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Rapid Communication

Effects of substrate temperature on properties of ITO–ZnO composition spread films fabricated by combinatorial RF magnetron sputtering

Gi-Seok Heo, In-Gi Gim, Jong-Woon Park, Kwang-Young Kim, Tae-Won Kim *

Nanoelectronics Team, Honam Technology Service Division, Korea Institute of Industrial Technology, Gwangju 500-480, Republic of Korea

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ABSTRACT

We have fabricated ITO–ZnO composition spread films to investigate the effects of substrate temperature on their electrical and optical properties by using combinatorial RF magnetron sputtering. It turned out by X-ray measurement that the film with zinc contents above 16.0 at% [Zn/(In+Zn+Sn)] showed amorphous phase regardless of substrate temperature. The amorphous ITO–ZnO film had lower resistivity than polycrystalline films. When the films were deposited at 250 °C, the minimum resistivity of $3.0\times10^{-4}\,\Omega\,\text{cm}$ was obtained with the zinc contents of 16.0 at%. The indium content could be reduced as high as ~30 at% compared to that of ITO for the films having similar resistivity ($\sim10^{-4}\,\Omega\,\text{cm}$). However, a drastic increase of resistivity was observed for the ITO–ZnO films deposited at 350 °C, having zinc contents below 15.2 at%.

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1. Introduction

Transparent conducting oxides (TCOs) have been widely used for optoelectronic devices like OLED, LED, solar cell, flexible display and so on due to their low resistivity and high transmittance characteristics [1]. Tin-doped In_2O_3 (ITO, tin 10 wt%) is the most popular material among the TCO materials, because of its excellent optoelectronic properties, i.e. resistivity as low as $1\times10^{-4}\,\Omega\,\text{cm}$ and transmittance as high as 85% in the visible wavelength range [2]. Though it shows the excellent optoelectronic properties, its expensive cost, toxicity, and instability in high temperature are drawbacks to the application of various optoelectronic devices. For that reason, there have been many attempts to substitute ITO by alternative materials like doped-ZnO or to reduce indium content of ITO [3–7]. Recently, Minami et al. [8] and Saji et al. [9] reported that Zn doped-ITO films showed good electrical properties comparable to ITO films. They demonstrated that indium content in ITO could be reduced by introduction of ZnO. However, no systematic study has been reported concerning the thermal stability of the Zn doped ITO films.

In this study, we have investigated the effects of substrate temperature on ITO–ZnO composition spread films. The published results for ITO–ZnO are mostly focused on specific single doping concentration [10,11]. However, in this work, we report on a combinatorial investigation of ZnO as a dopant material in ITO films. The work presented here is the first time a combinatorial study has been performed on the dependence of the opto-electronic properties of ITO–ZnO as functions of substrate temperature and concentration.

2. Experimental

2.1. Synthesis

ITO–ZnO composition spread films were fabricated on glass substrate (Corning 1737) by combinatorial RF magnetron sputtering system. The sputtering system consists of a vacuum chamber (ULVAC MB07-4501) with four sputtering guns, which are located on either side of the substrate center. It is shown schematically in Fig. 1. The sputter guns are located to obtain a thickness gradient in the deposited films and therefore produce a compositionally graded film when co-sputtered from both guns at the same time. In order to synthesize ITO–ZnO composition spread films, we employed ITO [Sn (10 wt%) doped In_2O_3, 99.99%, ∅ 4 in] target, ZnO [99.99%, ∅ 4 in] target, and shadow mask. The composition ratio between ITO and ZnO could be changed by controlling the RF power applied to each target. Ar gas (99.999%) was used as a process gas, and the process pressure was 0.14 Pa. The distance from target to substrate (T_S) was maintained at 150 mm. RF power was fixed to be 200 W for each target, and sputtering time was 30 min. To investigate the effects of substrate temperature, we have deposited the ITO–ZnO thin film with changing substrate temperature from room temperature to 350 °C.

* Corresponding author. Fax: +82 62 600 6509.
E-mail address: twkim90@kitech.re.kr (T.-W. Kim).

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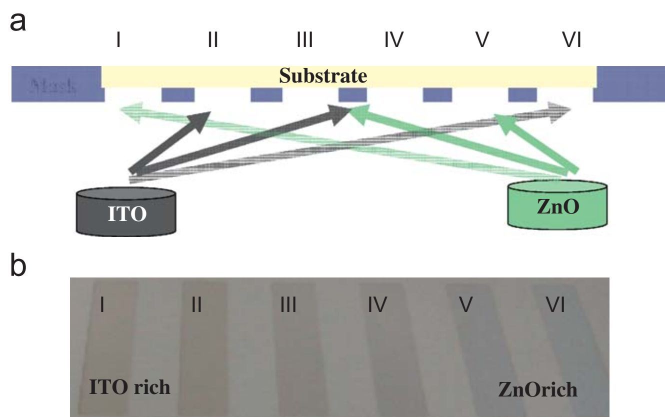

Fig. 1. Schematic overview of combinatorial deposition process.

Table 1
The zinc contents of the ITO–ZnO thin films with various substrate temperatures fabricated by combinatorial RF magnetron sputtering [Zn content, Zn/(Zn+In+Sn) at%].

Substrate temperature (°C)	Sample ID					
	I	II	III	IV	V	VI
RT	14.3	15.3	20.3	25.7	32.7	39.1
150	14.1	16.4	17.7	19.2	24.6	33.7
250	12.2	13.8	14.3	16.0	21.1	25.6
350	14.0	14.7	15.2	15.6	15.8	23.6

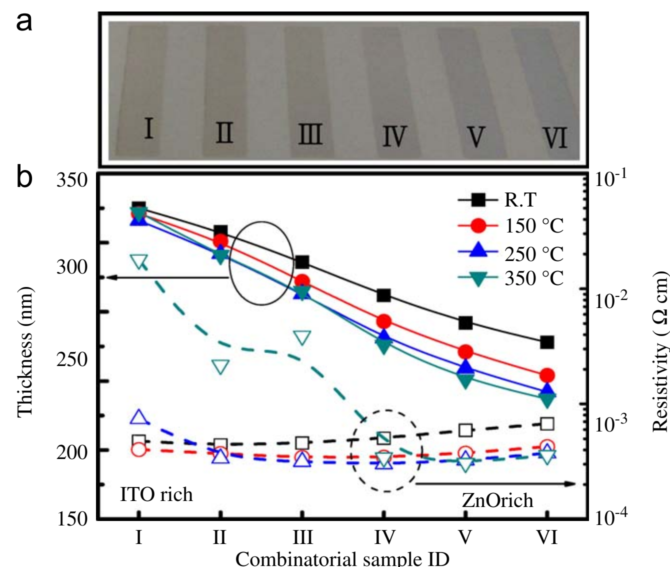

Fig. 2. The photograph of the ITO–ZnO composition spread film (a) and thickness and resistivity as a function of substrate temperature at each sample position (b).

2.2. Characterization

The thickness was determined by an optical thickness monitoring system (K-Mac ST 5000). Sheet resistance was measured using a conventional 4-point probe system. Resistivity, carrier concentration, and mobility were measured using the Van der Pauw method [LakeShore Cryotronics]. Transmittance was examined by a UV–vis–NIR spectrophotometer [Varian Cary 5000]. The film structure was checked by X-ray diffraction system (Panalytical X'pert MPD). The microstructures and compositional analysis of the films were performed using a field emission SEM/EDS [JEOL JSM-7000F].

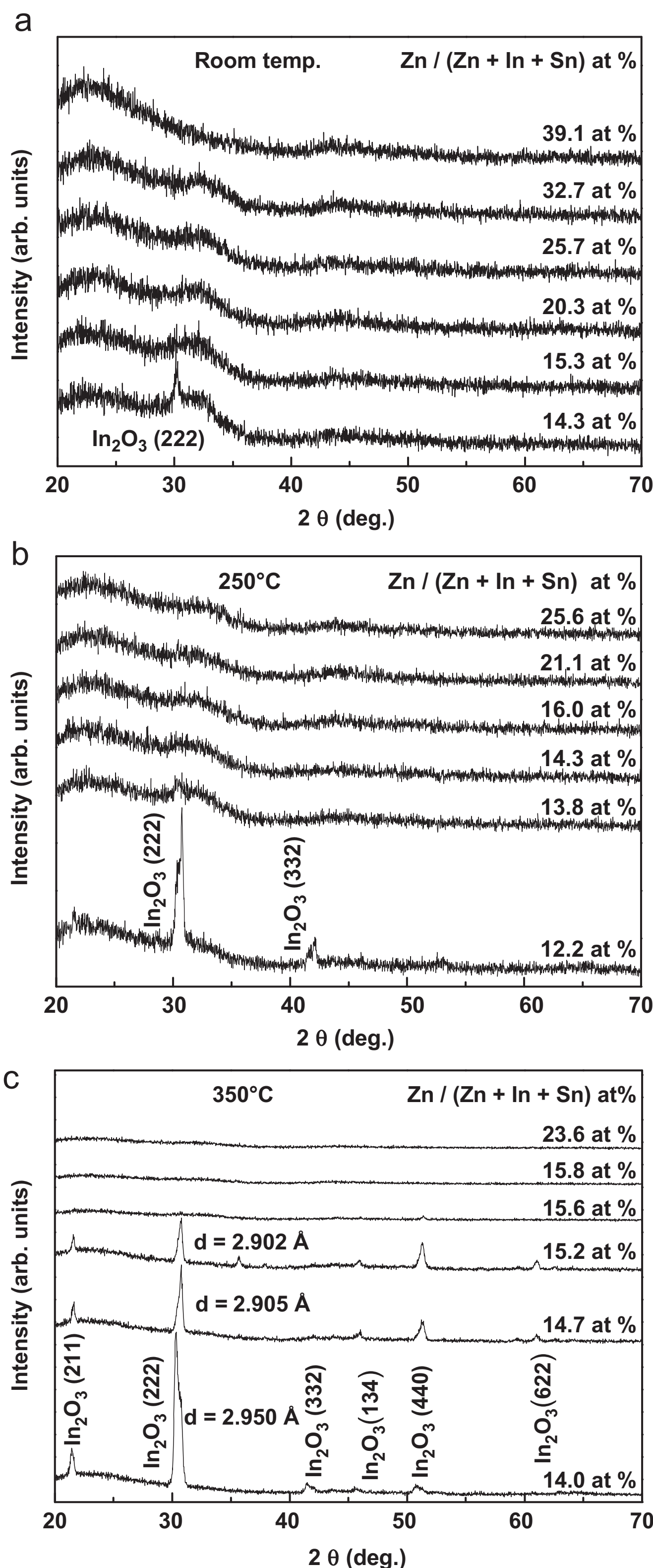

Fig. 3. X-ray diffraction patterns of: (a) the ITO–ZnO thin films deposited at room temperature, (b) at 250 °C, and (c) at 350 °C by combinatorial RF magnetron sputtering.

3. Results and discussion

3.1. Composition

Table 1 presents the zinc compositions of the fabricated ITO–ZnO thin films at each position. The composition ratio

[Zn/(In+Zn+Sn)] decreased as the substrate temperature was raised from RT to 350 °C, which can be ascribed to the fact that the incorporation of Zn into the films decreased with increasing substrate temperature.

3.2. Thickness versus resistivity

Fig. 2 shows the photographs of the ITO–ZnO composition spread films, thickness, and resistivity as a function of substrate temperature at each sample position. The thickness of the fabricated films was ranged from 180 to 330 nm. The film thickness decreased with increasing substrate temperature, which can be ascribed to the decrease of ZnO growth rates with increasing substrate temperature [12].

3.3. Structural properties

Fig. 3 shows X-ray diffraction patterns for the ITO–ZnO composition spread films deposited at $T_S = \mathrm{RT}$ and 250 °C, and 350 °C as a function of Zn contents. At $T_S = \mathrm{RT}$, the diffraction patterns show that the films were of amorphous in the wide range of Zn contents, 15.3–39.1 at%, but at low Zn contents, 14.3 at%, the film had a part of bixbyite type In_2O_3 or ITO composition peak. As shown in Fig. 2(c), increasing T_S up to 350 °C caused crystallization of films. The films Zn content below 15.2 at% were in the crystal phase. The diffraction peak at $2\theta = 30°–31°$ was shifted to the higher values [i.e. decrease of lattice constant (d)] with increasing Zn content, which can be ascribed to a smaller ionic radius of Zn^{2+} (0.74 Å) than that of In^{3+} (0.80 Å) [13]. Even though the substrate temperature increased, the Zn content, which converted from amorphous to polycrystalline phase was in the range of 13.8–15.6 at%. It means that the crystallinity of ITO–ZnO films are dominantly affected by Zn content compared to substrate temperature.

3.4. Electrical properties

Fig. 4 shows electrical properties of the films as a function of substrate temperature and composition. The resistivity below $1 \times 10^{-3}\,\Omega\,\mathrm{cm}$ was obtained for the films deposited at a temperature ranged from RT to 250 °C, while at 350 °C the resistivity was rapidly increased by decreasing Zn content below 15.2 at%. The minimum resistivity of $3.0 \times 10^{-4}\,\Omega\,\mathrm{cm}$ was obtained for the film with Zn content of 16.0 at% deposited at 250 °C, which is lower value than that ($3.9 \times 10^{-4}\,\Omega\,\mathrm{cm}$) of the ITO–ZnO films deposited at room temperature. It should be noted that the minimum resistivity was obtained for the amorphous phase film deposited at 250 °C. This result is in good agreement with that of previous report by Moriga et al. [6]. They have also reported that the ZnO–In_2O_3 film deposited at 300 °C showed inferior electrical properties to the film deposited at 150 °C [6]. In our case, a significant decrease in carrier mobility was also observed for the crystalline films, especially, fabricated at 350 °C. The mobility decrease can be explained as that grain boundary formation in the crystalline films caused an additional scattering for electrons. Consequently, the increase of the resistivity was observed for the crystalline films deposited at 350 °C. Thermal degradation of the films deposited at a higher temperature can be considered as an additional effect for the electrical properties, because at a higher temperature lattice defects could be easily introduced into the films and it might play as carrier traps. However, the thermal degradation and grain boundary effects were suppressed when the Zn content increased, i.e. for the film deposited at 350 °C, above 15.6 at%. As a result, the resistivity was maintained at a lower level of $\sim 10^{-4}\,\Omega\,\mathrm{cm}$. When the films were deposited at 250 °C, the indium content [In/(In+Zn+Sn)] of the film having the minimum resistivity ($3.0 \times 10^{-4}\,\Omega\,\mathrm{cm}$) was 75.5 at%. It is noteworthy that we could actually reduce the indium content as high as ~30 at% compared to that [indium content: 84.8 at% (In/In+Sn)] of ITO for the fabricated ITO–ZnO film ($\sim 10^{-4}\,\Omega\,\mathrm{cm}$) fabricated above 150 °C.

3.5. Optical properties

Fig. 5 shows the transmittance curves (normalized to the glass substrate) of ITO–ZnO composition spread films. All the films showed high transmittance over 82% at the range of 450–1500 nm. In general, optical properties of TCO in near-infrared region depends on carrier concentration. In particular, the plasma wavelength which separates the reflective from the transparent region can be defined as

$$\lambda_p = 2\pi C\left(\frac{\pi m}{e^2 N_f}\right)^{1/2}$$

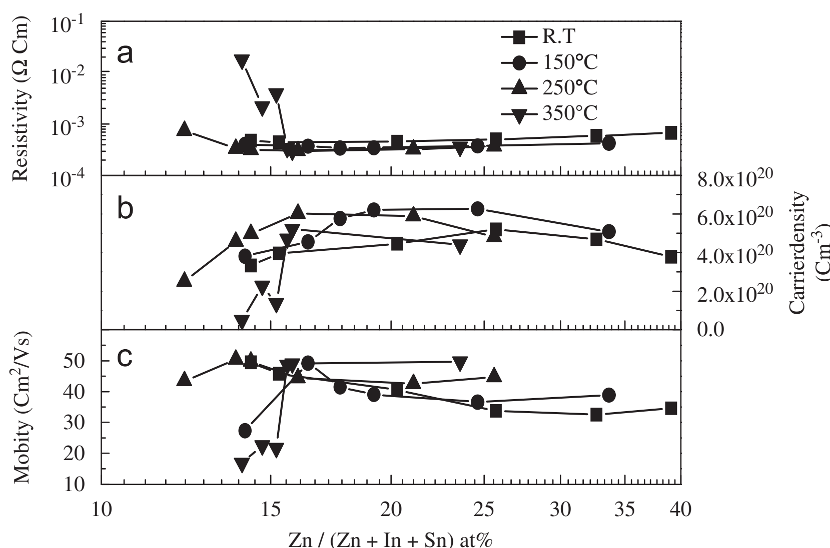

Fig. 4. Variations in: (a) resistivity, (b) carrier concentration, and (c) Hall mobility for ITO–ZnO thin films fabricated by combinatorial RF magnetron sputtering as a function of the substrate temperature.

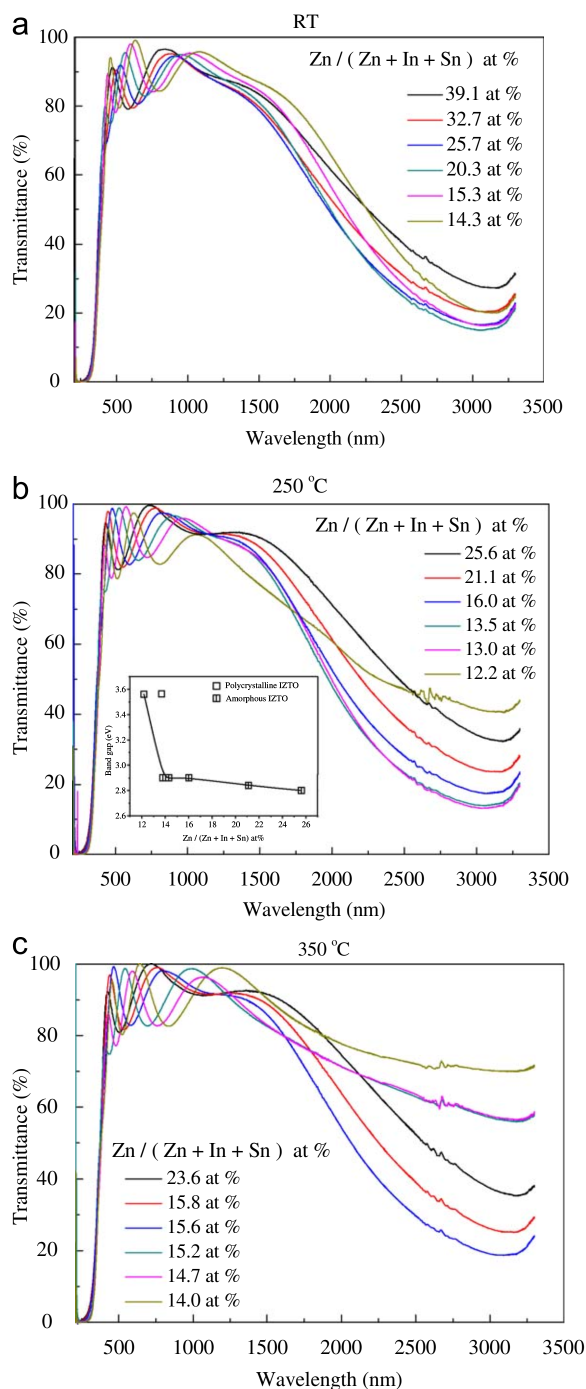

Fig. 5. Optical transmission spectra of: (a) the ITO–ZnO thin films deposited at room temperature, (b) at 250 °C, and (c) at 350 °C by combinatorial RF magnetron sputtering. The inset graph of (b) shows the optical band gaps versus Zn contents.

where C is the velocity of light, m the electron mass, e the electron charge, and N_f the free electrons per cubic centimeter [14]. As known the relation between λ_p and carrier concentration N_f, increasing N_f yields shorter λ_p. Our results also demonstrated that the films with higher carrier concentration showed lower transmittance in near-infrared region. For instance, the ITO–ZnO composition spread film deposited at 350 °C, which possesses carrier concentration above $2\times10^{20}\,\mathrm{cm}^{-3}$ were relatively low transparent in near-infrared region compared with the films having higher carrier concentrations. Inset in Fig. 5(b) shows the optical band gaps as a function of Zn content for the ITO–ZnO composition spread films deposited at 250 °C. Optical band gaps are obtained by linearly extrapolating the plot of $(\alpha h\nu)^{1/r}$ versus $h\nu$ ($r=1/2$ for direct transition, $r=2$ for indirect transition or amorphous semiconductor) [15,16]. From this relation, the band gaps of polycrystalline ITO–ZnO films were obtained by plotting $\alpha h\nu^2$ versus $h\nu$ and those of amorphous films were obtained by plotting $\alpha h\nu^{1/2}$ versus $h\nu$. The optical band gaps were ranged from 2.8 to 3.6 eV. It was also observed that the band gap of films decreased with increasing zinc content. Especially, it decreased rapidly when the phase converted from polycrystalline to amorphous.

3.6. Amorphous ITO–ZnO films

For the transparent amorphous oxide semiconductor, it is satisfied with this electronic configuration $[(n-1)d^{10}ns^0\ (n\geq4)]$ for an large overlap between conduction band orbitals [17,18]. At this case, the conduction band minimum (CBM) of most transparent metal oxides is made of spatially spread spherical metal *ns* orbital. In contrast, the valance band maximum (VBM) is made of oxygen 2*p* orbitals. We suggest that the CBM of ITO–ZnO film could be composed of Zn 4*s*, In 5*s*, or Sn 5*s* orbitals and the magnitude of overlap between neighboring metal (Zn, In, Sn) orbitals is considerably large. As a result, the fabricated ITO–ZnO films are amorphous and exhibit high electrical conductivity. But, we need more researches on electronic band structure of ITO–ZnO by XPS or UPS measurements to support our suggestion. The effects of orbitals overlap in amorphous ITO–ZnO films causes to the decrease of band gap compared to polycrystalline films, and it also continue to decrease with increasing Zn content in amorphous region. Regardless of substrate temperature, the decrease of band gap in amorphous ITO–ZnO phase was predominantly observed for all samples.

4. Conclusion

We have fabricated ITO–ZnO composition spread films with various substrate temperatures. The transmittance of film was not degraded compared to ITO film. The crystallinity of ITO–ZnO films were dominantly affected by zinc content compared to substrate temperature. The electrical properties were slightly improved compared to the films fabricated with room temperature. The indium content could be reduced as high as ~30 at% compared to that of ITO. These results show that the ITO–ZnO is not only substitute ITO by reducing the quantity of indium consumption but also could be possible candidate for various transparent amorphous oxide applications.

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