Effect of thickness and substrate temperature on the properties of transparent Ti-doped In$_2$O$_3$ films grown by direct current magnetron sputtering

Dong-Ju Kim $^a$, Bong-sueg Kim $^b$, Han-Ki Kim $^{a,*}$

$^a$ Department of Advanced Materials Engineering for Information and Electronics, Kyung-Hee University, 1 Seocheon-dong, Yongin-si, Gyeonggi-do 446-701, South Korea

$^b$ Z-TEC Co., Ltd., Star-Biz Building #105, 4th Gumi National Industrial Complex, Sandoong-myeon, Gumi-si, Gyeongsanbuk-do, 730-853, South Korea

**Abstract**

We reported on the effect of film thickness and substrate temperature on the properties of TiO$_2$-doped In$_2$O$_3$ (TIO) films deposited on a glass substrate by direct current (DC) magnetron sputtering for touch panel applications. The electrical, optical, surface and structural properties of TIO films grown at room temperature were significantly dependent on its thickness. At optimized TIO thickness (480 nm), the resistivity of the TIO film decreased with increasing substrate temperature due to effective activation of Ti dopant and crystallization of the In$_2$O$_3$ matrix. Furthermore, the increase in substrate temperature during DC sputtering leads to increase of optical bandgap of the TIO films due to Burstein–Moss effect, which is caused by change in carrier concentration of TIO films. At optimized conditions, the TIO film shows resistivity of $1.947 \times 10^{-4}$ Ω-cm and optical transmittance of 85.3% comparable conventional indium tin oxide films.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Transparent conducting oxide (TCO) films have been widely employed in a wide range of optoelectronic applications, such as flat panel displays, photovoltaics, light emitting diodes, and touch panels due to its low resistivity and high transmittance in a visible wavelength region. Among In$_2$O$_3$, ZnO, SnO$_2$, TiO$_2$-based TCO materials, In$_2$O$_3$-based TCO films, including Sn-doped In$_2$O$_3$ (ITO) and Zn-doped In$_2$O$_3$, and Zn, Sn co-doped In$_2$O$_3$ are most widely investigated due to predominant electrical and optical properties of In$_2$O$_3$ [1–5]. In particular, most research have been devoted to the study of ITO films with intention of their utilization in flat panel displays and photovoltaics in more than 50 years because they exhibited a remarkable combination of low resistivity ($-10^{-4}$ Ω-cm) and high transmittance ($>80$%) [6]. As an alternative dopant of Sn for the In$_2$O$_3$, several dopant such as Si, Ge, Ti, Te, Mg, F, Ca, Cu, S, As, Sb, Sr, Bi and B have been suggested [7–11]. In particular, Ti-doped In$_2$O$_3$ (TIO) has a great attention for application in touch panel displays due to stable crystalline structure and high stability against humidity. As discussed by Hest et al., one carrier is generated for every Ti for doping concentration between 1 and 3 at.% in TIO film unlike the case of Sn dopant [12]. They also reported that the maximum mobility of the TIO film increased up to 83.3 cm$^2$/V·s much higher than that of ITO. Abe et al. also suggested that Ti doped In$_2$O$_3$ had a low resistivity ($2.1 - 3.0 \times 10^{-4}$ Ω-cm) and high transmittance in the near infrared region [13]. Although the possibility of Ti dopant in the In$_2$O$_3$ film as TCO materials has been suggested, the investigation of the effect of thickness and substrate temperature on the properties of the TIO film is still lacking.

In this work, we investigated the effect of thickness and substrate temperature on the electrical, optical, surface and structural properties of the DC sputtered TIO films. With increasing thickness from 24 to 720 nm, sheet resistance and optical transmittance of the TIO films were measured to correlate the electrical and optical properties of the TIO film with its thickness. At optimized thickness (480 nm), the effect of substrate temperature during DC sputtering on the electrical, optical, surface and structural properties of the TIO film was further investigated. Based on calculated figure of merit values, we optimized the thickness and substrate temperature of the TIO films.

2. Experimental details

The Ti doped In$_2$O$_3$ (TIO) films were deposited on glass substrate by means of a specially designed DC magnetron sputtering system. Using the 3 inch TIO ceramic target as a sputtering source, TIO films were sputtered on glass substrate as a function of thickness and substrate temperature. During TIO sputtering, target-to-substrate distance was kept constant at 80 mm. Firstly, the TIO films were sputtered on a glass substrate with a dimension of 25 × 25 mm$^2$ as a function of thickness at room temperature. By adjusting the sputtering time, we controlled the thickness of the TIO film at constant Ar flow rate of 15 sccm, working pressure of 0.399 Pa (3 mTorr), and DC power of 60 W without addition of reactive oxygen gas. The sputtering time was varied from 1 min to 30 min and the resulting film thickness is of 24 nm to 720 nm, respectively. Secondly, to investigate the effect of substrate temperature on the properties of the TIO films, 480 nm thick TIO films were deposited on glass substrate as a function of substrate temperature from 100 °C...
to 550 °C at same sputtering conditions. The substrate temperature was intentionally heated by halogen lamp heater. The sputtering rate and thickness of the TIO films were obtained by means of a stylus profilometer (Tencor Alpha-step 250). The electrical properties of the TIO films were measured by the Hall measurements at room temperature as a function of the film thickness and substrate temperature. In addition, the optical transmittance of the TIO films was measured by UV/Visible spectrometer in a range of 220–800 nm. The structural properties of the TIO films were studied by X-ray diffraction (XRD-2θ mode, D/Max 2500) with Cu Kα radiation. Furthermore, the surface of the TIO films was analyzed by field emission scanning electron microscopy (FESEM; Hitachi-S4800) with operating voltage of 5 kV.

3. Results and discussion

Fig. 1a shows sheet resistance and resistivity of the as-deposited TIO films as a function of the film thickness. During DC sputtering of the TIO target, the DC power, working pressure, and Ar flow rate were kept constant at 60 W, 0.399 Pa (3 mTorr), and 15 sccm, respectively. At 24 nm thickness, the TIO film shows fairly high sheet resistance of 275 Ω/square and resistivity of 6.463 × 10^-4 Ω-cm. However, the 120 nm thick TIO film shows abruptly decreased sheet resistance of 55 Ω/square and resistivity of 6.146 × 10^-4 Ω-cm. Note that sheet resistance of TIO films above 120 nm thickness is similar (~50 Ω/square) regardless of film thickness due to increase of resistivity. Fig. 1b shows the optical transmittance of the as-deposited TIO films with increasing film thickness. As can be seen, that as the TIO film thickness increases, variation of the optical transmittance occurred due to interference phenomena. Regardless of the film thickness, all TIO films exhibited a fairly high optical transmittance in a visible wavelength range. The TIO film with a thickness between 120 and 480 nm showed the high transmittance nearly 90% at a wavelength of 550 nm. Due to the variation of the optical transmittance caused by optical interference, it is difficult to determine the exact relationship between TIO thickness and optical transmittance. However, the shift of the absorption edge of the TIO films towards longer wavelengths with increasing thickness is apparent, indicating bandgap narrowing [10,14].

Fig. 2a shows the sheet resistance and optical transmittance of the TIO films grown at a substrate temperature of 550 °C with increasing thickness. To decide the optimized thickness of TIO films, we compared the sheet resistance and optical transmittance of the TIO films grown at high substrate temperature of 550 °C. Compared to the as-deposited TIO film in Fig. 1a, the TIO film grown at substrate temperature of 550 °C showed a significantly reduced sheet resistance. In addition, the TIO film showed a decreased sheet resistance with increasing film thickness. The 480 nm and 720 nm thick TIO films showed the low sheet resistances of 4.0 and 3.3 Ω/square, respectively. However, the increase of film thickness led to a decrease in optical transmittance of the TIO film at 550 nm wavelength. Based on sheet resistance (Rsh) and optical transmittance (T) of the TIO films, we calculated the figure of merit value (FOM = T/mΩ·cm) of the TIO films with increasing film thickness as shown in Fig. 2b. With increasing the thickness, the TIO film showed an increase in the figure of merit value. Except the 720 nm thick TIO film, the 120, 240, and 480 nm thick TIO films showed a similar high figure of merit values due to low sheet resistance and high optical transmittance. Therefore, we decided the 480 nm-thick TIO film as an optimized thickness to investigate the effect of substrate temperature.

Fig. 3 shows XRD plot of the TIO films grown at room temperature with increasing thickness. In the case of the TIO film with thickness of 24 and 120 nm, similar XRD plots were observed. There is only a broad glass substrate peak indicating that the TIO film had an amorphous
structure. However, the 240 nm thick TIO film shows only a peak at \(2\theta = 34.47^\circ\) (400), indicative of crystalline structure with (400) preferred orientation. Further increase in thickness leads to appearance of additional XRD peaks as well as (400) peak. The XRD plots of the 720 nm thick TIO film exhibited several peaks at \(2\theta = 20.80^\circ\) (211), 29.71° (222), 34.47° (400), 49.57° (440), and 59.07° (622), indicative of a bixbyte structure of the TIO film. It was noteworthy that the TIO film grown at room temperature showed a strongly (400) preferred orientation, unlike conventional ITO films with (222) preferred orientation [15]. The different preferred orientation of the TIO film with thickness above 240 nm could be attributed to the process ambient effect [16].

The dependence of the surface morphology of the TIO films on the film thickness was investigated by FESEM as shown in Fig. 4. At thicknesses of 24 nm and 120 nm, both TIO films in Fig. 4a and b show a similar surface morphology because the structure of both samples is completely amorphous as expected from XRD results. However, the surface and cross-sectional FESEM images of the 240 nm thick TIO film in Fig. 4c exhibited crystalline feature. The surface of the 240 nm thick TIO film shows square shape grain indicative of (400) preferred orientation. With increasing thickness, the surface and cross-sectional FESEM image shows clear crystalline feature as shown in Fig. 4d and e. The TIO films with 480 and 720 nm thicknesses showed a [100] preferred columnar structure that consists of small sub-grains like sputter-deposited ITO films discussed by Shigesato et al. [17].

To investigate the substrate temperature effect on electrical, optical, and structural properties of TIO film, we deposited the TIO film with a constant thickness of 480 nm as a function of substrate temperature. Fig. 5 shows the Hall measurement results of the 480 nm thick TIO films as a function of substrate temperature from 100 °C to 550 °C. It is clearly shown that the increase of substrate temperature lead to a significant reduction of sheet resistance and resistivity of the TIO films due to effective activation of Ti dopant and crystallization of In$_2$O$_3$ matrix at high substrate temperature. The TIO film grown at 550 °C substrate temperature showed the lowest sheet resistance of 4.0Ω/square and resistivity of 1.95 \(\times\) 10\(^{-4}\) Ω-cm. The low resistivity of the TIO film grown at high substrate temperature could be attributed to high mobility and carrier concentration as shown in Fig. 5b. As expected from the resistivity of the TIO film, the increase of the substrate temperature leads to an increase of carrier concentration and mobility. With increasing substrate temperature, the Ti$^{4+}$ dopant more effectively substitute the In$^{3+}$ and increase the carrier concentration [12]. In addition, the crystallization of the TIO with increasing substrate temperature increases the mobility. Therefore the combined effect of the activation of Ti dopant and the crystallization of In$_2$O$_3$ matrix resulted in the decrease in the resistivity of the TIO film with increasing substrate temperature.

Fig. 6a shows optical transmittance spectra of the TIO film grown as a function of substrate temperature. Upper panels exhibited the pictures of the TIO films sputtered at different substrate temperatures. All TIO films show a high optical transmittance in a visible wavelength region regardless of the substrate temperature. However, the shift of the absorption edge of the TIO films towards shorter wavelengths with increasing substrate temperature is apparent, indicating bandgap widening. The optical energy band gap of the TIO films was evaluated from the variation of absorption coefficient (\(\alpha\)) as a function of photon energy (\(h\nu\)). The energy band gap of the films was determined using the relation [15],

\[
\alpha(h\nu) = C(h\nu - E_g)^{1/2} .
\]

where C is a constant that depends on the material, and \(E_g\) is its optical band gap. The optical band gap can be deduced by extrapolating the straight line portion of this plot to the energy axis as shown in Fig. 6b. By increasing the substrate temperature, the bandgap energy...
of the TIO film was shifted to the higher energy. It is clearly seen that the optical band gap of the TIO films increases linearly from 3.4 eV to 3.75 eV with increasing substrate temperature. The increase of carrier concentration in the TIO film with increasing substrate temperature is closely related to the band gap widening of the TIO film. The band gap widening as a result of the increase in the carrier concentration is related to the Burstein–Moss (BM) effect [13,15].

Fig. 7 shows the XRD plots of the TIO films as a function of substrate temperature. As we explained in Fig. 3, the TIO film grown at room temperature showed (400) preferred orientation due to effect of Ar ambient during sputtering. With increasing substrate temperature, the peak intensity of (400) significantly reduced. The TIO films grown at substrate temperature above 300 °C showed strong (211) and (222) peaks indicating preferred orientation similar to structure of conventional ITO film. As discussed by Thilakan et al., the preferential orientation in the bixbyite structure was dependent on the oxygen concentration in the film [16]. Therefore, it was thought that the changed oxygen concentration in the TIO film with increasing substrate temperature could affect the preferred orientation of the TIO films.

Fig. 8 shows surface FESEM images of the TIO film with increasing substrate temperature. It was clearly shown that sub-grain size of the TIO film increased with increasing substrate temperature. At room temperature, the TIO film shows fairly smooth surface even though it has a (400) preferred orientation. However, increase of the substrate temperature up to 550 °C increase in the sub-grain size nearly 107 nm. Sub-grain size increase of the TIO film with increasing substrate temperature could be explained by enhanced self-diffusion of sputtered atoms on the surface of substrate. The general microstructure of the sputter-deposited TCO film could be zone model [18]. The zone model described that the microstructure of sputtered films was closely related to the substrate temperature ($T_{\text{substrate}}/T_{\text{melting}}$). Based on the substrate temperature, the structure zone could be divided into four regimes, in which the microstructure of sputtered film is critically affected by shadowing, surface diffusion, bulk diffusion and desorption with increasing substrate temperature. The $T_{\text{substrate}}/T_{\text{melting}}$ for TIO film grown at a substrate temperature of 550 °C is about 0.48, which corresponds to the zone where surface and self-diffusion become active. This is consistent with our microstructure of TIO films grown by DC magnetron sputtering.
4. Conclusions

The effect of thickness and substrate temperature on the properties of TIO film grown by DC sputtering was investigated. In case of the TIO film grown at room temperature, the resistivity and optical transmittance were affected by thickness of the TIO film. With increasing the thickness, evolution of the crystalline structure lead to the change of electrical and optical properties. In addition, increase of substrate temperature during DC sputtering process influenced on the quality of the TIO films. At substrate temperature of 550 °C, the TIO film showed the sheet resistance of 4.0 Ω/square, resistivity of $1.947 \times 10^{-4}$ Ω-cm, and optical transmittance of 85.3%. Furthermore, the increase of substrate temperature led to increase of bandgap of the TIO film due to the BM effect which is critically affected by carrier concentration. Based on Hall measurement, UV–Visible spectrometry, XRD, and FESEM examinations, it was found that the electrical, optical, structural, and surface properties of the DC sputter grown TIO films clearly depend on the thickness and substrate temperature during sputtering process.

Acknowledgments

This work was supported by grant no. 10031768 from the Ministry of Knowledge Economy (MKE) and Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

References


Fig. 8. Surface FESEM images of the 480 nm thick TIO films with increasing substrate temperature; (a) room temperature, (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400, and (f) 550 °C.