International Journal of Enhanced Research in Science Technology & Engineering, ISSN: 2319-7463
Vol. 3 Issue 6, June-2014, pp: (381-385), Impact Factor: 1.252, Available online at: www.erpublications.com

Improvement of the Structural, Optical, and Electrical Properties of Indium-Tin-Oxide Thin Films by High-Temperature Annealing

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Abstract: **The present work demonstrated the improvement of indium-tin-oxide thin films using a high-temperature annealing technique. The films were deposited onto glass substrates with a sputter-coater system (RF) from a high-density target (In_2O_3-SnO_2, 90 wt.%–10 wt.%), and the structural, electrical, and optical properties of the films were investigated. These films were annealed at different temperatures (250, 350, 450, and 550 °C) in air for 1 h. The structure, resistance, and optical transmission of the films were systematically investigated as a function of post-annealing temperature. Results showed that the highest optical transmittance was 97.27%, the highest energy gap was 3.72 eV, the lowest resistivity was 3.8×10^{-4} Ω-cm, and the lowest sheet resistance was 9.5 Ω/sq. Grain size increased from 29.27 nm to 43.87 nm. X-ray diffraction and field-emission scanning electron microscopy analyses were performed to study the microstructure of the films.**

Keywords: ITO thin film; RF sputtering; annealing; optical properties; structure; XRD; transmission; resistivity; sheet resistance; energy gap.

Introduction

Indium-tin-oxide (ITO) thin film has been widely used for transparent conductive layers in various optoelectronic devices due to its high transparency to visible light and low electrical resistivity [1]. In applications that use ITO as a transparent conductor, which require liquid transparency and low resistivity, the parameters such as the thickness of the film, dopant type, its amount, and the other deposition conditions have to be optimized. To obtain high-quality ITO films, these films are conventionally annealed after deposition. Post-deposition annealing at temperatures from 250, 350, 450, and 550 °C in a furnace is effective on grain growth or crystallinity of ITO thin films, resulting in reduced structural defects. Therefore, a

High-temperature process technology has drawn an increasing amount of attention recently. The required exceptionally smooth surface morphology necessitated the use of ITO films OLED displays [2], liquid crystal display (LCD) [3], solar cells [4], and various light-sensitive solid state devices. High-quality ITO films have been prepared by various deposition methods such as electron beam evaporation [5], thermal evaporation CVD [6], spray pyrolysis [7], pulse laser deposition[8], DC and RF sputtering [9]. In this research, we report on the characteristics of ITO films deposited on glass substrates by a RF sputtering system and then followed by high temperature annealing. The high-temperature annealing in the present study shows that annealing greatly affects the final surface morphology of ITO thin films.

Experimental

Glass substrates containing indium-tin-oxide thin films were prepared by RF sputtering technique. The ITO target (99.9% purity) was a commercially available hot-pressed pallet composed of 90 wt.% In_2O_3 with 10 wt.% SnO_2. ITO films with a thickness of 200 nm were deposited by using RF sputtering device at a temperature of 200 °C and basic vacuum pressure of 3×10^{-5} Torr, then under plasma by Ar gas at 6×10^{-3} Torr. The glass substrates were cleaned by sonication with detergent (acetone, methanol), rinsed with deionized water for 15 min, blown dry by nitrogen gas, and finally dried in the oven at 120 °C for outgassing. Structural properties were studied by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FESEM) analyses. XRD was operated in the 2θ mode with Cu Kα radiation (XRD; Rigaku,D/MAX-Rc) at a wavelength of 1.54 Å. Resistivity measurements were obtained using 2400 Source Meter (KETHLEY). Transmission curves were obtained using a Varian-Cary system 5000 UV- Vis-NIR spectrophotometer. Annealing experiments were performed in air and at different temperatures (250, 350, 450, and 550 °C) for 1 h.

Results and discussions

To study the microstructure of the ITO thin films, X-ray diffract meter (XRD) measurements were performed. The film microstructure orientation was found to be sensitive to the thermal annealing condition. Fig. 1 shows the X-ray diffraction patterns of the IT0 thin films as deposited and annealing at different temperatures (250, 350, 450, and 550 °C). The diffraction patterns of the ITO thin film without annealing and at 250 °C annealing temperature did not exhibit a peak,which indicates an amorphous structure, whereas the diffraction patterns of the ITO thin films began to grow at 350 °C, and the intensity of the diffraction peaks increased with increasing annealing temperature. This indicates a change of the film structure from amorphous to polycrystalline. The highest intensity of the diffraction peaks was obtained at 450 °C annealing temperature.

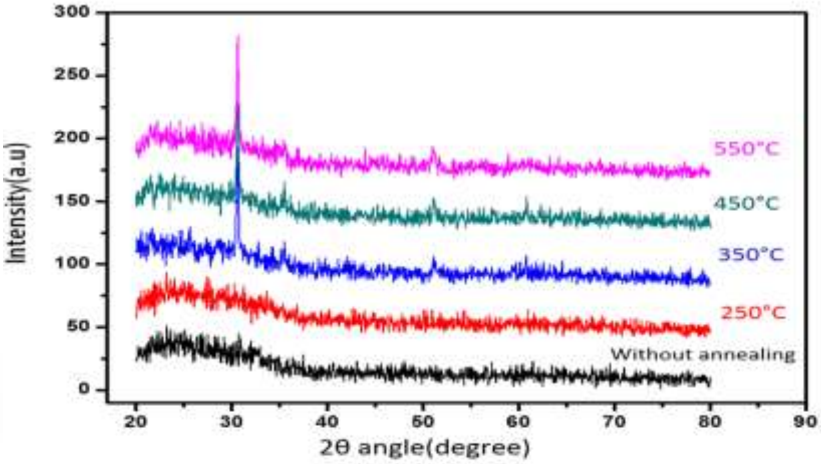


Fig. 1: High-angle XRD pattern of ITO thin films at different annealing temperatures.

Fig. 2 shows the XRD patterns of the ITO thin film at 450 °C annealing temperature. The XRD patterns of the ITO thin film at 450 °C annealing temperature indicate five major peaks (211), (222), (400), (440), and (622) [10]. The results suggest that the crystallinity of the ITO thin films was enhanced at 450 °C. Table 2 shows a comparison between measurement XRD result and standard. In particular, the strongest line at 2θ = 30.5 (corresponding to the reflection from the (222) crystalline plane) is close to the position of the strongest line of the reference indium oxide.

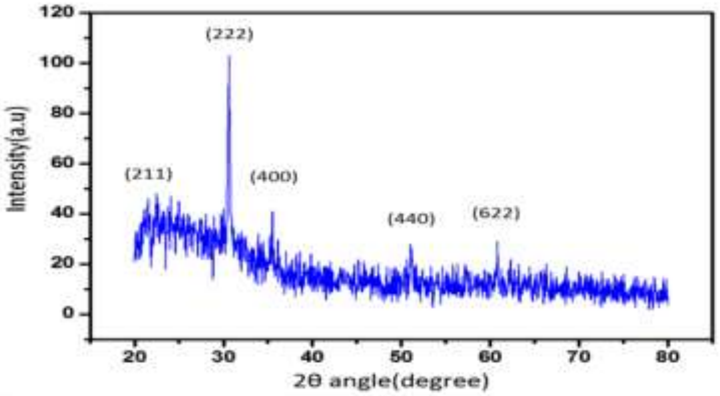
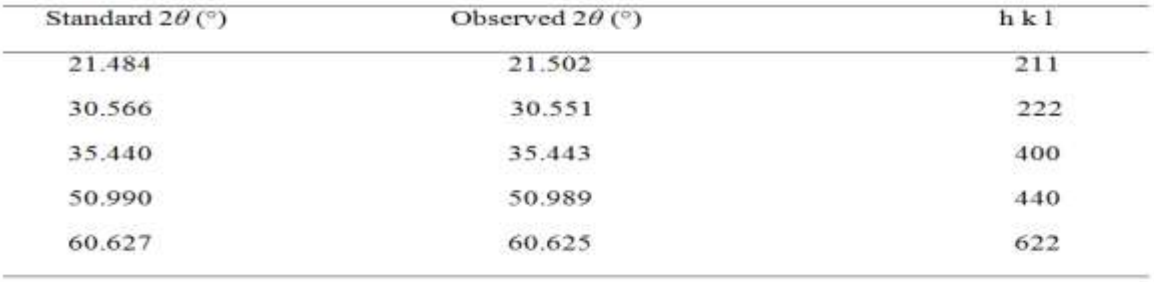


Fig. 2: High angle- XRD pattern of ITO thin film after annealing at 450 °C.

Table 1 Comparison between measurement XRD result and of ITO thin-film standard(450 °C).



Standard 2θ (°)	Observed 2θ (°)	h k l
21.484	21.502	211
30.566	30.551	222
35.440	35.443	400
50.990	50.989	440
60.627	60.625	622

The grain sizes were derived from the X-ray diffraction spectra following the Scherer method. Grain size D is given by: $D = K\lambda/\Delta(2\theta)\cos(\theta)$, where λ is the X-ray wavelength (λ = 1.5406 Å), the constant $K = 180/\pi = (0.94)$, θ is the diffraction angle at which the peak of a particular orientation occurs. The grain size increased from 29.27 nm to 46.87 nm, as shown in Table 2. Fig. 3 shows the FESEM images of ITO thin films.In Fig. 3(a), polycrystalline and granular structures cannot be seen because the surface morphology of ITO thin film without annealing is an amorphous structure. Fig. 3(b) shows the ITO thin-film image at 250 °C annealing temperature, where the beginnings of polycrystalline growth can be seen. Fig. 3(c) shows the image of the film at 350 °C annealing temperature, which creates the polycrystalline and granular structures. The most characteristic grains were observed in the film grown at 450 °C annealing temperature (Fig. 3(c)). Observed in Fig. 3(e) are large voids between the crystalline grains, as well as small cracks.

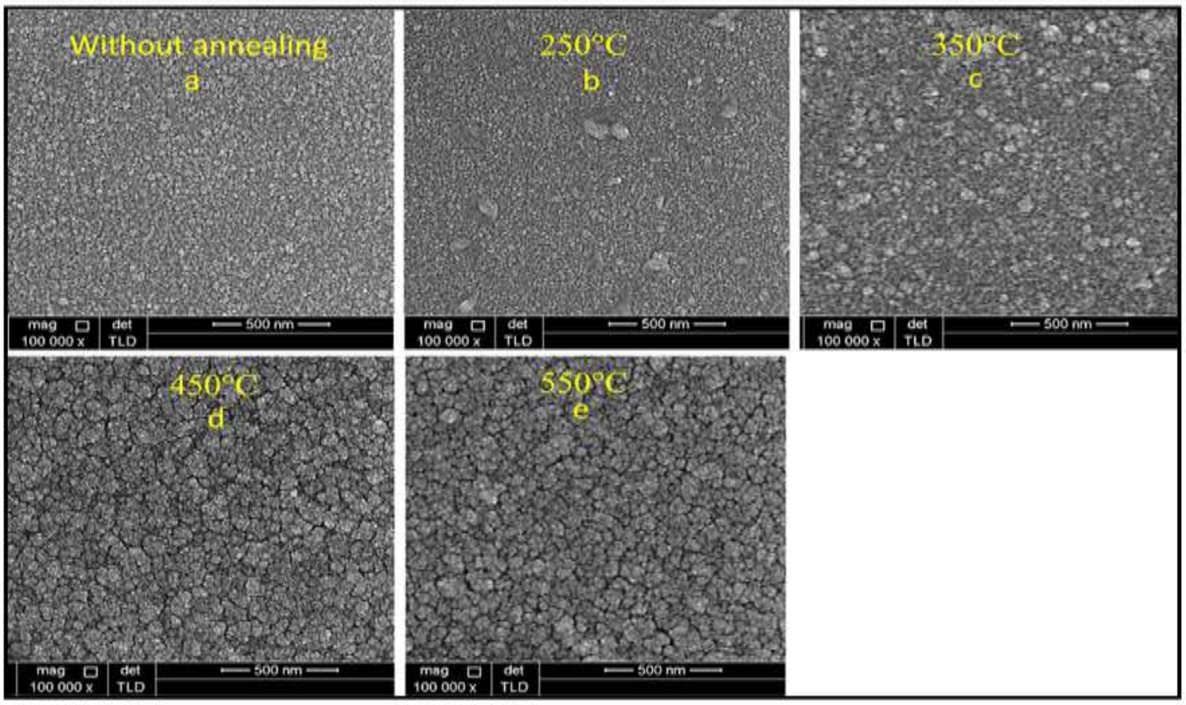


Fig. 3: FESEM image of the ITO films with different substrate temperature.

Fig. 4 shows the variation of resistivity as a function of the substrate temperature. The resistivity of the ITO films decreased with increasing substrate temperature, suggesting that the electrical properties of the ITO films were strongly influenced by the substrate temperature. The lowest resistivity of 3.8×10^{-4} Ω-cm was obtained from the film that was annealed at 450 °C, as shown in Table 2. The increase in resistivity at 550 °C annealing temperature is related to the film beginning to lose some of the structure, as well as its electrical and optical properties due to the high heat (550 °C**).** This leads to the small cracks and increases the voids between crystalline grains. Sheet resistance is given by the equation: ($R_S = \rho/T$) where R_s is the sheet resistance, ρ is the resistivity, and T is the thickness of the thin film [11], as shown in Table 2.

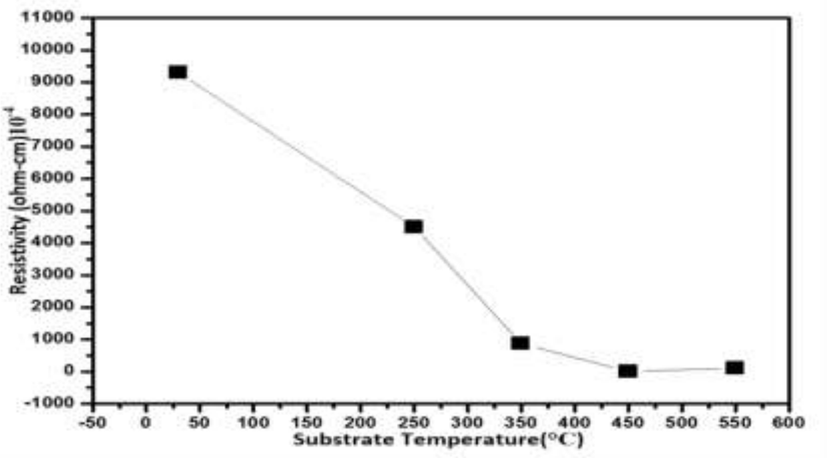


Fig. 4: Variation in resistivity of ITO films with different substrate temperature.

Fig. 5 shows the optical transmission of the ITO film in the wavelength range of 300 nm to 800 nm. The transmission of the deposited thin film without annealing over the spectral range of 300 nm to 400 nm was relatively low; this is due to the amorphous structure of the film. A further increase in optical transmission, which was 97.27%, could be recognized at a higher annealing temperature of 450 °C. Higher annealing temperature heat treatment leads to better crystallization and lower level of defects found near the grain,thus resulting inimprovement of structural homogeneity and the decrease of light reflection. The ripples in the spectrum resulted from the interference light, since the spectrum reflects wave forms that are characteristic of the interference light [9, 10]. A decrease in transmission can be observed in the near IR region because of the increase of carriers after annealing.

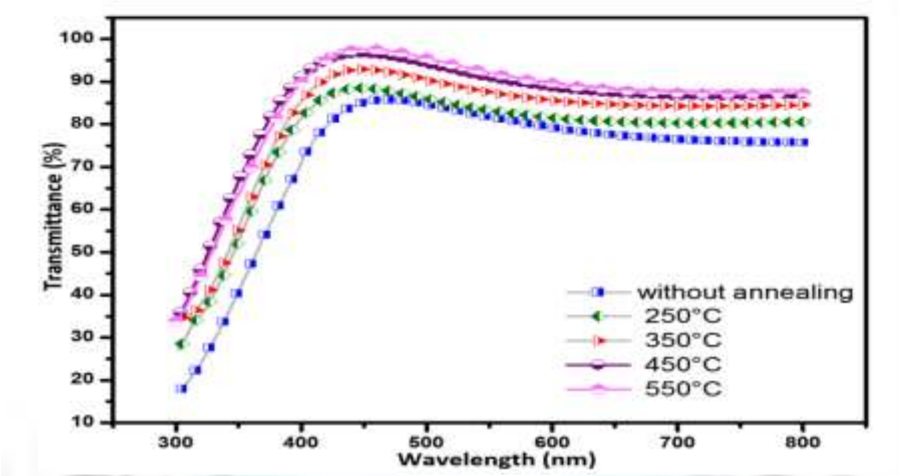
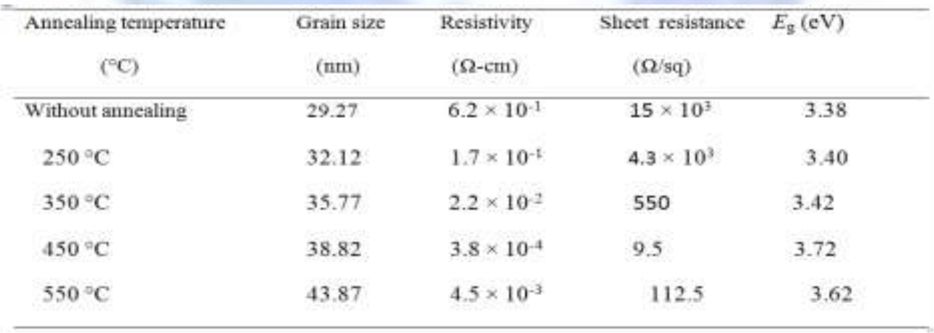


Fig. 5: Optical transmission spectra of ITO thin films.

Fig. 6 shows the energy gap of the ITO filmwith different annealing temperature. The energy gaps of the ITO thin films were values calculated from the plot of $(\alpha h\nu)^2$ versus hν for the ITO films. The absorption coefficients (α) were calculated from the optical transmission (T) by the following equation: $\alpha = (\ln 1/T)/D$, where D is the film thickness, and the photon energy (hν) was calculated from the following equation: $h\nu = 1240/\lambda$. The energy gap average was observed to increase correspondingly with increase in annealing temperature of the ITO thin film, as shown in Table 2.

Table 2: Grain size, resistivity, sheet resistance, energy gap for the ITO thin films at different annealing temperature.



Annealing temperature (°C)	Grain size (nm)	Resistivity (Ω-cm)	Sheet resistance (Ω/sq)	E_g (eV)
Without annealing	29.27	6.2×10^{-1}	15×10^{3}	3.38
250 °C	32.12	1.7×10^{-1}	4.3×10^{3}	3.40
350 °C	35.77	2.2×10^{-2}	550	3.42
450 °C	38.82	3.8×10^{-4}	9.5	3.72
550 °C	43.87	4.5×10^{-3}	112.5	3.62

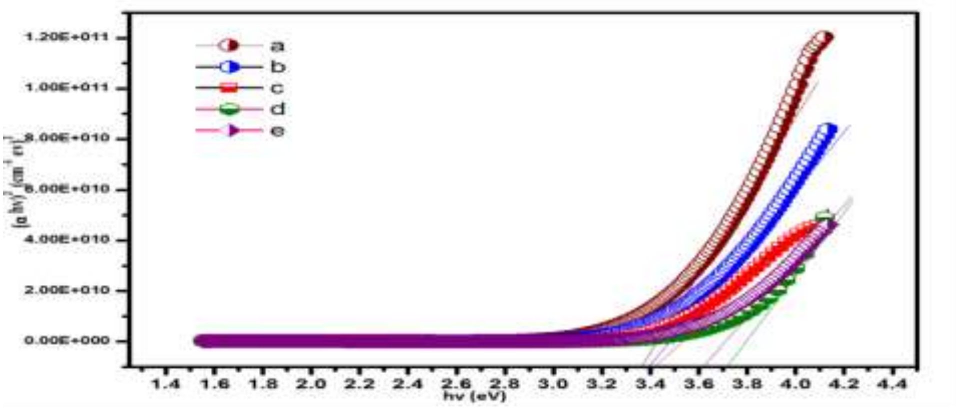


Fig. 6: Variation of the optical band gap of ITO thin films.

Most structural, optical, and electrical properties of ITO thin film was observed to decrease at 550 °C annealing temperature because of the increase in voids and small cracks between the crystalline grains (Fig. 3(e)) caused by high temperatures(550 °C).

4. Conclusion

ITO thin films were prepared by (RF) sputtering coater is deposited on glass. The effects of substrate temperature on the structural, electrical, and optical properties were investigated. From the obtained results, the following conclusions can be drawn.

1. The XRD results showed that the crystallinity of ITO thin films was improved with annealing, and grain size increased from 29.27 nm to 43.87 nm.
2. High-quality film with low resistivity of 3.8×10^{-4} Ω-cm and sheet resistance was 9.5 Ω/sq.
3. Highest optical transmittance was 97.27%.
4. High energy gap of the ITO thin film was 3.72 eV.

These results can be used in the preparation of ITO films for use as transparent conductive electrodes in various applications.

Acknowledgement

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We gratefully acknowledge the support of the school of physics University Saince Malaysia under short term grant no 304/PFIZK/6312076.

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