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Ambipolar SnO\textsubscript{x} Thin-Film Transistors Achieved at High Sputtering Power

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SnO is the only oxide semiconductor to date that has exhibited ambipolar behavior in thin-film transistors (TFTs). In this work, ambipolar behavior was observed in SnO\textsubscript{x} TFTs fabricated at a high sputtering power of 200 W and post-annealed at 150-250 °C in ambient air. X-ray-diffraction patterns show polycrystallisation of SnO and Sn in the annealed SnO\textsubscript{x} films. Scanning-electron-microscopy images revealed that microgrooves occurred after the films were annealed. Clusters subsequently segregated along the microgrooves, and our experiments suggested that they are most likely Sn clusters. Atomic-force-microscopy images indicated an abrupt increase in film roughness due to the cluster segregations. An important implication of this work is that excess Sn in the film, which has been generally thought to be detrimental to the film quality, may promote the ambipolar conduction when it is segregated from the film to enhance the stoichiometric balance.

Oxide semiconductors are highly attractive especially for the new generation flexible and wearable electronics due to their low cost, low deposition temperatures, high carrier mobilities (1~100 cm\textsuperscript{2}/Vs), good transparency in the visible-light region, and ease of large-area manufacturing.\textsuperscript{1-4} To date, n-type oxides, such as ZnO and InGaZnO, are highly developed and even commercialized. On the contrary, the development of their p-type counterparts is far behind, and ambipolar oxides that can exhibit both n- and p-type conduction are even rarer.\textsuperscript{5-9} To fabricate all-oxide-based complementary-metal-oxide-semiconductor (CMOS) -like circuits, it is essential to develop high-performance p-type or ambipolar oxide semiconductors. In particular, ambipolar semiconductors can significantly simplify the fabrication process of
CMOS circuits and allow more compact CMOS architectures. Hence, extraordinary efforts have been made to develop ambipolar semiconductors and related thin-film-transistors (TFTs). Up to now, nanocrystalline silicon, organic semiconductors, and carbon nanotubes have been found capable of operating in ambipolar mode, due to either a small bandgap or low density of subgap states. Recently, tin monoxide (SnO) has been found capable of operating in ambipolar mode, and this is the only oxide semiconductor capable of conducting both electrons and holes effectively in a TFT. Voltage gains of CMOS-like inverters based on such ambipolar SnO TFTs have been shown to be higher than 100.

Ambipolar behavior is generally difficult to achieve in most oxide TFTs because of their typically large fundamental bandgaps and a high density of subgap states. SnO is regarded as the most promising p-type oxide among the limited number of p-type oxides discovered so far. The ambipolar behavior of SnO has been thought to be due to its low electron effective mass (~0.4 \( m_0 \)), low hole effective mass (~0.6 \( m_0 \)), and small fundamental bandgap (~0.7 eV). However, the density of subgap states in some p-type SnO TFTs extracted by temperature-dependent field-effect results can be higher than \( 10^{19} \text{eV}^{-1}\text{cm}^{-3} \), which suppresses the ambipolar behavior. In 2011, Nomura et al. fabricated the first SnO-based ambipolar TFT. Subsequently, Cao et al. fabricated ambipolar SnO TFT with balanced electron and hole mobilities. In 2016, Chen et al. demonstrated controllability of ambipolar conduction in SnO TFTs by oxygen plasma treatment. In 2017, Kim et al. observed clear ambipolar operation in TFTs based on atomic-layer-deposited SnO films as the active layer. Despite these processes, studies on how the ambipolar conduction and associated microstructures change in SnO film under thermal treatment are still limited.

In this work, ambipolar SnO channel layers were achieved by using a high sputtering power of 200 W and post-annealing in ambient air without passivation. The ambipolar behavior appeared when microgrooves occurred and nanoclusters segregated along the microgrooves in the SnO film. Our study indicates that the appearance of ambipolar behavior is a result of both a reduction of density of subgap states by Sn interstitials (Sn\text{\textsubscript{\textit{i}}}) and suppression of interfacial trap states because of the segregation of Sn clusters.

The schematic diagram of our SnO TFTs is shown in Fig. 1(a). Heavily doped p-type silicon wafers were used as both substrates and gate electrodes. 300-nm-thick thermally grown
SiO₂ was employed as the gate dielectrics. SnOₓ active layers were deposited onto the SiO₂ surfaces using reactive radio-frequency magnetron sputtering method with a deposition power of 200 W from a 3 inches Sn target (99.99% purity). The Ar/O₂ mixture atmosphere was fixed at a ratio of 23/3 (sccm/sccm). The working pressure during the sputtering process was ~4.8 mTorr. The substrate temperature was kept at 100 °C. The thickness of the SnOₓ layers was 27 nm. 50-nm-thick Pd source and drain electrodes were deposited by electron-beam evaporation, and the length and width of the active channel were 60 and 2000 μm, respectively. Finally, the devices were annealed at 150, 175, 200, 225, and 250 °C for 1 hour in ambient air step by step.

![Schematic diagram of SnOₓ TFT](image)

FIG. 1. (a) Schematic diagram of SnOₓ TFT, (b) transfer curves of the as-deposited and annealed (at 150, 175, 200, 225, and 250 °C) SnOₓ TFTs, (c) output curves of the TFT post-annealed at 200 °C, (d) a zoomed view of figure (c) when \( V_G = 40-100 \) V.

Figure 1(b) shows the transfer curves of the TFT annealed at different temperatures. The channel layer of the as-deposited TFT was too conductive to be tuned by gate voltages \( V_G \). The source-drain current, \( I_D \), decreased by ~ 4 times after the TFT was annealed at 150 °C in air due to oxidation of excess metallic Sn, but still could not be tuned by gate voltage. After the TFT was annealed at 175 and 200 °C, ambipolar behavior was observed. The TFT showed p-type characteristics at negative gate biases and n-type conduction at high positive gate biases (> 40 V). The on/off ratio reached 288 and 1350 for post-annealing temperatures of 175 and 200 °C, respectively. As shown in Figs. 1(c) and 1(d), the TFT exhibited pronounced p-type
performance at $V_G$ from +20 to -100 V, and n-type transport was observed at positive $V_G$ from +40 to +100 V. Such ambipolar behavior disappeared with the disappearance of the n-type conduction when the TFT was further annealed at 225 and 250 °C.

Electrical parameters (on/off ratio $I_{on}/I_{off}$, electron mobility $\mu_e$, hole mobility $\mu_h$, subthreshold voltage swing $SS$, and density of subgap trap states $D_t$) of TFTs annealed at various temperatures were summarized in Table I. The field-effect mobility, $\mu$, was extracted from the linear region of the transfer curve by using

$$I_D = \frac{W}{L} C_{ox} \mu (V_G - V_{th}) V_D,$$

(1)

where $W$ and $L$ are the channel width and length, respectively; $C_{ox}$ is the capacitance per unit area of the dielectric; $V_{th}$ is the threshold voltage; and $V_D$ is the drain voltage. As shown in Table I, the n-type SnO$_x$ TFT showed an $\mu_e$ of 0.16 and 0.02 cm$^2$/(V·s) with annealing temperatures of 175 and 200 °C, respectively. For the p-type SnO$_x$ TFT, the $\mu_h$ was 0.97, 0.92, 0.74, and 0.52 cm$^2$/(V·s) with annealing temperatures of 175, 200, 225, and 250 °C, respectively.

The $SS$ of the TFT is given by

$$SS = \left[ \frac{\partial (\log i_D)}{\partial (V_G)} \right]^{-1} = \ln(10) \frac{kT}{q} \left( 1 + \frac{q^2 D_t}{C_{ox}} \right),$$

(2)

where $k$ is the Boltzmann constant; $T$ is the temperature; and $q$ is the electron charge. For the p-type SnO$_x$ TFT, $SS$ was 28.36, 18.29, 38.94, and 29.61 V/dec with annealing temperatures of 175, 200, 225, and 250 °C, respectively. $D_t$ extracted from the transfer curves was $3.42 \times 10^{13}$, $2.20 \times 10^{13}$, $4.70 \times 10^{13}$, and $3.57 \times 10^{13}$ cm$^{-2}$eV$^{-1}$ with annealing temperatures of 175, 200, 225, and 250 °C, respectively.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$I_{on}/I_{off}$</th>
<th>$\mu_e$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>$\mu_h$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>$SS$ (V/dec)</th>
<th>$D_t$ (cm$^{-2}$eV$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>175</td>
<td>288</td>
<td>0.16</td>
<td>0.97</td>
<td>28.36</td>
<td>$3.42\times10^{13}$</td>
</tr>
<tr>
<td>200</td>
<td>1350</td>
<td>0.02</td>
<td>0.92</td>
<td>18.29</td>
<td>$2.20\times10^{13}$</td>
</tr>
<tr>
<td>225</td>
<td>108</td>
<td>-</td>
<td>0.74</td>
<td>38.94</td>
<td>$4.70\times10^{13}$</td>
</tr>
<tr>
<td>250</td>
<td>728</td>
<td>-</td>
<td>0.52</td>
<td>29.61</td>
<td>$3.57\times10^{13}$</td>
</tr>
</tbody>
</table>
FIG. 2. XRD patterns of one-μm-thick as-deposited and annealed (at 175, 200, 225, and 250 °C) SnOₓ films which are sputtered at 200 W.

Figure 2 presents XRD patterns of the as-deposited and annealed one-μm-thick SnOₓ films. It indicates that there is crystalized Sn but no crystalized SnO in the as-deposited film. Peaks of (101), (110), (200), (112), and (211) directions of α-SnO (α-PbO structure) were detected after the films were annealed. Peaks of Sn were also detected in the annealed films. Sn₃O₄ which is an intermediate oxidation state and can be easily further oxidized to SnO₂ by annealing was detected after the film was annealed at 225 °C. The disappearance of such Sn₃O₄ peak after the film was annealed at 250 °C indicates the formation of SnO₂. SnO₂ is not expected to be shown in the XRD spectra because it is expected to be amorphous at the annealing temperatures in this work.

Figure 3 shows the surface morphologies of the 27-nm-thick SnOₓ thin films annealed at various temperatures. The as-deposited film was relatively homogeneous and smooth as shown in Fig. 3(a). For the film annealed at 150 °C, feather-like and bright regions (marked by white circle in Fig. 3(b)) were observed and some tiny microgrooves (black region) appeared simultaneously possibly due to formation of polycrystalline of SnO. As the annealing temperature went higher, such feather-like, bright regions and black microgrooves became more obvious (Fig. 3(c)), and needle-like grains started to grow along the microgrooves when
the film was annealed at temperatures above 162 °C. XRD patterns in Fig. 2 show the crystallization of SnO and metallic Sn in the annealed films. The dominated and continuous composition in films annealed at and above 175 °C should be SnO due to the observed ambipolar and p-type conduction of TFTs (Fig. 1(b)).

![Fig. 3. SEM images of (a) as-deposited SnO$_x$ film, and SnO$_x$ films annealed at (b) 150, (c) 155, (d) 162, (e) 175, and (f) 200 °C.](image)

Atomic-force-microscopy (AFM) images were taken to study the surface roughness of the films annealed at different temperatures. Figures 4(a) and 4(b) show AFM images of the as-deposited film and film annealed at 200 °C, respectively. Figure 4(c) shows how the root-mean-square (RMS) roughness changes with the annealing temperature. The RMS roughness of the film shows a sharp increase from 0.60 to 3.73 nm when the film was annealed from 150 to 175 °C. The drastic change of roughness correlates with the significantly improved transistor on/off ratio at similar annealing temperatures as in Fig. 1(b).
FIG. 4. AFM images of (a) as-deposited SnO\textsubscript{x} film and (b) film annealed at 200 °C. The scanning size of the AFM images is 1\textmu m × 1\textmu m. (c) Root-mean-square (RMS) roughness of the films as a function of annealing temperature.

To study the nature of the clusters shown in Figs. 3 and 4, we note that previous studies showed that Sn atoms tend to precipitate to the dislocations and grain boundaries and then form Sn quantum dots in the Sn-rich SiO\textsubscript{2} films during annealing\textsuperscript{24}. Lei \textit{et al.}\textsuperscript{25} also reported a void-mediated formation of Sn quantum dots in a Si matrix. In their studies, voids below Si surface were induced by the lattice mismatch strain and Sn atoms were found to diffuse into these voids. The phenomenon in our experiment may be quite similar to these experiments. In our case, the microgrooves appeared when grain boundaries of polycrystalline SnO was formed when the films were annealed at 175 °C as confirmed by XRD\textsuperscript{26}. As such, the microgrooves could well be the grain boundaries of polycrystalline SnO. These microgrooves could act as defects that promote the crystal nucleation of metallic Sn, and the high diffusivity of Sn enabled the Sn crystals to grow along the sidewalls of the microgrooves in the annealed films. Furthermore, metallic Sn nucleated along the sidewalls of the microgrooves is expected to reduce the interfacial trap states at the grain boundaries of polycrystalline SnO. During annealing process at and above 162 °C (Figs. 3(d-f)), the original dispersed and continuously spread excess Sn in the as-deposited film quite possibly gathered to form Sn clusters along the microgrooves as in Refs. 24 and 25. The diameters of the clusters are 30 ± 9 nm as estimated by SEM. Indeed, the XRD spectra reveal the formation of polycrystalline Sn at annealing temperatures at and above 175 °C. Also, the conductivity of the film dropped dramatically after the film was annealed in agreement with the formation of isolated (and hence not able to contribute to the film
conductivity) Sn clusters. Obviously, the segregation of Sn clusters leads to a drastic reduction of Sn in the SnO film. According to the first-principle calculations of native defects in SnO, Sn interstitial (Sn\textsubscript{i}) is found to induce a huge amount of defect states in the bandgap of SnO.\textsuperscript{27} As such, the reduction of Sn\textsubscript{i} due to segregation of Sn at the sidewalls of the microgrooves makes it easier to shift the Fermi level.\textsuperscript{6,11} Because the bandgap of SnO is only 0.7 eV, the reduction of subgap states may well enable the ambipolar behavior. Indeed, the TFTs annealed at 175 and 200 °C exhibited improved $SS$, low $I_{\text{off}}$, and ambipolar conduction. The TFT annealed at 225 °C showed much larger $I_{\text{off}}$ and $D_{t}$ than those annealed at 200 °C, and the ambipolar behavior disappeared with the disappearance of n-type conduction. This may be due to the excess trap states caused by the formation of oxidized impurities such as Sn\textsubscript{3}O\textsubscript{4} and SnO\textsubscript{2} (Sn\textsubscript{3}O\textsubscript{4} was detected by XRD when the TFT was annealed at 225 °C, and Sn\textsubscript{3}O\textsubscript{4} can easily transform to SnO\textsubscript{2}). These trap states, including both shallow and deep trap states, make it difficult to shift the Fermi level, and as a result, the ambipolar behavior disappeared. The shallow traps led to the deterioration of $\mu$, $SS$, and high $I_{\text{off}}$. With the annealing temperature increase from 225 °C to 250 °C, both $I_{\text{on}}$ and $I_{\text{off}}$ significantly decreased, and this should be due to the disproportionation reaction “SnO $\rightarrow$ SnO\textsubscript{2} + Sn” was activated at 250 °C.\textsuperscript{23} Consequently, the obviously reduced amount of SnO led to the clear decrease of the hole concentration and drain current.

In conclusion, we have fabricated ambipolar SnO\textsubscript{x} TFTs by applying a high sputtering power of 200 W and post-annealing treatments. The ambipolar behavior was studied and discussed in the light of characterisation of the film morphology and composition. The results suggest that segregation of excess Sn on the sidewalls of the microgrooves leads to the reduction of density of subgap trap states by Sn interstitials in SnO, making it possible to shift the Fermi level effectively by the gate voltage. As the ambipolar oxide TFT is highly attractive for CMOS-like applications, our results may have useful implications in achieving and optimizing ambipolar behavior in SnO\textsubscript{x} films for thin-film-based circuits. In addition, the optimum processing temperature for the ambipolar SnO\textsubscript{x} TFT is below 200 °C, so that the results are relevant to possible applications on flexible substrates such as polyimide.

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