Improvement of the positive bias stability of a-IGZO TFTs by the HCN treatment

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1. Introduction

Recently, oxide thin-film transistors (TFTs) have attracted much attention for applications in active-matrix liquid-crystal displays (AMLCDs) and active-matrix organic light-emitting diode displays (AMOLEDs) due to their various competitive advantages. In particular, amorphous indium gallium zinc oxide (a-IGZO) TFTs have a high mobility (>20 cm²/V) compared to conventional amorphous silicon TFTs (~0.5 cm²/V). As such, a-IGZO TFTs represent promising switching devices for flat panel displays that possess ultra-high-definition (resolution: 2000 x 4000), large size (>50 in.), and high frame rate operation (>240 Hz) [1,2]. In addition, a-IGZO TFTs have a higher transparency over the entire visible light range, as compared to silicon-based TFTs, because of their wide band gap. They also possess better uniformity than polysilicon TFTs because of their amorphous structure [3,4]. However, bias stability issues of a-IGZO TFTs under gate bias stress still need to be resolved in flat panel displays such as AMLCDs and AMOLEDs. According to many studies investigating the stability of a-IGZO TFTs, the bias stability is very sensitive to oxygen vacancies in a-IGZO films as well as to ambient oxygen molecules [5–7]. For these reasons, passivating the oxygen vacancy defect states and the a-IGZO back-channel layer is necessary in order to maintain good bias stability under gate bias stress.

Many studies have been made in attempts to improve the stability of oxide TFTs by reducing the number of oxygen vacancy defect states in oxide semiconductors. The approaches used in these studies typically utilize high pressure oxygen annealing or the addition of carrier suppressors, such as gallium (Ga), hafnium (Hf), and zirconium (Zr), to the oxide semiconductor. Carrier suppressors can prevent the formation of oxygen vacancies because they have high ionic field strengths, which allow oxygen to be bound more tightly. However, these methods result in degradation of the electrical characteristics, including the mobility and threshold voltage ($V_{th}$), of oxide TFTs [8–10]. Additionally, there have been many studies investigating ways to protect the back-channel layer of a-IGZO TFTs; this is typically done by employing a passivation layer. However, passivation layers, such as SiO₂ and SiNₓ, lead to $V_{th}$ shifts in a-IGZO TFTs because hydrogen radicals in the process chamber can diffuse into the a-IGZO bulk and act as donors during deposition [11,12].

Removing metal species by treating semiconductors with hydrogen cyanide (HCN) solutions has been found to be an effective method to improve the electrical characteristics and bias stability of semiconductor devices. To remove metal species on Si, for example, the HCN treatment is performed using extremely dilute (3 ppm) HCN solutions at room temperature; this results in the complete removal (below $\approx 3 \times 10^{10}$ atoms/cm²) of metal contaminants [13–15]. The removed metal species are present in the form of metal-cyano-complex ions, which are extremely stable in HCN solutions, allowing them to avoid re-adsorption [15]. In addition,
cyanide ions (CN⁻) in HCN solutions selectively react with defect states, such as Si and Cu dangling bonds, by forming Si-CN [13,16,17] and Cu-CN [18,19] bonds, respectively. This passivates the defect states. However, HCN treatments have yet to be attempted on oxide semiconductor-based devices.

In this study, we performed HCN treatments on a-IGZO TFTs to improve their bias stability under a positive gate bias stress (PBS). To confirm the bias stability improvement of the HCN-treated a-IGZO TFTs, the standard device electrical properties were evaluated. Under bias conditions, we focused on the $V_{th}$ shift of a-IGZO TFTs; this shift is closely related to the bias stability of a-IGZO TFTs. In order to understand the effect of the HCN treatment on the bias stability of a-IGZO TFTs, the chemical states were also evaluated through X-ray photoelectron spectroscopy (XPS). Finally, to observe variations of the CN⁻ ions in the a-IGZO bulk, we carried out time-of-flight secondary ion mass spectroscopy (TOF-SIMS) depth profile analysis before and after the HCN treatment.

2. Experimental

Schematic diagrams of the device cross-sections for the HCN treatment and the final structure of the device are shown in Fig. 1(a) and (b), respectively. A 50-nm-thick Mo layer was deposited as the gate electrode on a glass substrate via DC sputtering at room temperature. This was then patterned using a conventional photolithography process. Then, a 100-nm-thick SiN$_x$ gate dielectric was deposited on the substrate by plasma-enhanced chemical vapor deposition at 250 °C. a-IGZO was selected as the active material and a 50-nm-thick a-IGZO film was deposited using RF sputtering with a power of 40 W at room temperature. During deposition, we used an Ar:O$_2$ ratio of 7:3, and the pressure was maintained at 5 mTorr. After defining the active region, one group of TFT devices was fabricated as a reference by following the typical processing sequence (device A). The other group of samples was also treated with an HCN solution, as shown in Fig. 1(a) (device B). The HCN treatment was performed using a 0.1 M HCN solution with a pH of 10 at room temperature for 10 min. Next, a 50-nm-thick Mo film was deposited via DC sputtering at room temperature. The source and drain Mo electrodes were patterned using the lift-off method. Finally, the devices were subjected to thermal annealing at 300 °C for 1 h in N$_2$ ambient. The electrical characteristics were measured using current–voltage ($I$–$V$) measurements using an Agilent E5270B parameter analyzer, and the chemical compositions of the oxide thin films were analyzed using XPS (Theta probe base system, Thermo Fisher Scientific Co.). The binding energy of the C1s peak, caused by contaminant hydrocarbon species on the specimen surfaces, was taken as a reference for the binding energies (284.5 eV). To confirm variations of the various ionic species in the a-IGZO thin film, we conducted time-of-flight secondary ion mass spectroscopy (TOF-SIMS) depth profile analysis.

3. Results and discussion

Several important parameters of pristine devices A and B, such as the saturation mobility ($\mu_{sat}$), threshold voltage ($V_{th}$), and subthreshold swing (SS), were measured at room temperature (298 K). Device A exhibited a $\mu_{sat}$ of 16.9 cm$^2$/Vs, $V_{th}$ of 5.3 V, and SS value of 0.45 V/dec. Device B exhibited a $\mu_{sat}$ of 16.9 cm$^2$/Vs, $V_{th}$ of 5.7 V, and SS value of 0.42 V/dec. Both devices possessed very similar electrical characteristics. Such results indicate that the HCN treatment did not affect the device parameters of pristine devices. Next, we investigated how the HCN treatment influenced the bias stability. Fig. 2(a) and (b) shows the transfer characteristics of non-HCN-treated (device A) and HCN-treated (device B) a-IGZO TFTs as a function of the PBS time. Devices A and B were stressed under the following conditions: the $V_g$ was set to +20 V at room temperature and the maximum stress duration was 2000 s. Table 1 shows a summary of the changes in the $\mu_{sat}$, $V_{th}$, and SS value according to the PBS time in devices A and B. During the bias stability test, neither device showed noticeable changes in the $\mu_{sat}$ or SS value. However, device A suffered from a positive $V_{th}$ shift of ~3.7 V after applying a PBS for 2000 s, whereas device B showed no significant change in the $V_{th}$; a shift of only ~0.2 V was observed under the same PBS conditions. In other words, unlike other treatment methods (e.g., high oxygen pressure annealing or the addition of carrier suppressors), the HCN treatment improves the bias stability while also retaining the desired electrical characteristics. Additionally, the lack of change in the SS value indicates that extra defect states at shallow levels (i.e., the subgap density of states in the energy region that are close to the conduction band) were not created by the HCN treatment; shallow defect states are known to affect the SS value [6]. In general, the positive $V_{th}$ shift of oxide TFTs is attributed to either (i) electron trapping [8,9,20] or (ii) adsorption of oxygen on the back-channel layer [5,12,21].

The electron trapping model can be further classified depending on the electron trapping sites, such as the active/gate insulator interface or oxygen vacancy defects, in our devices. We can exclude the electron trapping model at the active/gate insulator interface because the HCN treatment is carried out on the back-channel layer of a-IGZO TFTs; therefore, it is unlikely to affect the active/gate insulator interface in our bottom-gate a-IGZO TFTs. However, the electron trapping model should be considered for the oxygen vacancy defect states because the bulk of the active layer can be influenced by the HCN treatment. According to Seo et al., the presence of oxygen vacancy defect states leads to poor bias stability under PBS and positive bias thermal stress (PBTS) conditions.

Fig. 1. Schematic diagrams of a-IGZO TFT cross-sections: (a) HCN treatment using a 0.1 M HCN solution with a pH of 10 at room temperature for 10 min and (b) a-IGZO TFT with source/drain electrodes. The channel width (W) and length (L) were 50 μm and 80 μm, respectively.
because the defect states act as electron trap sites in TFTs [22]. For this reason, the bias stability can be improved by passivating oxygen vacancy defect states in the active layer of oxide TFTs under PBS conditions.

Fig. 3 shows the O1s XPS spectra of the (a) non-HCN-treated a-IGZO thin film and (b) HCN-treated a-IGZO thin film. The O1s spectra were deconvoluted into three different peaks: (i) a strong peak at a lower energy, which represents a metal-oxide peak in the oxide lattice without an oxygen vacancy (529.8 eV); (ii) a metal-oxide peak in the oxide lattice with an oxygen vacancy (531.3 eV); and (iii) a metal-hydroxide peak (532.2 eV) [23]. It can be clearly seen that the peak related to the metal-oxide with an oxygen vacancy decreased after the HCN treatment. Presumably, this change is associated with CN⁻ ion penetration. Penetrating CN⁻ ions selectively react with oxygen vacancies. As a result, the unsaturated metal-oxide bonds that originate from oxygen vacancies are present in the form of metal-cyano bonds, which remain in the a-IGZO thin film [13,16,17]. This indicates that the unsaturated metal-oxide bonds near the surface of the a-IGZO thin film are passivated by CN⁻ ions.

Additionally, we carried out time-of-flight secondary ion mass spectroscopy (TOF-SIMS) depth profile analysis in order to observe variations in the various ionic species in a-IGZO thin films as a function of the HCN treatment. For the TOF-SIMS measurements, a 25 keV Bi⁺ ion beam was used as the analysis beam and a 3 keV Cs⁺ ion beam was used as the sputtering beam. Fig. 4 shows the TOF-SIMS depth profile analyses of Ga-O, In-O, Zn-O, SiO₂, CN, and Si ions in non-HCN-treated and HCN-treated a-IGZO thin films.

Table 1
Comparison of the electrical properties of devices A and B as a function of the gate bias stress time.

<table>
<thead>
<tr>
<th>Device</th>
<th>Gate bias stress time (s)</th>
<th>Mobility (cm²/Vs)</th>
<th>Threshold voltage (V)</th>
<th>Subthreshold swing (V/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>16.9</td>
<td>5.3</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>16.9</td>
<td>9.0</td>
<td>0.43</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>16.9</td>
<td>5.7</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>16.8</td>
<td>5.9</td>
<td>0.42</td>
</tr>
</tbody>
</table>
Although the Ga-O, In-O, Zn-O, SiO₂, and Si ions in the a-IGZO thin films did not change noticeably, the intensity of the CN ions was significantly increased in the a-IGZO region after the HCN treatment. This suggests that the HCN treatment affects the bulk of the a-IGZO thin film. In other words, the unsaturated metal-oxide bonds on the surface and in the bulk of the a-IGZO thin film were passivated by CN⁻ ions after the HCN treatment. It can be inferred that the presence of passivated, unsaturated metal-oxide bonds is one of the reasons for the improved bias stability of device B under PBS conditions.

The oxygen adsorption model can also be used to explain the positive Vth shift under PBS conditions. Fig. 5(a) shows the general adsorption process of oxygen molecules on the back-channel layer in the non-HCN-treated device (device A). In general, the interaction between the back-channel layer of a-IGZO TFTs and ambient oxygen is critical in determining the Vth instability because ambient oxygen molecules can capture electrons from the surface of the back-channel layer by the following chemical reaction [5,12,21]:

\[ \text{O}_2 \text{(gas)} + e^- \rightarrow 2\text{O}^{-} \text{(solid)} \]  

(1)

According to Le Chatelier’s principle, high ambient oxygen pressure at a fixed temperature causes an increase of the O⁻_solid. Similarly, when the PBS is applied in a gate electrode, the interaction between the back-channel layer and oxygen molecules can become more activated, which leads to the poor bias stability of a-IGZO TFTs [5,12,21]. For this reason, many researchers have formed passivation layers, such as SiO₂ and SiNx, to protect the back-channel layer of a-IGZO TFTs and prevent oxygen adsorption [12,24]. However, the HCN-treated device (device B) shows good bias stability under PBS conditions (Fig. 2(b)). This can be explained by the fact that the absorbed CN⁻ ions on the back-channel layer can passivate the back-channel layer and block the adsorption of oxygen molecules that induce the Vth shift (Fig. 5(b)). Therefore, applying the HCN treatment on the back-channel layer of a-IGZO TFTs can enhance the bias stability of a-IGZO TFTs under PBS conditions without necessitating the need for a passivation layer. This also demonstrates that the HCN treatment plays a significant role in improving the bias stability of TFTs under PBS conditions.

4. Conclusion

In this study, we investigated how the HCN treatment affected the instability of a-IGZO TFTs under PBS conditions. The HCN treatment caused no noticeable change in the SS value or saturation mobility. However, the non-HCN-treated device suffered from a positive Vth shift of ~3.7 V after applying the PBS for 2000 s. Alternatively, the HCN-treated device exhibited superior stability (ΔVth of ~0.2 V) under the same conditions. In other words, the HCN treatment can improve the bias stability of a-IGZO TFTs without degrading their electrical characteristics. XPS and TOF-SIMS depth profile analysis suggest that unsaturated metal-oxide bonds in the a-IGZO thin film are passivated by forming metal-cyano bonds. Such passivation leads to a significant reduction in the Vth shift in HCN-treated a-IGZO TFTs under PBS conditions. Moreover, it is believed that the absorbed CN⁻ ions can prevent the adsorption of oxygen molecules at the surface, which enables the production of passivation layer-free a-IGZO TFTs.

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