Hexaaqua Metal Complexes for Low-Temperature Formation of Fully Metal Oxide Thin-Film Transistors

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Supporting Information

ABSTRACT: We investigated aqueous metal complex-based oxide semiconductor films formed with various ligands, such as chloride, acetate, fluoride, and nitrate. Nitrate ligand-based indium(III) precursor was easily decomposed at low temperature due to the replacement of all nitrate ions with water during solvation to form the hexaaqua indium(III) cation ([In(H₂O)₆]³⁺). Hexaaqua indium(III) cation was a key complex to realize high-quality oxide films at low temperature. Additionally, Al₂O₃-based high-κ dielectric was also employed by using a nitrate precursor, and the hexaaqua aluminum(III) cation ([Al(H₂O)₆]³⁺) was confirmed. This complex-based Al₂O₃ film showed high breakdown voltage and stable capacitance under high frequency operation compared to organic solvent-based Al₂O₃ films. We successfully demonstrated aqueous-based In₂O₃ TFTs with Al₂O₃, high-κ gate dielectrics formed at 250 °C with a wide gate voltage operation and high saturation mobility and on/off ratio of 36.31 ± 2.29 cm² V⁻¹ s⁻¹ and over 10⁷, respectively.

INTRODUCTION

Amorphous metal oxide semiconductor (AOS)-based electronic devices have been developing rapidly for use as thin-film transistors (TFTs) in display backplanes, sensors, and logic devices.¹⁻³ In particular, the high field-effect mobility (>10 cm² V⁻¹ s⁻¹), transparency, and electrical stability of AOS TFTs are attractive for flexible transparent circuit applications. Recent research has focused mainly on developing new materials with high mobility and stability, diverse substrates, and facile processing methods.⁴⁻⁵ Various processing methods are used to deposit AOS such as atomic layer deposition, pulsed laser deposition, sputtering, and solution process. Except for the solution process, most processes are associated with the high cost and the use of vacuum facilities. In order to consider this issue, solution processing has emerged as a future technology with simple process and low cost. Although solution processing of AOS TFTs has great potential, the electrical properties of these devices strongly depend on the processing temperature, and their electrical performances are much lower than that achieved with vacuum processing even after annealing over 450 °C. To overcome this obstacle, several solutions have been proposed, including new material synthesis,⁶⁻⁸ different ligand-based precursor optimization,⁹ nanostructure-based film formation,¹⁰,¹¹ ultraviolet (UV) irradiation,¹² high pressure annealing,¹³ microwave irradiation,¹⁴ and ozone treatment.¹⁵ A recent study of metal oxide film formed by the aqueous route showed the possibility of a low-temperature process by reducing the amount of carbon-based organic solvent, additives, and ligands in the metal precursors to lessen the detrimental effects of carbon impurities.¹⁶,¹⁷ On the basis of an aqueous system, many kinds of metal precursors with different ligands could be selected to form metal oxide formation such as metal-based nitrate, acetate, chloride, fluoride, and so on. Besides, aqueous systems with various metal ligands can make different chemical bondings, which form different film morphologies. Therefore, it is challenging to find the route of low temperature and high performance semiconductor formation of the best precursor or/and formation mechanism in water.

Here, we report different complexes and their performance of metal oxide films and thin-film transistors with different ligands. Selected chloride-, acetate-, nitrate-, and fluoride-based metal precursors are popular ligands to synthesize solutions in organic solvent due to high solubility, controllability, and low cost. On the basis of our results, we found that ultrahigh mobility of fully aqueous-based In₂O₃ TFTs with indium(III) and aluminum(III) nitrate precursors specially formed hexaaqua metal(III) complexes of [In(H₂O)₆]³⁺ and [Al(H₂O)₆]³⁺ as the oxide semiconductor and gate dielectric layers, respectively. The metal atoms in the hexaaqua metal(III) complexes in water have a coordination number of six (Figure 1a). Furthermore, we confirmed that nitrate-based metal complex did not precipitate in water as M(OH)₃, which could represent high solubility in water as the monomeric [M((H₂O)₆)³⁺]⁺ and smooth surface of the films. This structure of the metal complexes could form high-quality oxide films at below 250 °C.

EXPERIMENTAL SECTION

Synthesis of Aqueous Metal Precursor Solutions. Indium oxide precursor solutions with varying ligands were synthesized by
Figure 1. (a) Structure and unique processing of hexaqua metal complexes. (b) Thermogravimetric analyses of the various aqueous metal precursors of In(C₂H₃O₂)₃, InCl₃, InF₃, and In(NO₃)₃. (c) Raman spectra of different ligand-based films.

dissolving 291.9, 221.1, 171.8, and 300 mg of indium acetate (In(C₂H₃O₂)₃, Aldrich, 99.99%), indium chloride (InCl₃ Aldrich, 99.999%), indium fluoride (InF₃, Aldrich, 99.9%), and indium nitrate hydrate (In(NO₃)₃·xH₂O, Aldrich, 99.999%), respectively, in 10 mL of water (H₂O, Aldrich). The aluminum oxide precursor solutions were synthesized by dissolving 1.12 g of aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O, Aldrich, 99.999%) in 10 mL of water (H₂O, Aldrich) or 2-methoxyethanol (C₂H₆O₂·H₂O, Aldrich, 99%), respectively. After stirring vigorously for 1 h at room temperature, the solutions appeared transparent and homogeneous.

Device Fabrication. The substrates were cleaned in acetone and isopropyl alcohol sequentially and then treated by ultraviolet (UV) irradiation for 10 min. The In₂O₃ precursor solution was spin-coated on SiO₂ (1000 Å)/heavily boron (B) doped p-type Si wafer at 3000 rpm for 30 s. The samples were then soft-baked at 100 °C for 5 min to eliminate water and then annealed at varying temperatures (150–250 °C) for 2 h. The annealed samples were treated using photolithography process. The aluminum (Al) source and drain (S/D) electrodes (thickness = 100 nm) were deposited by thermal evaporation with a metal shadow mask. The channel region was defined with a width (W) of 1000 μm and a length (L) of 200 μm. For the solution-processed Al₂O₃ film, the aluminum oxide precursor solution was spin-coated at 3000 rpm for 30 s. The sample was then sequentially annealed at 100 and 250 °C for 5 min each. These procedures were repeated several times to obtain a thickness of 100 nm, and then, sample was annealed at 250 °C for 2 h.

Material and Device Characterization. Thermogravimetric analyses of the different aqueous precursor solutions were performed using a TGA analyzer (SDT Q600, TA Instruments). Each 25 mg powder was prepared by drying the precursor at 60 °C in a vacuum oven. The chemical and structural properties of the oxide films were examined using a high-resolution Bragg–Brentano X-ray diffractometer (XRD, Bruker). The In₂O₃ and Al₂O₃ films showed amorphous structures (Figure S7). To determine the solvated structures of the metal ions, Raman spectra were recorded at room temperature with a Renishaw spectrometer at 154 nm, with notch filters cutting at 100 cm⁻¹. The solutions were dropped on glass substrates, and a 50X objective is used for measurements, which are performed at an incident power of 100 MW. The TFT characteristics of the devices were measured in a dark box in ambient air using an Agilent 4155C semiconductor parameter analyzer. The measurements of the TFTs on SiO₂/Si wafers were performed by inducing VGS of −30 to 40 V and VDS of 30 V. The capacitance–frequency (C–F) properties of the metal–insulator–metal (MIM) structure were measured using an Agilent 4284A precision LCR meter from 100 to 1 MHz.

RESULTS AND DISCUSSION

Thermogravimetric analysis (TGA) of the precursors allows a comparison of the thermal evolution of the different precursors (Figure 1b). For each precursor, two-step decompositions are present, representing dehydroxylation and condensation. In(NO₃)₃ has the lowest decomposition temperature at approximately 240 °C. On the other hand, the decomposition temperatures of InCl₃, In(C₂H₃O₂)₃, and InF₃ were 490, 443, and 326 °C, respectively. The different decomposition temperatures are related to the specific chemical structures of the precursors.

Raman spectroscopy was performed to directly probe the covalently bonded aqueous species (Figure 1c). The splitting of the C–C stretching for In(C₂H₃O₂)₃ indicates that acetate exists in three states in solution: acetic acid (C₂H₃O₂), free acetate ion (CH₃COO⁻), and complexed acetate at Raman peaks of 890, 928, and 960 cm⁻¹, respectively.21,22 In the case of InF₃, the broad Raman peak at 484 cm⁻¹ is caused by the In–F vibration.23 The high charge and moderate size of indium ion qualify it as a hard acid, and thus, it easily forms complexes with hard bases such as F⁻ and acetate.23 According to the measured pH value (~2), the major species was determined to be InF₃, which in turn agreed with the low solubility of InF₃ and we could thus predict the poor quality of the InF₃-derived In₂O₃ film and confirmed surface morphology (Figure S1). The broad Raman peak of InCl₃ appeared at 296 cm⁻¹, representing the In–Cl stretch in InCl₃(H₂O)₇–₉⁻ (n = 1–4). The peak assignment and fitting25 (Figure S2) and the major species was InCl₃(H₂O)₉−, as determined by the area under the peak,26 which was also expected to lead to low-quality In₂O₃ films owing to further decomposition steps. On the other hand, In(NO₃)₃ solution showed a vastly different behavior. The peak at 1050 cm⁻¹ corresponds to the symmetric N–O stretch of free nitrate ions, and no evidence of complexed nitrate (1040 cm⁻¹) is observed.27,28 This means that water replaces all the nitrate ions during solution to form the hexaqua indium(III) cation ([In(H₂O)₆]³⁺), as shown in Figure 1a.

We can consider water as playing two critical roles in the precursors. First, it acts as a solvent with a high polarity and dielectric constant (ε = 80) that enables the dissociation of ionic species. Second, it behaves as a σ-donor and reacts as a nucleophilic ligand to form solvated species of the type M(H₂O)ₙ.

\[
MXₙ + nH₂O → M(H₂O)ₙ + nX
\]  

(1)

For a fixed metal cation, the stability of MXₙ depends on the electronegativity of the anion and the pH.29 Here, stability constants can be used to explain the bonding strengths of coordination complexes in aqueous solution. Log Kₙ values for In–NO₃, In–Cl, In–(C₂H₃O₂)₃, and In–F are 0.18, 2.32, 3.50, and 3.75, respectively.20 Compared with the other anions, the small stability constant of In–NO₃ shows that nitrate anion is more easily displaced from indium cation than the other anions. The indium ions in aqueous In(NO₃)₃ are fully solvated with water molecules and have higher potential energies for the thermally driven hydrolysis and condensation reactions. On the other hand, the anions coordinated to the metal ion play a role as network modifier in the structure of the condensed phases, which would lead to a disrupted metal oxide network.25 Also, the incomplete decomposition of InCl₃, In(C₂H₃O₂)₃, and InF₃...
at 250 °C results in a large quantity of the hydrates, hydrogen halides, and acetates remaining in the thin film. The unique case of In(NO3)3 having a weak anion complexation makes it superior to the other precursors. That is, the formation of the hexaqua complex with In(NO3)3 results in a very low decomposition temperature, and a high-quality In2O3 film can be obtained at 250 °C, which is favorable for flexible substrates.

In order to compare the oxide quality and oxygen binding states for the different ligand types, X-ray photoelectron spectroscopy (XPS) analysis of the thin films annealed at 250 °C was conducted (Figure 2). The XPS O 1s spectrum of the

![Figure 2. XPS O 1s spectra of the different ligand-based In2O3 films with (a) In(C2H3O2)3, (b) InCl3, (c) InF3, and (d) In(NO3)3. Films were annealed at 250 °C. The areas of O1 (530.27 eV, red line), O2 (531.65 eV, green line), and O3 (532.70 eV, blue line) indicate the oxide lattice, oxygen deficiencies, and hydroxide bonding in In2O3, respectively.](image)

In(NO3)3-based film has the largest area (54.04%) of the oxide lattice (530.27 eV, O1), while InF3 has the smallest area (6.92%) of O2 and a large area of M–OH (O3). Furthermore, the O1 areas in the In(C2H3O2)3 and InCl3 spectra were 13.20% and 52.44%, respectively. That is, the decomposition route for oxide formation strongly depends on the ligands used in the different indium complex precursors. These results are consistent with the decomposition temperatures of the different precursors determined by TGA. Looking at different annealing temperatures of the In(NO3)3 precursor, even the film formed at 150 °C shows a higher oxide lattice formation compared to the films from the other ligands annealed at 250 °C (Figure S3). On the basis of these various chemical analyses, we confirmed that, among all the precursors, the nitrate-based solution provided the highest quality In2O3 film at low temperature, which in turn, could exhibit the highest field effect mobility as a TFT channel material. The transfer and output curves of the In2O3 TFTs from different precursors are shown in Figure 3. The μsat of the In2O3 TFTs from In(C2H3O2)3, InCl3, and InF3 exhibited mobilities of 0.07–1.2 cm2 V−1 s−1. Detailed parameters are given in Table 1. The In(C2H3O2)3-based TFT had the lowest mobility owing to the

![Figure 3. Transfer curves of In2O3 TFTs with different ligands of (a) In(C2H3O2)3, (b) InCl3, (c) InF3, and (d) In(NO3)3.](image)

In addition, the oxide lattice peak (530.29 eV, O1) in the XPS O 1s spectrum was much smaller than the hydroxide peak (532.70 eV, O3), as shown in Figure 2. This result can be attributed to an insufficient energy supply for the dehydroxylation and carbon elimination. Interestingly, the In(C2H3O2)3 precursor had a faster thermal decomposition than that of InF3, and the oxide lattice-related O 1s peak of the acetate-based film is much higher than that in the fluoride-based film.

However, the mobility of the In(C2H3O2)3-based In2O3 TFT (0.07 ± 0.02 cm2 V−1 s−1) is much lower than that of the TFT from InF3 (1.21 ± 0.10 cm2 V−1 s−1). The reason for this is that fluorine can occupy oxygen deficiencies in the In2O3 lattice at low temperature owing to the similar ionic size of fluorine and oxygen. Furthermore, In–F bonding was stable over 250 °C as shown by TGA. On the other hand, μsat (23.96 ± 1.85 cm2 V−1 s−1) of the In(NO3)3-based In2O3 TFT was more than 20 times higher than those of the films made from other ligands. Furthermore, the on/off ratio and subthreshold voltage swing (SS) were over 106 and below 1 V dec−1, respectively, and showed a clear pinch-off behavior (Figure S4). We examined the In(NO3)3-based In2O3 TFTs at different annealing

| Table 1. Extracted Device Parameters of the In2O3 TFTs with Different Ligands and Annealing Temperatures |
|-----------------|-----------------|-----------------|-----------------|
| precursor types | temp. (°C) | μsat (cm2 V−1 s−1) | Ion/off SS (V dec−1) |
| In(C3H7O2)3 | 250 | 0.07 ± 0.02 | ∼104 |
| InCl3 | 250 | 0.44 ± 0.14 | ∼104 |
| InF3 | 250 | 1.21 ± 0.10 | ∼106 |
| In(NO3)3 | 150 | 1.24 ± 0.07 | ∼106 |
| In(NO3)3 | 200 | 6.27 ± 0.74 | ∼107 |
| In(NO3)3 | 230 | 14.10 ± 0.97 | ∼104 |
| In(NO3)3 | 250 | 23.96 ± 1.85 | ∼104 |
| In(NO3)3 | 250 | 36.31 ± 2.29 | ∼107 |

With aqueous Al2O3 gate dielectric.

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temperatures (150–250 °C), and the device showed good switching behavior even when annealed at 150 °C (Figure S5). This device is thus expected to be applicable toward the low-temperature processing of flexible electronics on polymer substrates.

Analogous to In(NO₃)₃, Al(NO₃)₃ can form hexaaqua complex [Al(H₂O)₆]³⁺, which could enable the fabrication of high-quality dielectric materials at low temperature. Typically, a solution-processed high-k dielectric material requires high-temperature annealing (over 450 °C). However, several gate dielectrics show poor characteristics at even high temperature annealing because of crystallization. Additionally, films annealed at lower temperature (below 350 °C) have a low breakdown voltage and large variation in their capacitance values under different frequencies. On the other hand, our hexaaqua complex-based Al₂O₃ film and In₂O₃ TFTs had excellent electrical properties at 250 °C compared to organic solvent-based films and devices (Figures S6 and S8 and Table S1). The capacitance variation of the Al(NO₃)₃-based metal–insulator–metal (MIM) device was very small, from 100 to 1 MHz, as shown in Figure 4b. This could be attributed to the low amount of impurities (i.e., carbon and/or alkali elements) in the film owing to the carbon-free solvent and ligands. Furthermore, the breakdown electric field is over 4 MV cm⁻¹ (Figure 4a), which allows a wide operating voltage range as shown in Figure 4c,d.

Finally, we successfully demonstrated aqueous-based In₂O₃ TFTs with Al₂O₃ gate dielectrics formed at 250 °C (Figure 4c,d). We demonstrated a wide range of gate voltages (V𝐺𝑆 = −20 to 40 V) during TFT operation with a drain voltage (V𝐷) of 10 V and a low leakage current level of below 1 nA. The μ𝑉, on/off ratio, and SS of the TFT were 36.31 ± 2.29 cm² V⁻¹ s⁻¹, 10⁷, and 0.76 ± 0.24 V dec⁻¹, respectively. This high mobility and wide-window voltage performance is the current state of the art in low-temperature solution-processed metal oxide TFTs, indicating that the proposed hexaaqua complex-based technology is key to enable ultrahigh performance of solution-processed electronic devices and circuits.

■ CONCLUSION

In summary, we utilized various ligand-based metal complexes from acetate-, chloride-, fluoride-, and nitrate-based aqueous precursors, and nitrate-based aqueous precursor could be easily decomposed at low temperature, to form a high-quality semiconductor and dielectric materials. Our low-temperature In₂O₃ TFT showed ultrahigh performance with a maximum mobility of over 25 cm² V⁻¹ s⁻¹. Furthermore, our hexaaqua-based high-k Al₂O₃ dielectric film also showed excellent breakdown voltage and stability under a wide frequency range. As a result, we achieved high mobility and good switching characteristics of our In₂O₃ TFT with an Al₂O₃ dielectric under a wide voltage range. The low-temperature formation of hexaaqua complexes was achieved through free carbon residues and simple dehydroxylation. These results highlight the utility of this method for eco-friendly, all solution-processed high performance transparent electronic devices for flexible applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b02505.

Optical images of films with different ligands; Raman and XPS results of aqueous films with different conditions; device performances with various conditions (PDF)

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The authors declare no competing financial interest.

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