The role of Tin Oxide Concentration on The X-ray Diffraction, Morphology and Optical Properties of In2O3:SnO2 Thin Films

Bushra A. Hasan, Rusul M. Abdallah
University of Baghdad, College of Science, Department of Physics
bushra_abhasan@yahoo.com

Abstract. Alloys were performed from In2O3 doped SnO2 with different doping ratio by quenching from the melt technique. Pulsed Laser Deposition PLD was used to deposit thin films of different doping ratio In2O3 : SnO2 (0, 1, 3, 5, 7 and 9 % wt.) on glass substrate at ambient temperature under vacuum of 10^-3 bar thickness of ~100nm. The structural type, grain size and morphology of the prepared alloys compounds and thin films were examined using X-ray diffraction and atomic force microscopy. The results showed that all alloys have polycrystalline structures and the peaks belonged to the preferred plane for crystal growth were identical with the ITO (Indium – Tin – Oxide) standard cards whereas another peaks were observed belonged to SnO2 phase. The structures of thin films was also polycrystalline, and the predominate peaks are identical with standard cards ITO. On the other side the prepared thin films declared a reduction of degree of crystallinity with the increase of doping ratio. Atomic Force Microscopy AFM measurements showed the average grain size and average surface roughness exhibit to change in systematic manner with the increase of doping ratio with tin oxide. The optical measurements show that the In2O3 :SnO2 thin films have a direct energy gap \( E_g^{opt} \) in the first stage decreases with the increase of doping ratio and then get to increase with further increase of doping ration, whereas reverse to that the optical constants such as refractive index \( (n) \), extinction coefficient \( (k) \) and dielectric constant \( (\varepsilon_r, \varepsilon_i) \) have a regular increase with the doping ratio by tin oxide and then decreases.

Keywords: thin films of In2O3:SnO2, XRD, AFM, PLD, Optical Properties
1. Introduction

Indium tin oxide (ITO) is well-known as transparent conducting oxide (TCO) have a wide band gap (~3.7eV). n-type semiconductor and it posses a low electrical resistivity [1-3]. Thin Films ITO is transparent but it have color when it is in bulk form bulk. The behavior of ITO similar to meats due to high conductivity, thin films exhibit to show high reflectivity in the near infrared region [4-5]. The lowest electrical resistivity and hence highest transparency transparency in the visible range suitable for many application can provided from ITO films. It is well known that the unique electrical and optical properties of ITO are depend upon the deposition method which can be modified by controlling the deposition parameters. There are many deposition techniques to obtain high quality ITO films such as pulsed laser deposition[6], sol-gel [7], RF and DC sputtering [8-9]. In the present work, ITO films were prepared by PLD on glass substrate and the, structural,morphology and optical properties of ITO films were examined.

2. Experimental Part

The alloy of In$_2$O$_3$:SnO$_2$ is were prepared by mixing the appropriate amount of high purity (99.99)indium oxide and tin oxide. An electronic balance with accuracy (10$^{-4}$gm)was used to weight the powder of the matrix material (Indium oxide) and the dopant material (tin oxide). A quartz ampoule with length and internal diameter ~ 25 cm and ~ 8 mm respectively was used to heat the material to 1000°C and left at this temperature for 8 hours. In order to obtain homogeneous alloy the ampoules are constantly agitated. Cleaning glass slides substrates were used which were subjected to several steps to remove any contamination such as dust, oily material, grease and some oxides using soap solution, then the glass slides were placed in a clean beaker containing distilled water and with ethanol solution then the glass slides were dried by blowing air. Thin films were deposited using pulsed laser deposition technique under vacuum of (10$^{-3}$ Torr). Thin films were obtained by focusing Nd:YAG (Huafai Tongda Technology–Diamond-288 pattern EPLS) Q-switching operating type, wavelength1064 /532) nm, repetition frequency (1, 2, 3,4,5,6), with applied voltage 220 volt. The incoming laser beam from a window will fall on a target make at angle 45° with it .X-ray diffraction (XRD) was used to check the structures of the prepared alloys and thin films. In the present work x-ray diffractometer type (Miniflex II), with Cu-K$_\alpha$ x-ray tube ($\lambda = 1.54056$ Å) is used. The morphology is obtained using atomic force microscopy AFM. UV/Visible spectrophotometer type SP-8001 was used to study the optical properties of In$_2$O$_3$:SnO$_2$ films in the wavelength range 300-1100 nm. The optical parameters optical energy gap and the optical constants which imply the refractive index (n), extinction coefficient (k) and real and imaginary parts of dielectric constants($\varepsilon_r,\varepsilon_i$) were measured using the transmittance and absorbance as function of wavelength using the following equation respectively:

The refractive index value can be calculated from the formula :

$$n = \sqrt{\frac{4R}{(R-1)^2} - k^2} - \frac{(R + 1)}{(R - 1)} \text{........................................(1)}$$

Where R is the reflectance, and can be expressed by the relation [10]:
\[ R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \] ..................................................(2)

The extinction coefficient is given by the relation[11]:

\[ k = \frac{\alpha \lambda}{4\pi} \] ..................................................(3)

Where \( \lambda \) is the wavelength of the incident radiation which is related to the absorption coefficient \( (\alpha) \) which define as the reduction of light intensity per unit length, \( (\alpha) \) is estimated from the equation:

\[ \alpha = 2.303 \frac{A}{t} \] ..................................................(4)

Where \( A \) is the absorbance and \( t \) is the sample thickness. The film thickness was measured by the Tolanasky interference method with an accuracy of \( \pm10 \) nm[12]. The real and imaginary part of dielectric constant can be measured by using the following equations [13]:

\[ (n - ik)^2 = \varepsilon_r - i\varepsilon_i \] ..................................................(5)

Where

\[ \varepsilon_r = n^2 - k^2 \] ..................................................(6)

and 

\[ \varepsilon_i = 2nk \] ..................................................(7)

3. Results and Discussion

'Figure 1' shows the X-ray diffraction patterns for \( \text{In}_2\text{O}_3 \) doped with different \( \text{SnO}_2 \) concentration powders. All the peaks of XRD patterns were analyzed and indexed using JCDD data base and compared with standards. All the ITO films are polycrystalline with body-centered cubic structure of \( \text{In}_2\text{O}_3 \). As can be seen from Fig. 1, the (222) peak is the most prominent, and the weak peaks are the (211), (400), and (622) planes. The similar result was reported previously [14]. Intensity of (222),(321),(400),(440), and (622) planes which are the dominate planes of the ITO become more prominent as \( \text{SnO}_2 \) was introduced to the host material, i.e. with increase of wt.% of \( \text{SnO}_2 \) to 1% as shown in same figure which indicates the improvement of crystallinity of the compound [15]. The intensity of the same planes decreased with further increase of \( \text{SnO}_2 \) concentration up 5%, which indicates the crystallinity deformation of the compound. The crystallinity of the compound increases with the increase of doping ratio from 5 to 9%. The grain size of the predominant plane increased
from 22.9nm to 48.1 nm as SnO$_2$ was added to In$_2$O$_3$, while the grain size was reduced with the continuous addition of SnO$_2$ up 5%. Then the grain size increases from with further increase of doping ratio and reach steady value at high doping ratio. Indeed the grain size increases 40.1 to 45.1 nm as when the doping ration increases from 5 to 9%.
Figure 1: shows the XRD patterns of the pure In$_2$O$_3$ and doped with different concentrations of SnO$_2$ powder.

The X-ray diffraction patterns of pure In$_2$O$_3$ and In$_2$O$_3$:SnO$_2$ thin films deposited on glass substrates prepared by the PLD technique with different doping concentrations of SnO$_2$ (1, 3, 5, 7 and 9) wt.% are shown in Fig. 2. The XRD diffractograms revealed that In$_2$O$_3$:SnO$_2$ films become polycrystalline when deposited at room temperature substrate and crystallized in a cubic bixbyite structure (In$_2$O$_3$) [16-17]. The peaks observed for (2θ = 30.4°) are associated to the plane (222) and other planes related to the ITO composite (400)(440) and (622). The preferential growth of the In$_2$O$_3$:SnO$_2$ films is the (222) plane and this orientation is dependent on the deposition conditions [17]. In Table 1 it can be noticed the structural parameters: 2θ, $d_{hkl}$, (hkl), FWHM and G.S of deposited pure and In$_2$O$_3$ films at different SnO$_2$ doping ratio (1, 3, 5, 7 and 9) %. In general, there was an increase in full width of half maximum FWHM with the increase of the doping ratio i.e. decrease of the crystalline size as the SnO$_2$ was introduced to the In$_2$O$_3$, but then the FWHM decreased (crystalline size increased) with the increase of doping ratio up to 3 %, (increasing the doping ratio more caused a decrease of crystalline size). It can be noticed for the doping ratios (3%, 5%, 7%) the appearance of the peaks related to SnO$_2$ located at (2θ = 26.4°, 33.78°) corresponds to the diffractions planes (110), (101). Theses peaks disappeared at high doping ratio, i.e. 9% SnO$_2$ indicates to the decrease of crystallization degree as indicated from the decrease of grain size at high doping ratio.

Table 1: Illustrates the Structural parameters: 2θ, $d_{hkl}$, (hkl), FWHM and G.S of deposited In$_2$O$_3$ films at different SnO$_2$ doping ratio (1, 3, 5, 7 and 9) %.

| % SnO$_2$ | 2θ (Deg.) | FWHM (Deg.) | $d_{hkl}$ Exp.(Å) | G.S (nm) | $d_{hkl}$ Std.(Å) | Phase | hkl |
|-----------|-----------|-------------|-------------------|----------|-------------------|-------|-----|
| Pure      | 30.5088   | 0.2892      | 2.9277            | 28.5     | 2.9214            | Cub. In$_2$O$_3$ | (222) |
| 1%        | 30.4767   | 0.3918      | 2.9307            | 21.0     | 2.9214            | Cub. In$_2$O$_3$ | (222) |
| 3%        | 26.5238   | 0.1750      | 3.3579            | 46.6     | 3.3503            | Tet. SnO$_2$    | (110) |
|           | 30.5410   | 0.3049      | 2.9247            | 27.0     | 2.9214            | Cub. In$_2$O$_3$ | (222) |
| %   | 33.8190 | 0.1264 | 2.6483 | 65.7  | 2.6441 | Tet.SnO$_2$ | (101) |
|-----|---------|--------|--------|-------|--------|-------------|-------|
| 5%  | 26.4596 | 0.2250 | 3.3659 | 36.3  | 3.3503 | Tet.SnO$_2$ | (110) |
|     | 30.4446 | 0.3649 | 2.9338 | 22.6  | 2.9214 | Cub. In$_2$O$_3$ | (222) |
|     | 33.7868 | 0.1928 | 2.6508 | 43.1  | 2.6441 | Tet.SnO$_2$ | (101) |
|     | 35.3294 | 0.1782 | 2.5385 | 46.8  | 2.5300 | Cub. In$_2$O$_3$ | (400) |
|     | 37.9004 | 0.1585 | 2.3720 | 53.0  | 2.3853 | Cub. In$_2$O$_3$ | (330) |
|     | 50.9480 | 0.1588 | 1.7910 | 55.4  | 1.7890 | Cub. In$_2$O$_3$ | (440) |
|     | 60.6856 | 0.1788 | 1.5248 | 51.5  | 1.5256 | Cub. In$_2$O$_3$ | (622) |
| 7%  | 26.5560 | 0.2350 | 3.3539 | 34.7  | 3.3503 | Tet.SnO$_2$ | (110) |
|     | 30.5088 | 0.3744 | 2.9277 | 22.0  | 2.9214 | Cub. In$_2$O$_3$ | (222) |
|     | 33.8190 | 0.2571 | 2.6483 | 32.3  | 2.6441 | Tet.SnO$_2$ | (101) |
|     | 35.3937 | 0.1892 | 2.5340 | 44.1  | 2.5300 | Cub. In$_2$O$_3$ | (400) |
|     | 37.9646 | 0.1607 | 2.3681 | 52.3  | 2.3853 | Cub. In$_2$O$_3$ | (330) |
|     | 50.9480 | 0.1590 | 1.7910 | 55.3  | 1.7890 | Cub. In$_2$O$_3$ | (440) |
|     | 60.7177 | 0.1801 | 1.5241 | 51.1  | 1.5256 | Cub. In$_2$O$_3$ | (622) |
| 9%  | 30.5731 | 0.3822 | 2.9217 | 21.5  | 2.9214 | Cub. In$_2$O$_3$ | (222) |
|     | 35.4580 | 0.1928 | 2.5296 | 43.3  | 2.5300 | Cub. In$_2$O$_3$ | (400) |
|     | 51.0123 | 0.1599 | 1.7889 | 55.0  | 1.7890 | Cub. In$_2$O$_3$ | (440) |
|     | 60.6213 | 0.1858 | 1.5263 | 49.5  | 1.5256 | Cub. In$_2$O$_3$ | (622) |
Fig. 2: X-ray diffraction patterns of deposited pure In$_2$O$_3$ and doped with SnO$_2$ films in different ratio (1, 3, 5, 7, and 9) %.

4. Atomic Force Microscopy Analysis (AFM)

The surface morphologies of In$_2$O$_3$:SnO$_2$ films are investigated using Atomic Force Microscopy (AFM). Fig. 3 shows their surface morphologies pictures obtained from AFM. The obtained data are listed such as grain size and RMS roughness and peak–peak value are listed in Table 2. This Table illustrates an increment in average diameter with doping ratio 1% then go down in 3% and increase at (5,7)% then go down. The roughness of the films shows increment by increasing doping but go down at 7%, while the doped film by 9% SnO$_2$ have maximum values of roughness and peak–peak value.
Table 2: AFM parameters for pure and doped \( \text{In}_2\text{O}_3 \) at different \( \text{SnO}_2 \) ratios deposited at room temperature.

| % \( \text{SnO}_2 \) | Average diameter (nm) | Average roughness (nm) | Peak-peak (nm) |
|-------------------|-----------------------|------------------------|---------------|
| 0                 | 52.48                 | 0.458                  | 2.21          |
| 1                 | 100.22                | 14.6                   | 62.9          |
| 3                 | 79.12                 | 22                     | 102           |
| 5                 | 87.57                 | 24.3                   | 109           |
| 7                 | 105.59                | 11.5                   | 109           |
| 9                 | 90.95                 | 26.8                   | 112           |
Figure 3 AFM images for pure In$_2$O$_3$ thin film and In$_2$O$_3$ doped with SnO$_2$ in different doping ratio.

5. The Optical Properties of In$_2$O$_3$:SnO$_2$ Films

The optical properties of pure In$_2$O$_3$ and doped with SnO$_2$ at different ratio of (1, 3, 5, 7, and 9) wt. % films deposited on glass at room temperature have been determined using UV-visible near infrared region (300-1100) nm. The energy gap and optical constants have determined using the transmittance and the absorbance spectrum. Fig(4) transmittance spectra pure In$_2$O$_3$ and doped with different concentrations of SnO$_2$. In general, we can observe from Fig.4 that transmittance is inversely proportional to concentration of tin oxide; hence the transmission decreases with increasing SnO$_2$ concentration ratio until (7%) and then the transmission increases, which result from the increment of the reflection and absorption, this giving rise to shift the absorption edge to longer wavelength (red shift
but the continues addition of tin oxide to the host material lead to shifts absorption edge toward shorter wavelength (higher energies) the behavior accompanied the increment of tin oxide concentration is related with reduction of grain size which in turn increases the lattice parameters and hence wide the energy gap as we seen in the next section.

Figure 4: The transmittance as a function of wavelength for pure In$_2$O$_3$ and doped with different concentrations of SnO$_2$ thin films deposited at R.T.

6. The Optical Energy Gap

The type of the optical transition as well as the optical energy gap values $E_{opt}^{gap}$ for thin films have been determined by applying the empirical Tauc equation. The plot diagram is shown in figure 5. Between $(\alpha hv)^{1/r}$ and $(hv)$ were $r=1/2$ for allowed direct transition. The extrapolation of the portion at $[(\alpha hv)^{1/r} = 0]$ gives the optical energy gap is shown in Fig.5. It can be observe that direct band gap for pure In$_2$O$_3$ films is 3.6 eV. The energy gap was decreasing with increase of doping concentration, indeed the optical energy gap decreases from 3.35 to 3.08 eV as the doping ratio increases from 1% to 7%, this result in agreement with the energy gap of ITO. This reduction of energy gap values attributed to creation of new states of donor levels within the energy gap near the conduction band by the impurity addition to the host material, take place as a donor levels within the energy gap near the conduction band. Thus, causes the visual decrease of energy gap such that the material will absorb photon of lower energy. The optical energy gap decrease by increasing concentration of SnO$_2$ in the films, can see it in the figures and Table 2. The optical energy gap return to increase with further increase of
doping ratio, indeed $E_g$ increases to 3.23 eV at SnO$_2$ 9%. This due to compensate the donor stated which were prohibited initially.

![Graph](image)

**Figure 5**: The variation of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for pure and doped In$_2$O$_3$ films with different concentrations of SnO$_2$ deposited at R.T.

The plot of the refractive index as a function of wavelength in the range (300-1100) nm for pure In$_2$O$_3$ and In$_2$O$_3$:SnO$_2$ thin films with different concentration of SnO$_2$ is shown in figure (6). The refractive index calculated according to the equation (3). It can be noticed from these figures that pure $n$ at $\lambda=500$nm of In$_2$O$_3$ is 1.68 increases with increasing of the concentration of SnO$_2$. Indeed $n$ increases to 2.644 with the increase of doping ratio from 0 to 7% while $n$ decrease to 2.292 at 9% doping ratio. The increase of $n$ attributed to the reduction of transmittance giving rise to high opaque material while the reduction of $n$ is related to the inverse manner. The values of refractive index are given in table (2)
Figure 6: Refractive index as a function of wavelength for pure \( \text{In}_2\text{O}_3 \) and doped \( \text{In}_2\text{O}_3 \) films with different concentrations of \( \text{SnO}_2 \) deposited at R.T.

Variation of the extinction coefficient as a function of wavelength for undoped and doped \( \text{In}_2\text{O}_3 \) films with different concentrations are shown in Fig. (7). It is evident from this figure and Table (2) that the extinction coefficient exhibit to change in non regular manner with the increase of doping concentration. Indeed \( k \) at \( \lambda = 500 \text{nm} \) for pure \( \text{In}_2\text{O}_3 \) is 0.026 increases to 0.163 as the doping concentration increases from 0 to 7% but the \( k \) return to decreases to 0.078 at 9% doping ratio. The increase and the decrease of \( k \) is related with increase and decrease of absorption coefficient.

Figure 7: Extinction coefficient as a function of wavelength for pure and doped \( \text{In}_2\text{O}_3 \) thin films with different concentrations of \( \text{SnO}_2 \) deposited at R.T.
The plot diagram of the real ($\varepsilon_r$) and imaginary ($\varepsilon_i$) parts of the dielectric constant values as a function of wavelength in the range (300–1100)$\mu$m for In$_2$O$_3$:SnO$_2$ films deposited at R.T with different concentration of SnO$_2$, are shown in Figs (8 and 9). Real part of dielectric constant $\varepsilon_r$ exhibits to change in similar manner to that of the refractive index because of the smaller value of $k^2$ compared with $n^2$, while imaginary part of dielectric constant $\varepsilon_i$ has similar trend to that of extinction coefficient $k$. It can be observed that the real dielectric constant ($\varepsilon_r$) for pure equal to 2.83 increased to 4.68 when SnO$_2$ concentration changed from 0 to 7% and then return to decreased to 2.64 with further increase of dopant material as shown in Table(3), and It is found that $\varepsilon_i$, increased with increasing of SnO$_2$ concentration and then return to fall with further increase of doping concentration. The behavior of $\varepsilon_r$ and $\varepsilon_i$ can be explained in similar ways to that of $n$ and $k$.

Figure.8: Variation of $\varepsilon_r$ with wavelength of for pure and doped In$_2$O$_3$ thin films with different concentrations of SnO$_2$ deposited at R.T
Figure 9: Variation of $\varepsilon_r$ with $\lambda$ of pure In$_2$O$_3$ and In$_2$O$_3$: SnO$_2$ thin films at different concentration of SnO$_2$ deposited at R.T.

Table (3) Values of $E_g$ and optical constants at $\lambda=500$ nm for pure and doped In$_2$O$_3$ with SnO$_2$ thin films with different doping concentrations (1, 3, 5, 7 and 9)%.

| %SnO$_2$ | T%  | $\alpha$ (cm$^{-1}$) | k    | n    | $\varepsilon_r$ | $\varepsilon_i$ | $E_g$ (eV) |
|----------|-----|----------------------|------|------|-----------------|-----------------|-----------|
| 0        | 87.90 | 6448              | 0.026 | 1.684 | 2.836           | 0.086           | 3.60      |
| 1%       | 72.94 | 15776             | 0.063 | 2.152 | 4.627           | 0.270           | 3.35      |
| 3%       | 62.51 | 23491             | 0.094 | 2.409 | 5.796           | 0.451           | 3.25      |
| 5%       | 52.54 | 32184             | 0.128 | 2.583 | 6.654           | 0.662           | 3.15      |
| 7%       | 44.15 | 40878             | 0.163 | 2.644 | 6.963           | 0.860           | 3.08      |
| 9%       | 67.60 | 19576             | 0.078 | 2.292 | 5.245           | 0.357           | 3.23      |

7. Conclusions
1- The prepared In$_2$O$_3$:SnO$_2$ compounds and thin films are polycrystalline with a cubic structure with a preferential orientation along (222) direction.
2- The grain size, the average diameter and average roughness increases as tin oxide increases added to hast material but then reduced and the increases to reach steady state.
3- Maximum diameter and average roughness obtained are 105.59 and 26.8 nm respectively.
4- The increasing of tin oxide concentration made all the prepared thin films more opaque throughout increasing the packing density and shifting the absorption edge to lower energies.
5- Increasing of tin oxide content in the prepared samples creates new states in the band gap which consequently giving rise to the visual decrease of the optical energy gap.
The transmittance and the optical energy increases, while the optical constants decreases when compensation take place at high tin oxide concentration i.e. 9%.

References
[1] N.G. Pramod, S.N. Pandey, and P.P. Sahay, Journal of Thermal Spray Technology, Volume 22(6) August (2013), 1035.
[2] Kyung-Soo Park, Young-Jin Choi, Jin-Gu Kang, Yun-Mo Sung and Jae-Gwan Park, Nanotechnology, 22 (2011) 285712 (5pp)
[3] A. Ambrosini, A. Duarte, K.R. Poeppelmeier, M. Lane, C.R. Kannewurf, T.O. Mason, J. Solid State Chem. 153 (2000) 41.
[4] S.H. Brewer, S. Franzen, J. Phys. Chem. B 106 (2002) 12986
[5] O.N. Mryasov, A.J. Freeman, Phys. Rev. B (2001) 6423, Art. No.233111.
[6] J. B. Choi, J. H. Kim, K.A. Jeon, S. Y. Lee, Mat. science and Eng. B102 (2003) 376-379.
[7] T.F. Stoica, V.S. Teodorescu, M.G. Blanchin, M. Gortner, M. Losurdo, M. Zaharescu, Mater. Sci. Eng. B101 (2003)222.
[8] L. Kerkache, A. Layadi, A. Mosser, journal of Alloys and Compounds 485(2009) 46-50
[9] M. Nisha, M.K. Jayaraj, Appl. Surf. Sci 255(2008)1790-1795.
[10] J.L. PANKOV, Optical Process in Semiconductors (London 1971).
[11] W. KLOPFFER, Introduction to Polymer Spectroscopy (SpringerVerlag, 1984).
[12] 9-T. Matsushita, A.Suzuki, M.Okuda, H.Naitoh and T.Nakau, Jap.J.App1.Phys., 22, 762 (1983).
[13] M. ALENSO, J. VENN, Physics, 2nd ed. (JohnWiley, 1971).
[14] J. George, C.S. Menon, Surf. Coat. Technol. 132, 45–48 (2000)
[15] H.L. Ma, D.H. Zhang, P. Ma, S.Z. Win, S.Y. Li, Thin Solid Films, 263, 105–110 (1995)
[16] Dewei Chua, Yu-Ping Zeng, Dongliang Jiang, Yoshitake Masuda, Sensors and Actuators B 137 (2009) 630–636.
[17] N.G. Patel, P.D. Patel, V.S. Vaishnav, Sensors and Actuators B 96 (2003) 180–189.