Journal of Ovonic Research Vol. 14, No. 3, May - June 2018, p. 225 - 233

# INFLUENCE OF GAMMA RAY ONTO TRANSPARENT INDIUM TIN OXIDE THIN FILMS

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Transparent Conducting Indium Tin Oxide (ITO) thin films were deposited with Pulsed Laser Deposition PLD at 300°C. The ITO films have small grain size of 22-26 nm, an average surface roughness of 5.5 nm and a high value transmission (95%) in the wavelength range from 300 to 700 nm with a low resistivity of $2.25 \times 10^{-4}$ Ω.cm. Spectral, structural and morphological properties were investigated for the films irradiated at low doses (5-25kGy). Improvement to the crystallinity was observed for the (ITO) films annealed at $300^0$C and above with a slight decrease in the optical transmittance. Annealing greatly decreased the resistivity of the films. A lower resistivity and better spectra selectivity is a measurement of the quality and potential use of transparent ITO films for the application as anode electrodes for optoelectronic devices such as solar cells and organic light-emitting diodes.

(Received April 5, 2018; Accepted June 20, 2018)

*Keywords*: Thin films, Gamma irradiation, Atomic force microscopy, Optical coatings, Pulsed laser deposition

## 1. Introduction

In recent years, there has been an increase in the number of applications of transparent conducting oxides such as ITO thin films, due to their unique optical, electrical and mechanical properties which are different to those of bulk material. Indium tin oxide (ITO) is an n-type transparent semiconductor with a wide band gap (*Eg* = 4 eV). These properties have led them to play an irreplaceable and increasing role in many areas of today's very demanding and rapidly developing technology, especially in the electronic displays and optical industries [1-2].

Interest in transparent films with an oxide layer such as indium tin oxide (ITO) has increased for a wide range of applications including heat-reflecting mirrors [3], the field of flat panel displays [4] anti-reflection Coatings [1], organic light-emitting diodes [3], gas sensors [2], and as transparent electrodes in solar cells [4-6].

ITO films can be prepared by different methods such as chemical vapour deposition (CVD) [7], electron-beam evaporation [8–9], sputtering [10–11], pulsed laser deposition (PLD) [12–15] and sol-gel methods [16].

Kim et al [4] demonstrated that by using a PLD process, a highly conductive and transparent ITO film can be deposited, with an optical transmittance of 88% and a resistivity of $2.49\times10^{-4}$ Ω cm for the film thickness of 180 nm.

In general the desired properties for conducting oxide films used as anodes in optoelectronic devices are as follows [5-6, 18-20]:

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(1) Low specific resistivity ( $<1.50 \times 10^{-6}$ Ω cm) (2) Good thermal stability (3) High uniformity across the flat substrate (4) Low particle contamination (5) Good adherence to substrate (6) Low manufacturing costs.

In this investigation, we deposited transparent conducting ITO films by a Pulsed Laser Deposition technique. A set of the freshly made ITO films were annealed for 1 hour at different temperatures (100 - 600 $^0$C) in an air atmosphere.

Then, another set freshly deposited ITO films were then irradiated with low gamma doses 5-25 kGy. Our aim was to make a comparative study between the as-deposited and irradiated ITO films grown at (300 $^0$C) by investigating their morphologies; and their electrical and optical properties, and to investigate the possibility for using the transparent conducting ITO films as protective coating for windows or as anode in an organic light emitting diode and solar cell based on conjugated polymers.

## 2. Experimental details

For the deposition of ITO films, a KrF excimer Laser was used as the Pulsed Laser Deposition source (PLD). A laser repetition rate of 10 Hz was used, with a target to substrate distance of 15 cm and a laser pulse energy density of 2.7 J/cm$^2$. The thin film growth chamber exhibits a base pressure of $10^{-6}$Torr. Glass was used as the substrate material in this study. Film growth was performed at a temperature of 300ºC in an oxygen pressure of 10 mTorr for 20 minutes.

Indium Tin Oxide target was fabricated using high purity $In_2O_3$ (99.995%) with $SnO_2$ (99.998%) as received from the supplier (Sigma-Aldrich). The target was pressed and sintered at room temperature for 24 hours in air. Further experimental details, processing conditions and research results were presented in a recent publication [17].

The ITO target was fabricated with $In_2O_3$ (90%):$SnO_2$ (10%).

The ITO films have an average thickness of 150 nm for all the samples used in our work. Thickness measurements were conducted using a Deck Tack 150.

The ITO films were irradiated in King Abdul Aziz City for Science and Technology, Atomic Energy Institute at various irradiation doses using a $^{60}$Co Gamma Cell GC-220 Excel (manufactured by MDS Nordion, Canada) with absorbed dose rate of 6.7 kGy/h, at room temperature. The humidity and temperature during irradiation were kept constant with an air chiller system (turbo-Jet, Kinetics, USA) as described previously in details [17].

X-ray diffraction (XRD) measurements have been performed to investigate the crystallography and the phase structures of ITO thin films. The optical transmission and absorption spectra of the oxide films were measured using a spectrophotometer over the range from 300 to ~ 800 nm. The Atomic Force Microscopy (AFM) was used to evaluate the morphology and surface roughness of the as-deposited and irradiated films. AFM images were taken on freshly as-deposited, irradiated ITO samples to avoid possible effects of humidity on the morphology. The sheet resistance ($R_s$) of the deposited films was measured using a four-point probe method at room temperature.

## 3. Results and discussion

### 3.1 X-rays results of the ITO thin films

XRD was used to study the effect of high gamma doses on the crystal structure. The XRD patterns of (as-deposited) 0 kGy, 5kGy, 10kGy and 25kGy are very similar with no significant change in the peaks or patterns, so only the results of the ITO film irradiated at 5kGy are represented in Fig. 1. For the ITO irradiated at 5kGy, the spectrum shows that all the patterns peaks (211), (222), (400), (411), (431), (440) and (622) for ITO films reflect the very high quality of films under investigation despite the relatively low temperature growth (300$^o$C). The intensity of ITO (222) diffraction peak at 30.5$^o$ was the strongest; the second strongest intensity (440) peak was at 51$^o$ and the third strongest one (400) was at 35$^o$. Kim *et al* [1] attributed the increase in the

lattice parameter to the substitution of $Sn^{4+}$ ions into $In^{3+}$sites; also it can be due to the incorporation of Sn ions in the interstitial positions. There was no detectable phase of $SnO_2$ resulting that Sn atoms were dissolved in the $In_2O_3$. However, the presence of different peaks suggested that the crystalline structure has different orientations. The grain size was calculated using formula (1) [17]:

$$D= 0.9\,\lambda\,/\beta\cos\theta \tag{1}$$

where, $D$ is the grain size, λ is the X-ray wavelength (Cu-Kα, 0.154 nm); $\theta$ is the diffraction angle and $\beta$ is the line broadening at half the maximum intensity (FWHM). This quantity ($\beta$) is sometimes denoted as $\Delta(2\theta)$; For the relation between the grain size and the doses, the grain size was26 nm for the as-deposited films and decreased to 22.6nm at the25kGy dose. Fig. 1 also, shows that the preferable orientation is (222) for samples without irradiations and at irradiation dose of 5kGy. However, it changes to (400) at 20 kGy and then changes slightly to (222) orientation up to 25 kGy, where the preferable orientations at all used doses are (222) and (400).

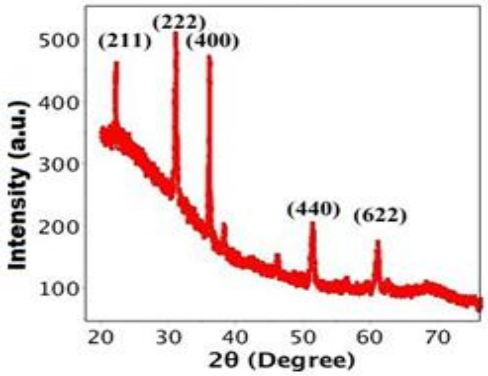


*Fig 1. XRD patterns of the ITO film produced by PLD and irradiated at 5kGy.*

### 3.2 Morphology of ITO thin films:

Atomic force microscopy (AFM) was used to find the morphology and surface roughness of the as-deposited and irradiated ITO thin films as shown in Figs. 2 and 3 respectively.

The roughness increases slightly from 3.1 nm for non-irradiated samples to 5.5 nm on average for doses up to 15 kGy and the surface improved slightly with roughness 4.2 nm at 20 kGy, for the 25kGy the surface became 5.6 nm. By comparing these results with the preferable orientation discussed in the previous section, we conclude that when the orientation is in the direction of (222), the surface is slightly smoother than the (400) direction.

The surface roughness and work function of conducting oxide films deposited on glass substrates are very important to enhance the stability and efficiency of electronic devices. So surface morphology of substrate is directly transferred to the deposited oxides and uneven interface is not desirable for the efficiency and stability of electronic devices based on such oxide films.

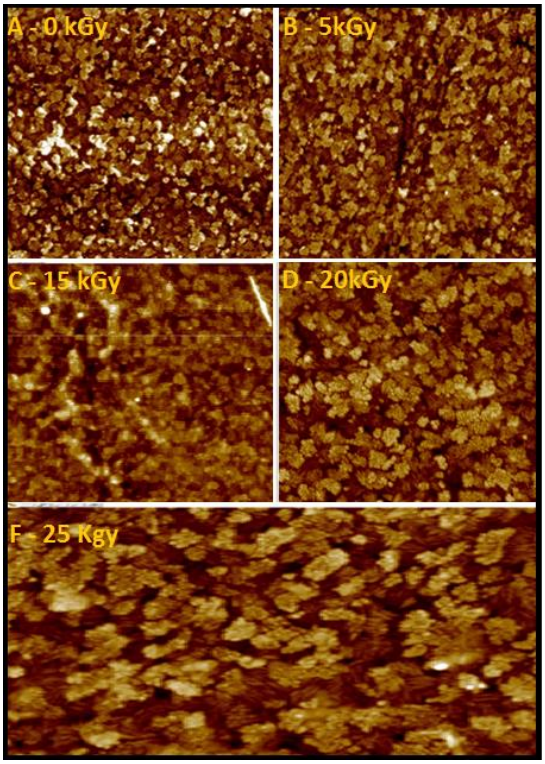


*Figure 2: AFM images of the ITO thin films deposited onto glass substrates irradiated with different gamma ray doses from 5- 25 kGy.*

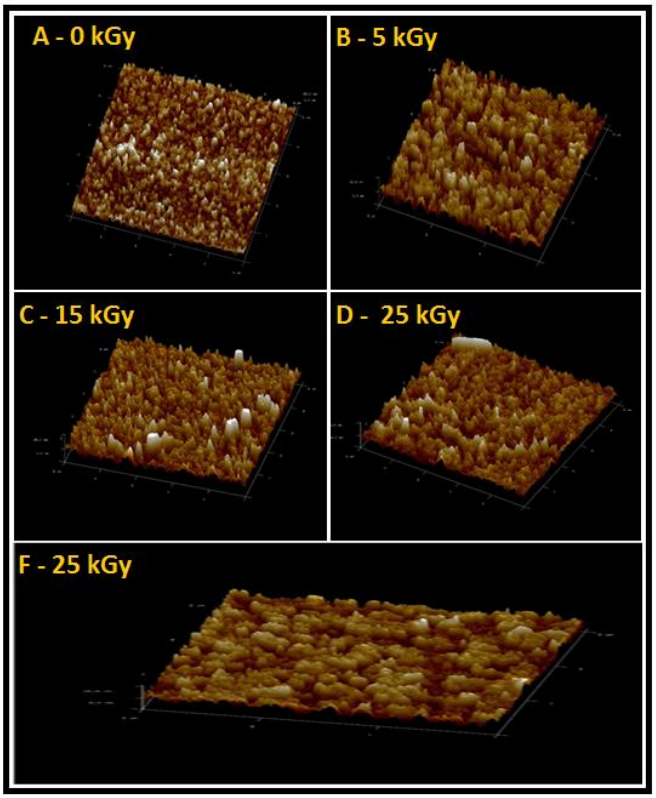


*Figure 3: AFM surface roughness images of the ITO thin films deposited onto glass substrates irradiated with different gamma ray doses from 5- 25 kGy.*

### 3.3 Optical properties

Fig. 4 represents the transmission spectra for the conducting transparent indium tin oxide (ITO) films. The ITO film showed high transmission higher than 90%in the visible range. The absorption spectra of the same samples are shown in figure 5. The transmittance values at the visible (550nm) and infrared (700 nm) regions are shown in table 1, as can be seen, the transmittance of the irradiated ITO films showed a slight decrease from 88% of the as-deposited film to 60 % of the irradiated one at 25kGy in the visible region and from 93% to 86% in the infrared region. The reduction in the transmittance of the irradiated films can be attributed to the increase in the lattice defects and hence the increase of the absorption.

The absorption spectrum of the ITO films in the band gap edge region has been obtained from the optical transmission and reflection measurements at room temperature, the Energy gap was found to be ( $E_g$ = 3.57 eV) for the films deposited at 300 ºC.

A summary of the transmission, roughness and grain size of the as-deposited and irradiated ITO films is represented in Table 1.

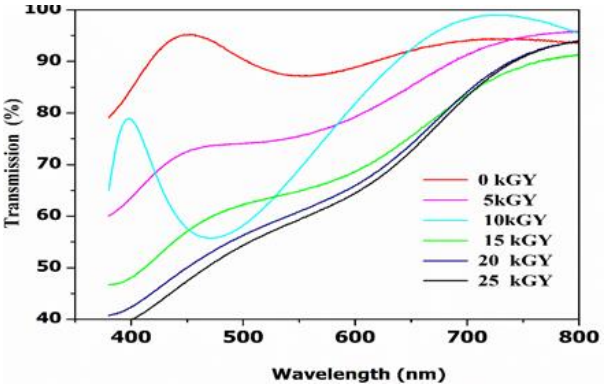


*Figure 4. The variation of transmittance spectra of the ITO films irradiated at various doses.*

*Table 1. Summary of the transmission, roughness and grain size of the as-deposited and irradiated ITO films.*

| Dose (kGy) | T % at 550 (nm) | T % at 700 (nm) | Roughness (nm) | Roughness error (±) | Grain size ($A^o$) |
|---|---|---|---|---|---|
| **0** | 88 | 93 | 3.1 | 0.51 | 262.34 |
| **5** | 76 | 90 | 5.5 | 0.72 | 209.58 |
| **10** | 67 | 97 | 5.4 | 0.63 | 209.81 |
| **15** | 65 | 83 | 5.4 | 0.61 | 199.68 |
| **20** | 61 | 85 | 4.1 | 0.40 | 233.17 |
| **25** | 60 | 86 | 4.2 | 0.23 | 227.70 |

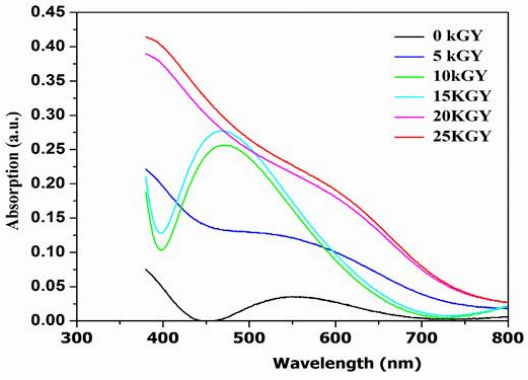


*Figure 5. The variation of the absorption spectra for the ITO films irradiated with various doses.*

The transmittance (T) and reflectance (R) data can also be used to calculate the absorption coefficients (α) of the as-deposited and irradiated ITO films. The absorption coefficient (α) is given by the equation (2):

$$T = (1-R)\exp(-\alpha d) \tag{2}$$

where (d) is the thickness of thin film.

The energy gap can be calculated from the absorption coefficient α using equation (3):

$$I = I_o e^{-\alpha d} \tag{3}$$

where $I$ is the intensity of the transmitted light, $I_o$ is the intensity of incident light and $d$ is the thickness of the film. Energy gap is determined using MOH and Davis' model equation (4) [21] and for direct band gap:

$$\alpha h\nu \propto \sqrt{h\nu - E_g} \tag{4}$$

where $E_g$ is the energy gap, $h\nu$ is the energy of the incident photon. By plotting $(\alpha h\nu)^2$ versus $h\nu$ we can determine the optical band gap by using the linear region, the intersection of the $h\nu$ axis from the plot in Fig. 6.

Table 2 represents the ITO energy gap calculated values for the various doses. As can be seen from figure (7) the energy decreases from ~3.56 eV for the as-deposited ITO film to ~ 3.4 eV for the film irradiated at 25 kGy dose.

*Table 2. Represents the ITO energy gap values for the various doses.*

| Dose | Energy gap (eV) |
|---|---|
| 0( kGy) | 3.57 |
| 5(kGy) | 3.3 |
| 10( kGy) | 3.5 |
| 15( kGy) | 3.5 |
| 20( kGy) | 3.4 |
| 25( kGy) | 3.64 |

### 3.4 Electrical properties of ITO thin films

The sheet resistance $R_s$ of the ITO films was measured using a four-point probe method at room temperature. By assuming that the thickness of the films was uniform, the resistivity ρ of the films was calculated from the simple equation $\rho = R_s\, d$, where d is the oxide film thickness. The

average sheet resistance $R_s$ of each ITO film was measured from three different positions of the film's surface.

The measured resistivity for the as-deposited ITO film (150 nm) at ambient temperature was ($2.10 \times 10^{-3} \Omega \cdot cm$) and it has decreased to $4.2 \times 10^{-4}$ Ω.cm for the gamma irradiated film at 25 kGy.

The low resistivity of ITO may be attributed to the presence of oxygen vacancies and substitutional tin, created during the growth of the film. A summary of the typical properties obtained for the ITO films is represented in Table 3.

*Table 3. Typical properties obtained for the as-deposited ITO oxide films.*

| **Property** | **Results** |
|---|---|
| Transmittance (%) | 94-95 % |
| Optical Band gap (eV) | 3.4 |
| Resistivity(Ω.cm) | $2.10 \times 10^{-3}$ |
| Surface roughness | 5nm |
| Grain sizes | 5-10nm |
| Thickness | 150 nm |
| Substrate temperature ($^0$C) | 300 |

A low resistivity of thin films used in the fabrication of electronic devices is very crucial in the present electronics and photonics applications. However, there is a limitation of increasing the concentration of (Sn) in the ITO films; this is due to the fact that any excessive concentration of (Sn) atoms will lead to a decrease in both carrier density and mobility [17]. As we mentioned earlier, oxygen vacancies are another way to reduce the resistivity. It is known that the resistivity of metal oxides is very sensitive to ionizing radiation and the behaviour of these oxides depend on the type of radiation used.

Annealed films had lower resistivity than the as -deposited ITO ones ranging from 20 $\times 10^{-4}$ Ω·cm to $2.2 \times 10^{-4}$ Ω·cm. Probably due to increase in carrier concentration with the Indium Tin oxides entering into the ITO lattice caused a shift in absorption edge and the average transmittance increased to 85% in the visible region. Resistivities and band gap values for ITO films annealed at various temperatures are shown in Table 4.

*Table 4. Resistivities and band gap values for ITO films annealed at various temperatures.*

| **Resistivity (Ω·cm) $\times 10^{-4}$ for ITO films** | **Annealing temperature ($^0$C)** | **Energy gap. $E_g$ (eV)** |
|---|---|---|
| 20 | 150 | 3.68 |
| 6.4 | 200 | 3.71 |
| 5.2 | 250 | 3.78 |
| 3.6 | 300 | 3.81 |
| 2.6 | 350 | 3.86 |

### 3.5 Energy dispersive X-ray spectroscopy (EDX)

EDX analyses showed that Indium (In), tin (Sn) and oxygen (O) elements in the ITO samples, present in the solid film. The Si, Mg, and Ca elements that are not expected to be in solid

films may probably result from the glass substrates. For the ITO samples, the elemental weights (wt. %) are listed in Table 5.

*Table 5. The elemental weights of the ITO samples.*

| | Oxygen (wt%) | Indium (wt%) | Tin (wt%) |
|---|---|---|---|
| ITO | 0.06 | 0.85 | 0.09 |

## 4. Conclusions

In summary, this paper presents the deposition of conducting and transparent ITO thin films on glass substrates by a pulsed laser deposition process. The AFM of deposited film showed smooth surface and small grain sizes. Average roughness $R_{av}$ of the ITO deposited film was 5 nm for film thickness of (150 nm). The deposited films were dense, and had good adhesion to glass substrates. Annealing the nano-structured film would improve the adhesion of the physical interfaces between the deposited films and the substrate. Annealing the ITO films greatly decreased the resistivity of the films.

Optical spectra measured by a spectrophotometer showed high transmission of the deposited ITO films (90-96%) in the visible range.

Super-smooth and dense films are particularly desirable for solar cell device. The adhesion quality of deposited films onto substrates is directly dependent on the cleanliness of the substrate. These properties would enhance their chemical stability, especially when used in long term operation of a solar cell [22].

Optical spectral property, morphology and the low resistivity ITO film prepared by Pulsed Laser Deposition are maintained even after low dose gamma irradiation.

High transparency, good conductivity and super smooth properties of ITO oxide thin films are particularly desirable in optoelectronic devices particularly when used as an anode in a solar cell, light emitting diode or as protective coatings.

## Acknowledgments

The authors would like to thank Al-Imam Mohammad Ibn Saud Islamic University for the financial support of this project 351225.

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