Full Length Article

Low-temperature growth and electronic structures of ambipolar Yb-doped zinc tin oxide transparent thin films

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ABSTRACT

The compositional dependence of the crystal structure, optical transmittance, and surface electric properties of the zinc tin oxide (Zn-Sn-O, shortened ZTO) thin films were investigated. ZTO thin films with different compositional ratios were fabricated on glass and p-silicon wafers using radio frequency magnetron sputtering. The binding energy of amorphous ZTO thin films was examined by a X-ray photoelectron spectroscopy. The optical transmittance over 70% in the visible region for all the ZTO films was observed. The optical band gap of the ZTO films was changed as a result of the competition between the Burstein-Moss effect and renormalization. An electron concentration in the films and surface work function distribution were measured by a Hall measurement and Kelvin probe force microscopy, respectively. The mobility of the n- and p-type ZTO thin films have more than 130 cm²/V s and 15 cm²/V s, respectively. We finally constructed the band structure which contains band gap, work function, and band edges such as valence band maximum and conduction band minimum of ZTO thin films. The present study results suggest that the ZTO thin film is competitive compared with the indium tin oxide, which is a representative material of the transparent conducting oxides, regarding optoelectronic devices applications.

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1. Introduction

The band gap of the transparent conducting oxide (TCO) films is a wider than ~3 eV and can be used for the transmission of the visible light and low resistivity from doped charge carriers. Doping with impurities, mainly rare-earth elements, into the transparent oxide attributes both of the high conductivity and the stability at high temperature. TCOs have been used in many applications including the transparent electrode in flat-panel optoelectronic devices such as solar cells, liquid-crystal displays, and light-emitting diodes [1–3]. The focus of the majority of the TCO research has been Sn doped In₂O₃ (ITO), and it has been common to apply transparent electrodes. However, the finding of an alternative material has been necessary due to the high cost and toxic nature of the indium in ITO. Here, an amorphous multicomponent oxide Zn-Sn-O (ZTO) system has attracted much attention as a new alternative to ITO materials, since it is inexpensive compared to TCO materials including rare earth metals and do not contain

toxic elements [4,5]. Furthermore, ZTO films can have smooth and hard surface morphology. Hence, they are suitable for barrier layers for electronic devices or optical products because they exhibit good thermal and chemical stabilities [6]. ZTO films show a different crystal structure with respect to the ratio of Zn and Sn. Crystalline ZnSnO₃ and Zn₂SnO₄ have the ilmenite and the inverse spinel structure, respectively [7,8]. ZTO films in elemental composition can have an amorphous structure which can be fabricated at low substrate temperature, even room temperature [9]. Inherent advantages exist regarding the amorphous TCO films for applications such as organic light emitting diodes and thin film transistor-liquid crystal displays. Zinc oxide (ZnO) and tin oxide (SnO₂)-based TCO films are easily doped as n-type semiconductors, but it is also necessary to obtain p-type TCOs, which are difficult to grow because of the self-compensating native donor defects such as the oxygen vacancies and the interstitials in the TCO structure [10,11]. In principle, the p-type conductivity can be realized by doping with the group-IV element in the plane of the Zn site in the ZTO system [12,13]. In the p-type TCO film, compositional control is one of the most important issues, because a specific physical condition has been required for specialized applications. In this

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study, the effect of the Sn concentration on the electrical and optical properties of amorphous ZTO films is reported. The ZTO films with the different Sn/(Zn + Sn) compositional ratios were used to investigate the tunable physical properties for optoelectronic applications.

2. Method

The ZTO thin films were deposited onto glass and p-silicon substrates at 300 °C with zinc and tin metallic targets in an Orion 3 RF (Radio-Frequency) reactive magnetron sputtering system from AJA International Co. A Zn target covered with small discs of pure Yb was used. Argon and oxygen gas were introduced in the sputtering chamber as reactive gases to deposit the Yb:ZnSnO_x films. For all depositions, the target-substrate distance was kept at about 12 cm; the working pressure was set at 3.4 mTorr. The substrate holder was rotating in order to insure an improved homogeneity of the layers. The base pressure is 1×10^{-8} mbar, and the argon (Ar) and oxygen (O₂) gases were introduced into the sputtering chamber with constant flow rates of 8 sccm for the Ar and 3 sccm for the O₂ using a standard mass flow controller. The RF power of the Sn varied from 10 to 70 W with a constant Zn:Yb power of 70 W. The film thickness and the cationic composition of the ZTO thin films, which are shown in Table 1, were determined using the field-emission scanning electron microscopy (FE-SEM) (S-4200, Hitachi) device equipped with an energy dispersion spectroscopy (EDS) functionality. The crystallographic structure of the ZTO thin film was determined using typical θ -2 θ scans and grazing incidence X-ray diffraction (XRD) experiments at room temperature using the Rigaku DMAX-2500 device with Cu-K α radiation (0.154 nm) over the range of 10–90°. The surface morphology and the local electrical properties of the ZTO films were examined using the Kelvin probe force microscopy (KPFM) (n-Tracer, Nanofocus) using Pt/Ir-coated Si atomic force microscopy (AFM) tip with a resonant frequency of 71–72 kHz. The WSxM software provided support in the KPFM analysis.

The carrier concentration was obtained from the Hall effect measurement (model HMS-5300, Ecopia) using the Van der Pauw method with a constant magnetic field of 0.5 Tesla at room temperature. The optical transmittance was measured with a Lambda 950 Perkin-Elmer UV–visible-NIR (UV–Vis-NIR) spectrophotometer in the wavelength range of 250–1500 nm [14]. The measurements using the X-ray photoelectron spectroscopy (XPS) (AXIS His, Kratos) were conducted under a base pressure below 10^{-8} Torr, with a monochromatized Al K α radiation ($h\nu = 1486$ eV) and at a constant dwelling time of 100 ms and a flood gun was operated at a 1 eV energy and an anode current of 0.1 mA. All XPS peaks were calibrated using the C 1s binding energy of 284.6 eV as a reference. The elemental composition was determined by calculating the relative XPS peak intensities at the specific binding energies of the Zn 2p and Sn 3d states.

3. Results and discussion

The θ -2 θ XRD patterns versus the Sn contents in the ZTO films that were deposited on the Si (100) substrate are shown in Fig. 1(a). Except for the Sn10 sample, the XRD profiles of the ZTO films do not show a crystalline structure. In the case of the Sn10 film, the XRD peaks at $2\theta = 33.9^\circ$ and 71.3° can be attributed to the (002) and (004) reflections of ZnO (001) structure. The grazing incident XRD was also measured to confirm the amorphous phase of the ZTO films, because the asymmetric geometry of the grazing incident XRD measurement could exclude the substrate signal, while the geometry of the θ -2 θ XRD measurement is symmetric geometry and was used to determine the normal plane crystalline structure. The ZnO phase in the Sn10 film was also detected through the use of a grazing incident XRD pattern, while a phase is not present in the Sn30 film, as shown in Fig. 1(b). The amorphous phase of the ZTO thin films is attributed to the high Sn concentration. The report indicates that the Sn-doped ZnO thin films were decrystallized with the increasing of the Sn concentration from 0 to 5 at.% [15]. The proposed ZTO thin films, except Sn10, contain concentrations that are more than 15 at.% which is a relatively high status compared with the previous work.

The XPS analysis was performed on the ZTO thin films to determine the variations of the chemical states of the Zn and the Sn. Fig. 2 shows the Zn 2p and Sn 3d XPS spectra of the amorphous ZTO thin films with different Sn concentrations. The XPS spectra were obtained after the pre-cleaning of the sample surface to prevent the contamination of the films. The C 1s with a binding energy of 284.6 eV were taken as a reference to calibrate the binding energies [16]. In Fig. 2(a), the XPS peaks that are evident at around 1021.4 eV and 1044.5 eV and correspond to the binding energies of the Zn 2p_{3/2} and Zn 2p_{1/2} levels, respectively, are consistent with the Zn²⁺ ion binding in the ZTO films [17,18]. It is notable that no significant XPS signals were observed for Yb binding states in the whole measurement range. Influence of Yb on physical properties of ZTO films is negligible, if any. The intensities of the XPS peaks of Zn 2p_{3/2} and Zn 2p_{1/2} were reduced with the increase of Sn concentration. Furthermore, the Sn 3d_{5/2} and Sn 3d_{3/2} peaks in Fig. 2(b) are located at 485.4 eV and 497.1 eV, respectively, which can be attributed to the Sn⁴⁺ ions in the ZTO film that resulted from the SnO₂ phase [19]. As expected, the trends for the XPS peaks of Sn appear contrary to the Zn's case, the intensity of the XPS peaks of Sn 3d_{5/2} and 3d_{3/2} increased with the increase of Sn concentration. In addition, XPS peaks of O 1s were observed at 530–533 eV and could be divided into two different peaks. One peak observed at 531 eV corresponds to the binding energy of photoelectrons coming from O with Zn²⁺ and Sn⁴⁺ [20,21]. The binding energies of photoelectrons from O-Zn²⁺ and O-Sn⁴⁺ are not distinguishable regardless of crystalline or amorphous ZTO films [22]. The other peak observed at 532.5 eV is attributed to chemisorbed oxygen at grain boundaries or loosely bound oxygen at the surface of the films [20,21].

Table 1

Thickness and composition ratios of the ZTO thin films, deposited by RF magnetron sputtering system, were measured using cross-sectional SEM and EDS. The compositional ratios of the right side of the table has been defined as the Sn contents over the total cation contents.

Sample label	Sn power [W]	Thickness [nm]	Compositional ratio (Zn:Sn:O:Yb)	Sn/(Sn + Zn + Yb) [at.%]
Sn10	10	57.3	1.00:0.00:4.17:0.10	0
Sn20	20	65.6	1.00:0.24:6.40:0.14	17.4
Sn30	30	95.8	1.00:0.56:6.95:0.13	33.1
Sn50	50	81.3	1.00:2.20:15.89:0.35	62.0
Sn60	60	72.9	1.00:2.55:21.14:0.45	63.8
Sn70	70	88.5	1.00:4.79:32.20:0.56	75.4

Fig. 1. (a) The θ - 2θ XRD patterns of the ZTO/Si(100) films with different Sn contents. (b) Grazing incidence XRD patterns of the Sn10 and the Sn30 where the incidence angle is 0.5° .

The dependence of the Sn concentration on the work functions (ϕ) of the ZTO thin films were measured using KPFM. KPFM is a non-contact electrical force microscopy that uses

AFM, and it is used to measure the two-dimensional image of the contact potential difference (V_{CPD}) between a sample and the conductive AFM tip with a resolution in the nanometer range [23]. Fig. 3(b) shows the V_{CPD} maps of the ZTO films with different Sn concentration. The V_{CPD} images were measured with a constant height after the scanning surface topography that is shown in Fig. 3(a). All of the ZTO films show an even potential distribution without any domain in the KPFM images, and their surfaces are flat with a root mean square (RMS) roughness that is less than 1.5 nm. For computing the work functions from the V_{CPD} values, the V_{CPD} distributions depending on the Sn concentration in the ZTO film are shown in Fig. 3(c). The work functions of the ZTO films could be calculated using the following equation because the V_{CPD} is equal to the work function difference between the AFM tip and the sample:

$$\phi_{sample} = -eV_{CPD,HOPG} + \phi_{HOPG} + eV_{CPD,sample} \quad (1)$$

where $V_{CPD,HOPG}$ and $V_{CPD,sample}$ represent the potential differences regarding the AFM tip potential, and the highly oriented pyrolytic graphite (HOPG) work function (4.6 eV) was used as a reference value. In Fig. 3(d), the work function was reduced with the increasing of the Sn concentration in the ZTO films.

The Hall measurement of the ZTO thin films was performed under a constant magnetic field using a 0.5 Tesla. The Hall coefficient (R_H) and the corresponding carrier concentrations (n), which could be obtained from the n or $p = 1/eR_H$, a dependent on the Sn concentration, as shown in Fig. 4. For the statistical analysis, the experiment was repeated over 50 times for each sample. For the Sn10 sample, the Hall coefficient was not obtained because of a high resistivity. The ZTO carrier type was changed from the n-type to the p-type at the critical point between the 33.1% and 62% Sn concentrations; moreover, the carrier concentrations for all of the ZTO films were increased with the increasing of the Sn concentration. The highest carrier concentration in the ZTO film is $4.73 \times 10^{19} \text{ cm}^{-3}$, where the Sn at.% is 33.1. Such behavior can be explained by a consideration of the element that is dominant in the ZTO film using the following chemical formula with the Kroger-Vink notation [24];

Below the critical point, the ZnO concentration is higher than the SnO_2 concentration in the ZTO film, namely $x > y$ in Eq. (2).

Fig. 2. XPS spectra in ZTO thin films for the following levels: (a) Zn 2p, (b) O 1s, and (c) Sn 3d.

Fig. 3. (a) Topographic images and (b) corresponding surface potential images of the ZTO thin films. (c) V_{CPD} distribution of the ZTO thin films. (d) Work function depending on the Sn concentration that was calibrated from the V_{CPD} .

The electrons that were generated from the substitution of the Sn at the Zn sites formed the major carrier. The substitution occurred easily since the ionic radii of the Zn and Sn atoms are similar to each other, as $r(\text{Sn}^{4+}) = 0.69 \text{ \AA}$ and $r(\text{Zn}^{2+}) = 0.74 \text{ \AA}$ [25,26]. On the contrary, above the critical point, the ZnO concentration is lower than the SnO_2 concentration, namely $x < y$, and as a consequence, free holes formed the major carrier in the ZTO film. It is notable that the n-type carrier concentration is higher than the p-type carrier concentration due to the free electrons that were generated from the oxygen vacancies within the whole Sn concentration range. In addition, the band edge values such as the conduction band minimum (CBM, E_c) and the valence band maximum (VBM, E_v) could be estimated using the carrier concentration that was obtained from the Hall measurement. The semiconductor carrier concentration under the thermal equilibrium can be expressed as follows:

$$n = N_c \exp \left[-\frac{(E_c - E_F)}{k_B T} \right] \text{ and } p = N_v \exp \left[\frac{(E_v - E_F)}{k_B T} \right] \quad (3)$$

where N_c and N_v are the intrinsic values that are described as $N_c \sim N_v = 2 \left(\frac{2\pi m_e k_B T}{h^2} \right)^{3/2}$. The CBM or the VBM of the ZTO thin films with an average carrier concentration, which is based on a Fermi level that is equal to 0 eV is shown in Table 2. With the increasing of the carrier concentration, the ZTO films mobility, which is shown in Fig. 4(b) and was obtained from the

division of the Hall coefficient by the resistivity, decreased along with the increasing of the Sn concentration. The electrical conductivity σ of the ZTO thin films depends on the carrier concentration n and on their mobility μ which could be simultaneously measured. The relationship between two parameters is described as $\sigma = n e \mu$ where $\mu = e \tau / m^*$. e is the electron charge, τ is the mean time between collisions, and m^* is the effective electron mass. The mobilities of the n- and p-type ZTO thin films have more than $130 \text{ cm}^2/\text{Vs}$ and $15 \text{ cm}^2/\text{Vs}$, respectively. The mobility of the n-type ZTO film has a similar value with ITO, whereas the p-type ZTO film has a lower value. The conductivity of the ZTO films is affected either by oxygen vacancies or by Yb dopants. However, since the Yb content ratio is constant over all the ZTO films, the variation in carrier concentration and mobility with the increase of the Sn content, shown in Fig. 4, is mostly due to the composition ratios of Sn and Zn. The relationship between the mobility and the carrier concentration is attributed to either the ionized impurity scattering or grain boundary scattering [27]. The effect of grain boundary scattering is negligible because the ZTO films have no grain boundary as shown in surface morphologies. Therefore, the mobility of the amorphous ZTO thin film with the low-temperature growth is mainly dominated by the ionized impurity scattering from Yb^{3+} or Sn^{4+} .

Fig. 5(a) shows the optical transmission (T) and reflection (R) spectra for the ZTO films consisting of different Sn concentrations

Fig. 4. (a) Distributions of the Hall coefficients and (b) carrier concentrations and mobilities of the ZTO thin films.

Table 2

The average carrier concentration (n or p) and the CBM or the VBM of the ZTO thin films with different Sn concentrations based on a Fermi level that is equal to 0 eV.

Sn conc. [at.%]	Carrier concentration [10 ¹⁹ cm ⁻³]	Band edge [eV]
0.0	N/A	N/A
17.4	n = 2.19	E _c = +0.35
33.1	n = 4.73	E _c = +0.33
62.0	p = 1.41	E _v = -0.36
63.8	p = 1.86	E _v = -0.35
75.4	p = 2.96	E _v = -0.34

in the wavelength range from 250 to 1500 nm using UV–Vis–NIR spectroscopy. The high transparency for all of the ZTO films were observed over ~70% in the UV–Vis light range. The absorption coefficient (α) was calculated from T and R by using $\alpha = \frac{1}{d} \ln \frac{1-R}{T}$, and the optical band gap (E_g) was determined by using the Tauc relation $(\alpha E)^x = C(h\nu - E_g)$, where h and ν are the Planck constant and the photon frequency, respectively. Although non-direct optical transitions are allowed and the exponent x is 0.5 for the most amorphous semiconductors [28], the direct band gap model provides a sound description of an optical absorption band edge with $x = 2$ [29]. Thus, $(\alpha E)^2$ is plotted versus the photon energy in Fig. 5 (b) for the ZTO films with different Sn concentrations, in which the x-intercept with the linear fitting yields the optical band gap [30]. Fig. 5(c) shows the variation of the optical band gap with the increasing of the Sn concentration, and this is attributed to the interplay between the Burstein–Moss effect and the renormalization effect [31–33]. The increment of the optical band gap is attributed to the Burstein–Moss effects that results from the increase of the carrier concentration, while the optical band gap was renormalized by the Coulomb repulsion between the added holes in the valence band. A few studies reported that influence of RF

Fig. 5. (a) Transmittance spectra for the ZTO thin films with different Sn concentrations. (b) Extrapolation of the linear part of the $(\alpha E)^2$ against the energy E for the ZTO thin films. (c) Variations of the band gap with the Sn concentration in the ZTO films.

power on bandgap is substantial to make a change of bandgap by 0.05 eV per 150 W RF power during growth of ZnO films [34]. Yet, the variation of Sn power in this work is relatively smaller than the previous work.

To extend the previously mentioned results of this section, the CBM, VBM, and vacuum level are shown in Fig. 6 as function of the Sn concentration in ZTO films. The Fermi level has been set to 0 eV, and therefore the vacuum level is equal to the work function that was obtained using KPFM. The CBM and VBM were calculated with the carrier concentration and band gap that obtained using the Hall measurement and UV–Vis spectroscopy, respectively.

Fig. 6. Variations of the E_c , E_v , and E_{vac} with the Sn contents in ZTO films.

4. Conclusion

The compositional dependence of ZTO thin films on the optical and electrical properties was investigated in this work. The ZTO thin films were prepared using RF magnetron sputtering at different Sn power levels on glass and p-silicon substrates at a 300 °C substrate temperature. The amorphous phase in the ZTO thin films was confirmed using symmetric and asymmetric X-ray diffraction θ -2 θ scans. The change of the carrier type from the n-type to the p-type with the increasing of the Sn concentration was observed through a measurement of the Hall effect because the Sn^{4+} ions contributed to the generation of the free hole carriers in the ZTO film. The work functions of the ZTO films were measured using KPFM, and they were decreased with increasing of the Sn concentration. The optical transmittance over 70% in the visible region for all of the ZTO films was observed using the UV–Vis–NIR spectrometer. The optical band gaps of the ZTO films were changed owing to the competition between the Burstein-Moss effect and the renormalization. The Sn dependence of the binding energy was examined according to the measurements of the Zn 2p and Sn 3d XPS spectra. Finally, the band structure that contains the optical band gap, work function, and band edges such as the VBM and the CBM of ZTO thin films was constructed. The results of the present study suggest that the ZTO thin film is competitive compared with indium tin oxide, a representative material of transparent conducting oxides, in terms of optoelectronic devices applications.

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