Amorphous In–Ga–Zn Oxide Semiconducting Thin Films with High Mobility from Electrochemically Generated Aqueous Nanocluster Inks

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1. INTRODUCTION

Amorphous oxide semiconductors (AOSs) have high mobilities, large band gaps, and visible light transparency and are thus attractive for use in many current and emerging optoelectronic devices.1–5 They have been utilized as active channel materials for TFTs in many technological applications, such as flat panel displays and active matrix liquid crystal displays.6,7 Indium–gallium–zinc oxide (IGZO) is a promising candidate because of its high carrier mobility and tunable carrier concentration.5,9 Typically, IGZO films are deposited using vacuum techniques, including sputtering8,11 and pulsed laser deposition.8,12 In contrast, solution methods allow deposition of thin films in air. The ability to achieve excellent uniformity over large areas suggests a path to simple, scalable, and low-cost alternatives to vacuum deposition.5,13–19

The most-common solution approach to deposit IGZO and related thin films is to use organic solvents with a “sol–gel” type process.13,20–29 These approaches typically require relatively high temperature annealing to achieve reasonable mobilities. Alternative routes have been explored to deposit IGZO from solution with lower processing temperatures, for example, on flexible plastic substrates, while achieving comparable device performance. Hwang and co-workers studied simple In and Zn nitrate salts dissolved in water as precursors for indium oxide (IO) and indium zinc oxide (IZO) films.30 They suggest that the hexaquo ions formed spontaneously by In nitrate in water are good precursors due to the ease at which they can be thermally cross-linked to form an oxide. Kim and co-workers suggested that process temperatures can be lowered by using “self-energy generating combustion chemistry” associated with oxidation of urea or acetylacetone by nitrate during heating.15 Photochemical

ABSTRACT: Solution processing is a scalable means of depositing large-area electronics for applications in displays, sensors, smart windows, and photovoltaics. However, solution routes typically yield films with electronic quality inferior to traditional vacuum deposition, as the solution precursors contain excess organic ligands, counterions, and/or solvent that leads to porosity in the final film. We show that electrolysis of aq. mixed metal nitrate salt solutions drives the formation of indium gallium zinc oxide (IGZO) precursor solutions, without purification, that consist of ~1 nm radii metal–hydroxo clusters, minimal nitrate counterions, and no organic ligands. Films deposited from cluster precursors over a wide range of composition are smooth (roughness of 0.24 nm), homogeneous, dense (80% of crystalline phase), and crack-free. The transistor performance of IGZO films deposited from electrochemically synthesized clusters is compared to those from the starting nitrate salt solution, sol–gel precursor solutions, and no organic ligands. Films deposited from cluster precursors over a wide range of composition are smooth (roughness of 0.24 nm), homogeneous, dense (80% of crystalline phase), and crack-free. The transistor performance of IGZO films deposited from electrochemically synthesized clusters is compared to those from the starting nitrate salt solution, sol–gel precursor solutions, and, as a control, vacuum-sputter-deposited films. The average channel mobility ($\mu_{AVE}$) of air-annealed cluster films (In:Ga:Zn = 69:12:19) at 400 °C was ~9 cm$^2$ V$^{-1}$ s$^{-1}$, whereas those of control nitrate salt and sol–gel precursor films were ~5 and ~2 cm$^2$ V$^{-1}$ s$^{-1}$, respectively. By incorporating an ultrathin indium–tin–zinc oxide interface layer prior to IGZO film deposition and air-annealing at 550 °C, a $\mu_{AVE}$ of ~30 cm$^2$ V$^{-1}$ s$^{-1}$ was achieved, exceeding that of sputtered IGZO control films. These data show that electrochemically derived cluster precursors yield films that are structurally and electrically superior to those deposited from metal nitrate salt and related organic sol–gel precursor solutions and approach the quality of sputtered films.
activation using deep UV irradiation also promotes film formation from \( \text{In, Ga, Zn} \) nitrate salts at temperatures near 150 °C.\(^{31} \) Banger et al. showed that mobilities > 10 cm² V⁻¹ s⁻¹ can be achieved using a “sol–gel on a chip” process, whereby metal alkoxide films are cast from alcohol under an inert atmosphere and then annealed at ~250 °C under water vapor to drive hydrolysis and cross-linking to form the semiconductor films.\(^{16,19} \) Despite these advances, achieving high-performance films via solution processing remains challenging. The precursor solutions contain organic solvents, organic stabilizing ligands, and/or counterions, which often result in porous films after calcination, negatively affecting device performance.\(^{32} \) New precursor chemistries are important to provide simple, scalable routes to films with electrical performance rivaling those obtained by vacuum sputtering.

An ideal solution precursor might be characterized by the following attributes: (1) high solubility (≥1 M) in so-called “green” solvents like water (or, e.g., ethanol), enabling tunable thickness via changing the precursor concentration; (2) minimal counterions and no organic ligands that ultimately must be removed; (3) no crystallization of the precursor upon solvent removal, minimizing film roughness; (4) stability in solution; and (5) readily cross-linkable after spin-coating to yield dense films with mild heating.\(^{33} \) Inks of aqueous (aq.) inorganic clusters\(^{34}−39 \) and other molecular inorganic precursors\(^{35,36,40}−42 \) with fewer counterions (compared to simple salts) and no organic ligands have recently been developed for depositing high-quality thin films. The films have electrical properties in many cases comparable to those deposited using vacuum techniques.\(^{40,41} \) In particular, the group 13 nanoscale clusters have been explored for use in thin-film semiconductor\(^{42} \) and dielectric\(^{43} \) applications. Recently, we reported the electrochemical synthesis of \( \text{Ga}_x \text{In}_{1-x} \) clusters and subsequent deposition of IGO films using these clusters as an aq. precursor ink.\(^{44} \) While these films displayed a uniform morphology from TEM studies, they demonstrated only a moderate channel mobility of ∼5 cm² V⁻¹ s⁻¹ as active channel layers in TFTs, in contrast to the >10 cm² V⁻¹ s⁻¹ of conventional amorphous oxide films of similar compositions via vacuum deposition.\(^{9} \)

A further shortcoming associated with previous work optimizing solution-processed films is in the lack of standardized comparison to sputtered materials that have been processed in a comparable manner. This is important because the electrical performance is strongly affected by the metal composition ratio, dielectric–semiconductor interface, and annealing conditions.

Here, we report the electrochemical synthesis of aq. \( \text{In–Ga–Zn} \) precursor solutions which contain metal–oxo clusters with a radius of 0.8–1.0 nm, low nitrate counterion content, and no organic ligands. The resulting clusters were used as precursor inks for deposition of amorphous transparent IGZO thin films. We compare the electrical properties of IGZO films derived from these clusters against those of nominally identical composition and device processing conditions obtained from sputtering and competing solution processes. The TFTs derived from electrochemically generated cluster precursors exhibited better average channel mobility \( (\mu_{\text{AVE}}) \) values than those obtained from the starting nitrate salts or a standard sol–gel recipe. However, the \( \mu_{\text{AVE}} \) of the TFTs made using cluster films as an active channel layer was one-third of that obtained from sputtered films with similar compositions. The cluster films also showed a turn-on voltage \( (V_{\text{ON}}) \) of ~20 V, compared to sputtered films with a \( V_{\text{ON}} \) of ~0 V. The incorporation of an ultrathin indium tin oxide (ITZO) interface layer\(^{21} \) prior to cluster-derived IGZO deposition yielded an improvement in electrical properties, displaying a \( V_{\text{ON}} \) of ~5 V and a \( \mu_{\text{AVE}} \) of ~30 cm² V⁻¹ s⁻¹, more than twice that of sputtered IGZO films, demonstrating the important role of the interface in determining channel mobility. The reported electrochemical synthesis thus allows for the development of aq. solution precursors to enable a variety of functional mixed-metal-oxide conducting/semiconducting films.

### 2.1. Precursor Synthesis and Characterization

\( \text{In(NO}_3)_3, \text{Ga(NO}_3)_3 \), and Zn(NO₃)₂ (Sigma-Aldrich) were dissolved with the desired molar ratios in 18.2 M 2-cm H₂O in order to achieve a total metal concentration of 0.5 M, referred to as the starting nitrate salt solution. Prior to use, these nitrate salt precursors were calcined at 700 °C for 8 h in order to determine their water content. The \( \text{In:Ga:Zn} \) molar ratios reported here for the films are those of the starting salt solution. A Pt mesh working electrode with a surface area of ~80 cm², a Pt counter electrode enclosed in a porous glass frit, and an Ag/AgCl(sat.) reference electrode were placed in 30 mL of the starting salt solution. A Bio-Logic SP-200 potentiostat was used to apply a constant voltage of −0.49 V vs Ag/AgCl(sat.) at the working electrode, and the solution was rapidly stirred. Solution aliquots were removed before the constant voltage was applied and after either 60 and 120 min of electrochemistry or 60 and 75 min of electrochemistry in the case of In-rich solutions. The pH of these aliquots was measured (IQ Scientific Instrument 280GB), and each aliquot was used directly without purification as a solution precursor for spin-coating IGZO thin films. The solution aliquots were also passed through 0.1 μm pore filters to remove dust particles and then transferred to a cuvette. Dynamic light scattering (DLS, Mbiouis Wyatt Technology) was used to characterize these solutions with 532 nm laser excitation at room temperature.

“Sol–gel” control precursors were prepared, in an identical method to that reported by Street et al.\(^{20} \) \( \text{In(NO}_3)_3, \text{Ga(NO}_3)_3 \), and Zn(NO₃)₂ were dissolved with the desired molar ratios in a 25:1 (v:v) solution of 2-methoxyethanol and monoethanolamine to provide a total metal concentration of 0.5 M. Solutions were then sonicated (Branson 1510) until the metal salts completely dissolved.

The precursor for ITZO interface layers was made as described by Rim and co-workers.\(^{22} \) A 0.03 M ITZO solution was prepared by dissolving a 9:1:1 molar ratio of \( \text{In(NO}_3)_3, \text{SnCl}_2, \) and \( \text{Zn(O}_2\text{CCH}_3)_2 \) in 2-methoxyethanol. The resulting solution was stirred at room temperature for 1 h to yield a transparent and homogenou solution.

### 2.2. Thin-Film Deposition

\( \text{Si (SUMCO Corporation), Au/Ti-coated QCM} \) crystals (Stanford Research Systems), and 100 nm thermally grown \( \text{SiO}_2 \) on p⁺-Si (η ~ 0.007 Ω cm) were used as substrates. Si substrates were cleaned by sonication in a 6.25% (v:v) solution of Conrad 70 detergent (Decon Laboratories) and 18.2 M 2-cm H₂O for 1 h at 60 °C. Au/Ti-coated QCM crystals were cleaned by oxygen plasma treatment for 15 min. The transistor substrates (100 nm thermally grown \( \text{SiO}_2 \) on p⁺-Si) were cleaned in a 70 °C 1:1 (v:v) solution of conc. aq. H₂SO₄ and H₂O₂ for 10 min, followed by a 15 min oxygen plasma treatment. The precursor solutions were passed through a 0.45 μm PTFE-45/25 filter prior to deposition. Spin-coating was performed by flooding the substrate surface with precursor solution, then spinning at 1500 rpm for 30 s, followed by spinning at 3000 rpm for 40 s. The resulting films were immediately annealed on a hot plate at 50 °C for 1 min and then at 300 °C for 5 min. The same hot plate annealing conditions were applied between each coat. The samples were then annealed in either an air or a humid atmosphere at various temperatures (as indicated below) for 2 h after a 2 h ramp-up to the annealing temperature from room temperature. For TFT devices, a single coating step was used to obtain films of approximately 10–16 nm in thickness (see Figure 3a, below). Thicker films of ~50 nm were deposited with three coats for SEM and XRD analyses.
In order to create control devices, TFTs were fabricated by radio frequency (RF) sputtering of an IGZO channel layer onto p'-Si substrates with 100 nm of thermal SiO₂ as the gate dielectric. The sputter deposition was performed with a 2° IGZO target (In:Ga:Zn = 33:33:33) at room temperature with a RF power of 75 W, frequency of 13.56 MHz, Ar/O₂ gas flow of 9/1 sccm, and deposition pressure of 5 mTorr. The film thickness was ~15 nm. The resulting IGZO films were annealed in air for 2 h at the temperatures indicated.

2.3. Morphological, Structural, and Chemical Characterization. The thickness and density of the films were determined using X-ray reflectometry (XRR) with a Bruker D8 Discover. A Zeiss Ultra-55 scanning electron microscope (SEM) was used for imaging of the films at 45° orientation and an accelerating voltage of 5 keV. Atomic force microscopy (AFM) images were collected using a Nanoscope IIIa. A first-order flatten and third-order plane fit were applied prior to the roughness calculation. XRD patterns were collected using a Rigaku RINT-1500 X-ray diffractometer with a Cu Kα source with a grazing angle incidence of 0.5°. Transmission electron microscopy (TEM) analysis was performed using an FEI Titan with a 300 keV accelerating voltage. Films were transferred onto 300 mesh lacey carbon/Cu TEM grids using an FEI Helios NanoLab Dual Beam FIB/SEM (quartz grid). The films were then exposed to a UV light (~365 nm, 13.56 MHz, Ar/O₂ gas flow of 9/1 sccm, and deposition pressure of 5 mTorr). The film thickness was ~15 nm. The resulting IGZO films were annealed in air for 2 h at the temperatures indicated.

2.4. Device Fabrication and Characterization. To fabricate transistors, a heavily boron (p')-doped Si wafer with 100 nm of thermally grown SiO₂ was used as a substrate. The substrates were cleaned using a 3:1 conc. aq. H₂SO₄:H₂O₂ and sequentially treated by acetone and isopropyl alcohol. The substrates were then baked at 175 °C for 15 min to remove the photoresist solvents. The sample was then exposed to a UV light (~17 mW cm⁻²) for 12 s through a mask and subsequently developed using a 1:1 18.2 MΩ·cm H₂O:Microposit-351 developer for 1 min. The TFT channel was patterned by a wet etch process using a conc. HCl for 10 s. Unexposed photoresist was removed with acetone. The sample was then baked at 300 °C for 15 min to remove the photoresistography solvents. Al source and drain electrodes were deposited by thermal evaporation using a metal shadow mask. The Al gate contact was deposited on the back side of the Si gate electrode by thermal evaporation.

In some instances, prior to depositing the IGZO channel, an ITZO interface layer was deposited on the SiO₂/Si by spin-coating. The resulting layer was immediately annealed on a hot plate at 350 °C for 5 min prior to the deposition of a second layer. The same device design procedures were conducted to create TFT devices with ITZO–IGZO heterojunction channels. The output and transfer characteristics of TFTs were measured using an Agilent 4155C semiconductor parameter analyzer. The mobility of the semiconductor channel was extracted from transfer curve measurements, where a gate-to-source bias, VGS, was applied across the gate and source terminals and swept between a range of voltages (i.e., VGS = −60 to 60 V) while the source-to-drain bias, VDS, was held at a constant voltage (VDS = 0.1 V).

As formulated by Hoffman et al.,[47–49] MMAX (which is a function of VGS) can be extracted from a transfer curve when utilizing the following expression

\[
\Delta \text{V}_{\text{TH}} = \frac{G_{\text{f}}}{\frac{C_{\text{g}}}{C_{\text{f}}}} \left[ V_{\text{GS}} - V_{\text{ON}} \right]
\]

where \( G_{\text{f}} = I_{\text{d}}/V_{\text{DS}} \) is the channel conductance (that depends on VGS), \( V_{\text{ON}} \) is the turn-on voltage, and \( C_{\text{g}} \) is the gate insulator capacitance density (34.5 nF cm⁻² for 100 nm of thermally grown SiO₂). For output measurements, the VDS was swept from 0 to 60 V while VGS was kept at a constant.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Synthesis and Solution Characterization. The electrochemical synthesis of the IGZO nanocluster precursor solution is performed in a stirred two-compartment electrochemical cell with a large Pt working electrode driving a reduction current and the Pt counter electrode driving oxidation current behind a glass frist. Figure 1a shows that the solution pH increases over the course of the electrolysis, but does not cross the predominance boundaries of the group 13 metals, as shown by the Pourbaix diagrams in Figure 1a.[50] The pH increase in the working electrode compartment as a function of charge per metal ion for solutions containing different In:Ga:Zn ratios. (b) The pH at the working electrode compartment as a function of charge per metal ion for solutions containing different In:Ga:Zn ratios. (c) Size distributions of IGZO solution nanoclusters as a function of the electrolysis time obtained from DLS. (d) Size distributions of the nanoclusters at various times after the synthesis via electrolysis for 2 h. These clusters are stable for >1 h at room temperature, after which cluster size increases with time due to additional cross-linking.

Figure 1. (a) Potential (E vs NHE)–pH Pourbaix diagrams for In, Ga, and Zn aq. species. Soluble species concentrations = 1 M.[50] (b) The pH at the working electrode compartment as a function of charge per metal ion for solutions containing different In:Ga:Zn ratios. (c) Size distributions of IGZO solution nanoclusters as a function of the electrolysis time obtained from DLS. (d) Size distributions of the nanoclusters at various times after the synthesis via electrolysis for 2 h. These clusters are stable for >1 h at room temperature, after which cluster size increases with time due to additional cross-linking.
observed. Therefore, we assume that \( \text{NO}_3^- \) reduction is the predominant electrochemical reaction at the working electrode compartment, consistent with our previous studies. Reduction of \( \text{NO}_3^- \) can produce a number of species, such as \( \text{HNO}_2, \text{NH}_4^+, \text{and NO}_2^- \), and each of these processes raises the pH by consumption of \( H^+ \) as in eq 2. The decrease in \( H^+ \) and \( \text{NO}_3^- \) drives the formation of clusters as in eq 3.

\[
\text{NO}_3^- + 2e^- + 3H^+ \rightarrow \text{HNO}_2 + H_2O \tag{2}
\]

\[
13M(H_2O)_x(NO_3)_y \leftrightarrow [M_{13}(\mu_3-OH)_6(\mu-OH)_{18}(H_2O)_{24}](NO_3)_{15} + 30H_2O + 24\text{HNO}_3 \tag{3}
\]

The oxidation state of \( \text{Zn} (+2) \) is different than that of group 13 metals (+3). In addition, \( \text{Zn}^{2+} (aq) \) ions are stable for a larger pH window than the group 13 ions, as shown by the Pourbaix diagrams in Figure 1a. For these reasons, the substitution of \( \text{Zn} \) into the cluster seems unlikely (although we cannot rule it out). We hypothesize that electrolysis drives the formation of \( \text{Ga}^- \)-In clusters mixed with \( \text{Zn} \) aquo species. The solutions derived in this way are kinetically stable. Figure 1d shows that, for a solution prepared by 2 h of electrolysis and then left in ambient conditions at room temperature, cluster oligomers/polymers form after 90 min. Increasing the relative concentration of \( \text{In} \) was found to cause electrolyzed solutions to precipitate sooner with time compared to solutions with \( \text{In}:\text{Ga}:\text{Zn} \) near 33:33:33.

3.2. Thin-Film Characterization. Morphology. Figure 2a–h shows scanning electron micrographs of IGZO thin films annealed at 450 °C for 2 h on Si for various compositions and deposition methods. Films deposited from the starting salt solutions exhibit rough surfaces with visible islands. These islands are particularly prevalent in films made with salt solutions with high \( \text{Zn} \) content (e.g., \( \text{In}:\text{Ga}:\text{Zn} = 32:26:42 \)), whereas those with low \( \text{Zn} \) (\( \text{In}:\text{Ga}:\text{Zn} = 41:33:26 \) and 81:6:13) have minimal or no island growth. High-resolution TEM imaging shows that these islands, however, are not \( \text{ZnO} \) but nanocrystalline \( \text{In}_2\text{O}_3 \) (Figure S1). Apparently higher \( \text{Zn} \) concentrations drive the phase segregation of \( \text{In} \), likely upon solvent removal during the initial "soft-baking" process.

In contrast, films deposited using electrochemically synthesized cluster precursors are homogeneous and smooth with minimal or no visible islands on the surface regardless of film composition (Figure 2b,d,e). The lack of island growth is attributed to mixed \( \text{Ga}^-\text{In} \) clusters preventing the phase segregation of \( \text{In}_2\text{O}_3 \) at low temperatures. Films made from cluster precursors are also thicker than those made from the starting salt solutions, likely due to both the increased concentration of the metal cations in the cathode compartment after electrolysis (to balance charge) and the increased solution viscosity caused by the oligomerization of the metal cations. Figure 2g shows a film made using solution from the fritted counter electrode compartment, which has increased nitrate counterions and a lower pH of ~1.3. When used as an active channel layer in TFTs, these films exhibited very poor electrical performance (\( \mu_{\text{AVE}} < 0.01 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \), Figure S3), likely due to increased porosity. A sol–gel method, using 2-methoxyethanol solvent and monoethanolamine stabilizing ligands based on ref 20, was used to deposit control films (Figure 2h).
AFM was used to characterize the smoothness of the various films (Figure S2). The cluster-derived films were remarkably smooth with a root-mean-square roughness of 0.24 nm, substantially better than films from the salt solutions (1.4 nm) and sol−gel (2.3 nm) preparations. The roughness is likely partially caused by the removal of the excess counterions and stabilizing ligands during the annealing process.

**Composition.** Electron probe microanalysis (EPMA) was used to measure the composition of films deposited by the various methods from precursors that nominally contained In:Ga:Zn = 33:33:33 (Table 1). The results show that the relative cation concentrations do not change within error during electrochemical cluster synthesis, allowing for the electrical and structural comparison of films that are made with starting salt solution and cluster precursors. Sputtered films (control samples) were slightly enriched in In (In:Ga:Zn = 37:33:30) relative to the target composition of 33:33:33. These compositions are sufficiently close to allow for direct comparison of electrical properties among the differently deposited samples.

**Structural Properties.** The densities and thicknesses of the IGZO films were obtained by fitting the XRR data using REFS (Bede Scientific) after annealing for 2 h at 450 °C. The fits are consistent with SEM images demonstrating that the sol−gel method produced the thickest, but least dense, films (Figure 3a), whereas the films derived from the cluster solutions after 1 h of electrolysis yielded the highest densities of ~80% (relative to dense crystalline oxides of the same average composition). The XRD patterns obtained for IGZO films made using 1 h electrochemically synthesized cluster precursors as a function of annealing temperature are shown in Figure 3b. Films annealed below 600 °C are amorphous, which was also confirmed by HRTEM and electron diffraction (Figure 3c,d). This is consistent with previous work—IGZO films begin crystallization at ~600 °C. Amorphous IGZO films have improved mobility by avoiding the scattering and trapping of carriers at the defects and grain boundaries present in polycrystalline films. All TFT devices discussed below are annealed at ≤550 °C to maintain an amorphous active channel layer structure.

**Chemistry of Annealing: Quartz Crystal Microgravimetry (QCM) and FT-IR Analyses.** The IGZO films created using the salt solution and cluster precursor (1 h) were deposited on QCM crystals in order to record the film mass as a function of annealing temperature from 30 to 300 °C (the temperature limit for the QCM substrate). The film mass after drying at 30 °C for 15 min was taken as the initial mass. Losses in the films’ mass were deduced from the frequency changes upon annealing. Both salt- and cluster-derived films complete the mass loss by ~250 °C (Figure 4a). The salt films lose ~60% of their mass, whereas cluster films lose only ~25%. This difference is caused by the chemical processes occurring during electrolysis that lower the nitrate-to-metal ratio (see above) and thus the fraction of the film that must be combusted.

FT-IR measurements were used to follow chemical changes related to densification. Figure 4b shows the nitrate (1200–1600 cm⁻¹) and hydroxyl (3000–3800 cm⁻¹) stretches from films annealed below 200 °C. The size of these stretches decreases with annealing and are absent after annealing at temperatures above 200 °C, demonstrating removal of the nitrate and water at low temperatures. This observation is in agreement with QCM data.

**Electrical Characteristics.** Solution-processed electronic materials will only have substantial impact if the resulting electronic properties approach those of films derived from standard vacuum processes, such as sputtering. We fabricated TFT test structures to understand the electronic quality of the solution-processed IGZO films in comparison to identically processed sputtered films. Panels (a) and (b) in Figure 5...
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**Figure 5.** (a) TFT transfer curves and (b) $\mu_{ave}$ of air-annealed (400 °C) In:Ga:Zn = 69:12:19 films made with different precursors.

The TFT results show that films made using electrochemically generated cluster precursors ($\mu_{ave}$ ~ 8.9 ± 0.6 cm² V⁻¹ s⁻¹) yield better films than the initial salt solution (~5.1 ± 1.2 cm² V⁻¹ s⁻¹) and sol-gel (~2.2 ± 0.4 cm² V⁻¹ s⁻¹) precursors do. The decreased mobility is correlated with the lower densities found from XRR analysis and increased roughness (from AFM) compared to the new cluster precursors reported here. We attribute the origin of this porosity/roughness to unwanted counterions and/or organics that must be removed during the annealing process. The data here with identically prepared devices thus show directly that aqueous precursors, tuned to minimize counterions, provide substantial performance advantages compared to traditional solution approaches. The composition of the cluster-derived films was then varied to include In-rich compositions, which are known to yield higher average mobilities for sputtered films (Figure 6). Films with In:Ga:Zn = 33:33:33 yielded enhancement-mode TFT devices (i.e., positive $V_{ON}$) with a $\mu_{ave}$ < 6 cm² V⁻¹ s⁻¹. Enhancement-mode TFTs typically result from low carrier concentration in the channel. The larger concentrations of small metal cations (e.g., Ga³⁺ and Zn²⁺) suppress the formation of oxygen vacancies, and thus free carriers, due to an increased metal—oxygen bond strength (relative to In³⁺). Increasing the Ga and Zn concentration also depresses carrier mobility because of weaker s—s orbital overlap of the small cations relative to the larger In³⁺.

The operation mode of TFTs was changed from enhancement to depletion mode (i.e., negative $V_{ON}$) with increasing In, concurrent with increased channel mobility and carrier concentration for the reasons described above. Films with In:Ga:Zn = 69:12:19 had the highest $\mu_{ave}$ ~ 15 cm² V⁻¹ s⁻¹, an $I_{DS-ON}/I_{DS-OFF}$ of >10⁵, and a $V_{ON}$ of ~ -30 V.

We note that channel mobility estimates for depletion-mode TFTs are fundamentally different than those for enhancement-mode devices, as discussed in detail by Wager and co-workers in the context of a comprehensive depletion-mode model (CDMM). This difference is due to the contribution of carriers in the “bulk” of the film to the conductance in a depletion-mode TFT. Bulk carriers typically have higher mobility than those confined to the dielectric interface, due to interface defects. Therefore, depletion-mode devices could show higher $\mu_{interface}$ than the true interface mobility ($\mu_{interface}$). However, the extracted $\mu_{interface}$ values from CDMM simulations are in good agreement with the simple square model calculations of $\mu_{ave}$ (Figures S6, S7, and S8).

**Figure 7.** (a) TFT transfer curves and (b) $\mu_{ave}$ of In:Ga:Zn = 69:12:19 films made using electrochemically generated cluster precursors. Films were annealed at various temperatures and in dry (D) and humid (H) conditions.

which were annealed at different temperatures and environments. At the low annealing temperature of 300 °C, the electrical performance is significantly improved by annealing first under humid conditions at 250 °C, increasing $\mu_{ave}$ from ~4 to 6 cm² V⁻¹ s⁻¹ at $V_{GS} = 60$ V and substantially reducing hysteresis. These observations are consistent with previous reports. Nomura and co-workers showed that humid-annealing reduces electron traps (e.g., oxygen-related defect states) compared to dry annealing, suggesting that oxygen species derived from water are more mobile than those from dry atmospheres. Hwang and co-workers reported improved electrical properties from solution-processed indium oxide TFTs by humid annealing and used X-ray photoelectron spectroscopy to show that the humidity facilitates the conversion of indium hydroxide into oxide and that this chemical conversion correlates with improved electrical properties.

**Figure 6.** (a) TFT transfer curves and (b) $\mu_{ave}$ of air-annealed (550 °C) IGZO films made with 1 h electrochemically synthesized cluster precursors with In:Ga:Zn ratio indicated.

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The increased mobility can be explained by reorganization of M–O–M networks and increased film densification at high temperature,\textsuperscript{16,31} thereby reducing the trap sites by distortional relaxation and/or filling the trap sites due to increased carrier concentration.\textsuperscript{15,62} The TFTs transfer curves show a change from enhancement to depletion mode with increasing anneal temperature, also consistent with an increase in the carrier concentration.

**Comparison to Sputtered IGZO.** The electrical properties of solution-processed films were compared with those of sputtered IGZO films (Figure 8). The devices from the 1 h electrochemically synthesized cluster precursor and by sputtering and were annealed at 550 °C in air for 2 h. Both solution-processed and sputtered IGZO films are composed of nominally In:Ga:Zn = 33:33:33 (see Table 1). The ITZO interface layer is composed of In:Sn:Zn = 9:1:1.

![Figure 8](image.png)

**Figure 8.** (a) TFT transfer curves and (b) \(\mu_{\text{AVE}}\) of TFT devices with and without the ITZO interface layer. The IGZO films were made of an electrochemically synthesized cluster precursor and by sputtering and were annealed at 550 °C in air for 2 h. Both solution-processed and sputtered IGZO films are composed of nominally In:Ga:Zn = 33:33:33 (see Table 1). The ITZO interface layer is composed of In:Sn:Zn = 9:1:1.

chemically synthesized cluster precursor with In:Ga:Zn = 33:33:33 exhibited a \(\mu_{\text{AVE}} \sim 4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\), a \(V_{\text{ON}}\) of \(\sim 20 \text{ V}\), and an \(I_{\text{DS-ON}}/I_{\text{DS-OFF}}\) of \(>10^5\). Devices with sputtered IGZO of similar composition films had a \(\mu_{\text{AVE}} \sim 12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\), a \(V_{\text{ON}}\) of \(\sim 0 \text{ V}\), and an \(I_{\text{DS-ON}}/I_{\text{DS-OFF}}\) of \(>10^6\). The two sets of devices were processed identically. This direct comparison indicates that there remains substantial materials quality differences between sputtered and solution-processed films.

**Enhanced Performance for Solution-Processed Films Using Interface Layers.** Rim and co-workers reported increased mobility in solution-processed TFTs by incorporating a thin indium–tin–zinc oxide (ITZO) interface layer at the dielectric IGZO interface.\textsuperscript{22} Saturation mobilities (\(\mu_{\text{SAT}}\)) of \(\sim 22 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) at \(V_{\text{GS}} = 40 \text{ V}\) were obtained using a SiO\(_2\) gate dielectric and a 3 nm thick ITZO interface layer using an IGZO channel with In:Ga:Zn = 2:1:1. \(\mu_{\text{SAT}}\) of \(\sim 1.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) were found without the interface layer, and \(\mu_{\text{SAT}}\) were obtained in the saturation regime with \(V_{\text{DS}} = 10 \text{ V}\). The enhanced performance is attributed to the filling of structural defects (e.g., pores) at the dielectric–semiconductor interface and to an electron energy barrier of \(\sim 0.15 \text{ eV}\) between the conduction band of the ITZO interface layer and the IGZO channel. Jeong and co-workers also reported solution-processed Al–In–Zn oxide/In–Zn oxide dual-active-channel layer TFTs with a field-effect mobility of \(\sim 5.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\), suggesting that heterojunction stacks are useful for enhanced performance in solution-processed TFTs.\textsuperscript{65}

We introduced an ITZO interface layer under the IGZO film and found \(\mu_{\text{AVE}} \sim 30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\), a \(V_{\text{ON}}\) of \(\sim 5 \text{ V}\), and an \(I_{\text{DS-ON}}/I_{\text{DS-OFF}}\) of \(>10^5\). The comprehensive depletion-mode model was used to extract values for \(\mu_{\text{SAT}}\) in close agreement with \(\mu_{\text{AVE}}\) (Figure S9). Control devices with the ITZO interface layer alone had much lower \(\mu_{\text{AVE}} < 6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) (Figure S5). The addition of the solution-processed ITZO interface layer prior to sputter deposition of IGZO yielded a \(\mu_{\text{AVE}}\) similar to that of solution-processed ITZO–IGZO TFTs (\(\sim 30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\)) but also resulted in a large clockwise drain current hysteresis and a negative \(V_{\text{ON}}\) of \(\sim 40 \text{ V}\). The large hysteresis is likely due to electron-trapping states at the interface layer, which may occur from plasma damage of the ITZO interface layer during sputter deposition of IGZO.\textsuperscript{32} The similar \(\mu_{\text{AVE}}\) values between the sputtered and the solution-processed films in the presence of the interface layer suggest that the intrinsic materials quality of the films derived from the optimized aq. solution/cluster process is approaching that of the sputter-deposited films. We note, however, that the sputtered film had lower In content than the particular solution-processed film shown in Figure 8.

**Aging Effects.** Figure 9 shows the changes in electrical properties for solution-processed IGZO with aging time in ambient air without encapsulation by a passivation layer. The output characteristics after aging for 21 days (Figure 9b) show improved transistor behavior compared to those measured initially (Figure 9a). The transfer characteristics further show that the aged devices show minimal clockwise drain current hysteresis compared to those that have not been aged (Figure 9c). Clockwise hysteresis is generally attributed to charge trapping states in the semiconductor bulk.\textsuperscript{66} We attribute the decreases in hysteresis with aging due to the reduction of such charge trapping states, perhaps due to diffusion of moisture into the film pores, which might react with and passivate surface/interface defect states. Finally, \(\mu_{\text{AVE}}\) decreases slightly after a week and remains constant for nearly a month (Figure 9d).

**4. CONCLUSIONS**

Electrolysis of aq. mixed metal nitrate salt solutions drives the formation of IGZO precursor solutions, without purification, that consist of \(\sim 1 \text{ nm}\) radii metal–hydroxo clusters, minimal nonfunctional counterions (e.g., nitrate), and no organic ligands or solvents. The resulting films deposited from cluster precursors are smooth (RMS roughness of 0.24 nm—approximately the M–O bond distance), homogeneous, dense, and crack-free. They are structurally and electrically superior to films deposited from metal nitrate salt and related organic sol–gel precursor solutions. We compared the solution-
processed IGZO films to sputtered ones with nominally the same composition in identical transistor test structures. We found that even the optimized solution-processed film had less than half the mobility of sputtered films. However, when an ITZO interface layer was incorporated with solution-processed IGZO, competitive mobilities near 30 cm² V⁻¹ s⁻¹ were achieved with small hysteresis in the transfer characteristics and turn-on voltages near 0 V, suggesting that a significant difference between the sputtered and solution-deposited films lies at the gate dielectric/semiconductor channel interface. The approach demonstrated, which combines clean electrochemical synthesis to minimize nonfunctional counterions with detailed characterization of the resulting precursor solutions, and the films and devices processed from those solutions, should be applicable for the synthesis of a variety of mixed-metal-oxide films with properties competitive with vapor-deposited films.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b01813.

Electrochemical synthesis parameters for the range of solution precursor compositions studied, TEM analysis of film inhomogeneities, AFM surface topography images, and additional thin-film transistor data along with fits to the comprehensive depletion-mode model (PDF)

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Notes
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