Review Article: Atomic layer deposition for oxide semiconductor thin film transistors: Advances in research and development

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I. INTRODUCTION

Atomic layer deposition (ALD) is a process that was developed to enable thin film deposition over a large area with good uniformity. This is achieved due to its basic self-limiting characteristics; in other words, unlike other deposition techniques, ALD proceeds via self-limiting reactions between precursor chemicals and the substrate (as shown in Fig. 1).\(^1\) Basically, ALD consists of four essential steps: (1) precursor exposure to the substrate, (2) evacuation or purging of the precursors as well as byproducts from the chamber, (3) reactant species exposure, typically oxidants or other reagents, and (4) evacuation or purging of the reactants and byproduct molecules from the chamber.\(^2\) During these surface reactions and the layer by layer growth cycle, the ALD process exhibits some important properties for nanofabrication: excellent conformality, atomic scale thickness control, and low growth temperature. Despite the similarities between conventionally used chemical vapor deposition and ALD, the distinctive and clear feature of ALD lies in the self-limiting nature of precursor adsorption and reaction. The sequential, alternating exposure of precursors and reactants results in the unique characteristics of the ALD process.\(^3\)

In the early stage of ALD development, applications of ALD were limited to the deposition of epitaxial layers of II–VI or III–V semiconductors, since the inherently low growth rate was considered to be a major hurdle for other applications.\(^4\) On the other hand, ALD grown aluminum oxide, hafnium oxide, and titanium oxide as well as mixtures of those were also used as the dielectric layers of a double-insulator electroluminescent device.\(^4,5\) However, because of the required down-scaling of semiconductor device dimensions, ALD grown nanoscale thin films have found new applications in metal oxide semiconductor field effect transistors (MOSFETs), solar cells, and high-density memory devices. Furthermore, because it can meet the requirements of small pixel size and large panel area growth as well as low deposition temperature, the ALD method will be considered as an important deposition technique for next generation display technologies including mobile terminals, large sheet-shaped televisions, and flexible products. It remains a significant challenge to produce such devices with higher resolution, lighter weight, lower power consumption, lower thickness, and a free design form.\(^6\)

Regarding display operation, many researchers have paid attention to thin film transistor (TFT) fabrication processes, for which high mobility, on-off current modulation, low contact resistance, and even mechanical flexibility are important considerations.\(^7,8\) Hydrogenated amorphous silicon (a-Si:H) TFTs have been extensively investigated; however, device performance is limited by their low mobility (<1 cm\(^2\)/V s).\(^9\) Low-temperature polycrystalline silicon (LTPS) TFTs have also attracted attention due to their high electrical mobility values close to 100 cm\(^2\)/V s. However, the non-uniform spatial distribution of the poly-Si grain structure in LTPS films, which results in non-uniform device performance,\(^12\) as well as high production costs limit their application in next generation displays.\(^15\)\(^16\) Besides, interest in Si-based devices for transparent circuits has been waning due to their small bandgap. In contrast, degenerate band conductivity and large mobility (>10 cm\(^2\)/V s) are possible in amorphous oxide semiconductors (AOS) containing post-transition-metal cations, which are completely different from those of the covalent semiconductors.\(^17\)\(^18\)

Previous research on oxide TFTs has usually been based on sputter or solution phase deposition methods. Such methods have some shortcomings in contrast to ALD, such as unavoidable high-temperature annealing, infeasibility of
accurate composition adjustment and thickness control, and also difficulties with large area thin film deposition, which may result in device performance degradation.19

On the other hand, n-type oxide TFTs fabricated using ALD show a performance comparable to that of sputtered TFTs in previous reports, such as zinc oxide (ZnO) TFTs with a mobility of 30 cm²/V s,20 indium gallium zinc oxide (IGZO) TFTs with a mobility of 10 cm²/V s,21 and indium zinc oxide (IZO) TFTs with a mobility of 42.1 cm²/V s.22

In addition to the great success of ALD n-type oxide semiconducting materials in TFT applications, p-type oxide semiconducting materials grown by ALD have also attracted much attention. Complementary metal oxide semiconductor inverters, which comprise both p- and n-type TFTs as the basic building blocks for complex integrated circuits for system-on-chip devices, can be realized only if superior p-type materials are found.

In this paper, we provide an introduction to recent developments in ALD oxide TFT research, including n-type oxide semiconductor combinations and p-type active layers. It should be noted that the oxide semiconductor active layer of TFT that deposited by sputtering, solution, or other processes will not include in this paper, while there are several excellent review papers on such content in terms of the device fabrication process by Park’s group23 and Jeong’s group.24

II. N-TYPE OXIDE MATERIAL COMBINATIONS FOR ACTIVE LAYERS

Since the demonstration of flexible amorphous IGZO TFTs by Nomura et al.,18 tremendous efforts have been made in the research of n-type AOS TFT devices, especially for next generation flat panel display applications. The sputtering technique is the most commonly used method for preparing TFT oxide semiconductor films because of its higher performance and superior electrical or photo stability compared to the counterpart of the solution-based processing.25,26 Besides, multicomponent AOS materials, like IGZO (Ref. 27) and indium tin zinc oxide (ITZO) (Ref. 28), can be easily deposited via sputtering process once the target ratio is modified, which are its merits as well as demerits as the composition of the sputtered active layer cannot be adjusted freely. In addition, research into 3D vertical TFT fabrication on polymer films using ALD has been conducted for future non-glass 3D displays as well as flexible displays, where extremely small pixel sizes and low deposition temperatures with large area deposition are necessary.29 Unlike Si-based semiconductors that use ion doping to control charge carrier concentrations in a thin film, for n-type AOS materials, the bottom of the conduction band that is highly ionized is primarily composed of spatially spread metal ns orbitals with isotropic shapes, where n is the principal quantum number, and direct overlap among the neighboring metal ns orbitals is possible. The magnitude of this overlap is insensitive to the distorted metal-oxygen-metal (M-O-M) chemical bonds that intrinsically exist in amorphous materials, which leads to a similar Hall Effect mobility to that of the corresponding crystalline phase.18,30,31

In this section, we review the development of n-type AOS TFTs fabricated by ALD. Recent reports of n-type AOS TFTs are summarized in Table I.

A. ZnO-based active-layer materials

1. ZnO

When investigation into ALD oxide semiconductor TFTs began (around 2010 to 2012), almost all devices used ZnO as the active-layer material. When used as the active material of
a TFT, ALD ZnO is usually deposited using diethylzinc (DEZ) as a zinc precursor and deionized (DI) water as a reactant. As ALD ZnO thin films usually have a high carrier concentration as well as defect states, research has generally focused on the thickness, growth temperature, and post treatment methods, including UV exposure, post annealing processes, and O2 plasma treatment.

The electrical properties of ZnO thin films depend on the ALD growth temperature, as shown in Fig. 2(a), where the measured carrier concentration and Hall mobility increased and resistivity decreased with increasing deposition temperature. Generally, the appropriate carrier concentration for the channel layer of an oxide TFT is $10^{14}\text{–}10^{17}\text{ cm}^{-3}$, which implies as-grown ZnO thin films deposited at $>150{ }^\circ\text{C}$ are not appropriate for TFT applications. Generally, the higher carrier concentrations obtained at higher growth temperatures of n-type oxide semiconductors are attributed to the oxygen vacancies ($V_o$). The $V_o$ is widely reported to be created through the reaction: $O_o \rightarrow \frac{1}{2} O_2 + V_o + e^-$, which is supposed to happen at higher growth temperatures.

It should be noted that the local density approximation calculations showed an oxygen defect works as an electron acceptor, leading to an unintentional p-type doping in the thin films. The introduction of cations such as Mg2+, Ti3+, and In3+ can be used to control the dopant content and carrier type. The dopant content and carrier type can be controlled by adjusting the ratio of precursors or by adding additional precursors during deposition. The electrical properties of the doped films can be further optimized by post treatment methods such as UV exposure, post annealing processes, and O2 plasma treatment.

### Table I. Summary of recent reports for thermal ALD and plasma enhanced ALD oxide semiconductor TFTs.

| Date     | Material       | Precursor | Reactant          | Growth temp. (°C) | Mobility (max) (cm²/V s) | Reference |
|----------|----------------|-----------|-------------------|-------------------|--------------------------|-----------|
| 2009     | ZnO            | DEZ       | H₂O               | 200               | 15                       | 32        |
| 2010     | ZnO and Al₂O₃ | DEZ, TMA  | H₂O               | 100               | 2.5                      | 33        |
| 2010     | ZnO            | DEZ       | O₂, Ar, H₂O       | 100–200           | 1.8                      | 34–37     |
| 2011     | Al₂ZnO         | DEZ, TMA  | H₂O               | 110               | 3.9                      | 38        |
| 2011     | ZnON           | DEZ       | NH₄OH             | 125               | 2.9                      | 39        |
| 2012     | AZO            | DEZ, TMA  | H₂O               | 60–110            | 1.95                     | 40, 41    |
| 2012     | ZnO            | DEZ       | H₂O, O₂           | —                 | 3.5                      | 42        |
| 2013     | AZO            | DEZ, TMA  | H₂O               | 200               | —                        | 43        |
| 2013     | TiO₂           | TDMAT     | H₂O               | 150               | 0.67                     | 44        |
| 2014     | AZO            | DEZ, TMA  | H₂O               | 100–150           | 6                        | 45–47     |
| 2014     | a-HZO/ZnO      | DEZ, TMA  | H₂O               | 200               | 6.3                      | 48        |
| 2014     | TiO₂           | TDMAT     | H₂O               | 200               | 0.014                    | 49        |
| 2014     | ZTO            | DEZ, TDMASn | H₂O₂       | 150               | 13.2                     | 50        |
| 2014     | ZnO            | DEZ       | O₂, H₂O           | 150–200           | 21.3                     | 29, 51–54 |
| 2015     | AZO            | DEZ, TMA  | H₂O               | 100–200           | 30.2                     | 55–58     |
| 2015     | MgZnO          | DEZ, Mg(CpEt)₂ | H₂O       | 200               | 3.6                      | 59        |
| 2015     | ZnN₂           | DEZ       | NH₃               | 315               | 1.6                      | 60        |
| 2015     | ZnHFO          | DEZ, TDMAH | H₂O₂       | 160               | 13.4                     | 61        |
| 2015     | ZnO            | DEZ       | H₂O               | 20                | 62, 63                   |           |
| 2015     | ZnON           | DEZ       | NH₃               | 200               | 17                       | 64, 65    |
| 2016     | IGZO           | DEZ, TMA  | H₂O               | 200               | 3.5                      | 21        |
| 2016     | AZO            | DEZ, TMA  | H₂O               | 100–200           | 25                       | 66–70     |
| 2016     | NbZnO          | DEZ, Nb(OEt)₃ | H₂O       | 150–225           | 7.9                      | 71        |
| 2016     | ZnO            | DEZ       | H₂O               | 120–130           | 18.2                     | 72, 73    |
| 2016     | InO            | InCa-i    | H₂O₂             | 150               | 9.8                      | 74        |
| 2016     | IZO            | DEZ, InCa-i | H₂O₂       | 150–200           | 42.1                     | 22        |
| 2017     | AZO            | DEZ, TMA  | H₂O               | 80–200            | 2.3                      | 75–78     |
| 2017     | HfZnO          | DEZ, TMA  | H₂O               | 150               | 9.4                      | 79        |
| 2017     | IGO            | InCa-i, TMGa | H₂O₂       | 200               | 9.45                     | 80        |
| 2017     | IGZO           | DEZ, In-Ga precursor | O₁      | 130–170           | 14.8                     | 81        |
| 2017     | IGZO           | DEZ, In-Ga precursor | O₁      | 150               | 7.1                      | 82        |
| 2018     | InO₃           | In(Cp)    | H₂O₂             | 150–200           | 7.8                      | 83        |
| 2018     | TITO           | InCa-1, TMGa | H₂O₂       | 180               | 28                       | 84        |
| 2010     | ZnO            | DEZ       | O₂, CO₂, N₂O plasma | 100–200           | 30                       | 85–89     |
| 2010     | ZnO:N          | DEZ       | NH₄OH plasma     | 100–300           | 20.9                     | 90        |
| 2011     | ZnO            | DEZ       | O₂, CO₂, N₂O plasma | 70–300           | 24                       | 91–96     |
| 2012     | SnO₂           | Sn(dmamp)₂ | O₂ plasma     | 70–130            | 6.2                      | 97        |
| 2012     | ZnO            | DEZ       | O₂ plasma        | 150               | 0.35                     | 98, 99    |
| 2013     | ZnO            | DEZ       | Plasma           | 200               | 20                       | 100       |
| 2015     | ZnO            | DEZ       | N₂O plasma       | 200               | 15                       | 101, 102  |
| 2016     | InO            | Me₂In(EDPA), InCa-1 | O₂ plasma     | 70–250            | 39                       | 103, 104  |
| 2016     | ZnO            | DEZ       | N₂O plasma       | 200               | 12                       | 105       |
| 2017     | ZnO            | DEZ       | Plasma           | 200               | 10                       | 106       |
| 2018     | IZO            | DEZ, In(CH₃)₃ | O₂/N₂ plasma   | 160               | 30                       | 107       |
| 2018     | SnO₂           | Sn(CH₃)₃ | Ar/H₂O plasma    | RT                | $8.2 \times 10^{-5}$      | 108       |
trap as well as a shallow donor depending on its local structure, explained by singly ionized state ($V_O^+$) by $V_O \leftrightarrow V_O^+ + e^{-}$ or doubly ionized state ($V_O^{2+}$) by $V_O^+ \leftrightarrow V_O^{2+} + e^{-}$. Thus, the shallow donorlike oxygen vacancy helps carrier concentration generation and mobility development. On the other side, the deep oxygen defects have essential influence on device stability performance. When a bias is applied to the device, electron capture is favored because the induced positive vertical field raises $E_F$ closer to $E_C$. This case can be explained by $V_O^+ + e^{-} \leftrightarrow V_O$, where transit $V_O^+$ or $V_O^{2+}$ back to $V_O$.\(^{110-112}\)

Thus, many researchers choose a post annealing treatment in air or oxygen-rich atmosphere to reduce the carrier concentration by reversing the reaction mentioned above. As shown in Fig. 2(b), even though the dependence of carrier concentration and resistivity of ZnO thin films on growth temperature after post annealing (250 °C) follows the same trend as the as-deposited thin films, their values were significantly decreased from $10^{19}$ to $10^{17}$ cm$^{-3}$ (150 °C).

The post annealed ZnO thin films grown at different temperature were used to fabricate TFTs and the related device transfer curves and performance parameters are shown in Figs. 2(c) and 2(d), respectively. The transfer curves display on/off switching operation and appropriate performance (mobility up to 7 cm$^2$/V s above a growth temperature of 150 °C) owing to the $O_2$ annealing process. However, the impurities existing in the ZnO thin film grown at low temperature, and crystallization and high carrier concentration at high temperature result in device performance degradation, including mobility dropping, subthreshold slope rising, and stability decrease. To overcome such problems, researchers have begun to focus on “carrier suppressor”-doped ZnO.

2. Al/Hf-doped ZnO

The first typical doping material used in ZnO is Al, which is a donor material. It is reported that doping Al into ZnO can result in a transparent conducting oxide material with high carrier concentrations at normal deposition temperatures. Maeng et al. studied Al-doped ZnO thin films using ALD and confirmed that the lower deposition temperature could not supply enough activation energy for carrier generation based on analysis of Arrhenius plots of the dependence of carrier concentration on deposition temperature, and finally fabricated Al-doped ZnO TFTs with a mobility of 1.95 cm$^2$/V s deposited at 100 °C.\(^{40}\)

Better performing ALD Al-doped ZnO TFTs were fabricated by Ahnand Kim,\(^{38}\) where an Al-doped ZnO thin film was deposited at 110 °C and the device was annealed at 200 °C for 30 min. They performed a combinatorial study of doping concentration using Al and reported that the highest mobility can be obtained by 1% Al doping and the best reliability can be obtained using 5% Al doping. As shown in Figs. 3(a) and 3(b), the mobility decreased and threshold voltage was shifted positively when the Al doping concentration was raised, which was explained by carrier concentration suppression. On the other hand, the improved electrical stability was attributed to the coarsening of the crystal size and the preferred orientation along the nonpolar direction afforded by the addition of Al.
Specifically, the instability of ZnO-based TFTs is still a difficult problem to solve which is generally attributed to the defects contained in the bulk active layer as well as in the interface of the active layer and the insulator layer, as reviewed by Conley. To obtain highly stable ZnO-based TFTs, some papers have reported using Hf as a doping material for ALD ZnO TFTs. As shown in Figs. 3(c) and 3(d), HfZnO TFTs can be fabricated by ALD using DEZ and tetrakisethylmethylaminohafnium as Zn and Hf sources and DI water as an oxygen source at a deposition temperature.

![Fig. 3. (a) Electrical performance and (b) V_{th} shift during 3000 s under positive bias stress at a gate bias of 10 V for pure ZnO and AZO TFTs as a function of Al content. Reproduced with permission from C. H. Ahn and H. Kim, J. Electrochem. Soc. 158, H170 (2011). Copyright 2011, The Electrochemical Society. (c) Dependence of threshold voltage shift on stress time; (d) Calculated DOS distributions as a function of the energy (E_{C} – E) for ZnO and HZO-TFTs. Reprinted with permission from X. Ding et al., Nanoscale Res. Lett. 12, 63 (2017). Copyright 2017, Springer.]

![Fig. 4. (a) Schematic illustration of the cross section of a flexible TFT structure incorporating InOx as the active layer. (b) Representative transfer characteristics (I_D vs V_G) of the devices incorporating InOx films grown at 125 and 150 °C.]

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of 150 °C. Although the field effect mobility slightly decreased from 11.3 to 9.4 cm²/V s as Hf content was increased due to the higher oxygen binding energy of Hf ions compared to Zn ions, which suppressed the generation of oxygen-vacancy-related defects, the stability under gate bias with temperature stress was significantly improved. This is attributed to the reduced density of states (DOS) calculated based on the experimentally obtained activation energy (Eₐ).

B. InOₓ-based active-layer materials

1. InOₓ

Indium oxide (InOₓ) has also been reported to be a potential candidate active-layer material in TFT devices because of its high mobility n-type character originating from the single free electronlike band of the In 5s state.115–117 The electrical characteristics of InOₓ thin films, grown by an ALD method using [1,1,1-trimethyl-N-(trimethylsilyl) silanaminato]-indium (InCA-1) as the indium source and hydrogen peroxide (H₂O₂) as an oxidant, also exhibit a strong dependence on the growth temperature.118 As shown in Fig. 4, it has been reported that InOₓ films act like TCO films at growth temperatures higher than 200 °C due to their relatively low electrical resistivity (∼10⁻⁴ Ω cm) and high optical transparency (>85%). Low resistivity at high growth temperature is supposed to be attributed to the high carrier concentration resulting from its crystallinity and molecular orbital ordering. On the other hand, at relatively low growth temperatures below 150 °C, indium oxide behaves as a transparent semiconducting oxide so that the related TFT devices exhibit reasonably high performance with a saturation mobility exceeding 15 cm²/V s and a threshold voltage near 0 V. As the as-deposited InOₓ generally exhibits metal-like conduction, the total carrier concentration can be reduced not only by decreasing growth temperature but also by some other methods, such as annealing in an oxygen-rich environment,104 exposure to N₂O plasma,74 or doping with high oxygen affinity metal cations.80

2. Zn/Ga-doped InOₓ

A homogeneous laminated IZO active layer was reported by Park’s group, as shown in Fig. 5, which was grown using the concept of an IZO supercycle, containing one ZnO cycle and one In₂O₃ cycle, using InCA-1 and DEZ as metal sources and H₂O₂ as an oxidant. The electrical performance of IZO TFTs deposited at different temperatures (150–200 °C) were evaluated.22 The higher mobility and stability of IZO TFTs deposited at a higher temperature are supposed to be due to the larger amount of shallow donor states.

Table II. Growth rate and atomic composition of thin films grown via ALD with various sequences [growth rate and atomic percentages obtained via spectroscopic ellipsometry and Auger electron spectroscopy (AES)].

| Sequence        | Supercycle          | Growth rate (Å/cycle) | At. % C | At. % Ga | At. % In | At. % O |
|-----------------|---------------------|-----------------------|---------|----------|----------|---------|
| GaO             | (TMGa)–H₂O₂         | —                     | —       | —        | —        | —       |
| InO             | (InCA-1)–H₂O₂       | 0.97                  | 0.5     | 0        | 42.8     | 56.7    |
| In-Ga           | (InCA-1)–(TMGa)–H₂O₂| 0.77                  | 0.7     | 3.8      | 39.6     | 55.9    |
| Ga-In           | (TMGa)–(InCA-1)–H₂O₂| 0.33                  | 0.4     | 28.3     | 14.9     | 56.4    |
| InO-GaO         | (InCA-1)–H₂O₂–(TMGa)–H₂O₂| 0.42             | 0.6     | 20.6     | 22.7     | 56.2    |
corresponding to the higher carrier concentration, and fewer deep level states, corresponding to the better stability.

It should be noted that not only can the composition of the combined ALD thin film be adjusted by changing the number of sub-cycles, but the influence of the growth mechanism on the composition can be enhanced if the surface termination is changed by using different metal precursors. It was reported that a discrepancy appeared between the actual growth of IZO and the sum of the respective binary oxides, which increased at higher deposition temperatures. Two surface reaction cases were proposed for the $\text{In}_2\text{O}_3$ cycle, where higher temperature may cause the $\text{InCA-1}$ precursor to release an additional $\text{CH}_3$ ligand so that In bonds to two $\text{OH}$ sites. During the following ZnO cycle, the number of sub-cycles can be adjusted.

![Figure 6](image-url) - (a) Structure diagram of top gate bottom IGO TFT. (b) Transfer performance of the InO-GaO sequence in different InO sub-cycles. Reprinted with permission from J. Sheng et al., ACS Appl. Mater. Interfaces 9, 23934 (2017). Copyright 2017, American Chemical Society.

![Figure 7](image-url) - (a) XRD spectra of as-deposited ZnO, InZnO (16% and 23%), and InGaZnO; (b) $V_{th}$ and $\mu_E$ of TFTs with ZnO, a-IZO [In/(In + Zn) = 27%], and a-InGaZnO active channels with In/(Ga + In + Zn) = 20%, 24%, 15%, and Ga/(Ga + In + Zn) = 8%, 12%, 14%, respectively. Reprinted with permission from A. Illiberi et al. ACS Appl. Mater. Interfaces 7, 3671 (2015). Copyright 2015, American Chemical Society. (c) Variations in atomic ratios of the ALD-IGZO films and (d) transfer characteristics of the related TFTs prepared at different temperatures of 130, 150, and 170 °C. Reprinted with permission from S.-M. Yoon et al., ACS Appl. Mater. Interfaces 9, 22676 (2017). Copyright 2017, American Chemical Society.
of -OH sites on the surface is reduced, resulting in a suppressed ZnO growth rate at high growth temperatures despite the increased reactivity.

The growth mechanism was further examined in a study of ALD indium gallium oxide (IGO) TFTs. Table II displays the growth rate and chemical composition of ALD grown IGO thin films using trimethylgallium (TMGa) and InCA-1 as the gallium and indium sources. No growth of gallium oxide was detected when the GaO sequence was applied, while varying Ga compositions were observed when an InCA-1 pulse was included in the sequence and a reactant pulse was launched before and after the sequential metal precursor pulses. The mechanism behind these different reactivities was explained by density functional theory, showing that adsorption of TMGa on the hydroxylated InOx surface would be spontaneous and irreversible.

The IGO TFTs were fabricated in a top-gate bottom-contact structure, as shown in Fig. 6, using different supercycles composed of InOx and GaO subcycles to control the atomic composition as well as electrical characteristics, such as carrier concentration and resistivity. The ALD IGO TFT achieved an optimum mobility of 9.45 cm²/V·s with a 3InO-GaO supercycle, which is comparable to that achieved in previous reports of sputter deposited IGO TFTs.

C. Multicomposition active-layer materials

AOS, which are based on ternary and quaternary zinc compounds (e.g., InGaZnO and InZnSnO), can have their electrical properties fine-tuned by varying the composition ratio of metal ions. Basically, amorphous indium gallium zinc oxide (a-InGaZnO) is the most widely utilized AOS for the active channel in TFTs due to its reasonably large...
mobility ($\mu > 10 \text{ cm}^2/\text{V s}$), low off-currents due to good controllability of the carrier concentration over a wide range ($10^{15} - 10^{19} \text{ cm}^{-3}$), and long-term stability.\textsuperscript{18,119}

Recently, several papers reported on thermal ALD IGZO TFTs\textsuperscript{81,120} as well as spatial ALD IGZO TFTs.\textsuperscript{21,82} The nucleation and growth of InGaZnO thin films by spatial atmospheric ALD were investigated by Illiberi’s group, using DEZ, trimethyl indium (TMIn), triethyl gallium (TEGa), and water as metal precursors and oxygen precursors.\textsuperscript{21} The morphology of the films changes from polycrystalline, for ZnO and In-doped ZnO, to amorphous for In-rich IZO and InGaZnO. As the XRD spectra shown in Fig.\textsuperscript{7(a)}, ZnO has a polycrystalline structure with (002) and (100) main orientations and the incorporation of In-atoms into the ZnO lattice induces a decrease in the intensity of the crystalline peaks and a shift of the (100) peak positions toward lower angles and finally results in an amorphous thin film structure as the In-content is further increased. These changes are generally reported\textsuperscript{121–124} and can be explained by the creation of crystallographic defects by In-atoms. On the other hand, the use of these films as the active channel in TFTs has been demonstrated and the influence of In and Ga cations on the electrical characteristics of the TFTs has been studied, as shown in Fig. 7(b).

The influence of growth temperature on thermal ALD IGZO TFTs also has been investigated. The IGZO film composition was analyzed after deposition using an indium–gallium single precursor, DEZ, and ozone. The results are exhibited in Fig. 7(c) where the atomic ratio of In:Ga:Zn was kept at 1:1:3 for all temperature conditions (from 130 to 170 °C). The amounts of oxygen-related defects such as oxygen vacancies increased with increasing ALD temperature, which explains the carrier mobility in the saturation regions ($\mu_{\text{sat}}$) for the fabricated TFTs using the IGZO channel layers, which were estimated to be 6.1–14.8 cm$^2$/V s with increasing ALD temperature [Fig. 7(d)]. It should be noted that the obtained device characteristics were sufficiently comparable to those of the conventional sputter-deposited IGZO TFTs.

Traditional InGaZnO is now facing a crisis as the mobility is generally limited to approximately 10 cm$^2$/V s, which is insufficient for the increasing requirements of high resolution, high response speed displays.\textsuperscript{125,126} Physically, doping of SnO$_x$ to InZnO is expected to increase the mobility due to the increased orbital overlap and conduction band dispersion by the large 5s orbital of Sn$^{4+}$ and, at the same time, improve the physical and chemical stability of the devices, thanks to the larger bond-dissociation energy (528 kJ/mol).\textsuperscript{28,127} Thus, indium zinc tin oxide (IZTO) as a typical n-type semiconductor material has been suggested as a promising candidate due to its relatively high field effect mobility values close to 30 cm$^2$/V s and superior stability compared to IGZO TFTs.

InO$_x$ and ZnO were grown one cycle at a time in alternating sequences throughout the entire IZO thin film, while

\begin{table}[h]
\centering
\begin{tabular}{llllll}
\hline
Date & Material & Precursor & Reactant & Growth temp. (°C) & Mobility (cm$^2$/V s) & Reference \\
\hline
2012 & Cu$_2$O & Cu(I)(hfac)(TMVS) & H$_2$O & 225 & 5.3 (Hall) & 138 \\
2013 & Cu$_2$O & ffacCu(I)(DMB) & H$_2$/O$_2$ plasma & 110 & 37 (Hall) & 139 \\
2016 & Cu$_2$O & ffacCu(I)(DMB) & Ozone & 100 & 5.64 & 136 \\
2015 & Cu$_2$O & Cu(dmamp)$_2$ & H$_2$O & 120–240 & 8.05 (Hall) & 140 \\
2014 & SnO & Sn(dmamp)$_2$ & H$_2$O & 210 & 2.9 (Hall) & 141 \\
2017 & SnO & Bis[bis(trimethysilyl)amino]tin(II) & H$_2$O & 100–250 & — & 142 \\
2017 & SnO & Sn(dmamp)$_2$ & H$_2$O & 210 & 2 & 143 \\
2018 & SnO & N,N’-tert-butyli-1,1-dimethylethylediamine stannylene (II) & H$_2$O & 60–180 & 20 (Hall) & 144 \\
\hline
\end{tabular}
\caption{Brief summary of ALD deposited p-type materials.}
\end{table}
[TDMASn–H2O2] cycles (one cycle or two cycles) immediately followed after the [InCA–1–H2O2–DEZ–H2O2] cycle to obtain the IZTO(111) and IZTO(112) samples. The concentration of Sn rose from 9.0% to 15.8% when the number of SnOx sub-cycles was increased from 1 to 2, and all the thin films exhibited uniform and homogeneous growth [Fig. 8(a)]. The amorphous IZTO thin films deposited by ALD were found to contain large amounts of carriers and fewer deep oxygen defect sites compared to the ALD IZO thin films. The electronic structures were examined and simulated, attributing the superior electrical properties to the increased electron activity (value of EC−EF from 0.73 to 0.53 eV) and decreased number of oxygen related defect sites. Such superior properties contribute to device performance resulting in the improvement of the mobility and stability of IZTO TFTs from 19.2 to 26.8 cm²/V s and from ΔVth of 1.8 V to 0.7 V compared to IZO TFTs, as shown in Fig. 8(b).

III. P-TYPE MATERIALS FOR ACTIVE LAYERS

For the n-type oxide materials, oxygen vacancies could easily generate electron carriers. Also, the electronic configuration of the conduction-band minimum mainly consists of metal s orbitals, which means electrons are delocalized so that n-type oxide materials could have high electron concentrations and mobilities. On the other hand, for p-type oxide materials, the situation is quite different. The high formation energy of metal cation vacancies and low anion formation energy limits the generation of hole carriers. Additionally, the main pathway for the hole carriers, the valence-band minimum (VBM), consists of anisotropic, localized oxygen p orbitals. Owing to these properties, the mobility of hole carriers is low.

Although it is difficult to fabricate p-type oxide materials with good performance, there are a few candidates such as Cu-based oxides (binary and ternary Cu oxides) and tin monoxide. When the ALD method is applied to deposit p-type materials, owing to the characteristics of ALD, the composition of the thin films can easily be controlled by combining different ALD cycles to fabricate binary, ternary, or even quaternary compounds. Furthermore, phase engineering could be easily achieved via adapting different ALD processes. Besides, due to the size scaling requirement of electronic device, the precise thickness control and highly uniform growth of thin films are needed, ALD process will certainly become the strongest candidate for p-type oxide semiconductor deposition. Recent reports of ALD p-type oxide are summarized in Table III.

A. Copper oxide

Cuprous oxide (Cu2O) with a cubic crystal structure [Fig. 9(a)] has p-type characteristics with a high Hall mobility exceeding 100 cm²/V s. The p-type characteristics of Cu2O come from Cu vacancies (Vc) and interstitial oxygen (Oi). As shown in Fig. 9(b), the valence band of Cu2O consists of fully occupied Cu 3d and O 2p hybrid orbitals, which are less localized than the O 2p orbitals of most oxide materials. These hybridized orbitals act as a hole conducting pathway, so that Cu2O can exhibit a high Hall mobility.

In a previous report, CuOx thin films were deposited using a thermal ALD process at 100 °C. The TFT devices...
were fabricated using as-deposited Cu2O and thermally annealed CuO, and the transfer curves of the TFTs are shown in Fig. 10. The device annealed at 300 °C showed the highest field effect mobility of about 5.64 cm2/V s with a high on-off ratio (∼105), whereas CuO annealed at a different temperature exhibited low mobility. This might be explained by competition between the Cu2O phase and CuO phase. Depending on the annealing temperature, the ratio of Cu2O and CuO could be changed, thus changing the charge transfer characteristics owing to their different electrical properties. As a result, Cu2O is a promising candidate for p-type oxide active layers, which can also be deposited even at low temperatures, which means that it could be applied to flexible devices.

B. Tin monoxide

The other candidate p-type oxide material is tin monoxide. Tin oxide has two well-known stoichiometric forms: tin dioxide (SnO2) and tin monoxide (SnO). Tin dioxide is an n-type material with a high Hall mobility and high carrier concentration, while on the other hand, SnO is a p-type material with a layered structure, as shown in Fig. 11(a). The p-type nature of SnO comes from its low formation energy, VSn, and dispersed VBM electronic structure with hybridized Sn 5s and O 2p orbitals [Fig. 11(b)].

Kim’s group reported a TFT application using SnO as an active layer, deposited at 210 °C. Also, two different processes were employed to condition the TFTs: (1) thermal annealing at 250 °C under an Ar atmosphere for 1 h and (2) passivation of the SnO surface with ALD grown Al2O3. Figures 12(a)–12(c) show the transfer characteristics of the as-grown, annealed, and Al2O3-passivated SnO TFTs with active-layer thicknesses ranging from 6.4 to 14 nm. All of the TFTs are p-type TFTs, and the current value decreased with decreasing channel thickness. The post-annealing at 250 °C under an Ar atmosphere was beneficial in effectively suppressing Ioff, as can be observed in Fig. 12(b). The passivated TFT’s Ioff also decreased, owing to the decrease in excess oxygen content near the SnO surface. From these results, SnO could easily change to SnO2, so surface passivation or finding a way to prevent oxidation is important.

SnO has only recently been studied as a p-type material, which can be deposited using an ALD process; therefore, further investigation and optimization are required for its application as a high-performance p-type material.

IV. SUMMARY AND CONCLUSIONS

In this review, recent progress in oxide TFTs has been discussed with a focus on n-type and p-type active layers grown by ALD, anticipating the development of device performance. An n-type active layer can be improved by oxide semiconductor combinations from binary (ZnO) to ternary (IGZO, ITZO) compounds, since the ALD method allows for easy control over the atomic composition of nanstructured layers that can result in decreased bulk active defect states and improved device mobility as well as increased carrier concentration. However, the mechanisms of ALD growth for multicomponent oxides are often more complex than a simple sum of the growth metrics for constituent binary oxides. Therefore, current lack of understanding regarding multicomponent ALD growth for oxide semiconductor materials is limiting their applicability as the active layer of TFTs. In terms of p-type oxide semiconductor material, till now, there have been only a few reports investigating p-type oxide materials via ALD, and their electrical properties are inadequate for TFT device applications. However, since previous results have shown in ALD p-type TFT with great potential, further study should be conducted focusing on material and precursor optimization as well as device fabrication process development to show a grander prospect.

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