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# Low temperature deposited transparent conductive ITO and IZTO films for flat panel display applications

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ITO and IZTO films were deposited as a function of the substrate temperature using a sintered ceramic target by pulsed DC magnetron sputtering. The influence of the substrate temperature on the microstructure, surface morphology, electrical, and optical properties was investigated. The amorphous IZTO films deposited at low substrate temperature showed very smooth roughness ( $\sim 0.5$  nm) with very fine grains, while polycrystalline ITO films exhibited rough surface (> 8.0 nm). With increasing substrate temperature, the transparent conducting properties of ITO films were improved. However, opposite tendency occurred for IZTO thin films. The amorphous IZTO film deposited at room temperature showed high transmittance of 89.3% and low resistivity of  $5.6 \times 10^{4} \Omega \cdot \text{cm}$ . In addition, the measured work function of IZTO films had relatively higher value (> 5.0 eV) than that of ITO films (< 4.9 eV) regardless of substrate temperature. In conclusion, IZTO thin film can be used as an alternative material for ITO film as an electrode of flexible flat panel displays.

Key words: TCO (Transparent conducting oxide), ITO (Indium tin oxide), IZTO (Indium zinc tin oxide)

#### Introduction

Transparent conductive oxide (TCO) films have been widely used as an electrode for flat panel displays, such as liquid crystal displays (LCDs), organic light emitting diodes (OLEDs) and e-papers [1, 2]. For these applications, it is well known that the structural, electrical, and optical properties of TCO films are very important factors for display performances [3]. Indium tin oxide (ITO) films are the most popular material as transparent electrodes because of its low electrical resistivity and high optical transmittance in the visible wavelength range [4, 5]. However, polycrystalline ITO films for OLEDs have critical drawbacks as anode materials because of the high process temperature, low work function, and rough surface [6]. In addition, ITO films deposited on flexible substrates are limited due to the problems of foliation and deformation of the substrate [7]. ITO films deposited at low temperature could be fabricated under limited conditions, but the transparent conducting properties of those films could not satisfy the demand for flat panel display applications [8]. For this reason, In-Zn-Sn-O (IZTO) thin films have gained much attention due to its high optical transparency, good conductivity, and high work function compared to ITO films in spite of low deposition temperature [9]. However, the characteristics of both ITO and IZTO films deposited at low temperature have not been investigated in detail.

In this work, we have carried out the electrical, optical and structural comparison of ITO and IZTO films, as a function of the substrate temperature below 200°C. Furthermore, the interrelation between the chemical binding state of the surface and the characteristics of ITO and IZTO films were analyzed by X-ray photoelectron spectroscopy. The work function of the films was measured to evaluate the possibility of alternative TCO applications such as OLEDs. We can conclude the amorphous IZTO film deposited at RT showed comparable resistivity and transparency to those of ITO films based on the figure of merit value. As a result, this enables the deposition of amorphous IZTO films on plastic substrates.

#### Experiment

Both ITO and IZTO films with various substrate temperature were deposited by pulsed DC magnetron sputtering, using a sintered ceramic target of ITO ( $In_2O_3$  90 wt.%, SnO<sub>2</sub> 10 wt.%) and IZTO ( $In_2O_3$  75 wt.%, SnO<sub>2</sub> 15 wt.%, ZnO 10 wt.%). Prior to deposition, the sputtering chamber of base pressure was pumped down to  $7 \times 10^{-7}$  Torr. ITO and IZTO films were deposited on Corning 1737 glass substrate in the presence of a mixture of argon (16 sccm) and oxygen (0.5 sccm) at a deposition pressure of 6 mTorr. DC Plasma powers for ITO and IZTO were 4.9 W/cm<sup>2</sup> and 6.2 W/cm<sup>2</sup>, respectively.

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The substrate temperature was varied from room temperature to 200°C. The crystallographic structure and c-axis preferred orientation of all anode thin films were analyzed by X-ray diffraction (XRD; D8 Advance, Brunker, Germany). The surface morphology and roughness of the all anode films were observed by the field emission scanning electron microscopy (FE-SEM; S-4800, Hitachi, Japan) and atomic force microscopy (AFM; XE150, PSIA, Korea). The resistivity, carrier concentration and Hall mobility of the films were obtained from a Hall measurement and four point electrical probe system. The optical transmittance of thin films was measured by the UV-visible spectrometer with wavelengths ranging from 200-1100 nm. X-ray photoelectron spectroscopy (XPS; ESCA 2000, VG Microtech, UK) was used to confirm the surface chemical state of the IZTO films. A surface work function on all films was measured by ultraviolet photoemission spectroscopy (UPS; AXIS-NOVA, Kratos Inc., England).

## **Results and discussion**

Fig. 1 shows the X-ray diffraction patterns for ITO and IZTO thin films deposited at different substrate temperatures ranging from RT to 200°C by pulsed DC magnetron sputtering system. The XRD patterns of all deposited ITO thin films show planes corresponding to (211), (222), (400), (411), (422), (431), (440), and (622), which are related to the crystalline structure of a cubic In<sub>2</sub>O<sub>3</sub> phase [10]. The ITO film deposited at RT exhibits sharp peaks with a broad peaks  $(2\theta = 30-35^\circ)$ , which indicates that the ITO film at RT has both amorphous and crystalline structures. The crystallinity of the ITO films increases with increasing substrate temperatures. This might be caused by the low deposition temperature, which affects the crystallinity of films by supplying insufficient thermal energy. While the IZTO thin films deposited from RT to 100°C exhibit weak and broad peak, indicating an amorphous structure  $(2\theta = 30-35^\circ)$ , IZTO film fabricated at 200°C has weak poly-crystalline phase. In the case of the IZTO film, the



Fig. 1. X-ray diffraction patterns of ITO and IZTO thin films deposited at different substrate temperatures.

immiscibility of ZnO and SnO<sub>2</sub> in In<sub>2</sub>O<sub>3</sub> leads to a stable amorphous structure at low temperature [11]. The crystallization of the ITO film occurs even at RT while the IZTO thin film can maintain a more stable amorphous structure. This structural stability of the amorphous IZTO films deposited at RT is beneficial for the large area sputtering for mass production.

Fig. 2 shows the surface morphology of the ITO and IZTO films measured by FESEM. The surface morphology of the ITO films changed with increasing substrate temperature. The ITO film deposited at RT was partially crystallized. However, at substrate temperatures higher than 100°C, the films had polycrystalline domain grains with a finer columnar structure of sub grains. As the substrate temperature was increased from RT to 200°C, the roughness of the ITO films increased (rms roughness: 8.56-8.89 nm) On the contrary, the IZTO thin film deposited at RT was amorphous, and was partially crystalline at 100°C. As increasing the substrate temperature up to 200°C, both ordered crystalline region and amorphous region coexist, and the proportion of ordered crystalline structures to amorphous structures gradually increased. The surface morphology of the IZTO thin film (rms roughness: 0.44 nm) grown at RT is much smoother than that of the ITO films. Even though the roughness of IZTO films increased with increasing substrate temperature up to 4.19 nm at 200°C, the surface roughness of the IZTO film is much smoother than that of the ITO due to the high stability of IZTO materials. The surface morphology of the thin film as an anode layer in OLEDs can affect the characteristics of the device; the rough surface could induce the leakage current [12]. Therefore, the amorphous IZTO thin films deposited at RT is more suitable for OLEDs compared to crystallized ITO thin films.

Fig. 3 exhibits the electrical properties, such as resistivity, carrier concentration, and mobility of ITO and IZTO thin films at different substrate temperatures. The ITO film at RT showed a resistivity of  $11.9 \times 10^4 \Omega \cdot \text{cm}$ . The resistivity of ITO thin films decreased rapidly with the increase of the substrate temperature. As a result



Fig. 2. Surface morphology of ITO and IZTO thin films at different substrate temperatures.



**Fig. 3.** Variations of the resistivity, carrier concentration, and mobility of ITO and IZTO thin films at various substrate temperatures.

the minimum resistivity of  $3.0 \times 10^{-4} \Omega \cdot cm$  was obtained for the ITO film deposited at 200°C. On the contrary, the resistivity of IZTO thin films increased with the increase of the substrate temperature. The lowest resistivity of  $5.3 \times 10^{-4} \Omega \cdot cm$  was obtained for the IZTO thin film deposited at RT. It should be noted that the minimum resistivity was obtained for the amorphous phase film. This might be due to the difference of electrical carrier sources and crystalline structure between the films. For an impurity doped TCO films, the carriers generally originated from intrinsic donors or extrinsic dopants or both [13, 14]. Normally, the electrical carrier generation in ITO film involves the substitution mechanism by extrinsic doping; Sn<sup>4+</sup> ions for  $In^{3+}$  sites ions in the  $In^2O^3$  structure [15, 16]. However, for the ITO thin film deposited at low temperature, the supply of insufficient thermal energy leads to a degradation of the crystallinity and a decrease in the substitution process. In addition, the carrier mobility in ITO thin films is closely related to the electron carrier scattering at grain boundaries [17]. Up to the process temperature of 200°C, the carrier mobility in ITO films increased as the carrier scattering decreased with crystallized large grains. In contrast, the carrier source of IZTO films is mainly intrinsic donors, such as oxygen vacancies. The carrier concentration of IZTO films from RT to 100 did not change noticeably,



Fig. 4. Optical transmission spectra of the ITO and IZTO thin films as a function of the substrate temperatures.

but the carrier concentration of IZTO film deposited at 200°C decreased due to the oxygen absorption [18]. The absorbed oxygen may have reduced the number of oxygen vacancies in the film and resulted in a decrease of carrier concentration. Furthermore, the mobility of IZTO films decreased due to the increase of carrier scattering between both crystalline region and amorphous region with increasing substrate temperature. For the reason above, the resistivity of ITO thin films decreased noticeably with increasing substrate temperature, while the resistivity of IZTO thin films increased with increasing substrate temperature and the resistivity of IZTO film deposited at low substrate temperature shows relatively low resistivity compared to ITO films.

Fig. 4 shows the optical transmittance spectra of ITO and IZTO films deposited at different substrate temperature in the wavelength range of 200-1100 nm. This graph shows that the transmittance of the ITO and IZTO film is more than 80% including glass substrate regardless of its deposition temperature. Both the transmittance of both ITO and IZTO films increased with increasing substrate temperature. The average transmittance of IZTO thin films deposited at below 100°C in visible light range (400-800 nm) is comparable to that of the ITO thin films. Especially, the average optical transmittance (89.3%) of the IZTO thin film deposited at RT is higher than that (88.7%) of ITO thin films at RT.



Fig. 5. (a) Plot of  $(\alpha h \upsilon)^2$  vs. photon energy and (b) band gap energies for ITO and IZTO thin films grown at different substrate temperatures.



Fig. 6. XPS core level spectra of (a) In 3d, (b) O 1s, (c) Sn 3d, and (d) Zn 2p obtained from ITO and IZTO thin films grown on a glass substrate as a function of the substrate temperatures.

Fig. 5 shows the optical band gap (Eg) of the ITO and IZTO thin films as a function of substrate temperature. The optical band gap of thin films was evaluated from the variation of absorption coefficient ( $\alpha$ ) as a function of photon energy (h $\upsilon$ ). The optical band gap of the films was determined using the relation [19],

$$\alpha(h\upsilon) = D(h\upsilon - Eg)^{1/2}$$
(1)

where D is a constant that depends on the material and Eg is its optical band gap. The optical band gap can be deduced by extrapolating a straight line to the energy axis. The optical band gap (3.61 eV) of ITO thin film at RT increased with increasing substrate temperature to a maximum of 3.88 eV (200°C), whereas the optical band gap of IZTO thin film did not change. The band gap shift of all films could be related with the changes of the carrier concentration in films by Burnstein-Moss effect; when the carrier concentration increases, the band gap also increases due to the creation of partially filled states near the conduction band edge [20]. This result corresponds with the variation of carrier concentration in the both ITO and IZTO thin films.

The chemical binding state of the ITO and IZTO thin films deposited at different substrate temperatures were investigated by XPS analysis. The detailed binding energy was analyzed by the core level spectra of In 3d, Sn 3d, and O 1s from both ITO and IZTO films and Zn 2p only from IZTO films, as shown in Fig. 6(a-d). As the substrate temperature is increased, no obvious changes in the Zn 2p peaks were observed. The difference in binding energy of the In  $3d_{3/2}$  and  $3d_{5/2}$  peaks was constant and equal to  $7.5 \pm 0.2$  eV for the In

3d peaks for both ITO and IZTO films. In particular, three components at binding energies of  $444.2 \pm 0.1$ ,  $445.0 \pm 01$ , and  $446.0 \pm 0.1$  eV were achieved from the In  $3d_{3/2}$  peak. Carvalho reported that the first peak is assigned to crystalline indium oxide (In<sub>2</sub>O<sub>3</sub>), the second to amorphous indium oxide, and the third to In(OH)x species [21]. Inset of Fig. 6(a) shows the difference between the binding energies of crystallized ITO and amorphous IZTO thin films in regions of different crystallinity. The fitting of O1s peak presents two different components with two types of O<sup>2-</sup> ions. John et al. reported that a lower binding energy peak  $(O_{II})$ from the O<sup>2-</sup> ions have neighboring In atoms with their full complement and the higher binding energy peak (O<sub>I</sub>) corresponds to oxygen deficient [22]. In our study, the binding energy ratio  $(I(O_I) / I(O_{II}))$  of both ITO and IZTO films decreased with increasing substrate temperature; the binding energy ratio of the ITO films from RT to 200°C decreased from 1.78 to 1.64, and the binding energy ratio of IZTO films from RT to 200°C decreased from 2.65 to 1.73. The decrease of higher binding peaks in O 1s peak indicates that the oxygen vacancies decrease with increasing substrate temperature. The two spectra of Sn 3d,  $8.5 \pm 0.1$  eV apart, due to Sn  $3d_{3/2}$  and Sn  $3d_{5/2}$  were observed. The Sn peaks from both ITO and IZTO films shift to lower binding energies with increasing substrate temperature due to increased In-substituted Sn, and it is in accordance with the explanation by John et al [21]. Overall, Sn-rich regions in crystallized ITO films could easily nucleate Sn-Oxide phases in the presence of oxygen vacancies, which could increase the electrical resistivity and darken the films. The high substrate temperature could improve the electrical and optical properties of ITO film due to decreased second phases of Sn-Oxide enhacing the crystallinity of Sn doped  $In_2O_3$ . However, in IZTO thin films, the electrical resistivity rather increases at high substrate temperature due to decreased electrical carriers which are mostly from oxygen vacancies in amorphous structure.

The work function of the anode surface might be responsible for the difference of a device performance in OLED system [23]. The work functions of ITO and IZTO films deposited at different substrate temperature are calculated using the direct measurement of an inelastic secondary electron cutoff measured by UPS in ultrahigh vacuum as shown in Fig. 7(a). The work function values of ITO and IZTO films deposited with various substrate temperatures are shown in Fig. 7(b). The work function of the IZTO films is much higher than that of the ITO films. The work functions of IZTO films with optimum deposition conditions were  $\geq 5.3$  eV, i.e. closer to the typical values for highest occupied molecular orbital (HOMO) in organic electroluminescent semiconductors. This means that IZTO film deposited at room temperature is more advantageous than ITO films for electrode applications requiring a lower hole injection barrier into the HOMO level at the hole transport organic layer. Consequently, the high work function of IZTO films could contribute to the high efficiencies in OLEDs or flexible OLEDs displays.

Fig. 8 presents the figure of merit, mean optical transmittance and sheet resistance of the ITO and IZTO thin films with different substrate temperature. The figure of merit ( $\Phi_{TC}$ ) value, which was suggested by Haacke, can be calculated from equation below, where T is transmittance and  $R_{sh}$  is sheet resistance of the IZTO anode films [24].

$$\Phi_{\rm TC} = T^{10} / R_{\rm sh} \tag{2}$$

The  $\Phi_{TC}$  can provide information for comparing the performance of TCO films with similar optical transmittance and electrical resistivity. As expected from the electrical and optical properties of both films, the increase of the substrate temperature led to increase in the  $\Phi_{TC}$  value of the ITO films, while the increase of the substrate temperature decreased the  $\Phi_{TC}$  value of the IZTO films. From the evaluated  $\Phi_{TC}$  values of the ITO and IZTO thin films, it can be concluded that the IZTO film is a suitable electrode material for low deposition process below 100°C.

## Conclusions

We prepared the ITO and IZTO thin films on glass substrates using pulsed DC magnetron sputtering at low substrate temperature (Ts <  $200^{\circ}$ C) to investigate the properties as an electrode for flexible substrate. As the substrate temperature is increased, the optical and electrical properties of ITO thin films improved with the growth of its crystallinity. On the other hand, the IZTO thin films deposited at RT showed the highest figure of merit values, but its electrical properties were degraded with increasing substrate temperatures. In particular, the substrate temperature has a significant effect on the surface morphology and chemical binding states of both ITO and IZTO films. As a result, it is concluded that the IZTO thin film grown at RT is comparable to that of conventional ITO thin film as an electrode for flexible displays, not only because of good electrical and optical properties but also because of its smooth surface and high work function.

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