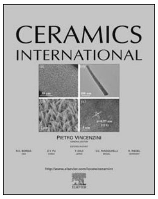
Ceramics International (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint



# Fully solution-processed metal oxide thin-film transistors via a low-temperature aqueous route

Wangying Xu[a,*], Mingzhu Long[b], Tiankai Zhang[b], Lingyan Liang[c], Hongtao Cao[c], Deliang Zhu[a], Jian-Bin Xu[b,*]

[a] Guangdong Research Center for Interfacial Engineering of Functional Materials, Shenzhen Key Laboratory of Special Functional Materials, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China

[b] Department of Electronic Engineering, Materials Science and Technology Research Center, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

[c] Division of Functional Materials and Nano Devices, Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Ningbo, China

## ARTICLE INFO

*Keywords:*
Solution-processed
Metal oxide thin-film transistors
Low-temperature
Aqueous route

## ABSTRACT

We report a facile and low-temperature aqueous route for the fabrication of various oxide thin films ($Al_2O_3$, $In_2O_3$ and InZnO). A detail study is carried out to reveal the formation and properties of these sol-gel-derived thin films. The results show that the water-based oxide thin films undergo the decomposition of nitrate group as well as conversion of metal hydroxides to form metal oxide framework. High quality oxide thin film could be achieved at low temperature by this aqueous route. Furthermore, these oxide thin films are integrated to form thin-film transistors (TFTs) and the electrical performance is systematically studied. In particular, we successfully demonstrate $In_2O_3/Al_2O_3$ TFTs with high mobility of 30.88 $cm^2 V^{-1} s^{-1}$ and low operation voltage of 4 V at a maximum processing temperature of 250 °C.

## 1. Introduction

Metal oxide semiconductors have attracted enormous attention in the area of active matrix devices such as liquid crystal displays (LCDs) and organic light-emitting diodes (OLEDs) because of their high mobility, good transparency to visible light, good uniformity and reasonable electrical stability [1–4]. Besides, the solution processes have been developed due to the possibility of low-cost and large-area fabrication without using vacuum deposition techniques [5–12].

Despite the substantial benefits and strong potential of the solution-based technique, the high-temperature annealing step is inevitable for oxidation and impurity removal in the solution process. Many researchers have attempted to develop low-temperature annealing processes for solution-processed oxide semiconductors. These approaches include sol-gel on chip [9], combustion process [8], photochemical activation [10], and annealing in an $O_2/O_3$ atmospheric environment [11]. Unfortunately, among most of the studies, toxic organic solvents such as 2-methoxyethanol (2-ME) were used, which will cause health risks and environmental hazards. Recently, a facile, novel and inexpensive ‘aqueous route’ has been proposed for the fabrication of $In_2O_3$-based thin-film transistors (TFTs) at low annealing temperature ( $< 250$ °C) [12]. This aqueous route makes significant contributions in terms of environmental protection and low temperature process [13–19].

On the other hand, most of these oxide TFTs were integrated with conventional $SiO_2$ dielectric and thus operated at high operating voltages ( $> 10$ V), which inhibit their applications in low power portable electronics. To overcome this bottleneck, various approaches have been explored to achieve large areal-capacitance dielectric [1–4,20]. Among these, the use of solution-processed high-*k* oxide dielectrics is the most attractive option as it enables the low leakage current, the low-voltage operation and the ease process integration with solution-processed oxide semiconductors. A few promising results on solution-processed oxide dielectrics have been reported, including $Al_2O_3$, $ZrO_2$, $La_2O_3$ and $Y_2O_3$ [20–37]. Among the various high-*k* dielectrics, $Al_2O_3$ is an excellent candidate, due to its abundance in nature, low cost, good chemical stability, relatively high dielectric constant, wide energy bandgap, smooth amorphous surface, and low interfacial trap density at the interface between the dielectric and active channel layers of oxide semiconductors [13,19,20,22,24,27–30]. However, the high annealing temperature ( $> 350$ °C) and multiple spin-coating processes ( $> 5$ times) inhibit their use for low-cost and large-scale flexible electronics. Encouraged by the success of aqueous route on $In_2O_3$-based oxide semiconductor, this technique may be

---

* Corresponding authors.
*E-mail addresses:* wyxu@szu.edu.cn (W. Xu), jbxu@ee.cuhk.edu.hk (J.-B. Xu).

http://dx.doi.org/10.1016/j.ceramint.2017.02.007
Received 19 November 2016; Received in revised form 4 January 2017; Accepted 1 February 2017

Please cite this article as: Xu, W., Ceramics International (2017), http://dx.doi.org/10.1016/j.ceramint.2017.02.007

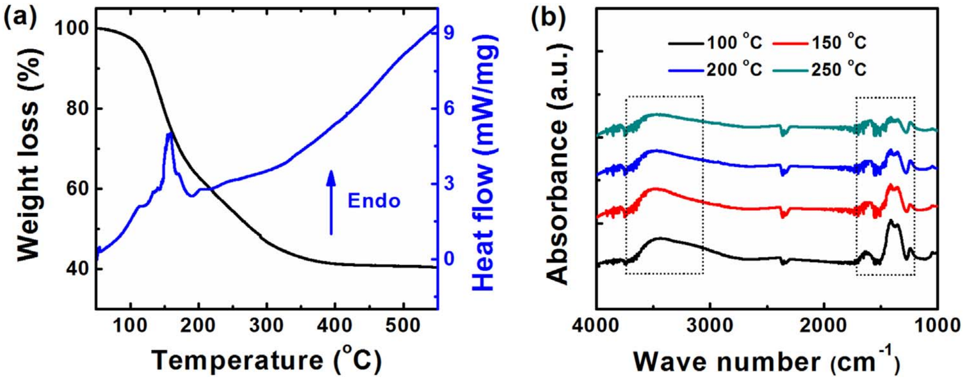


**Fig. 1.** (a) TG and DSC curves of $Al_2O_3$ precursor powder from 50 to 550 °C. (b) ATR-FTIR spectra of $Al_2O_3$ films annealed at indicated temperatures.

applicable to fabricate $Al_2O_3$ dielectrics at low temperature. Furthermore, the combination of aqueous-deposited high-*k* $Al_2O_3$ and $In_2O_3$-based oxide semiconductor may achieve fully solution-processed low-temperature oxide TFTs.

In this article, we reported on the fabrication of $Al_2O_3$, $In_2O_3$ and InZnO thin films using water as solvent by single-step spin-coated process. The formation and properties of aqueous solution-based oxide thin films were systematically investigated. Besides, the electrical performance of fully solution-processed oxide TFTs was studied in detail. In particular, the $In_2O_3/Al_2O_3$ TFTs annealed at 200 and 250 °C showed good mobilities of 2.04 and 30.88 $cm^2\ V^{-1}\ s^{-1}$ at low operation voltage of 4 V.

## 2. Experimental section

### 2.1. Precursor preparation

All chemicals were purchased from Sigma-Aldrich and used as received. The $Al_2O_3$ precursor solution was prepared by dissolving about 2.5 M aluminum nitrate hydrate ($Al(NO_3)_3 \cdot xH_2O$) in water. For the $In_2O_3$ solution, 0.15 M indium nitrate hydrate ($In(NO_3)_3 \cdot xH_2O$) was dissolved in water. For the InZnO solution, 0.1 M indium nitrate hydrate ($In(NO_3)_3 \cdot xH_2O$) and 0.05 M zinc nitrate hydrate ($Zn(NO_3)_2 \cdot xH_2O$) were mixed with water. All the precursors are fully dissolved in water since the nitrate salts show very good solubility in water. The picture of the solutions could be seen in Fig. S1. The solutions were filtered through 0.45 μm polyethersulfone (PES) syringe filters before spin coating.

### 2.2. Devices fabrications

Heavily doped Si substrates were exposed to oxygen plasma for 10 min to enhance the hydrophilicity before spin coating. The $Al_2O_3$ precursor solution was spun onto the substrate at 4500 rmp for 40 s and annealed at a selected temperature (100, 150, 200 and 250 °C) under ambient atmosphere for 1 h. For the metal-insulator-metal (MIM) devices, an Al electrode (100 nm) was deposited on the dielectric layer by thermal evaporation. The area of the circular Al electrode was 0.03 $mm^2$. To fabricate the TFTs with a bottom-gate top-contact configuration, the $In_2O_3$ and InZnO films were then spun onto the $Al_2O_3$ gate dielectric at 3000 rmp for 20 s and annealed at desired temperature (150, 200, and 250 °C) for 1 h to achieve thickness of about 10 nm. Subsequently, the Al source and drain top electrodes (100 nm) were deposited by thermal evaporation through the shadow mask. The channel width ($W$) and length ($L$) were 1500 and 100 μm, respectively. The large $W/L$ ratio over 15 in this work could efficiently limit mobility overestimation as suggested by previous studies [20,28].

### 2.3. Film and device characterization

The thermal behavior of the precursor powders, which were dried at 105 °C for 12 h, were measured by thermogravimetric analyzer (PerkinElmer, TGA 6) and differential scanning calorimeter (PerkinElmer, DSC 7) at a heating rate of 10 °C/min from 50 to 550 °C. The crystallization and structural information of the sol-gel derived thin films were obtained using *x*-ray diffraction (XRD, Sienmens D5005) with Cu $K_\alpha$ radiation. The chemical characteristics of the thin films were investigated by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Bruker Tensor 27) and *x*-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB 250). The thicknesses of the thin films were measured via a variable-angle spectroscopic ellipsometer (SE, J. A. Woollam Co., Inc.). The surface morphologies of the solution-processed films were observed by atomic force microscopy (AFM, Veeco Dimension V). The frequency-dependent capacitance characteristics of the dielectrics were performed using a HP 4284 A in a frequency range of 20–1 MHz. The leakage of the oxide dielectric films and the electrical characteristics of the TFTs were measured with a precision semiconductor analyzer (Keithley 4200) in the dark at room temperature. Threshold voltage ($V_{th}$) was extracted from measurements in the saturation region by plotting $(I_{DS})^{1/2}$ vs. $V_{GS}$ and extrapolating to $I_{DS}=0$ plots. The mobility ($\mu$) and subthreshold swing ($S$) were calculated by the following formulas:

$$I_{DS} = \left(\frac{\mu C_i W}{2L}\right)(V_{GS} - V_{th})^2$$

$$S = \left(\frac{d(\log_{10} I_{DS})}{dV_{GS}}\right)^{-1}$$

where $C_i$, $W$ and $L$ are the capacitance of the gate dielectrics per unit area, channel width and channel length, respectively.

## 3. Results and discussion

### 3.1. Fabrication and characterization of $Al_2O_3$ film

Fig. 1(a) displays the TG-DSC of $Al_2O_3$ precursor powder from 50 to 550 °C. An endothermic peak accompanying a small weight loss was observed at 113 °C, which could be attributed to the evaporation of solvent and/or the hydrolysis of the metal precursor [23]. The peak at 160 °C indicated the dehydroxylation behavior of the hydrolyzed metal hydroxide, which reacted with adjacent metal hydroxide molecules and formed metal oxide lattices [14,23,30]. Another peak at 204 °C could be related to the decomposition of residual nitrate [14,23,30].

To investigate the formation of the solution-deposited $Al_2O_3$, ATR-FTIR measurements were carried out, and the results are shown in Fig. 1(b). The broad peaks in the range of 3000–3500 $cm^{-1}$ could be