



Combined effect of the large ionic radius and low electronegativity of lanthanum additive on solution-processed zinc–tin–oxide thin-film transistors

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ABSTRACT

Solution-processed lanthanum–zinc–tin–oxide thin films were fabricated with varying La content. A peak shift to small angles was observed in X-ray diffractometer spectra due to the expansion of the zinc–tin–oxide lattice originated from the larger ionic radius of La^{3+} , while oxygen vacancies first increased, and then decreased with increasing La molar ratio. These results indicate that La, which has both low electronegativity and a large ionic radius, plays the role of either a generator or a suppressor of oxygen vacancies. Therefore, when choosing an additive to control the electrical properties of an oxide semiconductor, the ionic radius of the added atom should be carefully considered along with its electronegativity.

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1. Introduction

In recent years, metal–oxide semiconductors have shown considerable promise as transparent semiconductors for the thin-film transistors (TFTs) used in flat-panel display applications, due to their high field-effect mobility, excellent uniformity, high optical transparency, and good stability of the ambience [1–3]. Among the various metal–oxide semiconductors studied thus far, Zn–Sn–O (ZTO) has been widely investigated due to the lower cost of Sn compared with In-based oxide semiconductors, such as In–Zn–O (IZO) and In–Ga–Zn–O (IGZO) [4–6]. There have been a number of studies on the effects of various additives to a ZTO thin film with the aim of improving the electrical properties of metal–oxide semiconductors, e.g., Al–Zn–Sn–O [7,8], Hf–Zn–Sn–O [9], Zr–Zn–Sn–O [10], and La–Zn–Sn–O [11]. These papers reported that an additive can control oxygen vacancies as carrier sources in metal–oxide semiconductors, but focus solely upon the high electronegativity difference between the additive and oxygen, compared with that of Sn and Zn, as the cause of this phenomenon. However, the ionic radius difference between an additive and the core materials of a metal–oxide semiconductor can also alter the oxygen vacancy content in the semiconductor, in addition to causing lattice distortion [12,13]. Moreover, there has been very little research on the simultaneous effects of both the electronegativity and ionic radius of an additive.

Accordingly, in this study, we investigate the effect of La additive on a solution-processed ZTO thin film in terms of the microstructural, optical, and electrical properties. La was chosen because it has lower

electronegativity (1.1) and a larger ionic radius (La^{3+} 0.117 nm) compared with Zn (1.65, Zn^{2+} 0.088 nm) and Sn (1.96, Sn^{4+} 0.083 nm).

2. Experimental details

A 0.25 M La–Zn–Sn–O (LZTO) solution was synthesized, using lanthanum chloride [LaCl_3], zinc chloride [ZnCl_2], and tin (II) chloride [SnCl_2] dissolved in 2-methoxyethanol solvent. The molar ratio of Zn:Sn was fixed at 1:5, and the molar ratio of La was varied from 0 to 1. The LZTO precursors were stirred at 70 °C for 1 h to make a homogeneous solution. The solution was then filtered with a 0.2- μm syringe filter and aged for more than 24 h. To fabricate LZTO TFTs with a bottom-gate and top-contact structure, a LZTO thin film with a thickness of 30 nm was spin-coated at 3000 rpm for 30 s on a SiO_2 layer with a thickness of 120 nm (as a gate dielectric), which was thermally grown on a heavily boron-doped Si wafer (as a gate electrode). The resulting films were pre-baked at 150 °C in air for 10 min to remove the solvent, and then annealed at 500 °C in air for 2 h. Aluminum source/drain electrodes (200 nm) were deposited on the LZTO active layer by sputtering, using a shadow mask with a channel width of 1000 μm and a length of 150 μm . The microstructural properties of the LZTO thin film were analyzed via X-ray diffraction (XRD) using $\text{Cu-K}\alpha$ radiation at 40 kV and 200 mA (Rigaku, Ultima III), and the optical properties were analyzed via ultraviolet–visible (UV–Vis) spectroscopy (JASCO V-650). X-ray photoelectron spectroscopy (XPS) (Thermo VG) was carried out to confirm the changes in the chemical bonding state using $\text{Al-K}\alpha$ line (1486.6 eV) at 12 kV and 3 mA with an energy resolution of 0.78 eV. The binding energy was referenced to the C1s line at 284.8 eV for calibration. The peak fit analysis was performed using XI SDP32 software, version 4.1. Current–

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voltage (I–V) measurements were performed using a HP 4156 (Hewlett Packard) semiconductor parameter analyzer in the dark at room temperature to characterize the electrical properties of the LZTO TFTs.

3. Results and discussion

Fig. 1 shows the XRD patterns of LZTO thin films with various La molar ratios. To isolate the effect of La incorporation, the LZTO thin film was repeatedly spin-coated until a thickness of 120 nm was reached. Broad diffraction peaks identified all the LZTO thin films as amorphous phase, and it was possible to index the peaks to the SnO₂ structure, as was corroborated with JCPDS reference card #41-1445. As the molar ratio of La increased, the XRD peaks became slightly weaker and broader. This result can be attributed to the lattice distortion originated from the difference ionic radius in each metal cations. As the inset of Fig. 1 shows, the (110) peak of LZTO 0.1:1:5 shifted to small angles (from 26.72° to 26.52°) compared with that of the ZTO thin film without La additive. This indicates that La incorporation caused the expansion of the ZTO lattice, due to the larger ionic radius of La³⁺ (0.117 nm) compared to Sn⁴⁺ (0.083 nm) and Zn²⁺ (0.088 nm) [12,14].

Optical transmittance spectra of the LZTO thin films are shown in Fig. 2 as a function of La content. All samples had a high average optical transmittance of over 97% in the visible light range (400–700 nm). A blue shift of the absorption edge was observed as the amount of La increased, implying enhancement of the optical band gap energy (E_g). Eqs. (1) and (2) were used to estimate E_g for the LZTO thin film [15]. The absorption coefficient α was calculated via Eq. (1),

$$T = A \exp(-\alpha d), \quad (1)$$

where T is the transmittance of the thin film, A is a constant, and d is the thickness of the thin film. It was possible to extract the direct optical band gap from the axis of the incident photon energy ($h\nu$) with the tangent to $(\alpha h\nu)^2$, using Eq. (2),

$$(\alpha h\nu)^2 = B(h\nu - E_g), \quad (2)$$

where h is Planck's constant, ν is the frequency of the incident light, and B is a constant. The inset of Fig. 2 shows plots of $(\alpha h\nu)^2$ versus the incident photon energy of the LZTO thin films for varying La content. E_g was blue-shifted from 3.47 eV to 3.66 eV as the La content increased. This was attributed not only to the larger optical band gap of

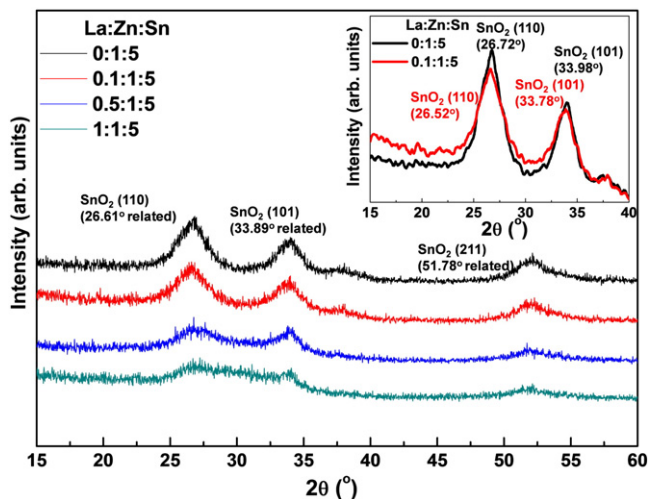


Fig. 1. XRD spectra of LZTO thin films with different La molar ratios, and (inset) magnified XRD patterns at La molar ratios of 0 and 0.1.

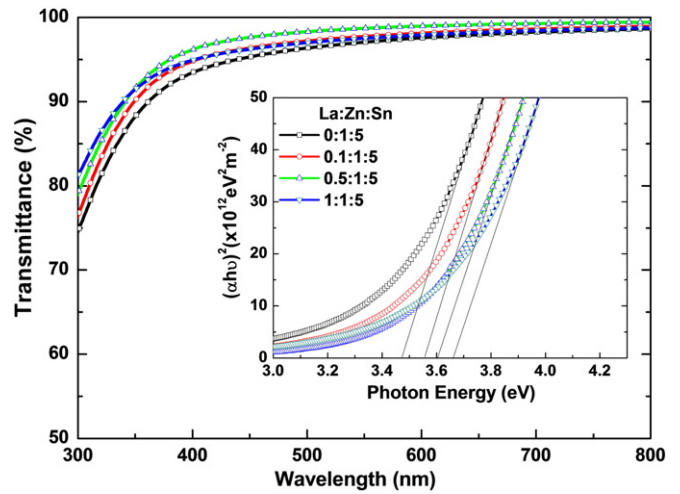


Fig. 2. Optical transmittance spectra of LZTO thin films with different La molar ratios, and (inset) plots of $(\alpha h\nu)^2$ vs. incident photon energy ($h\nu$).

La₂O₃ (5.5 eV) compared to ZTO (~3.6 eV) [16], but also to the extended localization in the conduction and valence bands of the ZTO thin film due to the amorphization of ZTO, indicated by the broadened XRD peaks of Fig. 1 [17,18].

The changes in the chemical bonding states of LZTO thin films with different La molar ratios were investigated by XPS. Fig. 3(a) shows the XPS peaks of La 3d_{5/2} with varying La molar ratios. As the La molar ratio increased, the La 3d_{5/2} peak was centered at 834.7 eV in accordance with the value of the La–O bond in La₂O₃ [19], indicating that the La atoms added to the ZTO thin film were completely oxidized and formed La₂O₃. The XPS peak of oxygen O 1s was analyzed to identify the changes in oxygen vacancies as carrier sources in a metal–oxide semiconductor [1,20]. Fig. 3(b) shows the O 1s XPS spectra as indicators of La content. The O 1s peak can be dissociated from the three Gaussian curves centered at approximately 530.3 eV (O_I), 531.7 eV (O_{II}), and 532.6 eV (O_{III}). The O_I peak at low binding energy represents the oxidation state of O²⁻ ions surrounded by metal cations. The O_{II} peak at middle-binding energy represents O²⁻ ions related to oxygen deficiency in the LZTO thin film. The O_{III} peak at high-binding energy is attributed to loosely-bound oxygen on the surface of the LZTO thin film, due to specific species (e.g., adsorbed H₂O or O₂, –CO₃) [10]. To examine the relative quantity of oxygen vacancies in the thin film, the peak area ratio (O_{II}/O_I) of the O_{II} peak area to O_I peak area was calculated as a function of the La molar ratio. Previous papers have reported that O_{II}/O_I decreased as the amount of an additive with low electronegativity was increased, due to the increasingly strong oxygen attraction compared with that of the core materials (which had relatively high electronegativity) [9,10,21]. Thus we expected that O_{II}/O_I for the LZTO thin film would decrease with increasing La content, due to the lower electronegativity of La (1.1) in comparison with Sn (1.96), and Zn (1.65). However, O_{II}/O_I was larger for LZTO 0.1:1:5 than for ZTO without La additive (from 11.6% to 14.1%). In view of the XRD peak shifts to small angles shown in the inset of Fig. 1, it could be explained that the expansion of the ZTO lattice by the large ionic radius of La³⁺ caused more dominantly the escape of oxygen atoms from the ZTO lattice than the reduction of oxygen vacancies by low electronegativity [12,13]. On the other hand, for LZTO 0.5:1:5 and 1:1:5, O_{II}/O_I decreased to 7.9% and 5.4%, respectively. This decreased O_{II}/O_I can be ascribed to the fragment of La oxide that made the formation of oxygen vacancies more difficult, due to the larger electronegativity difference between La and O. Thus, La (which has both low electronegativity and a large ionic radius compared with Sn and Zn) can play the role of either an oxygen vacancy generator via lattice expansion in case of La incorporation, or an oxygen vacancy suppressor via strong

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