Metal oxide semiconductors are considered as an active material for the next generation thin film transistor (TFT) technology due to their favorable mobility. One of the most promising applications for the metal oxide TFT is the active matrix (AM) backplane of liquid crystal displays (LCDs) and organic light emitting diode display (OLEDs)\(^\text{[12]}\). Various oxide semiconductor materials have been suggested, such as zinc tin oxide (ZTO), indium zinc oxide (IZO), and indium gallium zinc oxide (IGZO), which are fabricated by vacuum-based deposition.\(^\text{[1-4]}\) Among various oxide semiconductor materials, the IGZO has been widely studied due to its exceptional performance and stability with low temperature processes (even at room temperature). However, such processes require expensive facilities and restrict the size of the substrates due to the physical restrictions of the equipment.\(^\text{[5-8]}\)

The solution process technique for fabricating oxide TFTs offers additional benefits over vacuum-based techniques: simplicity, high throughput, low fabrication cost, and large area uniformity. In addition, the mild deposition condition rarely damages the underlying layer, usually the gate insulator in a TFT, while vacuum-based processes involve plasma or a high vacuum state. This process improves the interface, which is an important aspect for TFT applications in terms of device stability because carriers move through the interface between the semiconductor and the gate insulator in the bottom-gated TFT structure.\(^\text{[9]}\)

In many studies, indium (In) is considered a prerequisite component for high performance TFTs, especially in solution process, because In offers high mobility due to a small electron effective mass of 0.25–0.35 \(\mu\)m\(^2\)V\(^{-1}\)s\(^{-1}\) \((m_e =\text{mass of an electron})\) from a high degree of s-orbital overlapping.\(^\text{[1]}\) The other atoms, such as Zn; Al; Ga, are considered carrier suppressors, which usually result in improved stability. We have reported on aqueous solution processed In\(_x\)O\(_y\) TFTs on transparent flexible plastic substrates with good electrical properties and stability.\(^\text{[10]}\) The aqueous solution route allows the preparation of a precursor solution without additional additives and catalysts due to the high polarity, formation of oxide with low process temperature, and environmentally friendly deposition conditions.\(^\text{[10,11]}\) In addition, the metal oxide TFTs via an aqueous route exhibited better electrical characteristics than alcohol-based precursor solutions, such as higher mobility and stability. In this study, we focus on the bias stability of high performance oxide TFTs for AM backplane applications.

We characterized the electrical property and stability of the metal indium oxide (XIO, X = Zn, Ga, and Al) TFTs under negative bias stress (NBS) and positive bias stress (PBS) to understand the effect of the metal compositions. Since the carrier concentration for In\(_2\)O\(_3\) annealed at 350°C is over 10\(^{12}\)cm\(^{-2}\), the Fermi level is constructed to be very close to the conduction band minimum (CBM).\(^\text{[12]}\) This makes it impossible to deplete the channel layer of the In\(_2\)O\(_3\) TFT with acceptable gate voltage. The Zn, Ga, and Al metal components were introduced into the In\(_2\)O\(_3\) matrix to control the carrier concentration and activate the semiconductor.\(^\text{[2]}\) In order to obtain the optimized composition for the high performance metal oxide TFTs, the composition of Zn, Ga, and In was carefully controlled.

**Experimental**

The preparation of the aqueous precursor solution starts with dissolving the metal nitrate precursor in deionized water. The sources for In, Zn, Ga, and Al were In(NO\(_3\))\(_3\)\(\cdot\)xH\(_2\)O, Zn(NO\(_3\))\(_2\)\(\cdot\)xH\(_2\)O, Ga(NO\(_3\))\(_3\)\(\cdot\)xH\(_2\)O, and Al(NO\(_3\))\(_3\)\(\cdot\)xH\(_2\)O, respectively (purchased from Aldrich and used without further purification). The total concentration of the metal nitrate precursors in the final precursor solution was fixed to 0.2 M (The amount of water molecule attached to the precursor was not included in the calculation of precursor concentration). The precursor solutions were stirred at room temperature for 24 h to make a transparent and homogeneous solution. After sufficient reaction the solution was filtered through a 0.22 \(\mu\)m syringe filter (Polytetrafluoroethylene, GE) and spin-coated on the SiO\(_2\)/Si substrate for 30 s with a speed of 5000 rpm. A 100 nm aluminum source drain electrodes were deposited using an E-beam evaporator through a shadow mask under a pressure of 10\(^{-6}\) Torr. The channel length and width for the device were 100 and 1000 \(\mu\)m, respectively.

After fabricating the TFTs, their electrical performance was measured in an ambient atmosphere in a dark room at room temperature using an HP 4156A semiconductor parameter analyzer. X-ray photoelectron spectroscopy (XPS) spectra were detected using a Thermo VG Scientific Sigma Probe with a base pressure of 1,486.6 eV was used. The Atomic force microscopy (AFM) and scanning electron microscope (SEM) images were measured using a SPA400, Seiko Inc. and Philips XL 30 SFEG with an electron acceleration voltage and current of 10.0 kV and 3.0 \(\mu\)A, respectively. X-ray diffraction (XRD) patterns were recorded with a RIGAKU D/MAX-2500 using Cu K\(_\alpha\) radiation coupled to a multilayer mirror.

**Results and Discussion**

Fig. 1 shows the transfer characteristics of XIO TFTs according to the metal composition. The performance parameters, including the mobility and the threshold voltage, were calculated from a linear fitting to the plot of the square root of drain current (\(I_D\)) versus gate voltage (\(V_G\)) in the saturation region. The performance of the optimized oxide TFTs (Zn\(_x\)In\(_{1-x}\)O, Ga\(_x\)In\(_{1-x}\)O, and Al\(_x\)In\(_{1-x}\)O) is summarized in Table I.

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**Table I.**

<table>
<thead>
<tr>
<th>Metal Composition</th>
<th>Mobility ((\mu)m(^2)V(^{-1})s(^{-1}))</th>
<th>Threshold Voltage (V(_T))</th>
<th>On/Off Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>In(_2)O(_3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn(<em>x)In(</em>{1-x})O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga(<em>x)In(</em>{1-x})O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(<em>x)In(</em>{1-x})O</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Transfer characteristics of oxide TFT according to the metal composition. (a) AIO, (b) GIO, and (c) ZIO TFTs.

Table I. Electrical performance of the optimized XIO (X = Zn, Ga, and Al) TFTs.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Annealing Temperature (°C)</th>
<th>Mobility (cm²/V s)</th>
<th>$I_{on}/I_{off}$</th>
<th>S (V/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₈In₉O</td>
<td>350</td>
<td>4.5</td>
<td>$\sim 10^7$</td>
<td>0.36</td>
</tr>
<tr>
<td>Ga₄In₆O</td>
<td>350</td>
<td>12.1</td>
<td>$\sim 10^7$</td>
<td>0.51</td>
</tr>
<tr>
<td>Zn₅In₅O</td>
<td>350</td>
<td>13.0</td>
<td>$\sim 10^8$</td>
<td>0.41</td>
</tr>
</tbody>
</table>

optimized IZO TFT exhibited good electrical property, a mobility of 13.0 cm²/V s, an on-to-off current ratio over $10^7$, and an sub-threshold slope (S) of 0.41 V/decade.¹³

Oxide TFTs attract great attention especially in the display field due to the high potential for next generation displays. Since the TFT is the basic unit for integrated circuitry, the operation stability of the TFT is one of the most important aspects when considering display applications such as the backplane of AMLCDs and AMOLEDs. The typical unit pixel circuit for the driving backplane of an active-matrix LCD is comprised of a switching transistor and two capacitors. In conventional pixel circuits, the turn-off time (~16.7 ms) is $10^3$ times longer than that of the turn-on time (~21 μs) during one frame time.¹⁴ That means that the typical driving circuit for an AMLCD is persistently exposed to $-5$ V of negative bias stress for the most of the time. On the other hand, the unit pixel circuit for driving an active-matrix OLED is basically composed of switching and driving transistors. The switching transistor is responsible for determining the on- and off-state of the pixel, which does not require very strict stability. However, a high level of resistance to the external bias stress is necessary for the driving transistor. Since the brightness of the OLED is determined by the input current, a highly stable and accurate operation is required against stress time.¹⁴

The high ionicity of the metal oxide allows the high performance of TFTs. However, the ionic behavior of the metal oxide also enables the interaction between oxide and molecules in the air.¹⁵,¹⁶ The evaluation of bias stability was conducted in an N₂ atmosphere to exclude the effect of molecules in an ambient atmosphere such as water and O₂.

Fig. 2 displays the evolution of transfer characteristics of oxide TFTs, according to the negative bias stress (NBS, $V_G = -20$ V) time. The transfer curves tend to shift the negative voltage without changing...
AIO TFTs with 3.6 ks NBS (VG
threshold voltage (Vth) for the oxide TFTs are summarized in
film. related to the relatively larger amount of metal hydroxide in AIO thin
ductor and the gate insulator.18
charge trapping phenomenon at the interface between the semicon-
time followed the stretched exponential model, which describes the
\[ |\Delta V_{th}| = |\Delta V_{th0}| \left( 1 - \exp \left( -\left( \frac{t}{\tau} \right)^\beta \right) \right) \]
where \( \Delta V_{th0} \) is the \( V_{th} \) shift at infinite time, \( t \) is the time, \( \beta \) is the
stretched exponential exponent, and \( \tau \) is the relaxation time constant.
The ZIO TFT had longer characteristics carrier trapping time (\( \tau \)) compared to the AIO TFT. (ZIO > GIO > AIO) It seems that this is
related to the relatively larger amount of metal hydroxide in AIO thin
film.
The effect of the positive bias stress (PBS, \( V_G = +20 \) V) on oxide TFTs was investigated and is shown in Fig. 3. The parallel shift of the transfer characteristics was also observed. The shift of the threshold voltage under the PBS (\( V_G = +20 \) V) for 3.6 ks were 3.4 V, 1.2 V, and 0.4 V, respectively. The trapped electron at the interface reduced the effective applied gate voltage and resulted in a positive shift of transfer characteristics. The time evolution of \( V_{th} \) for the oxide TFTs are summarized and fitted with a stretched exponential model in Fig. 3d. In both cases, no significant change in S is observed under ~2 MV/cm of bias stress. This means that the oxide channel layer is rigid and solid to the external bias stress.17 The characteristics carrier trapping for AIO TFT under PBS is shorter than IZO TFT. The effective suppression of carrier by addition of Al allows the improvement of stability under PBS.

It is important to note that there is an opposite tendency of stability under PBS and NBS. An AIO TFT exhibits good resistance to PBS but a relatively large \( V_{th} \) shift under NBS. That means that a higher level of resistance to PBS does not promise good NBS stability.

XPS was conducted to understand the chemical composition of the resultant oxide thin-films. The XPS O 1s analysis of the films is displayed in Figs. 4a–4c. The deconvolution of the spectra represents the contributing peaks at ~530.0 (red), ~531.0 (blue), and ~532.0 eV (olive) from oxygen atoms in the metal oxide lattice, oxygen atoms near oxygen vacancy in metal oxide, and oxygen in metal hydride related species, respectively.7,19 The composition of the oxygen atoms and the bias stability results are summarized in Fig. 4d. The hydride related species rich film (AIO > GIO > ZIO) exhibits a large \( V_{th} \) shift under NBS and the \( V_G \) rich film (ZIO > GIO > AIO) shows a large \( V_{th} \) shift under PBS. In addition, the resulting XIO thin-films has very smooth surface with amorphous structure, as shown in Fig. 5 and 6.

It seems that the hydride related species and oxygen vacancy are responsible for the instability from NBS and PBS, respectively. The parallel shift of the transfer characteristics, without a change in the sub-threshold slope, is considered as a charge trapping phenomenon at the interface between the semiconductor and the gate insulator. That means that the instability from NBS and PBS is due to the hole and electron trapping, respectively. The hydride related species, which is negatively charged, can act as a hole trapping center and results in a negative parallel shift of transfer characteristics.20 The defects in the bandgap were primarily a deep donor state, which generally exist as a form of oxygen vacancy in oxide semiconducting materials.21 The ionized state of oxygen vacancies captures the electron and...
Figure 4. X-ray photoelectron spectroscopy O 1s analysis of (a) AIO, (b) GIO, and (c) ZIO thin-films. (d) Relation between $V_{th}$ shift and chemical composition of thin films.

Brings a parallel shift of transfer characteristics due to the screening effects.

The cations which form stronger chemical bonds suppress the carrier generation via oxygen vacancy formation. The Ga ion is a well-known carrier suppressor which could enhance the stability of the TFT. The Al ion is a more effective carrier suppressor than the Ga ion due to the stronger chemical bond with oxygen. A small amount of Al controls the carrier adequately by reducing the oxygen vacancy (which is also related to the generation of carrier), as shown in Fig. 4d, and relocates the turn-on voltage of the TFT to the positive voltage.

In the sol-gel process, the metal oxide framework is achieved by a thermally driven condensation reaction, including olation (Eq. 1) and oxolation (Eqs. 2, 3) reactions, which are based on a nucleophilic reaction between metal cations. The relatively large difference of electronegativity ($\chi$) between In ($\chi = 1.78$) and Zn ($\chi = 1.65$) facilitates the condensation reaction and results in a low level of hydroxide related species. In addition, the partial charge of oxygen, which could participate in the nucleophilic reaction, is more negative in a Zn matrix than a Ga ($\chi = 1.81$) matrix due to the larger difference in electronegativity ($\chi_{\text{oxygen}} = 3.44$). Since the oxolation reaction, which eliminates the H and completes the oxide formation in the reaction (Eq. (2.2)), is achieved by a nucleophilic reaction, the more negative partial charge of oxygen in OH stimulates the nucleophilic reaction and results in a lower level of OH species. We found that the number of hetero-cations also affects the quantity of hydroxide related species when considering the AIO thin-film case. Though the electronegativity of Al ($\chi = 1.61$) is comparable to Zn, a small quantity of Al cannot strongly affect the oxolation reaction.

Figure 5. Atomic force microscopy surface image of (a) AIO, (b) GIO, and (c) ZIO thin-films.
the number of hydroxide related species strongly affects the resistance against PBS, an effective reduction of the species is required for practical circuitry applications. Therefore, careful consideration and design of material, including chemical composition, is required for high performance oxide TFTs with good stability.

\begin{equation}
M_1 - OH + M_2 - OH_2 \rightarrow M_1 - OH - M_2 + H_2O \tag{1}
\end{equation}

\begin{equation}
M_1 - OH + M_2 - OH \rightarrow M_1 - O - M_2 + H_2O \tag{2}
\end{equation}

\begin{equation}
M_1 - OH - M_2 + M_1 - OH \rightarrow M_1 - O - M_2 - M_1 + H_2O \tag{3}
\end{equation}

Conclusion

We fabricated and characterized the performance and stability of XIO (X = Zn, Ga, and Al) TFTs via an aqueous route with 350°C annealing. The optimized IZO TFTs exhibited good electrical performance, a mobility of 13.0 cm²/V s, an on-to-off current ratio over 10⁵, and an S of 0.41 V/decade. The stability of the optimized oxide TFTs against NBS and PBS was evaluated and we concluded that the instability of the oxide TFT is due to the charge trapping phenomenon. The combinational study of bias stability and chemical composition, which was characterized using XPS analysis, indicates that the hole and electron trapping are due to the metal hydroxide species and oxygen vacancy, respectively. It was found that the addition of Al, Ga, and Zn atoms in an oxide matrix influenced the oxygen chemical composition and stability of the devices.

Acknowledgments

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References