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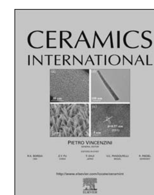

# Electrical and chemical stability engineering of solution-processed indium zinc oxide thin film transistors via a synergistic approach of annealing duration and self-combustion process

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ABSTRACT

The electrical and chemical stability of solution-processed indium zinc oxide (IZO) channel thin-film transistors (TFTs) were engineered via a synergistic approach of annealing duration and self-combustion process. In particular, the amorphous IZO TFTs that were thermally treated at 400 °C for 3 h using the specific precursor combination to generate internal self-combustion energy showed the best electrical performance [high saturation mobility ($\mu_{SAT}$)=2.7 cm$^2$/V s] and stability [low threshold voltage shift ($\Delta V_{TH}$) under positive bias stress of 10.5 V] owing to the formation of oxide films with excellent metal–oxide–metal (M–O–M) bonds, fewer impurities, and an amorphous phase compared to IZO TFTs using other precursor formulas and annealing times. Longer annealing times led to a saturated M–O bond ratio and crystallization via extreme thermal annealing, which induced electrical degradation (low $\mu_{SAT}$ and high $\Delta V_{TH}$) of IZO TFTs. In the wet chemical patterning of electrodes, conventional acidic and basic wet etchants cause severe damage to the surfaces of the IZO channels; thus, insufficiently annealed IZO TFTs exhibited considerable degradation in terms of their on-current level and mobility. Alternatively, the TFTs subjected to an excessively long-term thermal annealing showed only a moderate decrease in mobility with the formation of small nanocrystals.

## 1. Introduction

Zn-incorporated ternary and quaternary oxide semiconductors are promising channel candidates for thin-film transistors (TFTs) for driving and switching device applications in next-generation displays owing to their excellent electrical mobility and low off-current. However, their insufficient electrical and chemical stability are main impediments to realizing long-term stable operation and industrial integration of TFT devices in practical displays [1–5]. Through concentrated endeavors over the last ten years, vacuum-processed oxide TFTs have been fabricated that could ensure high electrical performance and stability by engineering oxygen-vacancy [6,7], hydrogen [8], and weak metal oxide bonds [9] of the oxide channel/gate-insulator interfaces and oxide back-channel regions. However, vacuum-based processes (sputtering and atomic layer deposition) require complex vacuum systems and limited deposition space with a vacuum atmosphere, which hinders cost efficiency and mass production for practical display fields [10].

The current focus for the development of oxide channels is based on simple, cost-efficient, atmospheric solution processes (sol–gel, spray, ink-jet, and printing methods). However, solution-processed oxide films suffer from inferior electrical performance and serious electrical/chemical instability due to incomplete chemical transformation from the metal precursors. In particular, Zn-based oxides are susceptible to conventional acidic and basic wet etchants, and solution-processed oxides include more defect sites (weakly bonded M-O-M networks and precursor-related impurities) than vacuum-deposited oxide films. As a result, solution-processed Zn-based oxide semiconductors experience severe chemical ionization on the oxide back-channel during the TFT circuit integration process using conventional acidic and basic wet etchants [11,12]. Thus, solution-processed Zn-based oxide TFTs have been fabricated with source/drain electrodes using chemical damage-free shadow mask-and-lift-off processes [13,14], instead of the wet chemical etchants that are usually used in vacuum-deposited oxide TFTs. To ensure superior electrical properties (performance and stability) and chemical stability, high quality oxide

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channel layers with well-linked metal-oxygen-metal (M-O-M) networks and low impurity contents should be formed via an effective chemical reaction route [15–20]. The sequential chemical reaction for sol-gel film formation is performed via the synergistic procedure of chemical activation energy and chemical reaction time. The sol-gel processed oxide TFTs were primarily explored to accomplish chemical activation energy reduction and high electrical mobility [15,16]. In contrast, annealing duration (chemical reaction time) for sol-gel processed oxide films has seldom been explored in contrast to annealing temperature (chemical reaction energy term) [21–23].

In terms of chemical activation energy, a huge energy budget on high temperatures and excessive oxidative gas at high pressure are required to supply sufficient chemical reaction energy to form well-linked M-O-M networks. However, epochal sol-gel processes (volatile nitrate precursor, combustion reaction, aqueous route, and photochemical activation) were introduced to make high-quality solution-processed oxide films with minimum external energy consumption [24–27]. Instead of convention metal precursors (with acetate or chloride ligands), volatile nitrate- and combustion-based metal precursors have been demonstrated to decrease the chemical activation energy [28–30]. In particular, combustion-processed sol-gel Zn-based films (InZnO, ZnSnO, and InGaZnO)—which supplement the external fuels (acetylacetonate or urea) and oxidizers (nitrate) in the precursor mixing solution (metal precursor + solvent)—could dramatically reduce the chemical activation energy with an internal exothermic combustion reaction and improve electrical mobility. Additionally, a more facile and reproducible self-combination process using the precursor mixing solution including fuel and oxidizer inside individual metal precursors (zinc acetylacetonate + indium nitrate) was developed for sol-gel processed ternary InZnO films with high saturation mobility ($\mu_{SAT}$: 8 $cm^2/Vs$) [31]. They indicate that chemical activation energy for sol-gel oxide film formation depends on the precursor-ligand formula. In contrast, in terms of chemical reaction time, only some studies on annealing time control were performed for sol–gel processed oxide films. Furthermore, they still paid attention to enhanced electrical mobility and low-temperature processing (chemical activation energy reduction) without considering superior electrical/chemical stability [21–23]. It is expected that prolonged annealing will provide sufficient chemical reaction time for sol-gel film formation and produce excellent M–O–M networks with minimal charge trap sites, which will improve electrical performance and electrical/chemical stability. Generally, thermal annealing of solution-processed oxide films has been performed for less than 3 h, regardless of metal precursor formula (Fig. S1) [21,24–26,31–33,41].

In this study, we engineered the electrical/chemical stability of solution-processed IZO films via the synergistic approach of annealing duration (chemical reaction time term) and self-combustion process (chemical activation energy term). To make oxide films with high electrical/chemical stability with minimal external energy consumption (chemical activation energy), solution-processed IZO films using various combinations of metal precursors were produced with a short annealing time (1 h). Chemical bond states and microstructures of the sol-gel processed IZO films were engineered with prolonged annealing time to realize solution-processed oxide TFT circuit integration with excellent electrical stability and wet-etched electrodes.

## 2. Experimental details

### 2.1. Preparation and characterization of the IZO precursor solutions

Various IZO films were produced via the sol-gel process using the same indium precursor and three types of zinc precursors. A conventionally derived IZO precursor was prepared using zinc acetate dihydrate [$Zn(C_2H_3O_2)_2 \cdot 2H_2O$, ≥98%; Sigma-Aldrich] and indium nitrate hydrate [$In(NO_3)_3 \cdot xH_2O$, ≥99%; Sigma-Aldrich]. A self-combustion-based IZO precursor was prepared using zinc acetylacetonate hydrate [$Zn(C_5H_7O_2)_2 \cdot xH_2O$, ≥99%; Sigma-Aldrich] and indium nitrate hydrate [$In(NO_3)_3 \cdot xH_2O$, ≥99%; Sigma-Aldrich]. A volatile nitrate-based IZO precursor was synthesized using zinc nitrate hydrate [$Zn(NO_3)_3 \cdot xH_2O$, ≥99%; Sigma-Aldrich] and indium nitrate hydrate [$In(NO_3)_3 \cdot xH_2O$, ≥99%; Sigma-Aldrich]. The molar ratio of In:Zn in the precursor solutions was 5:5, and the molar concentration of the IZO precursors was 0.1 M. After the metal salts were dissolved in 2-ME [$CH_3OCH_2CH_2OH$, ≥99%; Sigma-Aldrich], the precursor solutions were vigorously stirred at 400 rpm for 12 h at room temperature to form homogeneous and transparent solutions. The precursor solutions were filtered through a 0.2 µm syringe filter. Each of the IZO precursor solutions was spin coated at 3000 rpm for 30 s on a heavily doped $p^{++}$-Si wafer with a 200-nm-thick $SiO_2$ layer. The spin-coated IZO precursor solutions were soft baked at 200 °C for 10 min to promote the hydrolysis of the metal precursor to form M–OH bonds. Then, hard baking was performed at 400 °C for different durations on a hot plate in air to engineer the electrically and chemically stable solution-processed IZO films.

### 2.2. Fabrication of solution-processed IZO TFTs

The annealing time in the hard baking step was varied from 1 to 7 h to ensure the optimal electrical and chemical properties of the IZO thin films. To confirm the electrical stability of sol–gel IZO TFTs with bottom-gate and top-contact structures, the source and drain electrodes (100 nm thick, Al) were thermally evaporated using a chemical damage-free metal shadow mask process. A constant positive gate bias ($V_{GS}$ =20 V) was continuously applied to each device for 7.2 ks in the dark. Next, the back-channel etched *a*-IZO TFTs were fabricated with wet chemical-etched Mo electrodes to verify the chemical durability of the sol–gel IZO films (annealing time of 1–7 h). The Mo (100 nm) electrodes were deposited through sputtering as source/drain electrodes with the W/L dimension of 500/50 µm via a wet etching process. Then, the Mo electrodes were wet-chemical etched without Mo oxide residues in a $H_2O_2$-based wet etchant (comprising mainly hydrogen peroxide with sulfuric acid and several hydrogen peroxide stabilizers). A reference *a*-IZO TFT was fabricated using the conventional Mo lift-off process for comparison.

### 2.3. Characterization of the IZO precursor solutions, films, and TFTs

Thermal analyses of IZO precursor solutions were carried out under an air atmosphere at a heating rate of 5 °C/min up to 600 °C via thermogravimetric (TG) and differential thermal analysis (DTA) (Seiko Exstar 6000) to identify the subsequent chemical reaction route from the precursor solutions to IZO films. The film thicknesses and porosities were measured with a spectroscopic ellipsometer (SE MG-1000UV). The relative film porosity of the IZO layers was determined from the refractive index using the Lorentz–Lorenz relation [9,11].

$$\text{Porosity(volume) \%} = \left\{1-\left[\left(\frac{n^2-1}{n^2+2}\right)\times\left(\frac{n_0{}^2+2}{n_0{}^2-1}\right)\right]\right\}\times 100 \tag{1}$$

where $n$ is the measured refractive index of the IZO film and $n_O$ is the refractive index of the dense $(ZnO)_5In_2O_3$ film ($n_0$=2.0). Angle-resolved X-ray photoelectron spectroscopy (AR-XPS, Theta Probe, Thermo Fisher Scientific Co.) with an Al-$K_\alpha$ excitation source at 1486.6 eV was used to characterize the surface chemical bonding of the *a*-IZO thin films.

The electrical characteristics of the fabricated IZO TFTs were measured in the dark at room temperature using a semiconductor parameter analyzer (HP-4145B). The transfer curves of IZO TFTs were measured with gate voltages ($V_{GS}$) from −30 to 40 V and a drain voltage ($V_{DS}$) of 10 V. The threshold voltage ($V_{Th}$) was defined as the specific $V_{GS}$ value with a drain current ($I_{DS}$) of L/W ×10 nA. The saturation mobility ($\mu_{SAT}$) and sub-threshold swing (S.S.) values were extracted

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