Morphological and Optical Properties of In_2O_3: Sn Thin Films Deposited by Spray Pyrolysis

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Received: 20 September 2017 Accepted: 13 December 2017

Abstract

The morphological and optical properties of indium tin oxide (ITO) thin films have been studied in this paper. Tin doped indium oxide thin films were deposited successfully on glass substrates at (450 ± 10)℃ for various tin doping (0, 5, 10, 15, 20) % by spray pyrolysis technique. Atomic force microscopy has been used to study the surface morphology of In_2O_3: Sn thin films. The optical properties were calculated by the absorbance and transmittance spectra in the wavelength interval (300-1000) nm. The optical constants such as (absorption coefficient, refractive index, extinction coefficient, real and imaginary parts of dielectric constant and optical conductivity) have been calculated and discussed.

Keywords: Indium tin oxide, Film morphology, Optical properties, Spray pyrolysis.

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Morphological and Optical Properties of $In_2O_3:Sn$ Thin Films Deposited by Spray Pyrolysis

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الخصائص البصرية والطوبوغرافية لأغشية أوكسيد الانديوم المشوبة بالقصدير الرقيقة المحضرة بطريقة التحلل الكيميائي الحراري

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الخلاصة

في هذا البحث تمت دراسة الخصائص الطوبغرافية والبصرية لاغشية اوكسيد الانديوم المشوبة بالقصديرحيث تم بنجاح تحضير هذه الاغشية على قواعد من الزجاج عند درجة حرارة (450 ± 10)℃ ولنسب مختلفة من التشويب بالقصدير % (0, 5, 10, 15, 20) بواسطة تقنية التحلل الكيميائي الحراري. تم دراسة الخصائص الطوبوغرافية لسطح الاغشية بواسطة مجهر القوة الذرية. اما الخصائص البصرية فقد تمت دراستها بتسجيل طيفي النفاذية والامتصاصية ولمدى اطوال موجية يتراوح nm (300-1000). كما ان الثوابت البصرية كمعامل الامتصاص ومعامل الانكسار ومعامل الخمود والجزء الحقيقي والخيالي لثابت العزل والتوصيلية البصرية قد تم حسابها ومناقشتها.

الكلمات المفتاحية: أوكسيد الانديوم المشوب بالقصدير، طوبغرافية الأغشية، الخصائص البصرية، التحلل الكيميائي الحراري.

Introduction

Indium tin oxide (ITO) thin film is an electrically conductive material that is highly transparent in the range of visible wavelength. It is a well-known that indium tin oxide thin film is n-type semiconductor with a direct band gap >3.5 eV. Here tin acts as a cationic dopant in the Indium lattice and as a substitute on the Indium sites to bind with the interstitial oxygen [1]. Indium tin oxide thin films have been widely applied in optoelectronics, flat panel displays, electroluminescence, organic light emitting diodes (OLED) and solar cells [2-6]. A variety of deposition techniques have advantages and disadvantages such as RF, reactive electron beam (EB) and DC magnetron, sputtering and spray pyrolysis [7-10] the jet nebulizer spray pyrolysis has a noticeable advantage; it is non-vacuum technique for large area applications and a low cost and can produce high quality film with low precursor volume [11].

Experimental

Tin doped indium oxide (ITO) films were deposited on glass substrates for different tin doping (0, 5, 10, 15, 20) % by chemical spray pyrolysis method under ambient atmosphere. The spray solution prepared from Indium Chloride ($InCl_3$) dissolved in distilled water at (0.05M) concentration and Stannic Chloride ($SnCl_4.5H_2O$) was added into the solution as a dopant, two drops of hydrochloric acid (HCl) were added to the (100ml) solution to increase the solubility of the compounds. Other deposition conditions such as substrate temperature (450 ± 10)℃, Carrier gas Nitrogen (N_2) under ambient atmosphere, Gas pressure $(3\ bar)$, Spraying rate $(5 - 6\ ml/\text{min})$, the nozzle distance from the substrate equal to 30 cm and, concentration of solution (0.05 M), the spraying time period is 8 s with 80 s wait between the steps of spraying. The surface morphologies and root-mean square (RMS) roughness of the ITO thin films were investigated using (SPM AA3000 Angstrom Advanced Inc. made in USA). Optical properties were studied in the wavelength interval of (300 - 1000) nm by using ultraviolet - visible spectrophotometer (Shimadzu UV-1650 PC).

Results and discussion

The surface morphology of ITO thin films for various tin contents (0, 5, 10, 15, 20) % prepared on glass substrates at (450 ± 10)℃ have been investigated by atomic force microscopy. The three-dimensional topographic view of AFM images for In_2O_3: Sn thin films are illustrated in figures [1-5]. The films show a homogenous exterior surface and this means that a large number of grains are connected and lined up regularly on the surface of the film without holes and no cutoff grain in the film structure. The atomic force microscopic study shows that the root mean square roughness of tin doped indium oxide thin films decreased with increasing Sn- content in the films from (4.68 nm) at (Sn = 0 %) to (2 nm) at (Sn = 20 %) as shown in figure (6) due to the rearrangement of atoms in the films and reduction in the vacancy defect. This indicates that the surface topography of the film has high surface uniformity and good crystalline uniformity. Such a surface is used in applications of semiconductor devices such as solar cells and photodetector.

The grain size of tin doped indium oxide prepared on glass substrates by spray pyrolysis technique has been measured from AFM images and listed in table (1). In our study, the measured grain size (D) of In_2O_3: Sn thin films are (107, 95, 96, 100, 77) nm for tin- doping equal to (0, 5, 10, 15, 20) % respectively. The nanostructure film occurs when the grain size is less than 100 nm. It can be noted that the grain size of indium tin oxide changed from microstructure to nanostructure after adding tin atoms as a dopant in the films. The roughness and the grain size of the films are dependent on the content of the dopant.

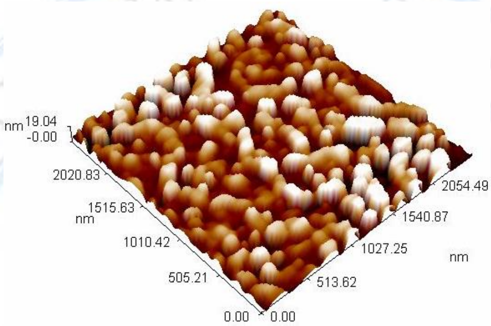

Figure 1: AFM images of In_2O_3 thin film

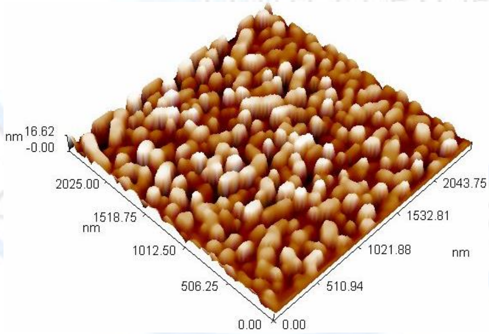

Figure 2: AFM images of ITO film (Sn=5%)

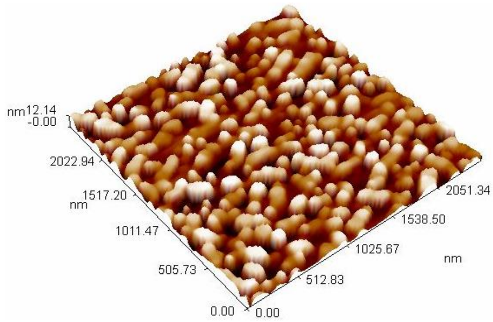

Figure 3: AFM images of ITO film (Sn=10%)

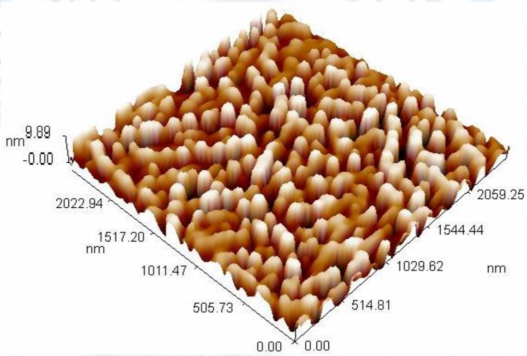

Figure 4: AFM images of ITO film (Sn = 15%)

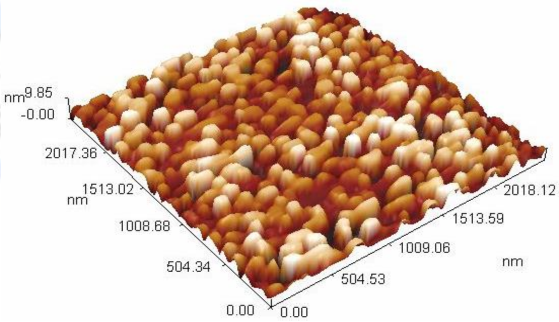

Figure 5: AFM images of ITO film (Sn = 20%)

DOI : http://dx.doi.org/10.24237/djps.1402.418B
P-ISSN: 2222-8373
E-ISSN: 2518-9255

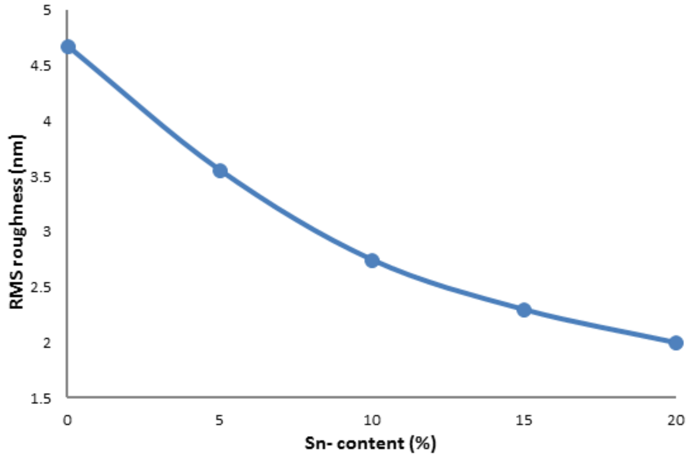

Figure 6: Variation of film roughness of ITO vs. tin-content

Schedule 1: RMS roughness, Grain size (D) and peak-peak height of ITO thin films

Sn-doping (%)	RMS roughness (nm)	Grain size (nm)	Peak-Peak height (nm)
0	4.68	107	19
5	3.56	95	16.6
10	2.75	96	12
15	2.3	100	9.85
20	2	77	9.85

Figures [7-11] shows the granularity distribution of tin doped indium oxide thin films deposited on glass substrates at (450 ± 10)°C by spray pyrolysis method under ambient atmosphere. It can be noted from the following figures that the distribution of the grains be more homogeneous after adding tin atoms as a dopant in the films, reach out to high homogeneous distribution in the size of grains at Sn- doping equal to 20 %. In other words, the granularity distribution of ITO grains becomes more homogeneous with increasing Sn- content in the films.

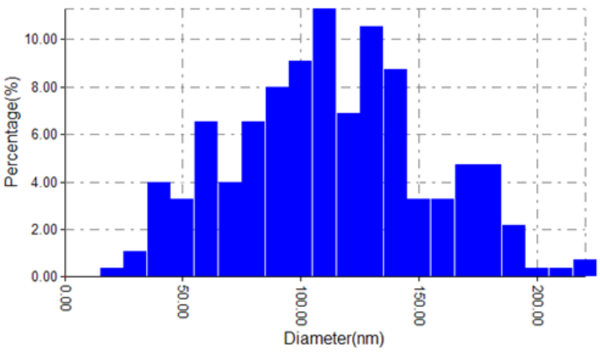

Figure 7: Granularity distribution of In_2O_3 film

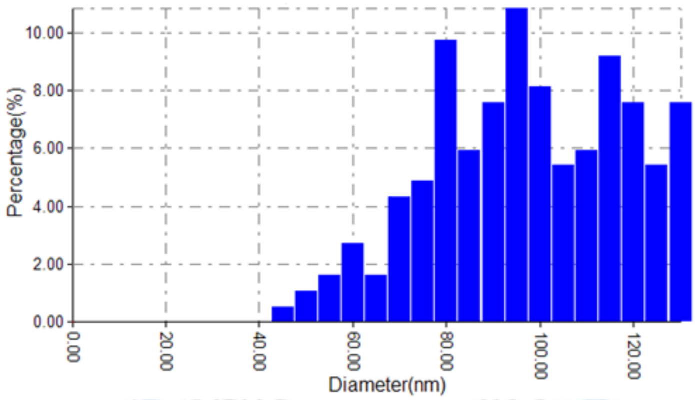

Figure 8: Granularity distribution of ITO film (Sn=5%)

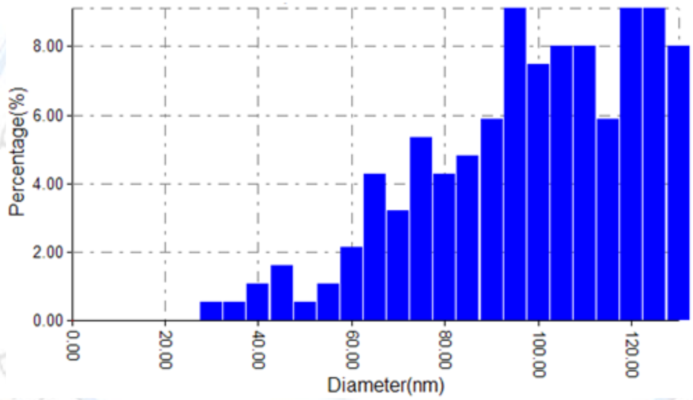

Figure 9: Granularity distribution of ITO film (Sn=10%)

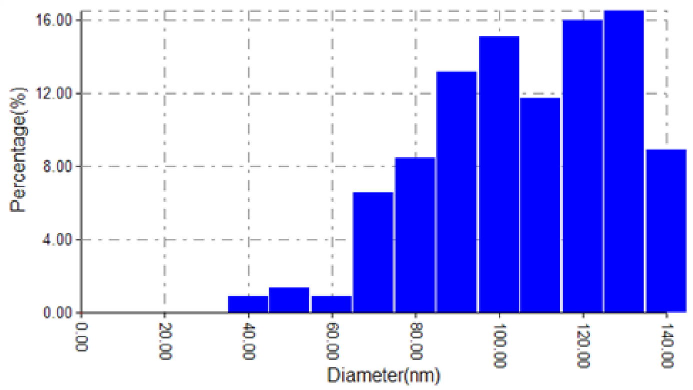

Figure 10: Granularity distribution of ITO film (Sn=15%)

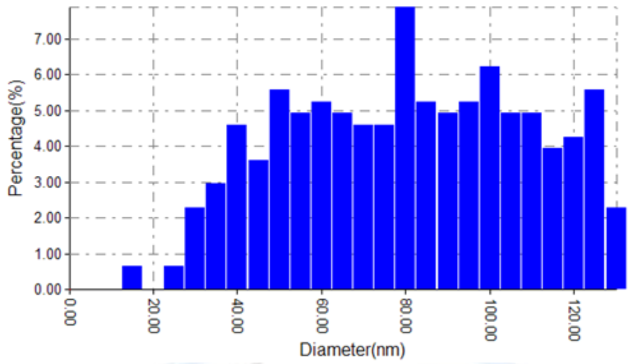

Figure 11: Granularity distribution of ITO film (Sn=20%)

The optical properties of indium tin oxide thin films deposited on glass substrates at (450 ± 10)℃ for various tin concentrations 0, 5, 10, 15, 20 % by spray pyrolysis technique have been studied by the room temperature transmission and absorption spectra.The absorbance spectra **(A)** of In_2O_3: Sn thin films deposited on glass substrates at different tin doping measured at room temperature have been shown in figure (12). Absorbance spectra of ITO thin films reveal that the films have low absorbance in the visible and near infrared regions, but the absorbance of the ITO films in the ultraviolet region is high. The absorbance of indium tin oxide thin films decreases with increasing tin content in the films up to 5 %, thereafter, it increases with increasing tin content as shown in figure (12). This may be due to impurities and the homogeneity of the film.

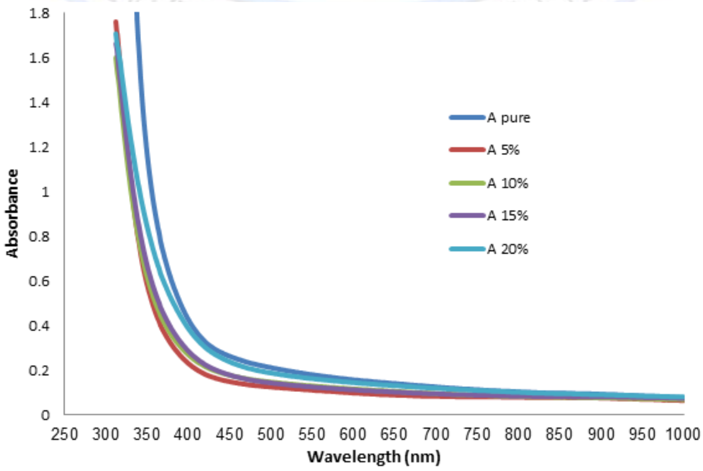

Figure 12: Absorbance spectra of In_2O_3: Sn thin films for various tin content

The transmittance spectra **(T)** of ITO thin film are shown in figure (13). It is observed that the transmittance of the In_2O_3: Sn thin films increases with increasing tin doping up to Sn = 5 %. Then, it decreases gradually with increasing tin content at Sn = 10, 15, 20 %. The transmittance of ITO thin film at visible region (550 nm) has been found (66, 77, 74, 73, 69) % for the tin doping (0, 5, 10, 15, 20) % respectively. When a high impurity is added, the transmittance of ITO thin film decreases due to increased photon scattered by crystal defects created by impurities, which is in agreement with the reports [12-14]. The optical characterization of tin doped indium oxide depends on the uniformity and roughness of the ITO film surface.

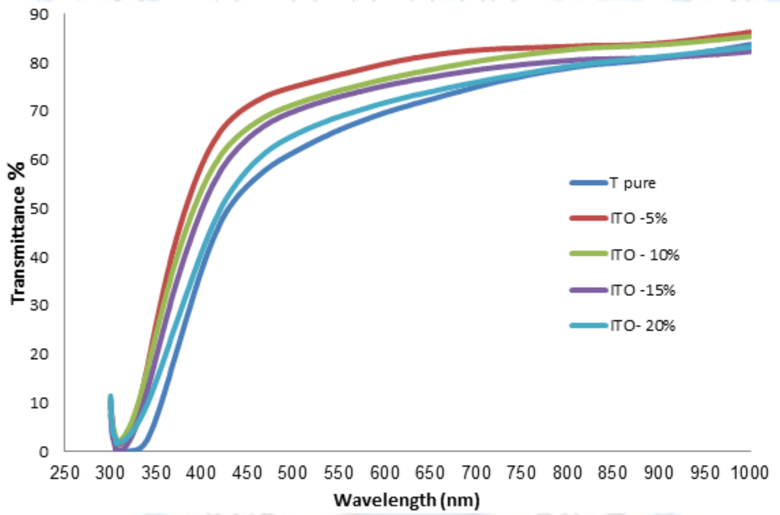

Figure 13: Transmittance spectra of In_2O_3: Sn thin films for various tin content

The absorption coefficient **(α)** is defined as the relative number of the photons absorbed per unit distance of semiconductor, as shown in the following equation [15]:

$$\alpha = \frac{2.303A}{t} \dots \dots (1)$$

Where:

A is the absorbance and t is the thickness of the film.

The absorption coefficient depends on the energy of the incident light, the band gap of semiconductor material and the kind of the transitions from valence band to conduction band.

Figure (14) depicts the variation of the absorption coefficient of the In_2O_3: Sn thin films for different tin doping. From the results the absorption coefficient decreased sharply in the UV/VIS region, and then it decreased gradually in the visible region with increasing the wavelength of incident photons. The value of absorption coefficient is larger than (10^4 cm^{-1}) which refers the direct transitions between the valence band and conduction band.

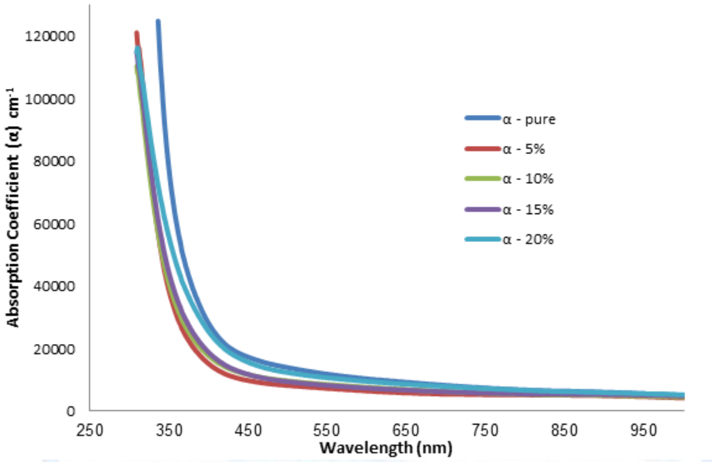

Figure 14: Absorbance Coefficient of In_2O_3: Sn thin films for various tin content

Extinction coefficient **(k)** refers to the extinction occurring in the electromagnetic wave inside the material is given by the following relation [18]:

$$K = \frac{\alpha\lambda}{4\pi} \quad .... (2)$$

Extinction coefficient of ITO thin films decreases with the increasing of tin doping from (0 – 5) % and then it increases afterward for further increasing in tin doping from (5 – 20) % as shown in figure (15).

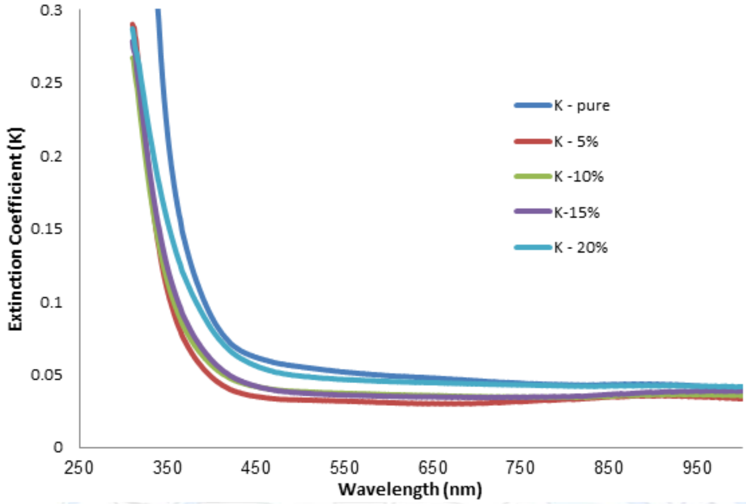

Figure 15: Extinction coefficient of In_2O_3: Sn thin films for various tin content

The refractive index **(n)** of ITO film was calculated from the following equation [19]:

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \; \ldots\ldots (3)$$

The refractive index of ITO thin films decreases with the increasing of tin doping from (0 – 5) % and then it increases afterward for further increasing in tin doping from (5 – 20) %. It is concluded that the refractive index depends on the production method, surface roughness, grain boundaries and morphologies of the produced film; and these properties are changed with tin doping as shown in figures (16), which is in agreement with the results reported by Hassoni et al. in 2015 [20].

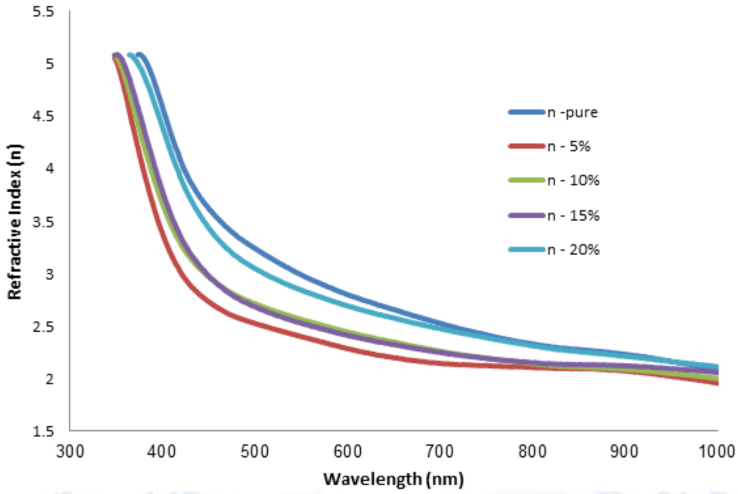

Figure 16: refractive index of In_2O_3: Sn thin films for various tin content

Optical conductivity (σ) is dependent upon many parameters, among them the refractive index, absorption coefficient, the extinction coefficient and the frequency of incident photons. It depends strongly on the optical band gap in semiconductors. The optical conductivity could be calculated using the following relation [21]:

$$\sigma = \frac{\alpha n c}{4\pi} (s^{-1}) \ldots\ldots (4)$$

The optical conductivity of indium tin oxide thin films decreases with the increasing of tin doping from (0 – 5) % and then it increases afterward for further increasing in tin doping from (5 – 20) %. From figure (17), we can see that the optical conductivity decreases with increasing the wavelength of incident photon and reaches a constant value. This suggests that the increase in optical conductivity is due to the excitation of electrons by photon energy.

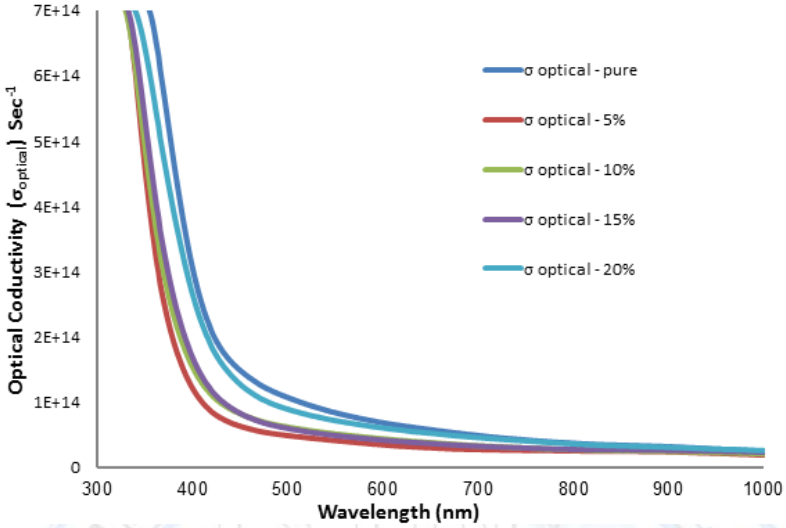

Figure 17: Optical Conductivity of In_2O_3: Sn thin films for various tin content

The complex dielectric constant describes the absorbing medium. The real **(ε_1)** and imaginary parts **(ε_2)** of dielectric constants of ITO thin films have been calculated using relations (5) and (6) as shown in figures (18) and (19).

$$\varepsilon_1 = (n^2 - k^2) \dots\dots (5)$$

$$\varepsilon_2 = 2nK \dots\dots (6)$$

However, ε_2 and ε_1 are related with n and k values and can be calculated by using the above equations [16, 17]. It can be noted that the values of real and imaginary parts of dielectric constant (ε_1, ε_2) are decreased with increasing wavelength of incident photons. The real and imaginary parts of dielectric constant of ITO thin films decrease with the increasing of tin doping from (0 – 5) % and then they increase afterward for further increasing in tin doping from (5 – 20) %.

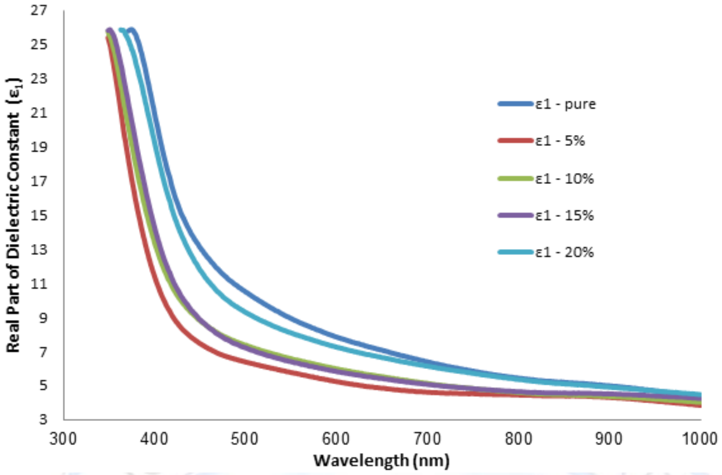

Figure 18: Real part of dielectric constant of In_2O_3: Sn thin films as a function of wavelength for different tin doping

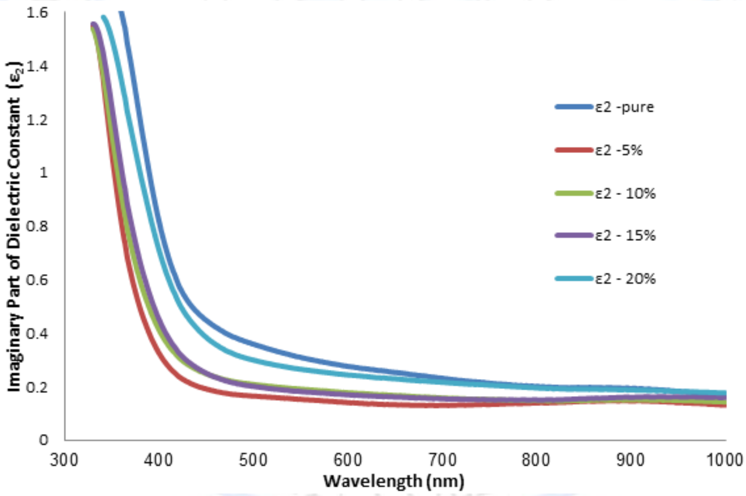

Figure 19: imaginary part of dielectric constant of In_2O_3: Sn thin films as a function of wavelength for different tin doping

Conclusions

Tin doped indium oxide (ITO) thin film was successfully deposited on glass substrates at 450 ℃ using spray pyrolysis method. The atomic force microscopic study shows that the RMS roughness of tin doped indium oxide thin films decreased with increasing Sn- content in the films from (4.68 nm) at (Sn = 0 %) to (2 nm) at (Sn = 20 %). The optical properties such as absorbance, reflectance, absorption coefficient, real and imaginary parts of dielectric constant, extinction coefficient, refractive index and optical conductivity of ITO thin films decrease with increasing tin-doping from (0 – 5) % and then they increase afterward for further increasing in tin doping from (5 – 20) %. When a high impurity is added, the transmittance of ITO thin film decreases due to increased photon scattered by crystal defects created by impurities. The optical characterization of tin doped indium oxide depends on the uniformity and roughness of the ITO film surface. When the surface is rough, the light will be scattered by the film surface and the films will be less transparent.

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