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# Effects of CW $CO_2$ Laser Annealing on Indium Tin Oxide Thin Films Characteristics

**Forat H. Alsultany, Naser M. Ahmed*, M. Z. Matjafri**

Nano-Optoelectronics Research and Technology Laboratory, School of Physics, Universiti Sains Malaysia, Penang, Malaysia
Email: *nas_tiji@yahoo.com

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## Abstract

**In this work ITO thin film annealing was carried out using a CW $CO_2$ laser beam for ITO thin film annealing over a 1 $cm^2$ area with a temperature higher than 250˚C to obtain ITO grains with excellent structural quality thin films. The obtained ITO films were characterized for crystallization, surface morphology, electrical and optical properties, which has theoretical significance and application value. ITO thin films are deposited on glass substrates by sputter coater system (RF) from a high density target ($In_2O_3$-$SnO_2$, 90 - 10 wt%). After deposition, ITO thin films have been irradiated by CW $CO_2$ laser ($\lambda$ = 10.6 µm) with power ranging from 1 to 10 watt. These films were annealed at temperatures 250˚C, 350˚C, and 450˚C in the air for 20 minutes using different laser power. The main incentive was to develop a low temperature process for ITO thin films, which typically required a 350˚C anneal to crystallize and achieve optimum optical and electrical properties. The XRD results showed that 350˚C temperature laser annealing could crystallize ITO with a strong (222) preferred orientation and its grain size increased from 29.27 nm to 48.63 nm. The structure, optical transmission, energy gap, resistivity and sheet resistance of the ITO thin films were systematically investigated as a function of laser post annealing temperature. It was found that the lowest resistivity was $2.9 \times 10^{-4}$ Ω-cm and that sheet resistance was 14.5 Ω/sq. And the highest optical transmittance (98.65%) of ITO films was obtained at 350˚C annealing temperature.**

## Keywords

**ITO Thin Film, RF Sputtering, Annealing, CW $CO_2$ Laser, Optical Properties, Structure, XRD, Transmission, Resistivity, Energy Gap**

*Corresponding author.

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## 1. Introduction

Laser materials processing is an enabling technology in many industries. The most prominent are automotive, semiconductor technology, flat panel display production, solar cell technology and medicine [1]. Typical laser-based processes are welding, soldering, cutting, drilling and laser annealing [2] written by laser micromachining [3], ablation and micro-lithography. What concerns us here is laser annealing on ITO thin film. Indium tin oxide (ITO) film has been widely used for transparent conductive layer in various optoelectronic devices due to its high transparency to visible light and its low electrical resistivity [4]. Applications which use ITO as a transparent conductor include liquid crystal display (LCD), solar cells and various light sensitive solid state devices [5]. High quality ITO films have been prepared by various deposition methods, such as electron beam evaporation [6], thermal evaporation CVD [7], spray pyrolysis [8], plus laser deposition [9], DC and RF sputtering [10].

In this study, we have actively investigated CW $CO_2$ laser annealing as an alternative method to obtain ITO grains with excellent structural quality thin films. Laser-treated samples of ITO films are characterized for extent of crystallization, surface morphology, electrical and optical properties.

## 2. Experimental

In the present study, ITO thin film was prepared on glass substrate from a ceramic is (90 wt% $In_2O_3$) and (10 wt% $SnO_2$) using RF sputtering method. The evaporation conditions were: RF power was 100 W for one hour sputtering time to get 200 nm thickness, the base pressure of the chamber was $10^{-7}$ mbar, and the working pressure of the chamber during sputtering was about $3 \times 10^{-2}$ mbar. The glass substrates were cleaned by sonication with detergent (acetone, methanol), rinsed with deionised water for 15 min, blown dry by nitrogen gas and finally dried in the oven at 120˚C for outgassing. A CW $CO_2$ laser with power from 1 to 10 W is employed as an annealing system. The laser beam is focused by a beam expander lens (100 mm focal length) and forms a focused spot of circular cross section with 1 $cm^2$ on the spin coated ITO thin film.

The annealing experiments were done, in the air, at different temperatures 250˚C, 350˚C and 450˚C for 20 mints. Structural properties have been studied by means of the X-ray diffraction technique and the Field Emission Scanning Electron Microscopy (FESEM). X-ray diffraction works in the $2\theta$ mode with the CuK$\alpha$ radiation (XRD; Rigaku, D/MAX-Rc) at a wavelength of 1.54 Å. The resistivity measurements were measured using (KETHLEY, 2400 Source Meter). The transmission curves were obtained using spectrophotometer type a Varian-Cary system 5000 UV-Vis-NIR. Spectrophotometer was used to determine the optical transmission spectra.

## 3. Results and Discussions

XRD patterns of the ITO films as-deposited and annealed at different annealing temperatures are shown in **Figure 1**. The pattern of the ITO thin film without annealing did not show a peak, indicating an amorphous structure, while the diffraction patterns of the ITO thin films began to grow at 250˚C and the intensity of the diffraction peaks increases with increase annealing temperature, this indicates to change the film's structure from amorphous to polycrystalline. The high intensity of the diffraction peaks was obtained at 350˚C annealing temperature.

**Figure 2** shows the XRD patterns of the ITO thin film of 350˚C annealing temperature, this pattern indicates to have five major peaks (220), (222), (400), (440) and (622) [11].

The preferred orientation of the (222) direction, peak becomes more intense and sharper at 350˚C annealing temperatures. This indicates that the crystallinity of the film was improved and the grain size became larger at high annealing temperature. **Table 1** shows the detailed structural information on samples obtained from the XRD patterns shown in **Figure 2**. These estimated values are compared with the standard values.

The grain sizes were derived from the X-ray diffraction spectra following the Scherer method [11]. Grain size $D$ is given by $D = K\lambda / \Delta(2\theta)\cos(\theta)$, where $\lambda$ is the X-ray wavelength ($\lambda$ = 1.5406 Å), the constant $K = (180/\pi) =$ (0.94), $\theta$ is the diffraction angle at which the peak of a particular orientation occurs [12]. The grain size increased from 29.27 nm to 48.63 nm, as shown in **Table 2**.

**Figure 3(a)** cannot be seen polycrystalline and granular structures due the surface morphology of the thin film without annealing grown an amorphous structure. **Figure 3(b)**, **Figure 3(c)** shows images of the films at 250˚C, 350˚C annealing temperature; one can see clearly many polycrystalline and granular structures. From **Figure 3(d)**, it can be seen that the voids between the crystalline grains and small cracks. The most characteristic grains were observed in the films grown at 350˚C annealing temperature.

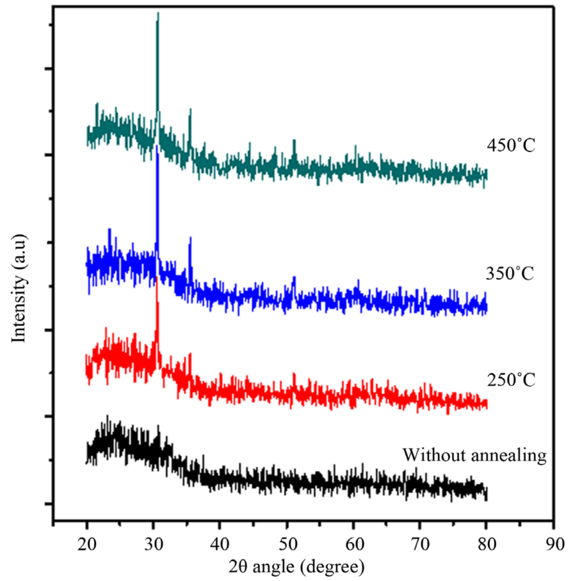


Figure 1. High angle-XRD pattern of ITO films at different annealing temperatures.

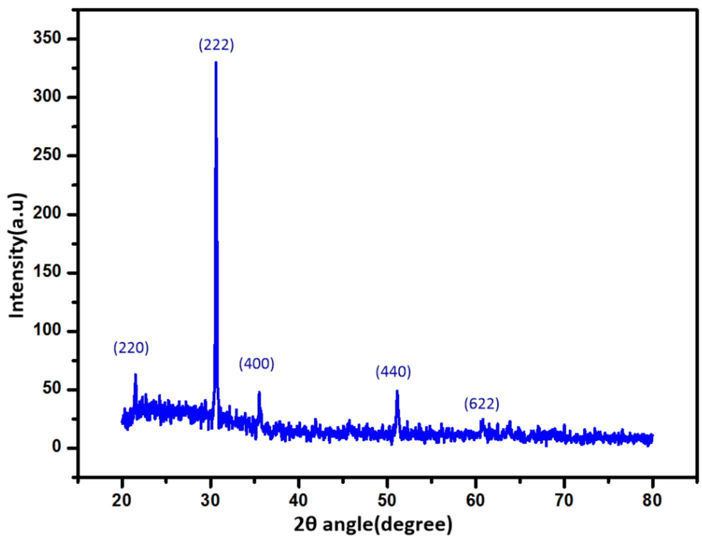


Figure 2. High angle-XRD pattern of ITO film after annealing at 350˚C.

Figure 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 and due to the large increase in carrier concentration and mobility. The lowest resistivity of $2.9 \times 10^{-4}$ Ω-cm was obtained from the film that was annealed at 350˚C, as shown in Table 2. The sheet resistance given by $\left(R_S = \rho/T\right)$ where $R_s$ is the sheet resistance, $\rho$ is the resistivity and $T$ is the thickness of the thin film, as shown in Table 2.

Figure 5 shows the optical transmission of the ITO film in the wavelength rang 300 nm - 800 nm. The transmission of the thin film grown without annealing over the spectral range from 300 nm to 400 nm was relatively low; this is due to the amorphous structure of the properties film. A further increase in the optical transmission could be recognized with increasing annealing temperature. Higher annealing temperature heat treatment leads to a better crystallization and lower level of defects near the grain found, thus resulting in the improvement of structural homogeneity and decrease of light reflection. It can be seen a decreasing in transmission in the near IR region because of the increasing of the carriers after annealing.

**Table 1.** Comparison between measurement XRD result and standard of ITO film (350˚C).

| Standard 2θ (˚) | Observed 2 (˚) | *hkl* |
|---|---|---|
| 24.857 | 24.822 | 220 |
| 30.566 | 30.551 | 222 |
| 35.440 | 35.443 | 400 |
| 50.990 | 50.989 | 440 |
| 60.627 | 60.625 | 622 |

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

| Annealing temperature (˚C) | Grain size (nm) | Resistivity (Ω-cm) | Sheet resistance (Ω/sq) | Eg (eV) |
|---|---|---|---|---|
| Without annealing | 29.27 | $6.2 \times 10^{-1}$ | $31 \times 10^{3}$ | 3.38 |
| 250˚C | 30.92 | $8.1 \times 10^{-1}$ | $4.3 \times 10^{3}$ | 3.47 |
| 350˚C | 36.94 | $2.9 \times 10^{-2}$ | 14.5 | 3.81 |
| 450˚C | 48.63 | $9.1 \times 10^{-4}$ | 45.6 | 3.76 |

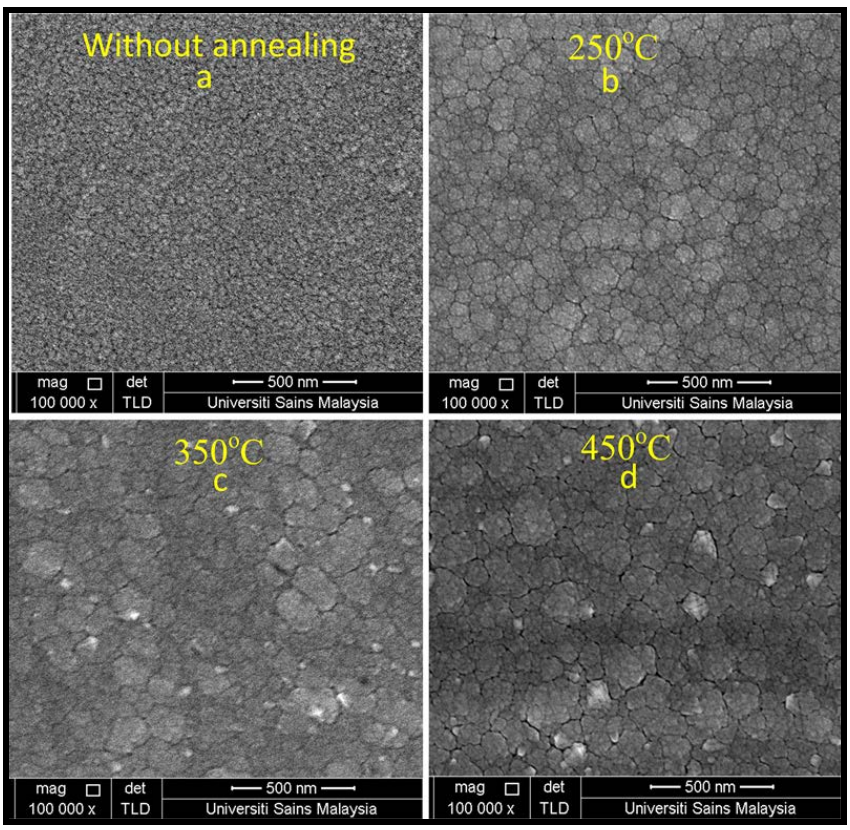


**Figure 3.** FESEM image of the ITO film with different annealing temperatures.

**Figure 6** shows the energy gap of the ITO film with different annealing temperature. The energy gaps of the ITO thin films were values calculated from the plot of $(\alpha h\nu)^2$ versus $h\nu$ for the ITO films. The absorption coefficients ($\alpha$) were calculated from the optical transmission ($T$) by the following equation $\alpha = (\ln 1/T)/D$, $D$ was the film thickness, and the photon energy ($h\nu$) was calculated from the following equation $h\nu = 1240/\lambda$. It

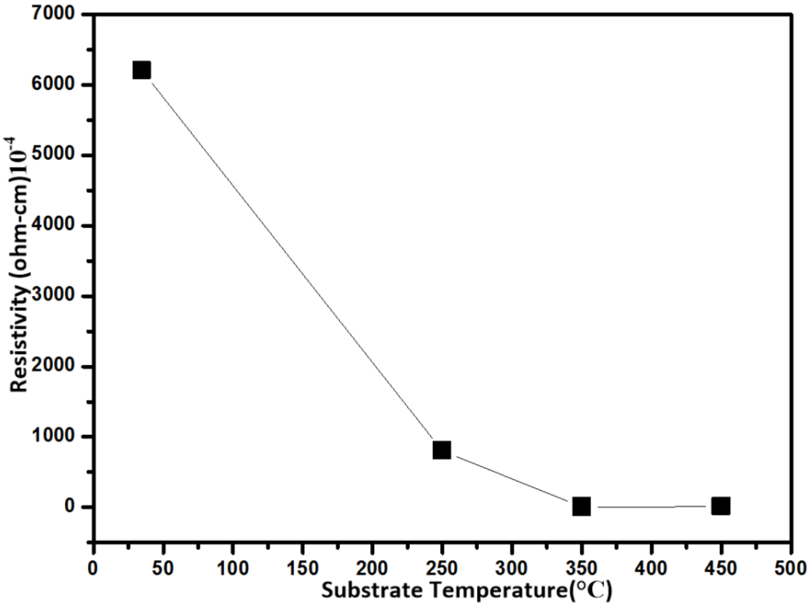


**Figure 4.** Variation in resistivity of ITO films with different substrate temperatures.

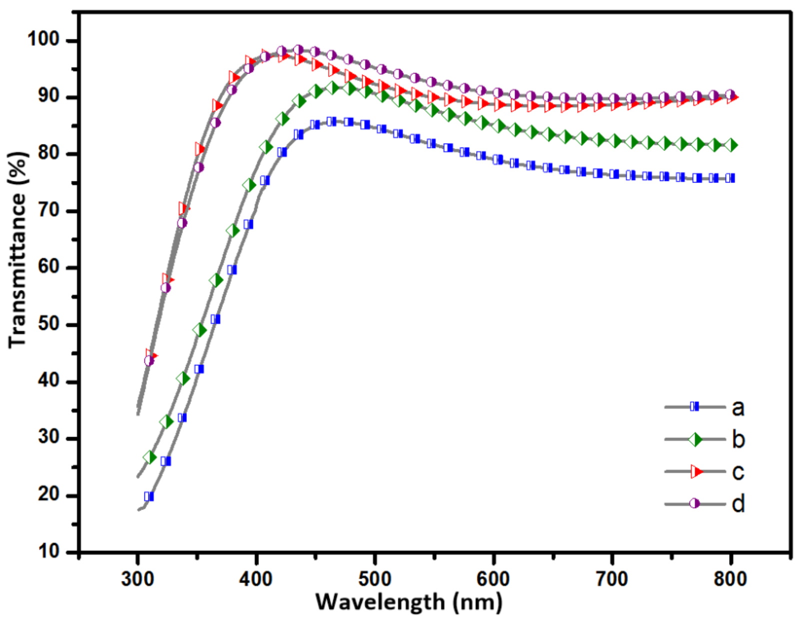


**Figure 5.** Optical transmission spectra of ITO thin films: (a) Without annealing; (b) 250˚C; (c) 350˚C; (d) 450˚C.

is observed that the energy gap average increases with increase annealing temperature of the ITO thin film, as shown in **Table 2**.

## 4. Conclusions

CW $CO_2$ laser annealing technique on ITO thin film is deposited on glass substrates by sputter coater system (RF) which has been used in this study. The effects of substrate temperature on the structural, electrical and optical properties are investigated. From the obtained results following conclusions can be drawn:

1) The XRD results show that the crystallinity of ITO thin films is improved with annealing and their grain size increase from 29.27 nm to 48.63 nm.

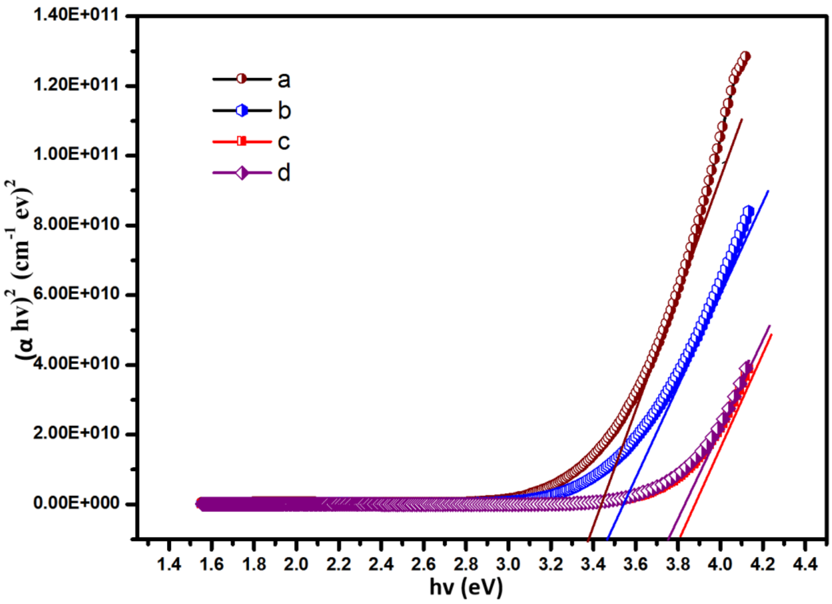


**Figure 6.** Variation of the optical band gap of ITO thin films: (a) Without annealing; (b) 250˚C; (c) 350˚C; (d) 450˚C.

2) High quality film with resistivity is as low as $2.9 \times 10^{-4}$ Ω-cm, and sheet resistance is 14.5 Ω/sq.
3) High optical transmittance is 98.65%.
4) High energy gap is 3.81 eV.

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

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