

Lanthanum Doping Enabling High Drain Current Modulation in a p-Type Tin Monoxide Thin-Film Transistor

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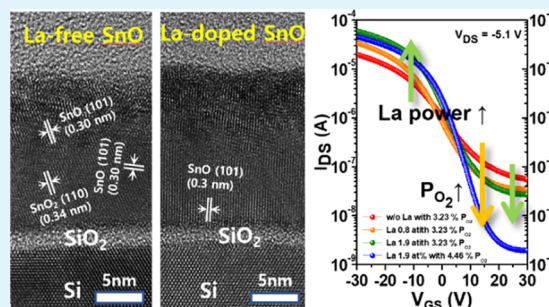
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Supporting Information

ABSTRACT: Effects of lanthanum (La) loading on the structural, optical, and electrical properties of tin monoxide (SnO) films were examined as a p-type semiconducting layer. La loading up to 1.9 atom % caused the texturing of the tetragonal SnO phase with a preferential orientation of (101), which was accompanied by the smoother surface morphology. Simultaneously, the incorporated La cation suppressed the formation of n-type SnO₂ in the La-doped SnO film and widened its optical band gap. These variations allowed the 1.9 atom % La-loaded SnO film to have a high hole mobility and carrier density, compared with the La-free control SnO film. The superior semiconducting property was reflected in the p-type thin-film transistor (TFT). The control SnO TFTs exhibited the field-effect mobility (μ_{SAT}) and $I_{\text{ON/OFF}}$ ratio of 0.29 cm² V⁻¹ s⁻¹ and 5.4 × 10², respectively. Enhancement in the μ_{SAT} value and $I_{\text{ON/OFF}}$ ratio was observed for the TFTs with the 1.9 atom % La-loaded SnO channel layer: they were improved to 1.2 cm² V⁻¹ s⁻¹ and 7.3 × 10³, respectively. The reason for this superior performance was discussed on the basis of smoother morphology, suppression of disproportionation conversion from Sn²⁺ to Sn + Sn⁴⁺, and reduced gap-state density.

KEYWORDS: cosputtering, p-type semiconductor, tin monoxide, lanthanum doping, thin-film transistor



1. INTRODUCTION

Indium gallium zinc oxide (IGZO) becomes the industrial standard channel substance of n-channel thin-film transistors (TFTs) for high-end advanced display devices such as ultrahigh-pixel-density liquid crystal screens and large-sized organic light-emitting diode television because it has several intriguing properties including high electron mobility (>10 cm² V⁻¹ s⁻¹), extremely low leakage current (<1 pA), low-temperature processing capability (<500 °C), and acceptable bias-thermal stability. On the other hand, the p-channel TFTs based on metal oxide (MO) semiconductors are inferior to the counterpart of n-channel TFTs in terms of device performance, which makes it difficult to realize the complementary metal oxide semiconductor (CMOS) inverter. Because the CMOS inverter is a building unit for versatile logic and digital/analog systems, the main application of metal oxide semiconductors is still limited to the niche market of display devices. Therefore, it is stringent and important to develop p-channel metal oxide TFTs, which is comparable to the device performance of n-channel MO TFTs. Among the various candidates for p-type MO semiconductors, tin monoxide (SnO) has been identified as a promising material because it has a lower hole effective mass (m_h^*)¹ and higher hole mobility² compared with the other p-type MOs such as NiO, CuO, CuAlO₂, and Bi₂O₃. This interesting feature is attributed to the formation of a

dispersed valance band (VB) edge arising from hybridization of oxygen 2p and Sn 5s orbitals. The wave-function overlapping of the symmetrical Sn 5s orbital near the top of VB provides an effective pathway for hole carrier transports in the SnO material.^{3–5} Besides, SnO has a reasonable hole dopability where the Sn vacancy (V_{Sn}) acting as an acceptor is easily created due to its relatively low formation energy.³ So far, various deposition methods have been used to prepare semiconducting p-type SnO thin films such as pulsed laser deposition,^{6,7} electron beam evaporation,^{8,9} solution process,¹⁰ reactive sputtering,^{11–31} atomic-layer-deposition,³² and thermal evaporation.^{33–35} The phase-stability map of β -Sn, SnO, and SnO₂ in the sputtered SnO system depending on the oxygen partial pressure and chamber pressure was constructed through hundreds of experiments.²⁰ The mixed-phase SnO film with the approximately 3 atom % β -Sn second phase allowed the high hole mobility, attributable to the enhancement in the metallic character near the top of the valance band by the Sn interstitial. The resulting TFT with the mixed-phase SnO channel exhibited a remarkably high mobility of 6.75 cm² V⁻¹ s⁻¹ and a $I_{\text{ON/OFF}}$ ratio of 6 × 10³.

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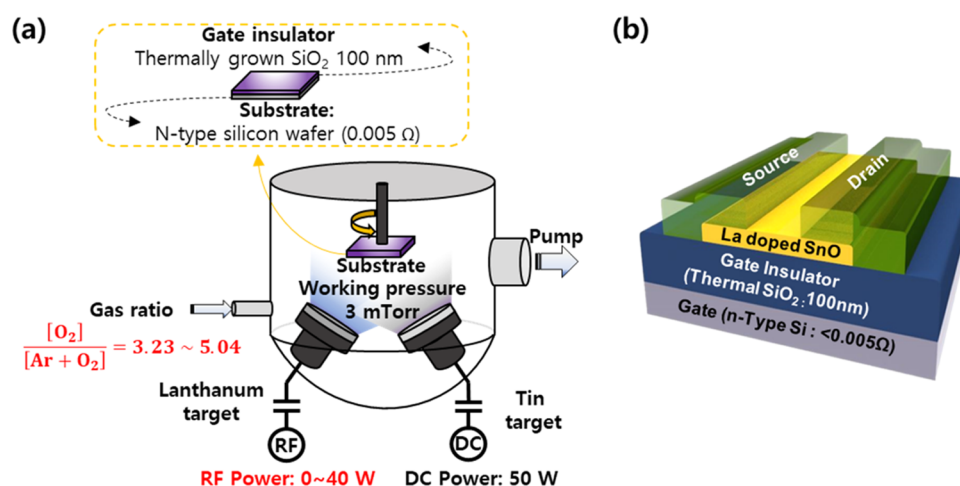


Figure 1. (a) Schematic diagram of a cosputtering method with Sn and La targets. (b) Schematic structure of the fabricated SnO TFTs with bottom gate and top contact configuration.

Regardless of the progress in the p-type SnO TFTs, the major problems still persist including the narrow temperature process window and low $I_{\text{ON/OFF}}$. The chemical state of Sn atoms greatly affects the microstructure and electrical properties of the resulting SnO film. Multiple valences of the Sn atom cause the mixing state of metallic Sn, SnO, and SnO₂ phases in as-deposited or/and annealed SnO films.²⁰ Metallic Sn existing in the SnO film shows a complicated behavior: excess Sn composition in the oxygen-deficient region during heat treatment often facilitates the dendritic phase and irregular protrusion structure, deteriorating the hole carrier transport.³¹ Conversely, the excess Sn cations in the uniform and homogeneous SnO film were found to enhance the hole mobility in the field-effect transistors.²⁰ When the annealing temperature for the SnO films increases more than 250 °C, the disproportionation chemical reaction occurs [$2\text{SnO} \rightarrow \text{SnO}_2 + \text{Sn}$] by virtue of the minimization principle of the total Gibbs free energy. Unfortunately, SnO₂ exhibits an n-type characteristic, which results in the partial loss of p-type character and/or occurrence of uncontrolled ambipolar conductivity. It is generally accepted that the bias-thermal-stress (BTS)-induced instability of n-channel IGZO TFTs is suppressed due to the reduction in the electric trap densities mainly coming from the nonstoichiometric nature of the IGZO film with increasing annealing or treatment temperatures (≥ 300 °C), which is a prerequisite for their implementation in commercial display products. Thus, the p-channel SnO TFTs, which are usually fabricated at a low temperature (< 250 °C) to prevent the conversion of Sn^{2+} to Sn^{4+} , are likely to also suffer from similar BTS-induced instability. Furthermore, the dissimilar processing/annealing temperatures between n-type IGZO and p-type SnO TFTs may complicate the integration of the MO-based CMOS devices. Therefore, it would be technologically important to secure the high performance of p-channel MO TFTs at an elevated temperature (≥ 300 °C). The second issue lies in the low $I_{\text{ON/OFF}}$ ratio ($\leq 10^3$) of the p-channel TFTs studied previously in the literature. In this regard, there have been a few approaches to improve the $I_{\text{ON/OFF}}$ ratio in the p-channel SnO TFTs on the basis of transition-metal doping. Liang et al. observed that yttrium (Y) incorporated into SnO films acts as a shallow acceptor to increase the hole carrier density (n_h), but the Y-doped SnO yielded low hole mobility due to the deterioration of its crystalline quality. Interestingly,

the off-state current (I_{OFF}) decreased with increasing Y doping for the resulting p-channel Y-doped SnO TFTs. However, the rationale for the plausible mechanism was not discussed.³⁶ Conversely, the doping of lead (Pb) in p-type SnO films was found to decrease the n_h and hole mobility simultaneously due to creation of deep hole traps and increase in grain-boundary energy barriers. The I_{OFF} value for the Pb-doped SnO TFTs was reduced, which was also explained by Fermi energy pinning caused by higher Pb-induced trap states, suggesting that the decoupling of the hole carrier dopability and adverse trap states is not trivial.³⁷ Very recently, the doping of Y into SnO was revisited for the purpose of improving the $I_{\text{ON/OFF}}$ ratio by reducing I_{OFF} in p-channel SnO TFTs. The incorporated Y was identified as an oxygen scavenger rather than a shallow acceptor in SnO thin films, causing the reduction in component of n-type SnO₂ and, thus, the I_{OFF} value.³⁸

In this work, we examined the effect of lanthanum (La) doping on the microstructural, chemical, optical, and electrical properties of p-type SnO thin films on SiO₂/Si substrates by reactive DC magnetron cosputtering. The reason for La doping lies in its high ionicity compared with the host Sn cation where the stronger bond between La and O would prevent the formation of an adverse hole compensation center such as oxygen vacancy. Our finding was that the La incorporated in the SnO film acts as a stabilizer of the metastable Sn^{2+} ion, which drastically reduced the I_{OFF} value (thus improving the $I_{\text{ON/OFF}}$ ratio) and widened the temperature process window by more than 300 °C for the p-channel SnO TFTs. This beneficial effect was supported by investigating the effect of La doping in the SnO films prepared at different oxygen pressures (P_{O_2}) and postdeposition annealing (PDA) temperatures.

2. EXPERIMENTAL SECTION

2.1. Fabrication of La-Doped SnO Thin Films and Their TFTs. The 30 nm-thick SnO films with different La loadings were prepared by a reactive cosputtering on the SiO₂/Si substrate using a 3 in. metallic Sn target and a La target at room temperature (Figure 1a). The cosputtering was carried out at the Ar gas flow rate of 30 sccm: the flow rates of O₂ were split into 1.0, 1.2, 1.4, and 1.6 sccm, corresponding to the oxygen partial pressures [$P_{\text{O}_2} = \text{O}_2/(\text{Ar} + \text{O}_2)$, vol %] of 3.2, 3.9, 4.5, and 5.1%. The input dc power of the Sn target was fixed at 50 W, while the input rf power of the La target was varied

from 0 to 40 W to control the fraction of La in the SnO films. The working pressure during the SnO deposition was 3 mTorr. Bottom gate TFTs with top contact configuration were fabricated to assess the suitability of the La-doped SnO film as a p-type semiconductor (Figure 1b). The 100 nm-thick SiO₂ film on a heavily doped n-type silicon substrate was grown using thermal oxidation. The thermal SiO₂ and conducting Si substrate were used as the gate insulator and electrode, respectively. After depositing the La-doped SnO film on the SiO₂/Si substrate, the 50 nm-thick Indium tin oxide (ITO) films were deposited as source/drain (S/D) electrodes using an identical sputtering system. Prior to the deposition of the S/D electrode, the samples were annealed at 250 or 300 °C for 1 h under a box furnace. The active area and the S/D electrode were defined using a shadow mask during the deposition of SnO and ITO films, respectively. The fabricated TFTs had a bottom gate structure, and their channel width (*W*) and length (*L*) were 1000 and 300 μm, respectively. Finally, the samples were annealed at 250 °C for 1 h on a hot plate to improve the contact property between the SnO channel and the ITO S/D electrode.

2.2. Characterization. The surface morphology and roughness of the La-doped SnO films were characterized by field-emission scanning electron microscopy (FE-SEM, Verios G4, Thermo Scientific) and tapping-mode atomic force microscopy (AFM, Nanoscope Multi-mode IV, Bruker). The structural properties of La-doped SnO films were examined by glancing incidence X-ray diffraction (GIXRD, X'Pert-PRO MRD with Cu Kα radiation). The mass density and thickness of the films were analyzed by X-ray reflectivity (XRR, SmartLab, Rigaku), where the film thickness was double-checked by using ellipsometry. The chemical state and composition of the La-doped SnO films were evaluated by X-ray photoelectron spectroscopy (XPS, K-Alpha+, Thermo Fisher Scientific) with an X-ray source of Al Kα of 1486.6 eV. Prior to the XPS measurement, the surface of La-doped SnO films was etched for 120 s with Ar⁺ plasma to eliminate unintentional surface contamination. The compositions of Sn, O, C, and N in the SnO films after PDA at 250 °C are summarized in Table 1. Microstructures of the undoped and La-doped SnO films were also

Table 1. Tin, Oxygen, Nitrogen, and Carbon Fractions of SnO Films Annealed at 250 °C with Different La Loadings

La loading in SnO film [atom %]	Sn [atom %]	O [atom %]	N [atom %]	C [atom %]
0	43.2	54.9	0.3	1.6
0.8	45.4	52.8	0.3	0.7
1.9	45.0	52.4	0.2	0.5
3.1	44.0	51.9	0.2	0.8

investigated using high-resolution transmission electron microscopy (HRTEM, JEM-ARM200F, JEOL Ltd) with the Cs corrected scanning mode. The optical properties of the La-doped SnO films were characterized using a UV–vis–near-infrared (NIR) spectrophotometer (v-530, JASCO) in the range of 400–800 nm. The Hall mobility (μ_{Hall}) and hole carrier concentration (n_{h}) of the La-doped SnO films were calculated from Hall effect measurement using the van der Pauw configuration (HL5500, BioRad). ITO films as an ohmic contact layer were deposited by dc magnetron sputtering through a shadow mask. The electrical characteristics of the fabricated La-doped SnO TFTs were performed at room temperature using a Keithley 2636B source meter.

2.3. Density Functional Theory Calculation. All calculations were performed by the Vienna ab initio simulation package (VASP)³⁹ using projector-augmented wave (PAW) pseudopotential with 500 eV cutoff energy. The hybrid functional method (HSE06)⁴⁰ was employed for the exchange–correlation energy, and the fraction was set to be 0.25. For defect calculations, we used a supercell with over 100 atoms, and only the Γ point was sampled. In the case of charged defects, the spurious interaction with periodic images of charged defect was corrected by using the Freysoldt, Neugebauer, and Van de Walle (FNV) scheme.⁴¹ The chemical potentials of Sn and O are

determined at the boundary between Sn metal and SnO ($\mu_{\text{Sn}} = E(\text{Sn})$, $\mu_{\text{O}} = E(\text{SnO}) - E(\text{Sn})$). In addition, we determined the chemical potential of La from La₂Sn₂O₇. Since the hydrogen-related defects could be a source of carrier,^{42,43} we calculated the defect formation energies of intrinsic defect, La substitutional defect, and hydrogen-related defects.

3. RESULTS AND DISCUSSION

Figure 2a shows the GIXRD patterns of the SnO films with different La loadings after PDA for 1 h at 250 °C. The control

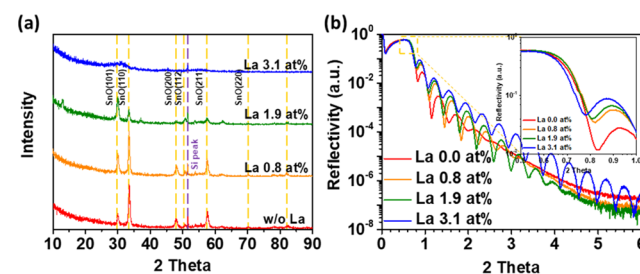


Figure 2. (a) GIXRD patterns and (b) XRR data of the SnO films with different La loadings after PDA for 1 h at 250 °C.

SnO film had discernible diffraction peaks at $2\theta = 30.0, 33.6, 48.2,$ and 57.6° , which can be, respectively, assigned to (101), (110), (200), and (211) reflections of the α -SnO phase (tetragonal litharge structure, JCPDS card No. 06-0395). It is noted that the peak intensity of α -SnO (110) is predominant among the other diffraction peaks, suggesting that the grown SnO film has the preferential orientation of (110) direction along the normal direction of the film surface.¹⁰ The intensities of these discernible peaks for the SnO thin films decreased with increasing La doping concentration except for the (101) reflection. The SnO film with 1.9 atom % La loading exhibited only a strong (101) reflection, indicating that the preferential orientation changed from the (110) face to the (101) face. The crystalline SnO is known to have an anisotropic band structure in the Brillouin zone. Its trigonal symmetry gives only two hole effective mass values: $0.59m_0$ along the Γ –Z direction (parallel to the *c*-axis) and $2.8m_0$ along the Γ –X direction (perpendicular to the *c*-axis, parallel to the *a*-axis).³ It means that the larger volume fraction of [001] oriented parallel to the in-plane direction yields a higher mobility in the thin-film device. This rationale predicts that the control SnO film with the preferential orientation of (110) should have higher mobility than the 1.9 atom % La-loaded SnO film with that of (101). Notably, the slightly higher Hall mobility was measured for the 1.9 atom % La-loaded SnO film compared with that of the control SnO film. It hints that the mobility variation is complicated by the scattering mechanism (for example, roughness-induced scattering) as well as the hole effective mass. On the other hand, all diffraction peaks for the SnO film with La doping concentration of 3.1 atom % disappeared, indicating that the moderate loading of La into SnO films frustrates its crystallization during film growth and annealing processes. It can be understood that the loading of La³⁺ with a smaller ionic radius (1.03 Å, coordination number = 6)⁴⁴ compared with the Sn²⁺ ion (1.18 Å, coordination number = 6) into Sn sublattices imparts enhanced disorder within the SnO network to facilitate a smoother surface and formation of an amorphous phase.⁴⁵ The evolution of structural properties of the SnO film as a function of La doping was also clearly confirmed in AFM analysis. The mass densities of the La-

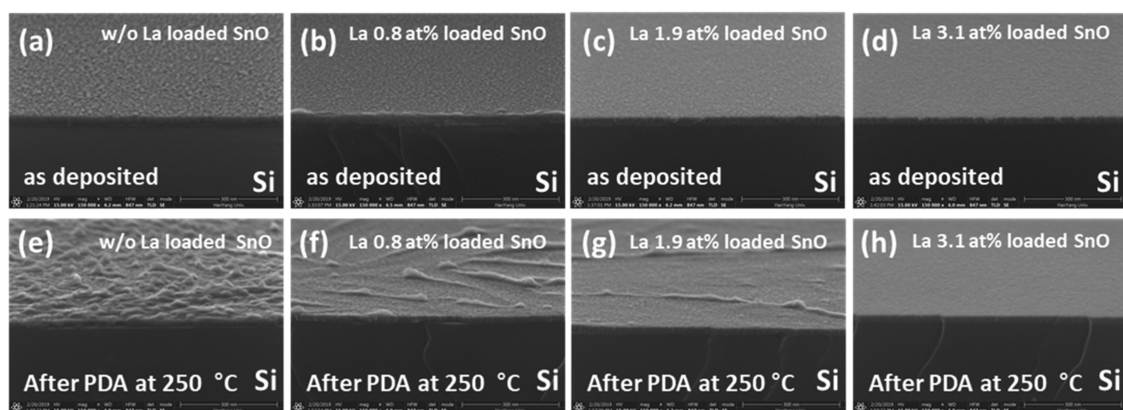


Figure 3. SEM images of as-deposited SnO thin films with different La loadings of (a) 0 atom %, (b) 0.8 atom %, (c) 1.9 atom %, and (d) 3.1 atom %. The image of SnO films after PDA at 250 °C with different La loadings of (e) 0 atom %, (f) 0.8 atom %, (g) 1.9 atom %, and (h) 3.1 atom %.

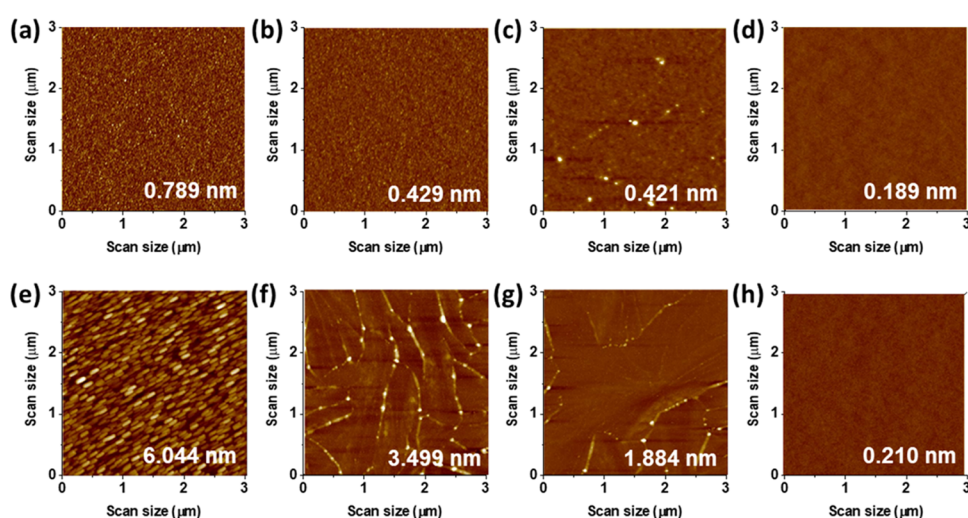


Figure 4. AFM images of as-deposited SnO thin films with different La loadings of (a) 0 atom %, (b) 0.8 atom %, (c) 1.9 atom %, and (d) 3.1 atom %. Corresponding AFM images of the SnO thin films annealed at 250 °C with different La loadings of (e) 0 atom %, (f) 0.8 atom %, (g) 1.9 atom %, and (h) 3.1 atom %. The scan area is 3 mm × 3 mm.

loaded SnO films were evaluated by X-ray reflectivity (XRR) analysis as shown in Figure 2b. The critical angle values for the SnO film with La loading of 0.8 and the 1.9 atom % La-loaded film were larger than that of the La-free SnO film. The mass densities of the SnO films with La loadings of 0, 0.8, and 1.9 atom % were 6.45, 6.85, and 6.83 g cm⁻³, respectively. Simultaneously, the oscillation fringe for the SnO film with La loading of 1.9 atom % became well developed, suggesting that the surface roughness of the La-loaded SnO films decreased. The reason why the La incorporation results in film densification with better morphologies will be discussed. However, the mass density for the SnO film with La loading of 3.1 atom % decreased to 6.30 g cm⁻³, which should be related to the formation of the amorphous phase.

Figure 3a–d shows the bird's-eye-view SEM images of the as-deposited SnO films with different La loadings of 0, 0.8, 1.9, and 3.1 atom %. The La-free film shows a uniform and small dispersed grainlike morphology. The uniform film became smoother with increasing La loading up to 3.1 atom % as shown in AFM images of Figure 4a–d. However, the PDA at 250 °C caused the La-free film to have an irregular surface morphology containing a large protrusion (Figure 3e). Thus, the La-free SnO film after PDA had rough morphologies (root-mean-square roughness, rms = 6.04 nm), as shown in Figure

4e. First, these protrusions in SnO were attributed to the migration of the excess Sn cluster in the as-deposited film toward the surface of the SnO film and subsequent oxidation during thermal annealing.³¹ It suggests that the incorporation of La into SnO films can reduce the excess Sn atom and/or mitigate the out-diffusion of the existing excess Sn atom. Interestingly, the areal density of these protrusions decreased with increasing La doping concentration (see Figures 3f–h and 4f–h). Most of the protrusions disappeared for the SnO film with the La doping of 1.9 atom % (Figure 3g), which improved its rms roughness to 1.88 nm, as shown in Figure 4g. In contrast, the SnO film with the largest La doping of 3.1 atom % exhibited a featureless smooth morphology: its rms value was reduced to 0.21 nm, which can be related to the formation of its completely amorphous phase (Figures 3h and 4h).

The evolution of chemical states for the SnO thin film with different La loadings was investigated by X-ray photoelectron spectra (XPS). Figure 5a shows the XPS survey spectra of the as-deposited SnO films with different La loadings. The C 1s peak (284.8 eV) for C–C bonds was used to calibrate the photoelectron binding energy. Each sample was subjected to Ar sputtering for 120 s prior to XPS analysis to reduce the contribution of native oxide layers on the top layer of the La-doped SnO films. The La-free SnO sample had Sn 3d, O 1s

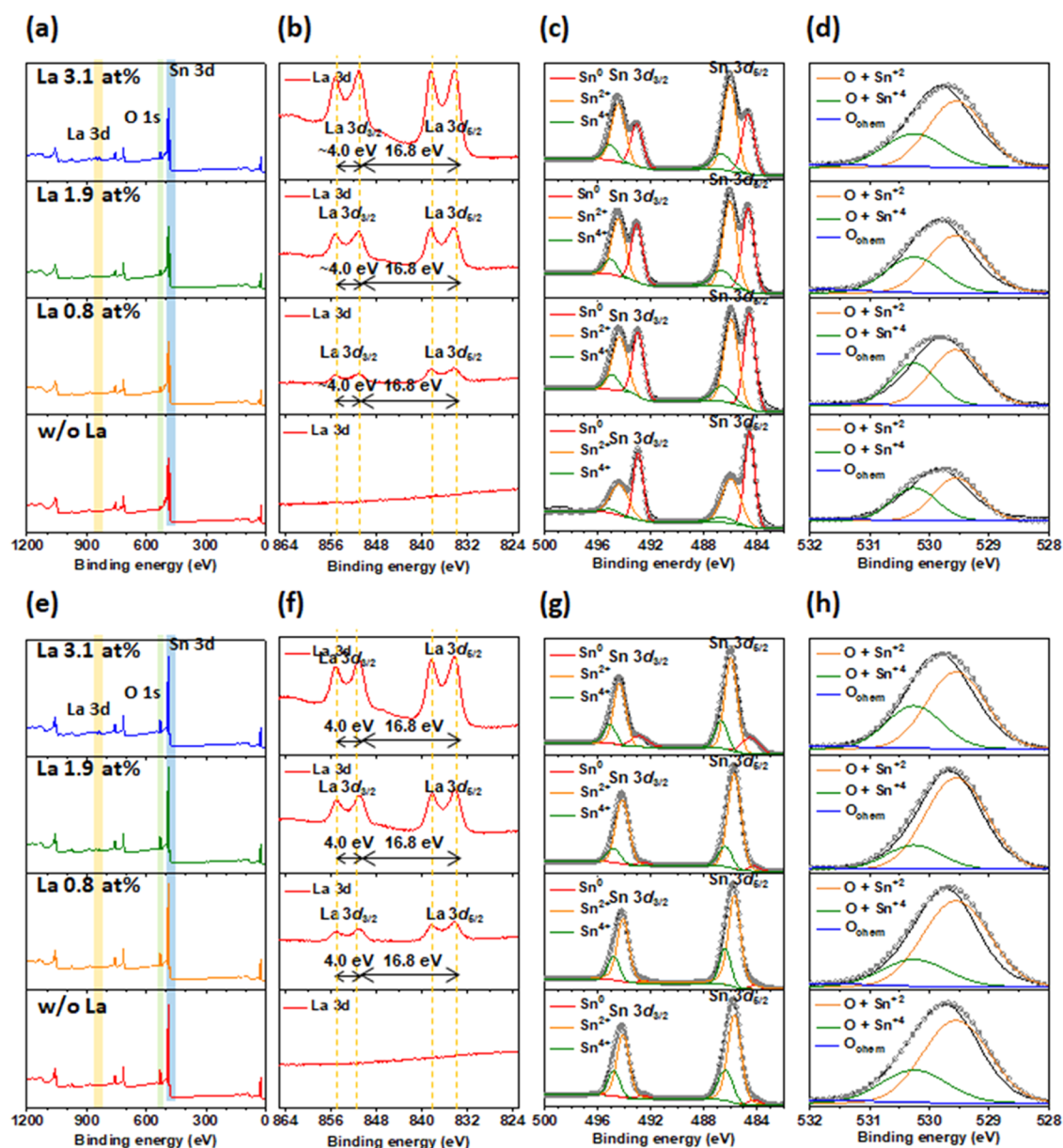


Figure 5. XPS survey spectra of different La-loaded SnO films (a) as-deposited and (e) annealed at 250 °C. XP spectra of (b, f) La 3d, (c, g) Sn 3d, and (d, h) O 1s of different La-loaded SnO films (b–d) as-deposited and (f–h) annealed at 250 °C.

peaks, whereas an additional La 3d peak was observed for the La-loaded SnO films (Figure 5b). Figure 5b shows the La 3d XP spectra of the as-deposited SnO films with different La loadings, in which no metallic peak was detected in the La 3d spectra. The peaks at 851.1 and 834.3 eV for the 0.8 atom % La-doped SnO film were assigned to La 3d_{3/2} and 3d_{5/2}, respectively, with a spin–orbit split of 16.8 eV. In particular, the multiplet splitting of each La 3d_{3/2} and 3d_{5/2} by ~4.4 eV indicates that the La³⁺ cation is coordinated with O²⁻ ions.^{46,47} The peak of La 3d XP spectra grew with increasing La loading, suggesting that the varying power of the La target has controllability of La doping in the SnO film. Sn 3d and O 1s XPS core-level spectra of 30 nm-thick SnO films with different La loadings are shown in Figure 5c,d respectively. The binding energy states of the Sn3d_{5/2} core level were deconvoluted into three bases of 484.2 ± 0.5, 485.7 ± 0.5, and 486.4 ± 0.5 eV, which can be assigned to Sn⁰, Sn²⁺, and Sn⁴⁺, respectively.⁴⁸ For accurate assignment of binding energies of Sn²⁺ and Sn⁴⁺,

the Sn 3d XP spectra for the reference SnO and SnO₂ films were also inserted in Figure S1, which were prepared at $T_A = 250$ and 400 °C under an air atmosphere, respectively. It can be clearly seen that the energy spacing between Sn²⁺ and Sn⁴⁺ states is approximately 0.7 eV. The comparable ratio between Sn²⁺ and Sn⁴⁺ for the undoped SnO films was also obtained from the Sn 4d XP spectra (see Table S1 and Figure S2). The striking feature of the control as-deposited SnO film lies in the dominance of the metallic Sn⁰ state: the portions of Sn⁰, Sn²⁺, and Sn⁴⁺ in the as-deposited SnO film were 51.4, 43.2, and 5.4%, respectively (Figures 5c, 6a, and Table S2). Notably, the Sn²⁺ portion for the as-deposited La-doped SnO films grew with increasing La loadings: those for the SnO films with La loadings of 1.9 and 3.1 atom % were 47.2 and 53.0%, respectively. It indicates that the incorporation of La with lower electronegativity compared with Sn facilitates the oxidation of Sn to Sn²⁺ due to its superior binding capability of the oxygen anion. This postulation can be confirmed in the

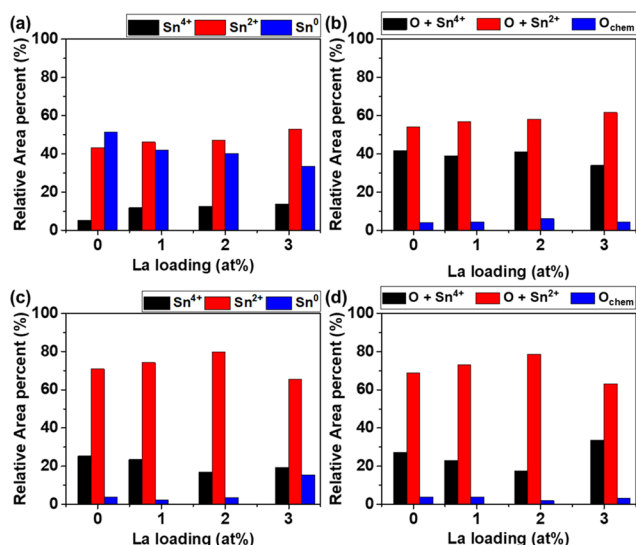


Figure 6. Variations in the chemical states including Sn^0 , Sn^{2+} , and Sn^{4+} of SnO films with different La loadings, which were calculated from the deconvolution of (a, c) Sn 3d and (b, d) O 1s spectra of SnO films (a, b) as-deposited and (c, d) annealed at 250 °C.

O 1s XP spectra for the as-deposited SnO films with different La loadings (Figure 5d and Table S2). The O 1s peaks could be deconvoluted to two components with binding energies of O– Sn^{2+} (529.6 eV) and O– Sn^{4+} (530.3 eV), without involving the peak at 531.8 eV, which corresponds to O_{chem} .⁴⁹ It can be understood that the chemisorbed oxygen ion was effectively eliminated during Ar sputtering prior to XPS analysis. The portion of Sn^{2+} increased for the La-doped SnO films compared with that of the La-free SnO film, as summarized in Figure 6b. The less formation of protrusion for the La-doped SnO films during PDA is well explained by the fact that the La loadings into the SnO film reduced the metallic Sn^0 portion as aforementioned. Figure 5e shows the XPS survey spectra of the La-doped SnO films annealed at 250 °C. There was no difference in the La 3d XP spectra of the annealed SnO films with different La loadings, compared with those of the corresponding as-deposited La-doped SnO films (Figure 5f). However, the metallic Sn^0 fraction in the La-free annealed SnO film rapidly decreased to 3.8%, whereas the portions of Sn^{2+} and Sn^{4+} increased to 70.9 and 25.3%, respectively, compared with the as-deposited SnO film (Figures 5g, 6c and Table S3). The large portion of Sn^{2+} compared with the other species with the different oxidation numbers indicates that the control SnO film should exhibit the p-type character. Our finding was that the increased La loading into the 250 °C-annealed SnO film was effective in reducing (increasing) the portion of Sn^{4+} (Sn^{2+}) up to the La loading of 1.9 atom %, while the variations in the small metallic Sn^0 portion were negligible as a function of La loading (Figure 5g and Table S3). The local incorporation of the n-type SnO_2 phase is known to diminish the free hole carrier density [so-called compensation effect] because the major carrier in n-type SnO_2 is an electron (not a hole). Therefore, the doping effect of La into the SnO film is beneficial in terms of electrical performance, which will be discussed later. The role of the chemically introduced La cation as a suppressor of Sn^{4+} was also confirmed in O 1s XP spectra shown in Figure 5h. The portion of O– Sn^{4+} for the 1.9 atom % La-loaded SnO film was reduced from 27.4% (for La-free control SnO) to 17.4%, which

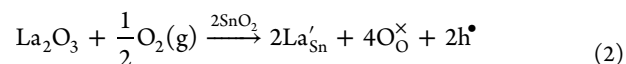
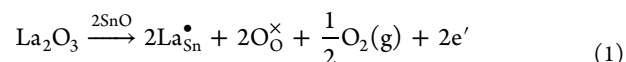
corroborates the postulation regarding the role of the La cation as the suppressor of Sn^{4+} (Figures 5h, 6d and Table S3). On the other hand, further loading of the La cation (3.1 atom %) in the SnO film rendered the portion of Sn^{2+} in the La-doped SnO film again to increase slightly. Simultaneously, the metallic Sn^0 portion for the 3.1 atom % La-loaded SnO film rapidly increased. These features may be related to emergence of its amorphous phase from the crystalline SnO phase as discussed in XRD data. These variations in the chemical states of Sn ions should be strongly correlated with the electrical properties of the resulting La-doped SnO films.

Feasibility of La-doped SnO films as a p-type semiconductor was assessed by Hall effect measurement. The control SnO film had a Hall mobility (μ_{Hall}) and an n_{h} value of $6.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $1.6 \times 10^{16} \text{ cm}^{-3}$, respectively, representing the typical p-type characteristics (Table 2). Interestingly, the μ_{Hall} value

Table 2. Hall Effect Measurements for the SnO Films Annealed at 250 °C with Different La Loading Concentrations

la loading in SnO film [atom %]	μ_{Hall} ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	N_{Hall} (cm^{-3})
0	6.4 ± 0.8	$1.6 (\pm 0.3) \times 10^{16}$
0.8	6.7 ± 0.8	$1.7 (\pm 0.7) \times 10^{16}$
1.9	8.1 ± 1.2	$4.5 (\pm 1.0) \times 10^{16}$
3.1		

slightly increased with increasing La loading: the 0.8 and 1.9 atom % La-loaded SnO films had μ_{Hall} values of $6.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $8.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, suggesting the promising feature of the La-doped SnO film in terms of carrier transport property (Table 2 and Figure S3). Simultaneously, the n_{h} value for the 1.9 atom % La-loaded SnO film increased from $1.6 \times 10^{16} \text{ cm}^{-3}$ (La-free SnO film) to $4.5 \times 10^{16} \text{ cm}^{-3}$ by more than 2-fold. It would be important to discuss why the La doping into the SnO film boosts the carrier mobility as well as hole carrier density. The substitutional doping of La^{3+} into the sublattices of Sn^{2+} and Sn^{4+} can be described by the following Kröger–Vink notations 1 and 2, respectively.



The first equation predicts that the increasing La_2O_3 fraction increases the electron density and thus diminishes the n_{h} value because the substitutional La atom acts as a donor ion due to the extra valence electron compared with Sn^{2+} . Obviously, the first scenario is not the case considering the La fraction-dependent n_{h} variations in La-loaded SnO films, suggesting that the La ion does not prefer to occupy the sublattice of Sn^{2+} . Indeed, according to the density functional theory (DFT) calculation result in Figure 7a, La substitutional defect at the Sn^{2+} site (La_{Sn}) is less stable than hole-generating defects like the Sn vacancy (V_{Sn}) and hydrogen-Sn vacancy defect complex ($\text{V}_{\text{Sn}}/\text{H}$). It is consistent with our observation that La_{Sn} does not compensate holes. The second scenario seems to be consistent with the experimental result because the La atom replacing the Sn^{4+} site (La_{Sn}) can produce the free hole carrier by eq 2. In DFT calculations, however, it is shown that the formation of La_{Sn} defects in the Sn^{4+} site is difficult due to its quite high formation energy as illustrated in Figure 7b.

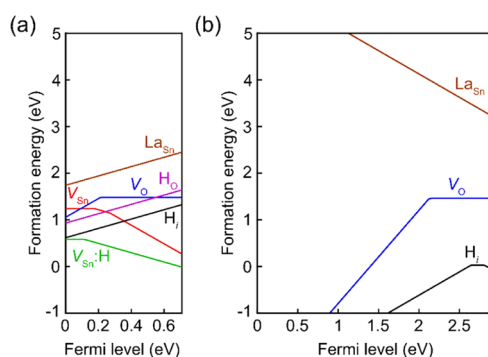


Figure 7. Defect formation energy diagram of intrinsic and hydrogen-related defects in (a) SnO and (b) SnO₂.

Therefore, the La substitutional doping in SnO₂ for the hole doping mechanism is not the case. As a plausible mechanism, we proposed that excess La can impede grain growth of SnO₂ by being located in boundaries. The grain growth of the thermodynamically favored SnO₂ phase under the given annealing condition can be kinetically hindered by the lattice distortion resulting from La.⁵⁰ The incorporated La is expected to exist in the grain boundary defects rather than the crystal lattices. The high-resolution scanning transmission electron microscopy (STEM) analysis for the undoped and 1.9 atom % La-loaded SnO films at $T_A = 250$ °C was conducted as shown in Figure 8. The undoped SnO film consists of rather random polycrystalline aggregates as aforementioned in the XRD analysis. The selective area diffraction patterns (SADPs) of SnO films were assigned to the mixture of crystalline SnO and SnO₂ phases. The volume fraction of the SnO₂ phase was roughly estimated to be ~28% on the basis of TEM observation. In contrast, the 1.9 atom % La-loaded SnO film exhibited a highly aligned microstructure of the SnO phase, which is consistent with its preferential orientation in XRD. Remarkably, the volume fraction of the SnO₂ phase in the La-loaded SnO film was significantly reduced to ~6%. This fact can be also confirmed by the weaker Bragg spot of SnO₂ compared with the strong Bragg spot of SnO in its SADPs. This result supports our postulation that the incorporated La acts as an inhibitor of SnO₂ grain growth, leading to the

enhancement in the hole carrier density of the resulting SnO film.

The adverse overoxidation of Sn²⁺ at the oxygen excess and high PDA temperature should be mitigated by the approaching of La loading, which widens the narrow p-type process margin of the SnO film (Figures S4 and S5). An alternative plausible explanation for the boosting of La-doping-induced n_h would be related to the reduction in the oxygen vacancy defect near the grain boundary of the SnO or SnO₂ phase. The Pauling electronegativity of La (~1.1) is smaller than those of Sn (1.8) and O (3.5), indicating that it can act as an effective oxygen binder such as Zr and Hf in a metal oxide semiconductor.⁵¹ Thus, it is quite reasonable to postulate that the incorporated La cation suppresses the formation of oxygen vacancy (V_O) defect in SnO substances due to its strong ionicity. Reduction in the V_O concentration will decrease the electron carrier density because the V_O is known to be an electron donor in the SnO material [$O_O^{\times} \rightarrow V_O^{\bullet\bullet} + 1/2 O_2(g) + 2e'$]. The net hole carrier density for the La-loaded SnO film increases as a result of the reduced V_O concentration, given that the concentration of the shallow acceptor center, tin vacancy (V_{Sn}), remains to be constant in the resulting film. This scenario also can explain our observation for the 1.9 atom % La-loaded SnO film with >2-fold enhanced n_h value. However, the Hall data could not be measured for the 3.1 atom % La-loaded SnO film because of the high electrical resistivity of the resulting film. It should be related with the phase change from the crystalline SnO phase to the completely amorphous phase. Generally, the amorphous phase film suffered from huge tail states above the VB edge, which captures the hole carriers in the solid film, and, thus, the insulating property rather than the semiconducting property will manifest itself. It is noted that the V_O concentration in the SnO system may be reduced by the hydrogen doping. Thus, the effect of forming gas annealing on the electrical properties of undoped and 1.9% La-doped SnO films was examined by Hall effect and the fabrication of field-effect transistors. The PDA at 250 °C for 1 h under the forming gas atmosphere allowed the given SnO films to exhibit the n-type character as summarized in Table S4. The consistent result can be also confirmed for the SnO TFTs with different La loadings of 0 and 1.9 atom % (Figure S6). These experimental results suggest that the intentional hydrogen doping into the SnO

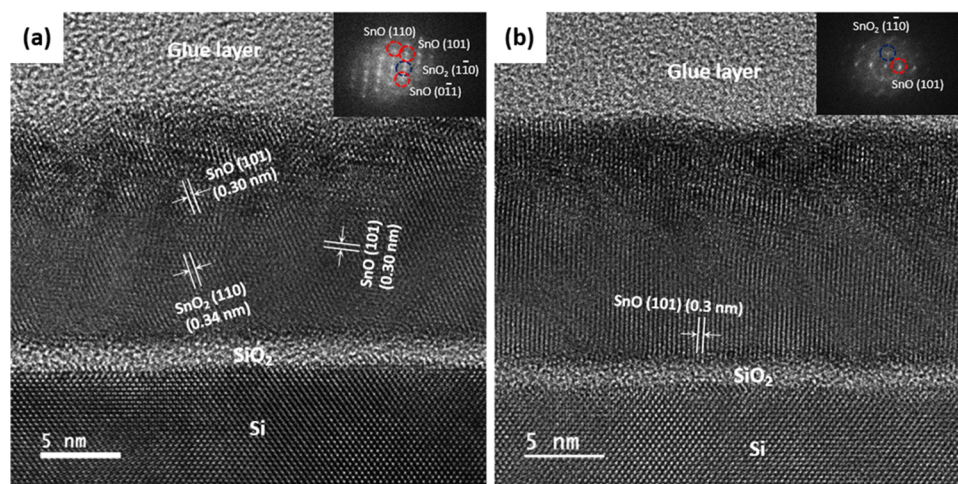


Figure 8. Cross-sectional high-resolution TEM images of the (a) undoped SnO and (b) La 1.9 atom %-loaded SnO samples. Fast Fourier transform (FFT) patterns of the selected area are inserted in the given TEM images, obtained from the bulk region of the SnO films.

system can cause the conversion from p-type to n-type due to its donor nature. Indeed, the interstitial hydrogen in the SnO and SnO₂ was predicted to be a donor according to the DFT result (Figure 7).

The role of incorporated La cations on the optical properties of the La-doped SnO films was investigated by fabricating La-doped SnO films on transparent quartz substrates. Figure 9a

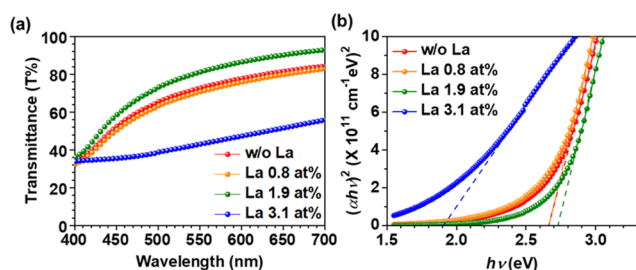


Figure 9. (a) Optical transmittance by UV–visible spectroscopy and (b) plot of $(\alpha h\nu)^2$ vs $h\nu$ of the SnO films annealed at 250 °C with different La loadings.

shows the optical transmittance of the La-doped SnO films with different La loadings by UV–visible spectroscopy. The transmittance values at the wavelengths of 500 and 650 nm for the 0.8 atom % La-loaded SnO film were approximately 63.4 and 79.8%, respectively, which is comparable to those for the La-free SnO film. An interesting finding was that the transmittance values at the wavelengths of 500 and 650 nm increased substantially to 73.2 and 90.2%, respectively, for the 1.9 atom % La-loaded SnO film. It hints that its optical band gap becomes wider with the effective incorporation of La cations. In contrast, the excessive La loading of 3.1 atom % caused the rapid reduction in the average transmittance: they were 38.9 and 51.6% for the wavelengths of 500 and 650 nm, respectively, suggesting that the electronic structure for the 3.1 atom % La-loaded SnO film can be modified considerably. To assess the optical properties for the La-loaded SnO films further, the optical band-gap (E_g^{opt}) values were extracted by extrapolating the best fit line in the plot of $(\alpha h\nu)^2$ versus $h\nu$ to the intercept (at $\alpha = 0$) for the La-loaded SnO films (Figure 9b). The E_g^{opt} values for the control SnO and 0.8 atom % La-loaded SnO films were similar—2.66 eV, which is comparable to the direct fundamental E_g^{opt} value of 2.7 eV for the SnO film reported in the literature.² When La loading into the SnO film was 1.9 atom %, the E_g^{opt} value for the 1.9 atom % La-loaded SnO film increased to 2.73 eV, which is consistent with its enhanced optical transmittance (also see Table 3). This blue shift can be supported by the fact that the E_g value (~ 5.5 eV) of La₂O₃ is considerably larger than that of SnO (in this work, 2.66 eV).^{36,52} Conversely, a significant reduction in E_g^{opt} (~ 1.91 eV) was observed for the 3.1 atom % La-loaded SnO film. The

Table 3. Optical Band Gap (E_g^{opt}) and Average Transmittance for the SnO Films Annealed at 250 °C with Different La Loadings^a

La loading in SnO film [atom %]	E_g^{opt} [eV]	average transmittance [%]
0	2.66	68.1
0.8	2.66	66.3
1.9	2.73	75.7
3.1	1.91	43.4

^aCalculated from Wavelengths Ranging from 400 to 700 nm.

origin of this abnormal behavior is not clear. The plausible rationale can be associated with its change of structural property from a tetragonal litharge crystalline structure to an amorphous phase (see XRD data). The electronic structure of crystalline SnO with an indirect band-gap nature means that the CB minima near the Γ point do not coincide with the VB maxima located in the M point in the reciprocal space of the Brillouin zone. The La-cation-induced amorphization of the SnO film may weaken the selection rule of phototransition, leading to the lowering of E_g^{opt} .⁵³

Figure 10 shows the representative transfer and output characteristics of the SnO TFTs with different La loadings.

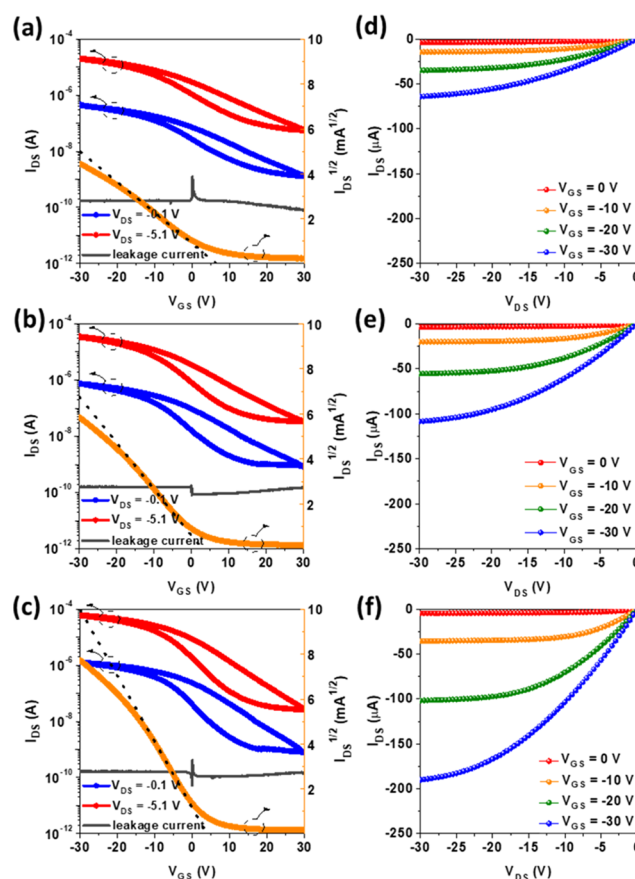


Figure 10. Transfer characteristics of the SnO TFTs with different La loadings of (a) 0 atom %, (b) 0.8 atom %, and (c) 1.9 atom %. The corresponding output characteristics of the annealed in 250 °C SnO TFTs with different La loadings of (d) 0 atom %, (e) 0.8 atom %, and (f) 1.9 atom %.

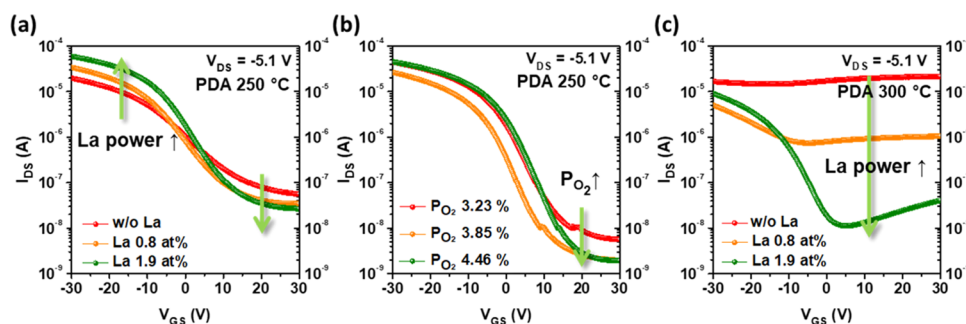
The saturation mobility (μ_{SAT}) was calculated by a maximum slope of a plot between $I_{\text{DS}}^{1/2}$ versus the gate voltage (V_{GS}) at $V_{\text{DS}} = -5.1$ V using the following equation

$$I_{\text{DS}} = \mu_{\text{SAT}} C_i \frac{W}{2L} (V_{\text{GS}} - V_{\text{TH}})^2 \quad (3)$$

where L is the channel length, W is the width, and C_i is the gate capacitance per unit area. The threshold voltage (V_{TH}) is extracted by the intercept of the extrapolated curve with a voltage axis. The subthreshold slope (S) is obtained by inverse of the maximum slope of the transfer curves in the subthreshold region ($|V_{\text{GS}}| < |V_{\text{TH}}|$) using the following equation

Table 4. Device Parameters Including μ_{SAT} , S , V_{TH} , $I_{\text{ON/OFF}}$ ratio, $N_{\text{T,max}}$ and $D_{\text{it,max}}$ for SnO TFTs with Different La Loadings and P_{O_2} , which Were Postannealed at 250 and 300 °C

channel information		μ_{SAT} (cm ² V ⁻¹ s ⁻¹)	S (V dec ⁻¹)	V_{TH} (V)	$I_{\text{ON/OFF}}$ ratio	$N_{\text{T,max}}$ (cm ⁻³ eV ⁻¹)	$D_{\text{it,max}}$ (cm ⁻² eV ⁻¹)
la loading (atom %)	P_{O_2} (%)						
SnO TFTs with Different La Loadings and P_{O_2} which Were Postannealed at 250 °C							
0	3.2	0.29 ± 0.07	11.9 ± 1.2	10.3 ± 4.1	5.4 (±0.2) × 10 ²	4.30 (±0.42) × 10 ²⁰	1.29 (±0.13) × 10 ¹⁵
0.8	3.2	0.91 ± 0.22	8.3 ± 0.5	9.5 ± 6.0	2.1 (±1.3) × 10 ³	3.00 (±0.19) × 10 ²⁰	8.99 (±0.55) × 10 ¹⁴
1.9	3.2	1.20 ± 0.21	6.9 ± 1.0	8.3 ± 4.4	7.3 (±5.7) × 10 ³	2.51 (±0.37) × 10 ²⁰	7.54 (±1.12) × 10 ¹⁴
1.9	3.6	1.05 ± 0.32	5.4 ± 1.6	7.1 ± 5.0	9.8 (±3.9) × 10 ³	1.97 (±0.59) × 10 ²⁰	5.91 (±1.78) × 10 ¹⁴
1.9	4.5	0.93 ± 0.21	5.4 ± 0.8	7.0 ± 0.4	1.1 (±0.9) × 10 ⁴	1.94 (±0.29) × 10 ²⁰	5.81 (±0.88) × 10 ¹⁴
SnO TFTs with Different La Loadings and P_{O_2} which Were Postannealed at 300 °C							
1.9	3.2	0.26 ± 0.01	6.5 ± 0.5	4.4 ± 0.2	8.0 (±1.9) × 10 ²	2.35 (±0.19) × 10 ²⁰	7.05 (±0.57) × 10 ¹⁴

**Figure 11.** Comparison of transfer characteristics of the SnO TFTs with different La loadings of 0 atom %, 0.8 atom %, and 1.9 atom % at P_{O_2} = 3.3% (a) annealed at 250 °C and (c) 300 °C, and (b) different P_{O_2} of 3.3, 3.9, and 4.5% at the La loading of 1.9 atom % annealed at 250 °C.

$$S = \left(\frac{\partial \log(I_{\text{DS}})}{\partial V_{\text{GS}}} \right)_{\text{max}}^{-1} \quad (4)$$

The fast bulk traps (N_{T}) and semiconductor–insulator interfacial traps (D_{it}) were calculated using the following equation⁵⁴

$$S = \frac{k_{\text{B}}T}{q} \ln 10 \left(1 + \frac{q(N_{\text{T}}t_{\text{ch}} + D_{\text{it}})}{C_{\text{i}}} \right) \quad (5)$$

where q is the electron charge, k_{B} is Boltzmann's constant, T is the absolute temperature, and t_{ch} is the channel layer thickness. $N_{\text{T,max}}$ and $D_{\text{it,max}}$ in the TFTs were calculated by setting one of the parameters to zero. Therefore, the $N_{\text{T,max}}$ and $D_{\text{it,max}}$ values must be considered the maximum trap density formed in a given system. $I_{\text{ON,MAX}}$ and $I_{\text{OFF,MIN}}$ values are extracted from transfer curves at $V_{\text{DS}} = -5.1$ V, corresponding to the maximum on-current and minimum off-current values, respectively. The $I_{\text{ON/OFF}}$ ratio is obtained by dividing the $I_{\text{ON,MAX}}$ current by the $I_{\text{OFF,MIN}}$ current. The carrier transport properties and current modulation capability of the devices were strongly dependent on the La loading in the SnO channel layer. The control SnO TFT annealed at 250 °C had the reasonable typical μ_{SAT} and $I_{\text{ON/OFF}}$ ratio of 0.29 cm² V⁻¹ s⁻¹ and 5.4 × 10², respectively (Figure 10a and Table 4). As expected from the Hall effect data, the enhancement in the μ_{SAT} value was observed for the TFTs with increasing La loading: they were 0.91 and 1.20 cm² V⁻¹ s⁻¹ for the devices with 0.8 and 1.9 atom % La loadings, respectively (Figure 10b,c and Table 4). Importantly, the $I_{\text{ON/OFF}}$ ratio also improved with increasing La loading in the SnO channel layer (also see Figure 11a). The $I_{\text{ON/OFF}}$ ratio for the devices with 0.8 and 1.9 atom % La loadings increased to 2.1 × 10³ and 7.3 × 10³,

respectively. The high I_{OFF} and, thus, low $I_{\text{ON/OFF}}$ ratio for the SnO TFTs remains a challenging issue for their practical application. It is attributed to their high trap density, which is concentrated near 0.2 eV above the VB edge, arising from the bulk defects and interfacial traps. In this study, the increasing $I_{\text{ON/OFF}}$ ratio with increasing La loading indicates that this adverse trap density could be reduced by La incorporation in the channel layer. Indeed, the S value for the devices with 0.8 and 1.9 atom % La loadings was reduced to 8.3 and 6.9 V/dec, respectively, compared with that (11.9 V/dec) for the control SnO device. The $N_{\text{T,max}}$ and $D_{\text{it,max}}$ values calculated from the S factor of each TFT are summarized in Table 4. It can be clearly seen that the $N_{\text{T,max}}$ value (2.51 × 10²⁰ cm⁻³ eV⁻¹) for the device with 1.9 atom % La loading was substantially smaller than that (4.30 × 10²⁰ cm⁻³ eV⁻¹) of the control La-free device. The beneficial effect of La loading as a suppressor of Sn⁴⁺ and adverse gap states can be further exploited by increasing P_{O_2} . In conventional SnO, the increasing P_{O_2} or annealing temperature accelerates the formation of Sn⁴⁺ via the well-known disproportionation chemical reaction. Conversely, the SnO system with 1.9 atom % La loading showed the opposite trend. When the P_{O_2} increased from 3.2 to 4.5% during cosputtering of the La-loaded SnO film, the Sn⁴⁺ fraction (~5.9%) in the channel layer was found to be smaller than that (15.3%) of the 1.9 atom % La-loaded SnO film prepared at $P_{\text{O}_2} = 3.2\%$ (Figure S7 and Table S5, Supporting Information). This result suggests that the incorporated La cation acts as an anticatalyst of the disproportionation reaction, which can be further confirmed by the fact that the fraction of metallic Sn⁰ in the 1.9 atom % La-loaded SnO film at $P_{\text{O}_2} = 4.5\%$ is negligible (also see Figure S7 and Table S5). Modulation capability characterized by the $I_{\text{ON/OFF}}$ ratio was further enhanced to 1.1 × 10⁴ for the device with the 1.9 atom

% La-loaded SnO film by increasing P_{O_2} from 3.2 to 4.5% (Figures 11b and S7), whereas the comparable μ_{SAT} ($\sim 0.93 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) was still available. Obviously, the significantly reduced I_{OFF} value was responsible for this improvement, which was corroborated by the smallest $N_{T,max}$ value of $1.94 \times 10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$. Therefore, improvement in terms of all important metrics including μ_{SAT} , S , V_{TH} , and $I_{ON/OFF}$ ratio without the trade-off relation can be achievable for the SnO TFTs with the appropriate incorporation of the La cation. Finally, it is noted that the La incorporation into the SnO channel layer widened the temperature process window for the stable p-channel behavior up to 300 °C (Figures S8 and 11c). The μ_{SAT} and $I_{ON/OFF}$ ratio values for the 1.9 atom % La-loaded SnO transistor annealed at 300 °C were $0.26 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 8.0×10^2 , respectively (see Figure S8c). Considering that the μ_{SAT} and $I_{ON/OFF}$ ratio values for the SnO transistors annealed at ≥ 300 °C in the literature were in the range of $0.1\text{--}1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $< 6.0 \times 10^2$, respectively (Figure S9), this result clearly demonstrated that the La-loaded SnO transistor exhibits good p-channel characteristics with better thermal immunity.

4. CONCLUSIONS

The p-type SnO thin films with different La loadings from 0 to 4.5 atom % were grown by a sputtering process adopting the metallic La and Sn targets. The preferential orientation of the annealed La-loaded SnO films was changed from (110) face to (101) face with increasing La loading up to 1.9 atom %, which was accompanied by a smooth morphology. One important finding was that the portions of O–Sn²⁺ and O–Sn⁴⁺ in the grown SnO film increased and decreased, respectively, with increasing La loading, leading to the enhancement of p-type semiconductor properties in terms of Hall mobility and hole carrier density. The fabricated SnO TFTs with 1.9 atom % La loading exhibited higher μ_{SAT} and an enhanced $I_{ON/OFF}$ ratio of $1.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 7.3×10^3 , compared with those ($0.29 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 5.4×10^2 , respectively) for the La-free SnO TFTs. From this result, the incorporated La cation in the SnO film is interpreted to act as a suppressor of the formation of Sn⁴⁺, which hints that the transition metal such as La with a strong ionicity can be an anticatalyst for the adverse disproportionation of an anticatalyst in the disproportionation reaction. However, the excessively La-loaded SnO film (La loading ≥ 3.1 atom %) lost the p-type semiconducting property: instead, insulating characteristics appeared, which can be attributed to the abrupt transition from the trigonal SnO to complete amorphous phase. The inevitable creation of huge tail states above the VB edge as a result of disordering will capture all hole carriers in the solid film, leading to the insulating property. The decoupling of boosting of carrier mobility and reducing the trap states in the p-type SnO film, which remains a challenging problem, can be alleviated by introduction of the La cation with low electronegativity. Therefore, the transition-metal-mediated engineering of p-type SnO semiconductor and related devices can be a useful guideline for the high-performance p-channel transistors.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.9b14462>.

XP spectra analysis of Sn 3d, Sn 4d, La 3d, and O 1s peaks; Hall effect data of 250 °C-annealed SnO films with different La loadings; transfer and output characteristics of SnO TFTs with different La loadings after the PDA at 250 °C for 1 h under the forming gas atmosphere; transfer and output characteristics of the 1.9 atom % La-loaded SnO TFTs annealed at 250 °C with different oxygen partial pressures; transfer characteristics of the SnO TFTs annealed at 300 °C with La loadings; comparison of the trade-off between the saturation mobility and $I_{ON/OFF}$ ratio for the SnO TFTs fabricated at the various annealing temperatures; references (PDF)

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Notes

The authors declare no competing financial interest.

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