Comparative Study of Antimony Doping Effects on the Performance of Solution-Processed ZIO and ZTO Field-Effect Transistors

Jong Han Baek,[‡][®] Hyunju Seol,[§][®] Kilwon Cho,[⊥][®] Hoichang Yang,^{*,∥}[®] and Jae Kyeong Jeong^{*,§}

[‡]Department of Materials Science and Engineering and ^{II}Department of Applied Organic Materials Engineering, Inha University, Incheon 402-751, South Korea

[§]Department of Electronic Engineering, Hanyang University, Seoul 133-791, South Korea

¹Department of Chemical Engineering, Pohang University of Science and Technology, Pohang 790-784, South Korea

Supporting Information

ACS APPLIED MATERIALS

& INTERFACES

ABSTRACT: ZnO-based oxide films are emerging as highperformance semiconductors for field-effect transistors (FETs) in optoelectronics. Carrier mobility and stability in these FETs are improved by introducing indium (In) and gallium (Ga) cations, respectively. However, the strong trade-off between the mobility and stability, which come from In or Ga incorporation, still limits the widespread use of metal oxide FETs in ultrahigh pixel density and device area-independent flat panel applications. We demonstrated that the incorporation of antimony (Sb) cations in amorphous zinc indium oxide (ZIO) simultaneously enhanced the field-effect mobility ($\mu_{\rm FET}$) and electrical stability of the resulting Sb-doped ZIO



Research Article

www.acsami.org

FET's. The rationale for the unexpected synergic effect was related to the unique electron configuration of Sb⁵⁺ ([Kr]4d¹⁰5s⁰5p⁰). However, the benefit of Sb doping was not observed in the zinc tin oxide (ZTO) system. All the Sb-doped ZTO FETs suffered from a reduction in μ_{FET} and a deterioration of gate bias stress stability with an increase in Sb loading. This can be attributed to the formation of heterogeneous defects due to Sb-induced phase separation and the creation of Sb³⁺ induced acceptor-like trap states.

KEYWORDS: antimony doping, solution process, field-effect transistor, zinc indium oxide, zinc tin oxide, bias stability

1. INTRODUCTION

Transparent conducting oxide (TCO) films such as indium oxide (In_2O_2) , indium tin oxide (ITO), and zinc indium oxide (ZIO) have been used extensively as a passive interconnection component for photovoltaic light-emitting diodes (LEDs) and active-matrix display devices because of their degenerate high carrier densities $(\geq 1 \times 10^{20} \text{ cm}^{-3})$ and good transparency to visible light.¹⁻³ Since the discovery of Ga-loaded ZIO as a semiconductor, the applications of conventional TCOs have been extended to the active components in field-effect transistors (FETs), smart identification cards, flexible electronics and transparent electronics.⁴ The success of Ga-loaded ZIO systems as a semiconductor is attributed to their ability to tailor the carrier density (N_e) down to $\leq 1 \times 10^{17}$ cm⁻³ via doping of Ga cations as carrier suppressors. The development of architecture and core processes has accelerated the commercialization of indium gallium zinc oxide (IGZO) FETs into consumer products such as the Apple iPad and LG active-matrix organic light-emitting diode display (AMOLED) TV, where the IGZO channel layers are prepared using a vacuum-based sputtering process.^{5,6}

However, several issues, including the need for expensive equipment and complicated lithography processes related to the vacuum-based preparation, make it necessary to explore solution-processable semiconducting metal oxides. The low processing cost, high throughput, substrate size scalability, and versatile composition manipulation provided by solution processing may allow the use of semiconducting oxide films for large-area, flexible electronics in next-generation applications. For this reason, high-performance solution-processed metal oxide FETs have been developed using novel hydrolysis synthesis,⁷ a combustion process,⁸ high pressure annealing,⁹ and photochemical activation annealing.¹⁰

Controlling the fraction of indium (In) plays an important role in boosting the field-effect mobility ($\mu_{\rm FET}$), which is one of the most important metrics for FETs. The intercalation of In *5s* orbitals provides an efficient conduction pathway in the semiconducting oxide film due to its relatively large ionic radius. Indeed, high mobilities of >40 cm² V⁻¹ s⁻¹ can often be observed for physical vapor deposited indium oxide-based TCO films with ≥80 at % In.^{11–13} Because the shallow oxygen vacancy donor states can be easily created by the weak bond

Received:January 22, 2017Accepted:March 6, 2017Published:March 6, 2017

strength of In–O, the huge N_e value (>1 × 10¹⁹ cm⁻³) observed for the TCO films results in simple conduction behavior rather than the strong drain current modulation required for FET devices. The mobility attainable in the oxide FETs is thus limited to moderate N_e conditions, which suggests there is a maximum fraction of In cations that can be tolerated in multicomponent oxide semiconductors. The moderate N_e value ($\leq 1 \times 10^{17}$ cm⁻³) in the semiconductor oxide film can be achieved by carefully doping with oxygen getter transition metals, which are well-known as carrier suppressors. In the case of IGZO, Ga³⁺ ions, which have a smaller ionic radius, are good oxygen getters because they have a higher ionic strength (Ze/r^2 , where Z is the valence number and r is the ionic radius) compared to those of In³⁺ or Zn^{2+,14,15}

compared to those of In³⁺ or Zn²⁺.^{14,15} Alternatively, elements such as Zr,¹⁶ Hf,^{17,18} Ba,¹⁹ and Ti^{20,21} with low electronegativity have been examined as carrier suppressors. Recently, Lewis acid strength (L) was proposed as a better figure-of-merit for the suitability of a material as a carrier suppressor.^{22–24} The doping of boron²² or carbon,²³ which have high L values, into a semiconducting ZIO film resulted in FETs with high $\mu_{\rm FET}$ values. Irrespective of the criterion used for choosing the dopants, oxide FETs showed positive V_{TH} displacement and an enhanced $I_{\text{ON/OFF}}$ ratio with an increase in carrier suppressor concentration, which induces a reduction in $N_{\rm e}^{16-21}$ Furthermore, the photobias instability, which is one of the critical issues for applications in optoelectronics, can be mitigated by introducing carrier suppressors.²⁵ Unfortunately, the increase in carrier suppressors in the semiconducting oxide film reduces the μ_{FET} values of the resulting FETs. The strong trade-off relationship between the mobility and photobias stability represents the main obstacle to the extensive application of metal oxide FETs.²⁶

A double channel/multiple channel concept consisting of front and capping layers has been proposed to resolve this trade-off relationship; in this strategy, the front layer serves as the carrier transporting layer and the capping layer serves to boost the photoelectric stability.^{27–31} However, preparing the channel is difficult in this strategy, and maintaining a constant front layer thickness over a large substrate area also needs to be addressed. Thus, simple and practical routes to enhance both the mobility and stability of metal oxide TFTs must still be suggested and investigated.

Here, we proposed the doping of antimony (Sb) during the solution processing of ZIO and ZTO films. The L value of Sb^{5+} , as a dopant, is relatively larger than those of In^{3+} and Zn^{2+} ; thus, we expected that Sb would act as an oxygen getter. Notably, the electron configuration of Sb^{5+} ([Kr]4d¹⁰5s⁰5p⁰) is similar to that of In^{3+} ([Kr]4d¹⁰5s⁰) in terms of the vacant 5s orbital availability. If the valence state of Sb⁵⁺ can be carefully tailored in the host oxide network, its introduction may provide an efficient percolation conduction path. Indeed, a synergistic effect of simultaneously boosting both mobility and stability was observed in the ZIO system. Specifically, the Sb-loaded ZIO FETs showed two times higher μ_{FET} values than those of Sb-free ZIO FETs. At the same time, the positive gate bias stress (PBS) and negative gate bias stress (NBS) instabilities of Sb-loaded ZIO FETs were improved (compared to an Sb-free system) by loading Sb cations in the channel layer. Conversely, the Sb doping into the ZTO system deteriorated the carrier mobility and electrical stability of the resulting ZTO FETs. The strongly Sb-dependent disparity was discussed in terms of the chemical state evolution of incorporated Sb doping and the microstructural evolution of the ZIO and ZTO films.

2. EXPERIMENTAL SECTION

2.1. Materials and Sample Preparation. A heavily doped p-type Si wafer and a 100 nm-thick thermal SiO₂ were used as the bottom gate electrode and gate insulator, respectively. All precursors and solvents were purchased from Sigma-Aldrich. Precursor solutions (0.1 and 0.3 M) were formulated for the Sb-loaded ZIO fabrication by dissolving indium nitrate hydrate (In(NO3)3·H2O, 5N purity), zinc nitrate hydrate (Zn(NO₃)₂·H₂O, 5N purity), and antimony acetate (Sb(CH₃COO)₃, 4N purity) in 5 mL of hydrated 2-methoxyethanol $(\geq 99.3\%$ purity). In the solutions, the ratio of the In to Zn precursors was 1.7 to 1, and then antimony acetate was added at concentrations of 0.1 and 0.15 wt %, respectively, for these precursors. Additionally, 0.1 and 0.3 M solutions to fabricate Sb-loaded ZTO films were prepared by dissolving zinc nitrate hydrate $(Zn(NO_3)_2 \cdot H_2O, 5N)$ purity), tin chloride dehydrate (SnCl₂·2H₂O, 98% purity), and Sb(CH₃COO)₃ in 5 mL of 2-methoxyethanol. Similarly, the ratio of Sn to Zn precursors was 1.7 to 1, and two different loadings of Sb(CH₃COO)₃ were used. All precursor solutions were stirred for 6 h at 75 °C and were then passed through 0.2 μ m membrane syringe filters before spin-coating. The 0.3 M solutions were used for fabrication of the Sb-loaded ZIO, ZTO films and their FETs if not specifically described.

The SiO₂/Si substrates were rinsed sequentially with acetone, isopropyl alcohol and deionized water, for 10 min each. Prior to spincoating the precursor solutions, the cleaned SiO₂/Si substrates were UVO₃-treated for approximately 30 min to provide a hydrophilic surface. Spin-coating was performed to fabricate metal oxide films at 3500 rpm for 40 s. The as-spun metal precursor films were prebaked on a hot plate for 5 min at 150 °C to remove the solvent residue in the films. The films were then annealed in an electric furnace for 1 h at 400 or 500 °C. An ITO film used as a source/drain (*S/D*) electrode was deposited on the Sb-loaded ZIO (or ZTO)/SiO₂/Si substrate by magnetron sputtering. The dc power and working pressure were 50 W and 5 mTorr, respectively, under an Ar atmosphere. The *S/D* electrode was patterned through a shadow mask during sputter deposition. The width and length of the TFTs were 1000 and 150 μ m, respectively.

2.2. Characterization. The chemical states of the different Sbloaded ZIO or ZTO thin films were characterized by X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific). The film thicknesses for the different Sb-loaded ZIO and ZTO layers were measured using ellipsometry, and the results are included in Table S1. Hall mobility (μ_{Hall}) and carrier concentration (N_e) of the Sb-ZIO or Sb-ZTO thin-film were evaluated from Hall effect measurement using the van der Pauw configuration (BioRad, HL5500). Surface morphologies of all the oxide films were characterized using atomic force microscopy (AFM, Multimode 8, Bruker) and scanning electron microscopy (SEM, Hitachi, S-4300). Synchrotron-based grazingincidence X-ray diffraction (GIXD) was conducted on the Sb-loaded ZIO and ZTO thin films at the 3C, 9A, and 6D beamlines, Pohang Accelerator Laboratory (PAL), Korea.³² The incident angle of the Xray beam in the sample remained below 0.18°. The electrical characteristics of the fabricated FETs were measured at room temperature using a Keithley 2636 source meter. The field-effect carrier mobility (μ_{FET}) was determined from the slope of the $I_{\text{DS}}^{-1/2}$ vs $V_{\rm GS}$ plot using the following equation

$$I_{\rm DS} = (WC_{\rm i}/2L)\mu_{\rm FET}(V_{\rm GS} - V_{\rm TH})^2$$
(1)

Here, *L* is the channel length, *W* is the width, and *C*_i is the gate capacitance per unit area (nFcm⁻²). The threshold voltage (V_{TH}) was defined as the gate voltage (V_{GS}) that induces a drain current of *L/W* × 10 nA at V_{DS} = 10.1. The subthreshold swing ($SS = dV_{GS}/d\log I_{DS}$) was extracted from the linear part of the log(I_{DS}) vs V_{GS} plot. The numbers of fast bulk traps (N_{SS}) and semiconductor–insulator interfacial traps (D_{it}) were calculated using the following equation³³

$$SS = \frac{qk_{\rm B}T(N_{\rm SS}t_{\rm ch} + D_{\rm it})}{C_{\rm i}\log(e)}$$
(2)



Figure 1. AFM topographies of different Sb-loaded (a-c) ZIO and (d-f) ZTO films annealed at 400 °C for 1 h: (a, d) 0, (b, e) 0.10, (c, f) 0.15 wt %.



Figure 2. 2D GIXD patterns of different Sb-loaded (a-c) ZIO and (d-f) ZTO films annealed at 400 °C for 1 h: (a, d) 0, (b, e) 0.10, (c, f) 0.15 wt %.

where q is the electron charge, $k_{\rm B}$ is Boltzmann's constant, T is the absolute temperature, and $t_{\rm ch}$ is the channel layer thickness. $N_{\rm SS}$ and $D_{\rm it}$ in the Sb-loaded ZIO or ZTO FETs were calculated by setting one of these parameters to zero. Therefore, the $N_{\rm SS}$ and $D_{\rm it}$ values are considered to be the maximum trap densities formed in a given system.

3. RESULTS AND DISCUSSION

Figure 1 shows AFM topographies of different Sb-loaded ZIO and ZTO films formed after annealing at 400 °C for 1 h. The presence of the Sb dopant in the metal oxide precursor films considerably affected the structures of each metal oxide film and had positive and adverse effects in terms of the structural uniformity. In the ZIO system, an enhancement in the film uniformity was observed with an increase in Sb loading. As shown in Figure 1a, nanosized domains in the Sb-free film agglomerated, yielding a surface roughness (R_q) greater than 8.5 nm, whereas the dispersion of the nanodomains was effectively enhanced with the presence of Sb. In particular, the 0.15 wt % Sb-loaded ZIO film showed a layer with wellpercolated nanodomains with a R_q below 5.0 nm (Figure 1c). Sb⁵⁺ ion has a smaller cation radius (0.6 Å) than In³⁺ (0.8 Å) and Zn²⁺ (0.74 Å), which would impart enhanced disorder within the ZIO network to facilitate a smoother surface and desirable formation of an amorphous phase. In contrast, the



Figure 3. O 1s XP spectra and their deconvolution results for Sb-loaded (a-c) ZIO and (d-f) ZTO films with different loadings: (a, d) 0 wt %, (b, e) 0.10 wt %, (c, f) 0.15 wt %.

ZTO system showed severely heterogeneous domains, which became larger with an increase in Sb loading (Figures 1d-f).

To characterize the film structures of both the ZIO and ZTO systems, the Sb-loaded metal oxide films were further characterized by 2D GIXD analysis. Figure 2 presents the 2D GIXD patterns of different Sb-loaded ZIO and ZTO films. The 2D GIXD patterns of Sb-free and Sb-loaded ZIO films both showed a diffused hollow ring at $Q = 2.30 \text{ Å}^{-1}$, independent of the Sb loading in the ZIO host matrix. This result strongly suggests that all the ZIO based films had amorphous-like phases.³⁴ In contrast, the 2D GIXD patterns of Sb-free and Sbloaded ZTO films showed intense X-ray reflections originating from the discernible crystal planes in the ZnO, SnO₂, and ZTO phases. The 2D GIXD patterns of 0 and 0.10 wt % Sb-loaded ZTO films showed intense diffraction peaks corresponding to the crystallographic planes in either rutile SnO₂ or wurtzite ZnO crystallites. Each indexed crystal plane was identified using a subscript that indicated a structure of either SnO₂ or ZnO. The introduction of 0.10 wt % Sb into the ZTO host matrix slightly decreased the intensities of ZnO crystal planes as compared to the Sb-free system. In contrast, the 0.15 wt % Sbloaded ZTO film showed diffraction patterns typical of ZTO polycrystallites with a preferred growth direction, as determined by anisotropic crystal reflections. These were indexed as (h00), (220), (311), (222), and (422) in a face-centered spinelstructured Zn_2SnO_4 (ZTO) with a = 8.657 Å.³⁵ Additionally, the X-ray reflections related to ZnO were marked with star symbols (Figure 2f).

The morphology and X-ray results suggested that the ZIO precursor solutions with $Sb(CH_3COO)_3$ provided improved uniformity and granular connectivity during sequential casting and annealing of the ZIO films. The amorphous semiconducting grains were well percolated, and we expected an improved charge-carrier transport in the Sb-doped ZIO FETs.

In the case of the ZTO system, however, the introduction of $Sb(CH_3COO)_3$ to the ZTO precursor solutions tended to accelerate the formation of the spinel Zn_2SnO phase, which is the only thermodynamically stable compound oxide in the ZnO and SnO_2 binary system. Simultaneously, the $Sb(CH_3COO)_3$ induced enlargement of the ZnO crystallite domains embedded in the crystalline ZTO matrix. We expected that the presence and increasing concentration of the heterogeneous ZnO crystallites would degrade the charge-carrier transport in the Sb-doped ZTO FETs.

Evolution of the chemical state of Sb-doped ZIO and ZTO films was evaluated using XPS analysis. The binding energies of photoelectrons were calibrated to the C 1s peak for the C-C bonds at 284.5 eV. Figure 3a shows the O 1s XPS profile for the control ZIO film after thermal annealing at 400 °C. The asymmetric peak of the O 1s spectrum was deconvoluted into three peaks at 530.1, 530.8, and 531.6 eV.^{10,36} The O 1s peak centered at 530.1 eV was assigned to oxygen bonded to fully coordinated metal ions (octahedrally coordinated in the case of In and tetrahedrally coordinated in the case of Zn, i.e., lattice oxygen), and the peak at 530.8 eV was assigned to oxygen bonded to under-coordinated metal cations. Although the oxygen vacancy (V_0) is not accurately defined in an amorphous matrix due to the absence of long-range order, the oxygen bonded to under-coordinated metal cations will be referred to as Vo for simplicity. The ZIO films with Sb had additional peaks at 539.6 and 529.9 eV, which are assigned to Sb $3d_{3/2}$ and Sb 3d_{5/2}, respectively (Figure 3b, c).³⁷ The Sb-related peaks at 539.6 and 529.9 eV were amplified with increasing Sb loading in the ZIO film, suggesting that the Sb cations are chemically well incorporated in the amorphous ZIO host matrix. Interestingly, the Sb-loaded ZIO films exhibited a considerably lower V_O and M–OH density compared to those of the Sb-free host. The relative percent area of V_0 and metal-OH (M-OH)

related peaks in the XPS spectra of the 0.15 wt % Sb-loaded ZIO film were calculated to be 14.0 and 10.0%, respectively. These were much lower than the 23.0% and 14.0% in the Sb-free ZIO film (Table 1). This result indicates that the

Table 1. Variations in the Oxidation States of the Different Sb-Loaded ZIO and ZTO Films As Calculated from the Deconvolution of O 1s Level in the Resulting XPS Spectra

| | | O 1s | | |
|---------------------|----------------------|----------------|----------------|-----------------|
| metal oxide film | Sb loading (wt %) | lattice (%) | vacancy (%) | hydroxyl (%) |
| ZIO | 0.0 | 63.0 | 23.0 | 14.0 |
| | 0.10 | 69.0 | 19.0 | 12.0 |
| | 0.15 | 76.0 | 14.0 | 10.0 |
| ZTO | 0.0 | 77.0 | 15.0 | 8.0 |
| | 0.10 | 77.0 | 16.0 | 7.0 |
| | 0.15 | 82.0 | 13.0 | 5.0 |

incorporated Sb cations promote metal–oxygen (M-O) lattice bond formation and suppress the creation of defect centers such as V_O and M-OH. These structural changes can provide fast charge carrier transport in the conducting channel layer because the coherency of the percolation path is enhanced by reducing carrier scattering centers. This was also discussed above in the discussion of AFM and 2D GIXD results.

In contrast, the Sb-loaded nanocrystalline ZTO matrix film did not show a decrease in the defect centers such as V_0 and M-OH (Figure 3d-f). Deconvolution of the XPS spectra related to the O 1s level showed that the Sb-related peaks at 539.6 and 529.9 eV were intensified with increasing Sb loading in the ZTO system. However, the portions of the V_0 and M-OH related peaks in the XPS spectra of the Sb-loaded ZTO system were comparable to those in the Sb-free ZTO film. For example, the relative percent area of V_0 and M-OH related peaks for the 0.10 wt % Sb loaded ZTO film were 16.0 and 7.0%, respectively, close to the values of 15 and 8% for the Sbfree ZTO film (Table 1). On the basis of these data, we inferred that the Sb cations in the Sb-loaded ZTO system act as a weak oxygen binder, whereas the physical role of Sb cations in Sbloaded ZIO system is to suppress the creation of V_0 .

It is important to clarify the oxidation states of Sb in the doped metal oxide systems; Sb³⁺ and Sb⁵⁺ are likely to act as acceptor-like traps and electron donors, respectively. Figure 4 represents XPS spectra of the Sb 3d_{3/2} level in the Sb-loaded ZIO and ZTO films. The XPS spectra were deconvoluted into two subprofiles with peaks at 538.7 and 539.6 eV, corresponding to the binding energies of Sb³⁺ and Sb⁵⁺, respectively. In the Sb-loaded ZIO film, the portion of Sb⁵⁺ was dominant at 87.7 \pm 0.5%, as shown in Figure 4a, b. Generally, a cation with a higher ionic strength is a good oxygen binder (i.e., charge carrier suppressor). Therefore, Sb5+ was predicted to be a better oxygen binder than Sb3+, because it has a higher valence state (+5) and smaller radius (0.60 Å) compared to the Sb³⁺ cation (0.76 Å).³⁸ This rationale was well corroborated by the fact that the Sb loading in the ZIO system caused a reduction in the substantial Vo density of the resulting Sbloaded ZIO films (Figure 3). In contrast, the portions of Sb^{3+} in the Sb-loaded ZTO system was enhanced to 17.5 \pm 0.5% (Figure 4c, d), which was higher than the 12.2 \pm 0.5% in the Sb-doped ZIO system. The Sb³⁺ cation is a relatively weak oxygen binder, therefore, Sb loading into the Sb-doped ZTO system did not reduce the V_O density.



Research Article

Figure 4. Sb $3d_{3/2}$ XP spectra and their deconvolution results for the Sb-loaded (a, b) ZIO and (c, d) ZTO with different loadings: (a, c) 0.10 wt %, (b, d) 0.15 wt %.

The functionality of the synthesized Sb-loaded ZIO and ZTO system as a charge carrier transporting layer was assessed by Hall effect measurements. Figure 5 shows the variation in



Figure 5. Variations in μ_{Hall} and N_{e} values of the different Sb-loaded (a) ZIO and (b) ZTO thin films.

 μ_{Hall} and the concentration of the free electron carrier (N_{e}) values for the Sb-loaded ZIO and ZTO thin films. The $\mu_{\rm Hall}$ and $N_{\rm e}$ values of the Sb-free ZIO films annealed at 400 $^{\circ}{\rm C}$ were 6.4 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $1.6 \times 10^{17} \text{ cm}^{-3}$, respectively. As expected, the 0.15 wt % Sb-loaded ZIO film exhibited enhanced $\mu_{\rm Hall}$ and $N_{\rm e}$ values of 20.2 cm² V⁻¹ s⁻¹ and 9.1 \times 10¹⁷ cm⁻³, respectively. The $N_{\rm e}$ values of the 0.15 wt % Sb-loaded ZIO films were 5 times higher than that of the Sb-free ZIO film, even though a high V_O density of approximately 14% was determined by XPS. Considering that only a small portion of all existing V_O act as shallow electron donors, the Sb-incorporated enhancement in μ_{Hall} seems to be inconsistent because the reduction in the V_O density decreased the N_e value in the Sb-loaded ZIO film. The unexpected increase in the N_e value for the Sb-loaded ZIO film may be attributed to the donor behavior of the Sb⁵⁺ cation. Zn^{2+} and In^{3+} cations in the stoichiometric crystals are



Figure 6. Typical $I_{DS}-V_{GS}$ transfer curves and I_G-V_{GS} curves of the Sb-loaded (a-c) ZIO and (d-f) ZTO FETs including different Sb loadings: (a, d) 0 wt %, (b, e) 0.10 wt %, (c, f) 0.15 wt % (these $I_{DS}-V_{GS}$ transfer curves were measured at $V_{DS} = 10.1$).

Table 2. Device Parameters Including μ_{FET} , SS, V_{TH} , $I_{\text{ON/OFF}}$, $D_{\text{it,max}}$ and $N_{\text{ss,max}}$ Values of the Different Sb-Loaded ZIO and ZTO Films

| system | Sb (wt %) | $\mu_{\rm FET}~({ m cm}^2/({ m V~s}))$ | SS (V decade ⁻¹) | $V_{\rm TH}$ (V) | $I_{\rm ON/OFF}$ | $D_{\mathrm{it,max}}~\mathrm{(eV^{-1}cm^{-2})}$ | $N_{\rm ss,max}~({\rm eV}^{-1}{\rm cm}^{-3})$ |
|--------|-----------|--|------------------------------|------------------|---------------------|---|---|
| ZIO | 0.0 | 0.55 ± 0.1 | 0.65 ± 0.30 | 3.6 ± 1.6 | 1.0×10^{6} | 2.4×10^{12} | 8.4×10^{17} |
| | 0.10 | 1.1 ± 0.1 | 0.32 ± 0.08 | 2.9 ± 1.0 | 5.0×10^{6} | 1.2×10^{12} | 4.1×10^{17} |
| | 0.15 | 1.8 ± 0.1 | 0.31 ± 0.05 | 0.2 ± 0.6 | 6.0×10^{6} | 1.1×10^{12} | 4.0×10^{17} |
| ZTO | 0.0 | 2.5 ± 0.1 | 0.85 ± 0.10 | 3.1 ± 0.1 | 3.0×10^{6} | 3.3×10^{12} | 1.2×10^{18} |
| | 0.10 | 1.7 ± 0.2 | 1.4 ± 0.24 | 4.7 ± 0.7 | 1.0×10^{6} | 5.1×10^{12} | 1.8×10^{18} |
| | 0.15 | 0.97 ± 0.3 | 1.2 ± 0.30 | 4.7 ± 0.8 | 3.0×10^{5} | 4.3×10^{12} | 1.6×10^{18} |

tetrahedrally and octahedrally coordinated by oxygen anions, respectively. This means that the corresponding coordination numbers (*CN*) of the Zn²⁺ and In³⁺ cations will be 4 and 6, respectively. The Sb⁵⁺ cation in the antimony pentoxide (Sb₂O₅) crystal is coordinated by six oxygen anions in a distorted octahedral arrangement.³⁹ The Sb⁵⁺ dopant incorporated in the amorphous ZIO matrix is likely to be coordinated in a manner similar to that of In³⁺. Therefore, the Sb⁵⁺ cation, which has five valence electrons, can contribute two free electrons to the conduction band. Based on this interpretation, the monotonic increase in μ_{Hall} of the Sb-loaded ZIO FETs with increasing Sb fraction is explained by the percolation conduction mechanism.

The entirely opposite behavior was observed for the Sbloaded ZTO system in terms of the increasing Sb loading as shown in Figure 5c, d. The Sb-free ZTO film had a μ_{Hall} of 12.9 cm² V⁻¹ s⁻¹ and a N_{e} of 1.1 × 10¹⁷ cm⁻³. As the Sb content increased in the ZTO films, the μ_{Hall} and N_{e} values simultaneously decreased, i.e., the 0.15 wt % Sb-loaded ZTO film had a μ_{Hall} of 3.9 cm² V⁻¹ s⁻¹ and a N_{e} of 5.1 × 10¹⁵ cm⁻³. This indicates that the existence of Sb⁵⁺ as a shallow donor in the Sb-loaded ZTO film was masked by the overwhelming creation of acceptor-like trap states. In a crystalline material, the cation dopant incorporated into the host material must be restricted by the structure of the specific crystal. The reduction in the $N_{\rm e}$ value of the higher Sb-loaded ZTO films suggests the replacement of Sb³⁺ for Sn⁴⁺ sites in a crystalline ZTO film, where the substituted sites can act as acceptor-like centers. This postulation is consistent with the fact that the portions of Sb³⁺ in the 0.15 wt % Sb-loaded ZTO system were higher than those of the 0.10 wt % Sb-loaded ZTO system. The formation of heterogeneous aggregates and the irregular film morphology in the Sb-loaded ZTO system can also create the additional trap states in the forbidden bandgap of the Sb-loaded semiconductor. This may be partially responsible for the reduction in $N_{\rm e}$ for the Sb-loaded ZTO materials.

The transfer characteristics of the different Sb-loaded ZIO FETs are shown in Figure 6a and Figure S1. First, the Sb-free ZIO FETs exhibited marginal electrical performance: μ_{FET} , SS, V_{TH} and $I_{\text{ON/OFF}}$ were 0.55 cm² V⁻¹ s⁻¹, 0.65 V decade⁻¹, 3.6 V, and 1.0 × 10⁶, respectively (Table 2). The carrier transport properties and switching capabilities were significantly improved for the Sb-loaded ZIO FETs. The resulting 0.15 wt % Sb-loaded ZIO FET showed a μ_{FET} of 1.8 cm² V⁻¹ s⁻¹ and an $I_{\text{ON/OFF}}$ of 3.0 × 10⁶ (Figure 6c and Figure S1). The output characteristics for the Sb-loaded ZIO FETs improved in terms

Research Article



Figure 7. Time-dependent variations in the transfer characteristics for the different Sb-loaded ZIO FETs under the (a-c) PBS and (d-f) NBS conditions: (a, d), (b, e) 0.10, and (c, f) 0.15 wt % Sb loading.

of the operating drain current level with increasing Sb loading (Figure S2). As shown in Figure 6a, a $V_{\rm TH}$ shift ($\Delta V_{\rm TH}$) of approximately 4.0 V was also observed for the control ZIO FETs. This result is attributed to the temporal gap-states at the bulk channel layer and/or near the gate insulator/channel interfaces. However, the hysteresis phenomenon nearly disappeared for the Sb-loaded ZIO FETs, yielding a decrease in the maximum bulk trap density ($N_{\rm SS,max}$) or interfacial trap density ($D_{\rm it,max}$). Specifically, the $N_{\rm SS,max}$ or $D_{\rm it,max}$ values for the 0.15 wt % Sb-loaded ZIO FET decreased to 4.0 × 10¹⁷ cm⁻³ eV⁻¹ and 1.1 × 10¹² cm⁻² eV⁻¹, respectively, in comparison to 8.4 × 10¹⁷ cm⁻³ eV⁻¹ and 2.4 × 10¹² cm⁻² eV⁻¹ for the Sb-free ZIO system (Table 2).

Unlike the ZIO system, the Sb-free ZTO FET showed better electrical properties: a μ_{FET} of 2.5 cm² V⁻¹ s⁻¹, a SS of 0.85 V decade⁻¹, a $V_{\rm TH}$ of 3.1 V, and an $I_{\rm ON/OFF}$ of 3.0 \times 10⁶ (Figure 6d). $\mu_{\rm FET}$ and $V_{\rm TH}$ values of the 0.15 wt % Sb-loaded ZTO FETs, however, decreased to 0.97 $\mbox{cm}^2\ \mbox{V}^{-1}\ \mbox{s}^{-1}$ and 4.7 V, respectively (Figure 6f and Figure S1). Additionally, $N_{SS,max}$ and $D_{\rm it,max}$ values increased up to $1.6 \times 10^{18} {\rm ~cm^{-3}~eV^{-1}}$ and $4.3 \times 10^{18} {\rm ~cm^{-3}~eV^{-1}}$ 10^{12} cm⁻² eV⁻¹, respectively, compared to the Sb-free ZTO FET $(N_{SS,max} = 1.2 \times 10^{18} \text{ cm}^{-3} \text{eV}^{-1} \text{ and } D_{it,max} = 3.3 \times 10^{12}$ $cm^{-2} eV^{-1}$). On the basis of these results, the Sb dopant in the ZTO adversely acted as either an electron carrier suppressor or carrier scattering center. Output characteristics for the Sbloaded ZTO FETs also showed degradation in the current level at each identical gate and drain voltage with an increase in Sb loading (Figure S2). The gate leakage current (I_G) values for the different Sb-loaded ZIO and ZTO FETs were included in the transfer characteristics. The measured I_G values were negligible compared to I_{DS} values independent of the Sb loadings.

The effect of Sb loading into the ZIO and ZTO system was further demonstrated by reducing the molar concentration of each precursor solution from 0.3 to 0.1 M. This reduction of solution concentration resulted in the formation of a thinner channel layer (Table S1); the thickness of the ZIO films decreased from 42.0 \pm 0.7 nm at 0.3 M to 17.6 \pm 0.5 nm at 0.1 M. Under the given Sb loading, the ZTO FETs prepared at 0.1 M exhibited substantially enhanced transport characteristics; for example, the μ_{FET} for the 0.15 wt % Sb-loaded ZIO FETs was improved from 1.8 cm² V⁻¹ s⁻¹ (at 0.3 M) to 4.2 cm² V⁻¹ s⁻¹ (see Figure S2). Simultaneously, the $N_{SS,max}$ and $D_{it,max}$ values for the 0.15 wt % Sb-loaded ZIO FETs at 0.1 M decreased to $4.7 \times 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$ and $8.2 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$, respectively, in comparison to 4.0×10^{17} cm⁻³ eV⁻¹ and 1.1×10^{12} cm⁻² eV⁻¹ for the 0.15 wt % Sb-loaded ZIO FETs at 0.3 M (Table S2). The synergistic effect of Sb loading may come from either the physical thinning or the more effective densification of the Sbloaded ZIO films due to its lower solution concentration. Conversely, the ZTO FETs with an identical Sb loading prepared at 0.1 M suffered from deterioration of the carrier transport properties and current modulation capabilities, which can be explained by their poorer microstructure due to the decrease of average crystalline size (see Figure S3 and Table S2).

The gate bias stress instability of the Sb-loaded ZIO and ZTO FETs were investigated to elucidate the role of Sb cation in the channel layers. Figure 7 shows variations in the $I_{\rm DS}-V_{\rm GS}$ transfer curves of the different Sb-loaded ZIO FETs measured under PBS and NBS conditions as a function of the stress time up to 1800 s. In this test, the devices were stressed under gate biases of +15 (for PBS) and -15 V (for NBS). The 0 wt % Sb-loaded ZIO FETs suffered from huge positive ($\Delta V_{\rm TH} = +12.0$ V) and negative $V_{\rm TH}$ shifts ($\Delta V_{\rm TH} = -6.3$ V) during PBS and

NBS testing, respectively (Figure 7a, d and Table 3). As expected, the 0.1 and 0.15 wt % Sb-loaded ZIO FETs showed

Table 3. Variations in the $V_{\rm TH}$ Shift after the Application of PBS and NBS for the Different Sb-Loaded ZIO and ZTO FETs

| system | Sb (wt %) | PBS induced ΔV_{TH} (V) | NBS induced $\Delta V_{\rm TH}$ (V) |
|---------------|--------------|--|-------------------------------------|
| Sb-loaded ZIO | 0.0 | +11.9 | -6.3 |
| FETs | 0.1 | +7.0 | -3.2 |
| | 0.15 | +1.7 | -2.0 |
| Sb-loaded ZTO | 0.0 | +1.4 | -0.9 |
| FETs | 0.1 | +4.7 | -2.4 |
| | 0.15 | +6.3 | -6.9 |
| | | | |

highly enhanced PBS and NBS stabilities. ΔV_{TH} values for the 0.15 wt % Sb-loaded ZIO FET were reduced to +1.7 and -2.0 V after the same PBS and NBS tests, respectively (Figures 7c, f and Table 3). This result is related to the reduction in the V_{0} density of the Sb-loaded ZIO films. Under the PBS condition, the accumulated electron carriers can be partially consumed by neutralizing the shallow V_0^{2+} in the deep V_0 state as V_0^{2+} + $2e^- \rightarrow V_0$, leading to a positive $V_{\rm TH}$ shift. Because the degree of positive V_{TH} shift tends to be proportional to the pre-existing Vo density, the 0.15 wt % Sb-loaded ZIO FETs with the lowest V_O density exhibited the most stable behavior against the external PBS. It should be noted that none of the fabricated FETs were passivated. The dynamic adsorption/desorption of ambient gases such as oxygen molecules and moisture depended on the applied electric-field, and these can also contribute to the $V_{\rm TH}$ shift observed for the different Sb-loaded ZIO FETs. However, we believe that the Sb-dependent $V_{\rm TH}$

shifts for the Sb-ZIO FETs were mainly related to the variation in the intrinsic defects density in the channel layer. The negative $V_{\rm TH}$ shift of the Sb-ZIO FETs under the NBS condition can also be explained by the reverse reaction $[V_O \rightarrow V_O^{2^+} + 2e^-]$, where a lower quasi-Fermi energy level (toward the valence band edge) induced by the applied NBS will energetically favor the conversion from V_O to $V_O^{2^+}$. Therefore, the simultaneous improvement in the PBS and NBS resulted in stable Sb-loaded ZIO FETs with increasing Sb loading, which is consistent with the fact that the corresponding V_O density in the Sb-loaded ZIO films decreased as a result of the incorporation of Sb⁵⁺ as an efficient oxygen binder.

Conversely, the PBS and NBS instability for the Sb-loaded ZTO FETs became worse with increasing Sb loading in the ZTO film as shown in Figure 8 and Table 3. The Sb-free ZTO FETs exhibited reasonable stability against the external PBS and NBS. The $\Delta V_{\rm TH}$ values for the 0 wt % Sb-loaded ZTO FET were +1.4 V and -0.9 V after the application of PBS and NBS durations, respectively (Figure 8a, d). The PBS and NBS instability for the ZTO FETs with 0.15 wt % Sb loading became worse, moving to +6.3 V and -6.9 V, respectively (Figures 8c, f and Table 3). The reason for these degradations in the crystalline Sb-loaded ZTO system is the unexpected creation of heterogeneous two-dimensional defects as a result of the enhanced aggregate formation. The Sb loading into the ZTO system caused the evolution of largely heterogeneous morphologies and interfaces where the heterogeneous ZnO nanocrystallites were increasingly embedded in the polycrystalline spinel Zn₂SnO phase. Those two-dimensional morphological and interfacial defect states likely act as the carrier trapping centers, leading to deterioration in PBS and NBS instability for the resulting Sb-loaded ZTO FETs.



Figure 8. Time-dependent variations in the transfer characteristics for the different Sb-loaded ZTO FETs under the (a-c) PBS and (d-f) NBS conditions: (a, d), (b, e) 0.10, and (c, f) 0.15 wt % Sb loading.

4. CONCLUSION

The effects of antimony doping in solution-processed zinc indium oxide (ZIO) and zinc tin oxide (ZTO) films were examined by AFM, SEM, 2D GIXD, XPS and Hall measurements. The 0.10 or 0.15 wt % Sb loading into the ZIO system allowed the Sb-loaded ZIO films to have enhanced nanodomains and reduced Vo density morphology without inducing crystallization. This led to improvements in the field-effect mobility and gate bias stress reliability, including PBS and NBS induced $V_{\rm TH}$ instabilities. Our results indicated that the Sb⁵⁺ cation incorporated in the Sb-loaded ZIO system acted as shallow donors, and thus as mobility promoters as well. This positive effect can be attributed to the vacant 5s orbital availability of the Sb⁵⁺ cation, which is similar to that of In³⁺ $([Kr]4d^{10}5s^{0})$. Simultaneously, the stronger ionic field strength of the Sb⁵⁺ cation makes it an efficient oxygen binder for the Sb-loaded ZIO system, which prevented the unwanted creation of V_O defects and intensified the resistance of the Sb-loaded ZIO FETs to the application of an external gate bias stress. Therefore, the synergistic effect of boosting both mobility and stability in the Sb-loaded ZIO system can be used in vacuum or solution processed metal oxide semiconductors and related FETs. Conversely, the introduction of Sb cations into the ZTO system caused the formation of a spinel Zn_2SnO_4 phase with a preferential orientation and enlargement of the wurtzite ZnO nanoscale inclusions from the host ZTO crystal. The functionality of Sb cations as Vo defect suppressors was not observed in the Sb-loaded ZTO system. This was due to enhanced Sb³⁺ cation incorporation, which presumably resulted in acceptor-like trap states. As a result, the field-effect mobility and gate bias stress induced reliabilities of Sb-loaded ZTO FETs became worse with increasing Sb fraction. Therefore, we concluded that the synergic effect of Sb loading into the metal oxide semiconductor system is expected when the Sb-loaded metal oxide materials remain in the amorphous state.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b01090.

Current-voltage output characteristics of different Sbloaded ZIO and ZTO FETs (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: jkjeong1@hanyang.ac.kr (J.K.J.). *E-mail: hcyang@inha.ac.kr (H.Y.).

ORCID ©

Jong Han Baek: 0000-0001-7794-215X Hyunju Seol: 0000-0003-2975-7560 Kilwon Cho: 0000-0003-0321-3629

Hoichang Yang: 0000-0003-0585-8527

Author Contributions

[†]J.H.B. and H.S. contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Industrial Strategic Technology Development Program through the Ministry of Knowledge Economy/Ministry of Energy, Industry and Trade under Grant 10048560 and the Center for Advanced Soft Electronics under the Global Frontier Research Program (2012M3A6A5055225).

REFERENCES

(1) Hoel, C. A.; Mason, T. O.; Gaillard, J.-F.; Poeppelmeier, K. R. Chem. Mater. 2010, 22, 3569.

(2) Fortunato, E.; Barquinha, P.; Martins, R. Oxide Semiconductor Thin-Film Transistors: A Review of Recent Advances. *Adv. Mater.* **2012**, *24*, 2945–2986.

(3) Kamiya, T.; Nomura, K.; Hosono, H. Present Status of Amorphous In-Ga-Zn-O Thin-Film Transistors. *Sci. Technol. Adv. Mater.* **2010**, *11*, 044305.

(4) Nomura, K.; Ohta, H.; Takagi, A.; Kamiya, T.; Hirano, M.; Hosono, H. Room-Temperature Fabrication of Transparent Flexible Thin-Film Transistors using Amorphous Oxide Semiconductors. *Nature* 2004, 432, 488–492.

(5) Official Sharp TV Website. https://www.sharptvusa.com (accessed February 28, 2017).

(6) OLED, Wikipedia [Online]. http://en.wikipedia.org/wiki/OLED (accessed August 10, 2016).

(7) Banger, K. K.; Yamashita, Y.; Mori, K.; Peterson, R. L.; Leedham, T.; Richard, J.; Sirringhaus, H. Low-Temperature, High-Performance Solution-Processed Metal Oxide Thin-Film Transistors Formed by a 'Sol-Gel on Chip' Process. *Nat. Mater.* **2011**, *10*, 45–50.

(8) Kim, M.-G.; Kanatzidis, M. G.; Facchetti, A.; Marks, T. J. Lowtemperature Fabrication of High-Performance Metal Oxide Thin-film Electronics via Combustion Processing. *Nat. Mater.* **2011**, *10*, 382– 388.

(9) Rim, Y. S.; Jeong, W. H.; Kim, D. L.; Lim, H. S.; Kim, K. M.; Kim, H. J. Simultaneous Modification of Pyrolysis and Densification for Low-Temperature Solution-Processed Flexible Oxide Thin-Film Transistors. J. Mater. Chem. 2012, 22, 12491–12497.

(10) Kim, Y. H.; Heo, J. S.; Kim, T. H.; Park, S.; Yoon, M. H.; Kim, J.; Oh, M. S.; Yi, G. R.; Noh, Y. Y.; Park, S. K. Flexible Metal-Oxide Devices Made by Room-Temperature Photochemical Activation of Sol-Gel Films. *Nature* **2012**, *489*, 128–132.

(11) Fortunato, E.; Barquinha, P.; Pimentel, A.; Pereira, L.; Goncalves, G.; Martins, R. Amorphous IZO TTFTs with Saturation Mobilities Exceeding 100 cm²/Vs. *Phys. Status Solidi RRL* **2007**, *1*, R34–R36.

(12) Oh, S.; Yang, B. S.; Kim, Y. J.; Oh, M. S.; Jang, M.; Yang, Y.; Jeong, J. K.; Hwang, C. S.; Kim, H. J. Anomalous Behavior of Negative Bias Illumination Stress Instability in an Indium Zinc Oxide Transistor: A Cation Combination Approach. *Appl. Phys. Lett.* **2012**, *101*, 092107.

(13) Wang, L.; Yoon, M.; Lu, G.; Yang, Y.; Facchetti, A.; Marks, T. J. High-Performance Transparent Inorganic/Organic Hybrid Thin-Film n-Type Transistors. *Nat. Mater.* **2006**, *5*, 893–900.

(14) Hosono, H. Ionic Amorphous Oxide Semiconductor: Material Design, Carrier Transport, and Device Application. J. Non-Cryst. Solids **2006**, 352, 851–858.

(15) Kamiya, T.; Nomura, K.; Hosono, H. Electronic Structures above Mobility Edges in Crystalline and Amorphous In-Ga-Zn-O: Percolation Conduction Examined by Analytical Model. *J. Disp. Technol.* **2009**, *5*, 462–467.

(16) Park, J.-S.; Kim, K. S.; Park, Y.-G.; Mo, Y.-G.; Kim, H. D.; Jeong, J. K. Novel ZrInZnO Thin-Film Transistor with Excellent Stability. *Adv. Mater.* **2009**, *21*, 329–333.

(17) Kim, C.-J.; Kim, S.; Lee, J.-H.; Park, J.-S.; Kim, S.; Park, J.; Lee, E.; Lee, J.; Park, Y.; Kim, J. H.; Shin, S. T.; Chung, U.-I. Amorphous Hafnium-Indium-Zinc Oxide Semiconductor Thin Film Transistors. *Appl. Phys. Lett.* **2009**, *95*, 252103.

(18) Kim, G. H.; Ahn, B. D.; Shin, H. S.; Jeong, W. H.; Kim, H. J.; Kim, H. J. Effect of indium composition ratio on solution-processed nanocrystalline InGaZnO thin film transistors. *Appl. Phys. Lett.* **2009**, *94*, 233501.

(19) Banger, K. K.; Peterson, R. L.; Mori, K.; Yamashita, Y.; Leedham, T.; Sirringhaus, H. High Performance, Low Temepratures Solution-Processed Barium and Strontium Doped Oxide Thin Film Transistors. *Chem. Mater.* **2014**, *26*, 1195–1203.

(20) Chong, H. Y.; Han, K. W.; No, Y. S.; Kim, T. W. Effect of the Ti Molar Ratio on the Electrical Characteristics of Titanium-Indium-Zinc Oxide Thin-Film Transistors Fabricated by using a Solution Process. *Appl. Phys. Lett.* **2011**, *99*, 161908.

(21) Do, J. C.; Ahn, C. H.; Cho, H. K.; Lee, H. S. Effect of Ti Addition on the Characteristics of Titanium-Zinc-Tin-Oxide Thin-Film Transistors Fabricated via a Solution Process. *J. Phys. D: Appl. Phys.* **2012**, 45, 225103.

(22) Parthiban, S.; Kwon, J.-Y. Amorphous Boron-Indium-Zinc-Oxide Active Channel Layers for Thin-Film Transistor Fabrication. *J. Mater. Chem. C* 2015, *3*, 1661–1665.

(23) Parthiban, S.; Park, K.; Kim, H.-J.; Yang, S.; Kwon, J.-Y. Carbon-Incorporated Amorphous Indium Zinc Oxide Thin-Film Transistors. *J. Electron. Mater.* **2014**, *43*, 4224–4228.

(24) Parthiban, S.; Kwon, J. Y. Role of Dopants as a Carrier Suppressor and Strong Oxygen Binder in Amorphous Indium-Oxide-Based Field Effect Transistor. *J. Mater. Res.* **2014**, *29*, 1585–1596.

(25) Yang, B. S.; Huh, M. S.; Oh, S.; Lee, U. S.; Kim, Y. J.; Oh, M. S.; Jeong, J. K.; Hwang, C. S.; Kim, H. J. Role of ZrO₂ Incorporation in the Suppression of Negative Bias Illumination-Induced Instability in Zn-Sn-O Thin Film Transistors. *Appl. Phys. Lett.* **2011**, *98*, 122110.

(26) Jeong, J. K. Photo-Bias Instability of Metal Oxide Thin Film Transistors for Advanced Active Matrix Displays. *J. Mater. Res.* 2013, 28, 2071–2084.

(27) Jung, H. Y.; Kang, Y.; Hwang, A. Y.; Lee, C. K.; Han, S.; Kim, D.-H.; Bae, J.-U.; Shin, W.-S.; Jeong, J. K. Origin of the Improved Mobility and Photo-Bias Stability in a Double-Channel Metal Oxide Transistor. *Sci. Rep.* **2014**, *4*, 3765.

(28) Ahn, C. H.; Cho, H. K.; Kim, H. Carrier Confinement Effect-Driven Channel Design and Achievement of Robust Electrical/ Photostability and High Mobility in Oxide Thin-Film Transistors. J. Mater. Chem. C 2016, 4, 727–735.

(29) Kim, J.-I.; Ji, K. H.; Jung, H. Y.; Park, S. Y.; Choi, R.; Jang, M.; Yang, H.; Kim, D.-H.; Bae, J.-U.; Kim, C. D.; Jeong, J. K. Improvement in Both Mobility and Bias Stability of ZnSnO Transistors by Inserting Ultra-Thin InSnO Layer at the Gate Insulator/Channel Interface. *Appl. Phys. Lett.* **2011**, *99*, 122102.

(30) Park, J. C.; Kim, S.; Kim, S.; Kim, C.; Song, I.; Park, Y.; Jung, U.; Kim, D. H.; Lee, J. Highly Stable Transparent Amorphous Oxide Semiconductor Thin-Film Transistors Having Double-Stacked Active Layer. *Adv. Mater.* **2010**, *22*, 5512.

(31) Liu, X.; Wang, C.; Cai, B.; Xiao, X.; Guo, S.; Fan, Z.; Li, J.; Duan, X.; Liao, L. Rational Design of Amorphous Indium Zinc Oxide/ Carbon Nanotube Hybrid Film for Unique Performance Transistor. *Nano Lett.* **2012**, *12*, 3596–3601.

(32) Jang, M.; Kim, S. H.; Lee, H. K.; Kim, Y.-H.; Yang, H. Layer-by-Layer Conjugated Extension of a Semiconducting Polymer for High-Performance Organic Field-Effect Transistor. *Adv. Funct. Mater.* **2015**, 25, 3833–3839.

(33) Greve, D. W. Field Effect Devices and Applications: Devices for Portable, Low-Power, and Imaging Systems, 1st ed.; Prentice Hall: Upper Saddle River, NJ, 1998; pp 379.

(34) Taylor, M. P.; Readey, D. W.; van Hest, M. F. A. M.; Teplin, C. W.; Alleman, J. L.; Dabney, M. S.; Gedvilas, L. M.; Keyes, B. M.; To, B.; Perkins, J. D.; Ginley, D. S. The Remarkable Thermal Stability of Amorphous In-Zn-O Transparent Conductors. *Adv. Funct. Mater.* **2008**, *18*, 3169–3178.

(35) Harvey, S. P.; Poeppelmeier, K. R.; Mason, T. O. Subsolidus Phase Relationships in the ZnO-In₂O₃-SnO₂ System. *J. Am. Ceram. Soc.* **2008**, *91*, 3683–3689.

(36) Kim, M. G.; Kim, H. S.; Ha, Y. G.; He, J.; Kanatzidis, M. G.; Facchetti, A.; Marks, T. J. High-Performance Solution-Processed Amorphous Zinc–Indium–Tin Oxide Thin-Film Transistors. J. Am. Chem. Soc. **2010**, 132, 10352–10364. (37) Manesse, M.; Sanjines, R.; Stambouli, V.; Jorel, C.; Pelissier, B.; Pisarek, M.; Boukherroub, R.; Szunerits, S. Preparation and Characterization of Silver Substrates Coated with Antimony-Doped SnO₂ Thin Films for Surface Plasmon Resonance Studies. *Langmuir* **2009**, *25*, 8036–8041.

(38) J., Kerr CRC Handbook of Chemistry and Physics 1999–2000: A Ready-Reference Book of Chemical and Physical Data, 81st ed.; CRC Press: Boca Raton, FL, 2000.

(39) Jansen, V. M. Die Kristallstruktur von Antimon (V)-oxid. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **1979**, 35, 539–542.