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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 $cm^2/V\,s$ and 15 $cm^2/V\,s$, 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.

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 In_2O_3 (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 $ZnSnO_3$ and Zn_2SnO_4 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 (SnO_2)-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 (O_2) gases were introduced into the sputtering chamber with constant flow rates of 8 sccm for the Ar and 3 sccm for the O_2 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-2θ 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-2θ 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 2θ = 33.9° and 71.3° can be attributed to the (002) and (004) reflections of ZnO (00l) 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-2θ 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 Zn^{2+} 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 Sn^{4+} ions in the ZTO film that resulted from the SnO_2 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 Zn^{2+} and Sn^{4+} [20,21]. The binding energies of photoelectrons from O-Zn^{2+} and O-Sn^{4+} 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