV-assisted annealing is currently being used [26, 30]. When citric acid is added as fuel low capacitance and high current density is observed, this is consistent with more porous AlO_x films and in fact their application as gate dielectric in TFTs was not successful as only short-circuited devices were obtained. Urea leads to consistent one domain capacitance characteristics and low current density within TFT operating voltage range as required for gate dielectric applications. The film properties are highly affected by processing temperature due to inefficient organics removal; at 250°C a two domain system is obtained, similar to that observed for non-combustion synthesis route, and at 200°C large hysteresis indicates an increase in charge defects concentration consistent with organic impurities within the film. Although from DSC analysis, the ignition temperature of AlO_x combustion reaction was determined to be 180°C, still higher temperature is required to obtain thin films with desirable dielectric properties. This inconsistency between thermal analysis and electrical properties obtained at

low temperature is attributed to the difference between bulk and film decomposition processes.

IGZO TFTs comprising combustion solution-based AlOₓ gate dielectric were produced by sputtering IGZO semiconductor layer onto annealed AlOₓ thin films and finally evaporating aluminium source/drain contacts. The use of a standard sputtered semiconductor allowed the assessment of the TFTs performance variation solely due to the dielectric layer's processing parameters influence. Electrical characterization of TFTs was performed by measuring the electrical characteristics of the devices in ambient conditions in the dark (**Figure 8**).

Figure 8. Electrical characterization of IGZO/AlOₓ TFTs produced at different temperatures using a) 2-methoxyethanol and b) water as solvent.

TFT performance is assessed trough the analysis of the turn-on voltage (V_{ON}), the threshold voltage (V_T), drain current on-off ratio (I_{ON}/I_{OFF}), subthreshold slope (S) and saturation mobility (μ_{SAT}), which was calculated using AlOₓ capacitance at the 10 kHz in order to minimize overestimation. Electrical characteristics of these devices are presented in **Table 1**.

| AlOₓ solvent	Temperature (°C)	V_{ON} (V)	I_{ON}/I_{OFF}	μ_{SAT} cm²/Vs
2-ME	350	−0.36	1×10^5	17.3
	250	−0.30	8×10^4	9.6
	200	−0.25	2×10^4	13.5
Water	350	0	5×10^5	9.2
	250	−0.10	5×10^5	6.9
	200	0	7×10^3	12.9

Table 1. Electrical characteristics of solution-based IGZO/AlOₓ TFTs.

Despite the non-ideal capacitance-voltage characteristics obtained for low-temperature AlOₓ thin films, IGZO/AlOₓ TFTs were successfully produced. Similarly to what is obtained for

capacitors the TFTs performance is highly dependent on annealing temperature. For both solvents used, 2-methoxyethanol and water, enhanced properties are obtained for 350°C and similar trend with temperature variation is observed which is in agreement with DSC-TG analysis. For lower temperatures, a hysteresis increase and on/off current ratio decrease is observed, being more significant for 200°C, due to oxide charge defects within the dielectric as a consequence of incomplete organic residues removal. Nevertheless, successful gate modulation at low operation voltage, due to the higher capacitance achieved with very thin AlO_x films, was obtained for all devices which demonstrated close to zero V_{ON}, high I_{ON}, high saturation mobility and low subthreshold swing as required for electronic applications.

3.3. Fully solution-based oxide TFTs

The realization of printed electronics requires all solution-based devices; consequently, semiconductor and dielectric materials must be combined in TFTs. Fully combustion-solution-based TFTs comprising the developed dielectric and semiconductor materials have been successfully fabricated. **Figure 9** shows transfer characteristics of these devices [5, 6].
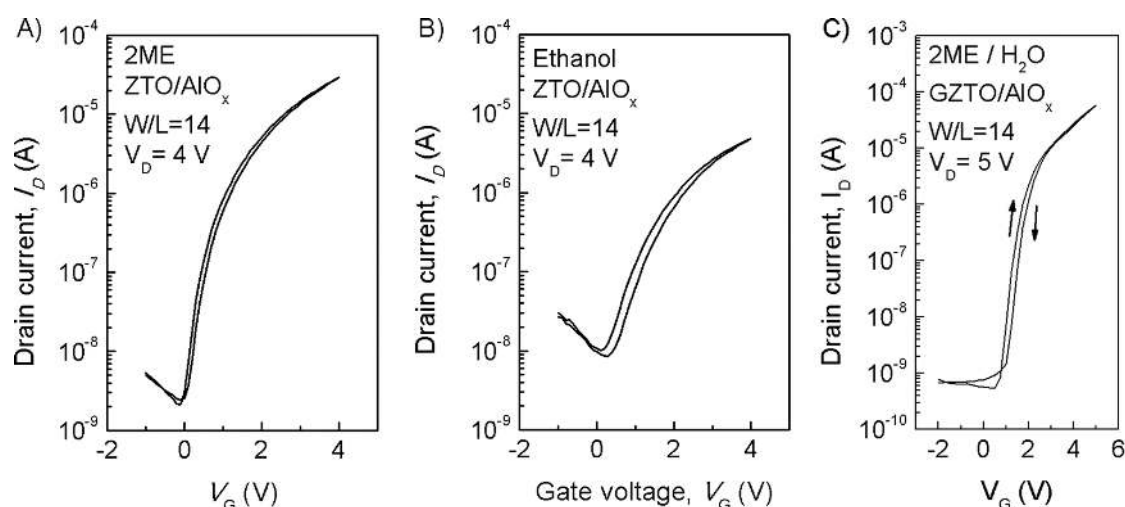
Figure 9. Transfer characteristics of fully combustion solution-based bottom gate TFTs produced at 350°C on highly doped p-Si (gate) with a) 2ME-based ZTO and AlO_x, b) ethanol-based ZTO and AlO_x, and c) 2ME-based GZTO and water-based AlO_x. Adapted from [5, 6].

The combination of solution-processed dielectric and semiconductors yielded TFTs with a good overall performance, demonstrating very low clockwise hysteresis, close to zero V_{ON} and I_{ON}/I_{OFF} above 10^4. Generally, 2ME-based devices show better performance when compared to more environmental friendly ethanol; saturation mobility increases from 0.8 cm²/V·s to 2.3 cm²/V·s for ZTO/AlO_x TFTs, also 2ME GZTO shows μ_{SAT} of 1.3 cm²/V·s when combined with water-based AlO_x. These differences in device performance are attributed to trapped charges at the semiconductor-insulator interface as consequence of the semiconductor films' composition and rougher morphology of ethanol-based films [5, 6]. The high I_{OFF} observed mainly arises from the use of non-patterned semiconductor layers which can be improved by implementing patterning techniques. The combination of AlO_x dielectrics and ZTO-based

semiconductors yielded very promising results for application in fully solution-processed electronics; however, the processing temperature required for good TFT performance was 350°C which is still too high for flexible substrates. Nevertheless, these results are within the state-of-the-art for solution-processed ZTO TFTs using different solvents (**Table 2**).

Ref	Solvent	Gate dielectric	T (°C)	Mobility (cm² V⁻¹ s⁻¹)	I_{ON}/I_{OFF}	V_{ON} (V)
[32]	Acetonitrile	HfO_y/AlO_x	400	3.84	10^5	~ −0.2
[31]	Acetonitrile	ZrO_2	500	~ • 10	10^9	~ −0.3
[33]	Acetonitrile	SiO_2	350	0.30	10^4	~ 5
[20]	Acetonitrile	Si_3N_4	500	7.7	10^8	~ −8
[4]	2-methoxyethanol	SiO_2	225	0.32	10^4	~ −30
			250	1.76	10^7	~ 10
[34]	2-methoxyethanol	SiO_2	450	1.95	10^7	~ −19
[35]	2-methoxyethanol	SiO_2	550	17.02	10^7	~ −4
[5]	2-methoxyethanol	AlO_x	350	2.6	10^4	~ 0
	Ethanol	AlO_x	350	0.8	10^2	~ 0.1
[7]	Water	SiO_2	250	0.12	10^5	~ 5
			300	3.03	10^7	~ −3

Table 2. Selected processing details for reported solution-based ZTO TFTs.
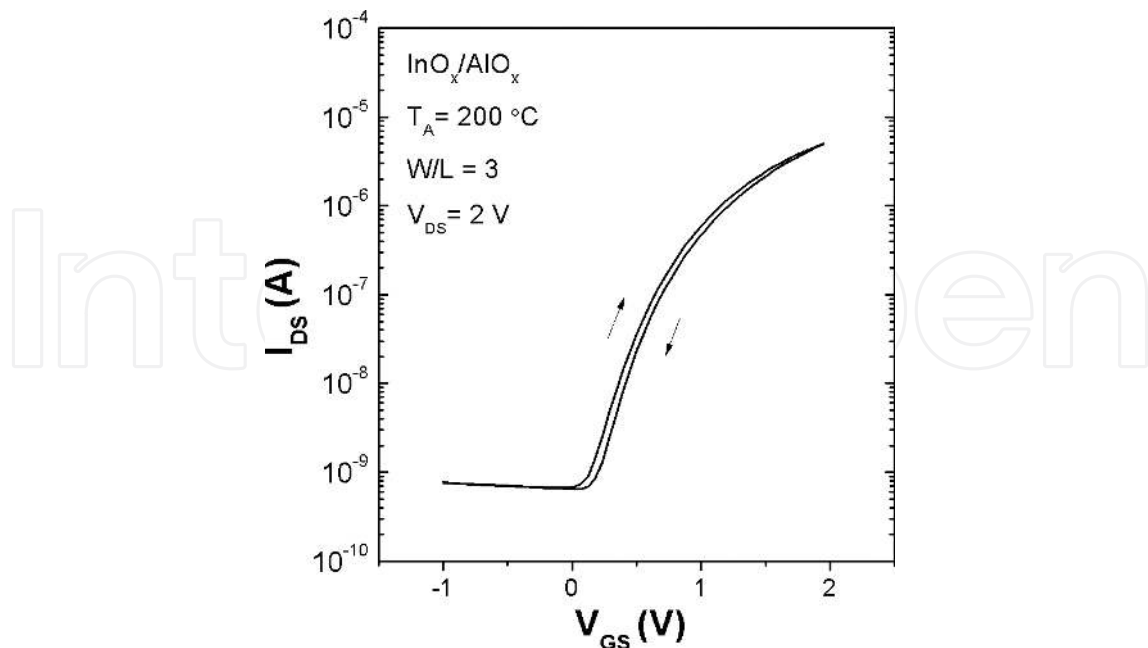
Figure 10. Transfer characteristics of fully combustion-solution-based InO$_x$/AlO$_x$ TFTs produced from 2ME precursors using a maximum processing temperature of 200°C.

The use of indium-free semiconductor materials, such as ZTO and GZTO, although environmentally relevant somehow lead to a compromise of solution-processed TFTs performance both in saturation mobility and processing temperature.

Fully solution-based TFTs were obtained at maximum processing temperature of 200°C when combining the developed 2-methoxyethanol-based AlO_x dielectric with solution-based indium oxide semiconductor produced using UV-assisted low-temperature annealing as reported in [36]. Transfer characteristics of low-temperature InO_x/AlO_x TFTs are depicted in **Figure 10**.

In O_x/AlO_x TFTs showed higher saturation mobility (μ_{SAT} = 5.6 cm^2 V^{-1} s^{-1}) when compared to indium-free devices processed at higher temperatures and otherwise similar electrical performance whilst at the same time being compatible with polymeric substrates for flexible electronics applications.

4. Conclusions

The application of solution combustion synthesis to prepare oxide materials for electronic devices was successfully achieved for dielectric and semiconductor thin films using varied processing parameters. We have clearly demonstrated that dielectric AlO_x thin films can be obtained using green solvents such as ethanol and water and successfully combined with ethanol-based ZTO semiconductor layers to yield fully combustion solution-based TFTs. Although electrical properties of these solution-processed TFTs are still far for what is required in AMTFT displays applications, successful preparation and combination of dielectric and semiconductor oxides films by a relatively low-temperature solution process represents a significant achievement and an advancement towards environmentally friendly production process. The facile applicability of SCS to other metal precursors opens numerous possibilities for low temperature synthesis of oxides materials and thin films required for the development of all solution-based devices. The mechanisms behind precursor degradation/oxide formation process are not yet fully understood so the challenge remains to unravel the ideal combination of solvent, oxidizer and organic fuel to obtain high-quality materials and properties. Nevertheless, this versatile synthesis method combined with innovative low-temperature annealing processes will continue to play a major role in the future development flexible electronics.

Acknowledgements

Author details

Rita Branquinho[*], Ana Santa, Emanuel Carlos, Daniela Salgueiro, Pedro Barquinha, Rodrigo Martins and Elvira Fortunato

*Address all correspondence to: ritasba@fct.unl.pt

i3N/CENIMAT, Department of Materials Science, Faculty of Science and Technology, NOVA University of Lisbon and CEMOP/UNINOVA, Caparica, Portugal

References

[1] M. Epifani, E. Melissano, G. Pace, and M. Schioppa, "Precursors for the combustion synthesis of metal oxides from the sol-gel processing of metal complexes," J. Eur. Ceram. Soc., vol. 27, no. 1, pp. 115–123, 2007.

[2] Z. Shao, W. Zhou, and Z. Zhu, "Advanced synthesis of materials for intermediate-temperature solid oxide fuel cells," Prog. Mater. Sci., vol. 57, no. 4, pp. 804–874, 2012.

[3] S. L. Gonzalez-Cortes and F. E. Imbert, "Fundamentals, properties and applications of solid catalysts prepared by solution combustion synthesis (SCS)," Appl. Catal. A Gen., vol. 452, pp. 117–131, 2013.

[4] M.-G. Kim, M. G. Kanatzidis, A. Facchetti, and T. J. Marks, "Low-temperature fabrication of high-performance metal oxide thin-film electronics via combustion processing," Nat. Mater., vol. 10, no. 5, pp. 382–388, 2011.

[5] R. Branquinho, D. Salgueiro, A. Santa, and A. Kiazadeh, "Towards environmental friendly solution-based ZTO/AlO x TFTs," Semicond. Sci. Technol., vol. 30, no. 2, p. 24007, 2015.

[6] R. Branquinho, D. Salgueiro, L. Santos, P. Barquinha, L. Pereira, R. F. D. P. Martins, and E. Fortunato, "Aqueous combustion synthesis of aluminium oxide thin films and application as gate dielectric in GZTO solution-based TFTs," ACS Appl. Mater. Interfaces, vol. 6, pp. 195592–195599, 2014.

[7] J. H. Park, W. J. Choi, J. Y. Oh, S. S. Chae, W. S. Jang, S. J. Lee, K. M. Song, and H. K. Baik, "Low-temperature, aqueous-solution-processed zinc tin oxide thin film transistor," Jpn. J. Appl. Phys., vol. 50, no. 7, p. 070201, 2011.

[8] S. R. Jain, K. C. Adiga, and V. R. Pai Verneker, "A new approach to thermochemical calculations of condensed fuel-oxidizer mixtures," Combust. Flame, vol. 40, pp. 71–79, 1981.

[9]   E. Fortunato, P. Barquinha, R. Branquinho, D. Salgueiro, E. Carlos, A. Liu, F. K. Shan, and R. Martins, "Is the new oxide electronics (r)evolution solution based?," J. Phys. D Appl. Phys., 2016, in press.

[10] J. F. Wager, "Oxide TFTs: A Progress Report," Inf. Disp. (1975), vol. 32, no. 1, pp. 16–21, 2016.

[11] P. Barquinha, L. Pereira, R. Martins, and E. Fortunato, Transparent Electronics: From Materials to Devices. John Wiley & Sons, Inc., Hoboken, New Jersey, 2012.

[12] E. Fortunato, P. Barquinha, and R. Martins, "Oxide semiconductor thin-film transistors: a review of recent advances," Adv. Mater., vol. 24, no. 22, pp. 2945–2986, 2012.

[13] B. Du Ahn, H.-J. Jeon, J. Sheng, J. Park, and J.-S. Park, "A review on the recent developments of solution processes for oxide thin film transistors," Semicond. Sci. Technol., vol. 30, no. 6, p. 064001, 2015.

[14] Y. H. Kang, S. Jeong, J. M. Ko, J.-Y. Lee, Y. Choi, C. Lee, and S. Y. Cho, "Two-component solution processing of oxide semiconductors for thin-film transistors via self-combustion reaction," J. Mater. Chem. C, vol. 2, no. 21, p. 4247, 2014.

[15] J. W. Hennek, M.-G. Kim, M. G. Kanatzidis, A. Facchetti, and T. J. Marks, "Exploratory combustion synthesis: amorphous indium yttrium oxide for thin-film transistors," J. Am. Chem. Soc., vol. 134, no. 23, pp. 9593–9596, 2012.

[16] J. W. Hennek, J. Smith, A. Yan, M.-G. Kim, W. Zhao, V. P. Dravid, A. Facchetti, and T. J. Marks, "Oxygen getter" effects on microstructure and carrier transport in low temperature combustion-processed a-InXZnO (X = Ga, Sc, Y, La) transistors," J. Am. Chem. Soc., vol. 135, no. 29, pp. 10729–10741, 2013.

[17] E. J. Bae, Y. H. Kang, M. Han, C. Lee, and S. Y. Cho, "Soluble oxide gate dielectrics prepared using the self-combustion reaction for high-performance thin-film transistors," J. Mater. Chem. C, vol. 2, no. 28, pp. 5695–5703, 2014.

[18] D. K. Schroder, Semiconductor Material and Device Characterization, 3rd ed. John Wiley & Sons, Inc., Hoboken, New Jersey, 2006.

[19] J. S. Lee, Y.-J. Kwack, W.-S. Choi, and C. Woon-Seop, "Low-temperature solution-processed zinc-tin-oxide thin-film transistor and its stability," J. Korean Phys. Soc., vol. 59, no. 5, p. 3055, 2011.

[20] R. D. Chandra, M. Rao, K. Zhang, R. R. Prabhakar, C. Shi, J. Zhang, S. G. Mhaisalkar, and N. Mathews, "Tuning electrical properties in amorphous zinc tin oxide thin films for solution processed electronics." ACS Appl. Mater. Interfaces, vol. 6, no. 2, pp. 773–7, 2014.

[21] A. Kiazadeh, D. Salgueiro, R. Branquinho, J. Pinto, H. L. Gomes, P. Barquinha, R. Martins, and E. Fortunato, "Operational stability of solution based zinc tin oxide/SiO2 thin film transistors under gate bias stress," APL Mater., vol. 3, no. 6, p. 062804, 2015.

[22] L. Pereira, P. Barquinha, E. Fortunato, R. Martins, D. Kang, C. J. Kim, H. Lim, I. Song, and Y. Park, "High k dielectrics for low temperature electronics," Thin Solid Films, vol. 516, no. 7, pp. 1544–1548, 2008.

[23] P. Barquinha, L. Pereira, G. Gonçalves, R. Martins, E. Fortunato, D. Kuscer, M. Kosec, A. Vilà, A. Olziersky, and J. R. Morante, "Low-temperature sputtered mixtures of high κ and high bandgap dielectrics for GIZO TFTs," J. Soc. Inf. Disp., vol. 18, no. 10, pp. 762–772, 2010.

[24] Y. B. Yoo, J. H. Park, K. H. Lee, H. W. Lee, K. M. Song, S. J. Lee, and H. K. Baik, "Solution-processed high-k HfO2 gate dielectric processed under softening temperature of polymer substrates," J. Mater. Chem. C, vol. 1, no. 8, p. 1651, 2013.

[25] J. Ko, J. Kim, S. Y. Park, E. Lee, K. Kim, K.-H. Lim, and Y. S. Kim, "Solution-processed amorphous hafnium-lanthanum oxide gate insulator for oxide thin-film transistors," J. Mater. Chem. C, vol. 2, no. 6, pp. 1050–1056, 2014.

[26] S. Park, K.-H. Kim, J.-W. Jo, S. Sung, K.-T. Kim, W.-J. Lee, J. Kim, H. J. Kim, G.-R. Yi, Y.-H. Kim, M.-H. Yoon, and S. K. Park, "In-depth studies on rapid photochemical activation of various sol-gel metal oxide films for flexible transparent electronics," Adv. Funct. Mater., vol. 25, pp. 2807–2815, 2015.

[27] C. Avis and J. Jang, "High-performance solution processed oxide TFT with aluminum oxide gate dielectric fabricated by a sol-gel method," J. Mater. Chem., vol. 21, no. 29, pp. 10649–10652, 2011.

[28] C. Avis, Y. G. Kim, and J. Jang, "Solution processed hafnium oxide as a gate insulator for low-voltage oxide thin-film transistors," J. Mater. Chem., vol. 22, no. 34, p. 17415, 2012.

[29] J. H. Park, K. Kim, Y. B. Yoo, S. Y. Park, K.-H. Lim, K. H. Lee, H. K. Baik, and Y. S. Kim, "Water adsorption effects of nitrate ion coordinated Al2O3 dielectric for high performance metal-oxide thin-film transistor," J. Mater. Chem. C, vol. 1, no. 43, pp. 7166–7174, 2013.

[30] Y.-H. Kim, J.-S. Heo, T.-H. Kim, S. K. Park, M.-H. Yoon, J. Kim, M. S. Oh, G.-R. Yi, Y.-Y. Noh, and S. K. Park, "Flexible metal-oxide devices made by room-temperature photochemical activation of sol-gel films," Nature, vol. 489, no. 7414, pp. 128–132, 2012.

[31] T.-J. Ha and A. Dodabalapur, "Photo stability of solution-processed low-voltage high mobility zinc-tin-oxide/ZrO2 thin-film transistors for transparent display applications," Appl. Phys. Lett., vol. 102, no. 12, p. 123506, 2013.

[32] Y. G. Kim, C. Avis, and J. Jang, "Low voltage driven, stable solution-processed zinc-tin-oxide TFT with HfOy and AlOx stack gate dielectric," ECS Solid State Lett., vol. 1, no. 2, pp. Q23–Q25, 2012.

[33] J.-S. Lee, S.-M. Song, D.-W. Kang, Y.-H. Kim, J.-Y. Kwon, and M.-K. Han, "Effects of ultra-violet treatment on electrical characteristics of solution-processed oxide thin-film transistors," ECS Trans., vol. 50, no. 8, pp. 121–127, 2013.

[34] W. Hu and R. L. Peterson, "Charge transport in solution-processed zinc tin oxide thin film transistors," J. Mater. Res., vol. 27, no. 17, pp. 2286–2292, 2012.

[35] C. Kim, N.-H. Lee, Y.-K. Kwon, and B. Kang, "Effects of film thickness and Sn concentration on electrical properties of solution-processed zinc tin oxide thin film transistors," Thin Solid Films, vol. 544, pp. 129–133, 2013.

[36] J. Leppäniemi, H. Majumdar, K. Ojanperä, T. Kololuoma, J. Dahl, M. Tuominen, P. Laukkanen, and A. Alastalo, "Rapid low-temperature processing of metal-oxide thin film transistors with combined far ultraviolet and thermal annealing," Appl. Phys. Lett., vol. 113514, pp. 1–10, 2014.