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Optical and morphological properties of post-deposition annealed Indium doped Tin Oxide (ITO) thin films.

A graduation project submitted to the department of physics in partial fulfillment of the requirements for the degree of bachelor's degree of science in physics.

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Transparent Conductive Oxide (TCO)
Indium Tin Oxide (ITO)
Scanning Electron Microscopy (SEM)
Atomic Force Microscopy (AFM)
Energy-dispersive X-ray spectroscopy (EDX)

شكر وتقدير Acknowledgment

بسم الله الرحمن الرحيم

الحمدالله رب العالمين والصلاة والسلام على أشرف الأنبياء والمرسلين نبينا محمد عليه أفضل الصلوات والتسليم من لا يشكر الناس لا يشكر الله عز وجل.

اود أن أعبر عن عميق امتناني وشكري لجميع من ساهم في وصولي إلى هذا الإنجاز العظيم، وهو حصولي على درجة البكالوريوس. لقد كانت رحلة مليئة بالتحديات، لكن بفضل الله ثم دعمكم المستمر، استطعت تخطي كل الصعاب وتحقيق هذا الحلم.

أود ان اشكر مشرف البحث الدكتور نذير مصطفى على دعمه ومساندتي خلال هذا البحث وأشكر الدكتور خالد بنعوف والدكتور محمد عبدالرافع على جهودهم التعاونية اثناء جمع البيانات.

كما أود أن أقدم شكرًا خاصًا لأسرتي وعلى وجه الخصوص الراحل الباقي في قلبي أبي رحمه الله.

اللهم أنفعني بما علمتني وزدني علما

والحمد لله رب العالمين

Abstract

Optical and morphological characteristics of post-deposition Indium doped Tin Oxide (ITO) annealed at 300, 450 °C deposited on glass substrates were investigated to assess the possibility of its use as an anode in optoelectronic devices such as solar cells and light emitting diodes. The project focused on the spectral properties of the post-deposition annealed ITO films such as Absorption, Transmission and Reflectance in the visible Range 380 – 780 nm. Energy gap for the as-deposited and annealed ITO films was calculated using Tauc model.

Chemical composition of the films was obtained. Morphology and surface roughness were examined using scanning electron mircoscopy (SEM) and atomic force microscopy (AFM).

الملخص

تمت دراسة الخصائص البصرية والتشكيلية لأكسيد الانديوم والقصدير المتكونة والمعالجة حراريا عند 300 و 450 درجة مئوية التي تم ترسيبها على شرائح الزجاج حيث تم التحقق من احتمالية استخدامها كقطب كهربائي في الأجهزة الكهروضوئية كالخلايا الشمسية والدايود المشع للضوء. في هذه البحث تم التركيز على المزايا الطيفية لأفلام أكسيد الانديوم والقصدير المتكونة والمعالجة حراريا كميزة الامتصاص والنفاذية والانعكاس في المدى المرئي 380-780 نانو متر. فجوة الطاقة لأفلام أكسيد الانديوم والقصدير المتكونة والمعالجة حراريا التي تم حسابها باستخدام نموذج تاوك. وكذلك التركيب الكيميائي المكون للأغشية.

التشكيل وخشونة السطح تم فحصهم باستخدام المجهر الماسح الإلكتروني ومجهر القوة الذرية.

Introduction

Transparent Conducting Oxide (TCO) Thin Films of Indium Doped Tin Oxide (ITO) are chemically stable transparent conducting oxides with several interesting properties namely high conductivity and transmittance (> 90%) in the visible to infra-red region (380–2500 nm) [1]. These features make ITO film useful for many optoelectronic applications including solar cells [2], light emitting diodes (LED's) [3] and display panels [4], [5]. Generally, the nature of ITO films is n-type and its energy band gap varies from 3.3 to 4.2 eV depending on the quality of film. Further, the high conductivity of ITO films is due to the large concentration of oxygen vacancies and substitutional tin dopants [6]. ITO films can be prepared by different methods such as chemical vapor deposition (CVD), sputtering, pulsed laser deposition (PLD) and sol-gel method [2-5].
ITO films can be included as protective coatings or anodes in solar cell panels generating electric power employed in space sciences. These instruments are exposed to high energetic particles that could induce damage on their performance [3]. In addition to the optical behavior of the ITO films, their resistance to radiation exposure is critical for a correct operation of the space instruments [3].
In fact, the deposition of ITO thin films was well described in the work of many researchers due to the various applications of such conducting transparent oxide thin films, and the necessity to explore their performance under different conditions in the fields of optics and electronics. In this work, the focus was on the effects of annealing temperature on the morphology and optical properties and optical band gap of the commercial ITO films deposited on glass substrates.

Chapter 1
Literature review
1.1 Transparent Conductive Oxide (TCO)

All the optically transparent and electrically conducting oxides (TCO) are binary or ternary compounds, containing one or two metallic elements. Their resistivity could be as low as 10^{-4} Ω.cm, and their extinction coefficient k in the optical visible range could be lower than 0.0001, owing to their wide optical band gap that could be greater than 3.6 eV. This remarkable combination of conductivity and transparency is usually impossible in intrinsic stoichiometric oxides. However, it's achieved by producing them with a non-stoichiometric composition or by introducing appropriate dopants [5].

1.2 Indium Tin Oxide (ITO)

Indium Tin Oxide ITO is a ternary composition of Indium, Tin and Oxygen in varying proportions. Depending on the oxygen content, it can either be described as a ceramic or alloy-tin oxide. It is typically encountered as an oxygen saturated composition with a formulation of 74% In, 18% O_2, and 8% Sn by weight. Oxygen saturated compositions are so typical, that unsaturated compositions are termed oxygen deficient ITO. It's transparent and colorless in thin layers while in bulk form it is yellowish to grey. In the infrared region of the spectrum it acts as a metal-like mirror. Indium Tin Oxide is one of the most widely used transparent conducting oxides because of its two main properties, its electrical conductivity and optical transparency, as well as the ease with which it can be deposited as a thin film. As with all transparent conducting films, a compromise must be made between conductivity and transparency, since increasing the thickness and increasing the concentration of charge carriers will increase the material's conductivity, but decreases its transparency [2].

1.3 Physical vapor deposition (PVD)

1.3.1 Sputtering

Magnetron sputtering is a domination technique to produce thin films because a large quantity of thin films can be produced at relatively high purity and low cost. This entails ejecting material from a source called a ”target” onto a ”substrate” like a silicon wafer. A schematic diagram of a sputtering process is shown in figure 1.1

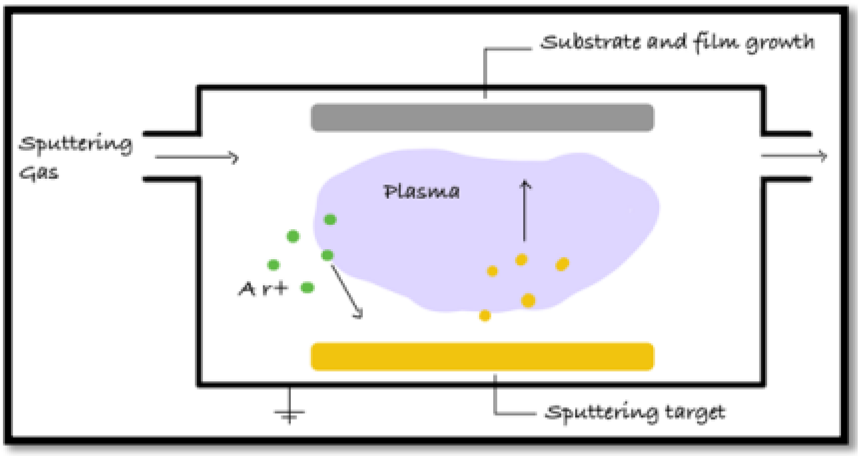


Figure 1.1: A schematic of a sputtering process system

Magnetron sputtering is a process of collision between incident particles and targets. Since high-speed sputtering is performed at low pressure, the ionization rate of the gas must be increased effectively. The incident particle undergoes a complex dispersion process in the target, collides with the target atom, and transmits part of the momentum to the target atom, which in turn collides with other target atoms to form a cascade process. During This cascade, certain target atoms near the surface gain sufficient momentum for outward motion and are spewed out of the target. Magnetron sputtering increases the plasma density by introducing a magnetic field on the surface of the target cathode and using the magnetic field constraints on the charged particles to increase the sputtering rate. Magnetron sputtering includes many types, such as direct current (DC) magnetron sputtering for conducting films and radio frequency (RF) for semiconducting and insulating films [4].

1.3.2 Pulsed laser deposition (PLD)

The experimental set-up for PLD experiment is based on two main equipment: a laser system and a vacuum chamber. The used laser systems were a Nd:YAG laser and ArF excimer laser. The target and collector substrate are mounted in the chamber in a vertical position, at variable distance. The angle of incidence of the laser beam is set at an angle of 45°. The substrate is fixed on a heating system. During deposition, the target was rotated and the laser beam was translated on surface of the target. The film deposition was performed in a dynamic ambient background gas (O_2, N_2, etc.) and the flow rates of gases can be precisely controlled through a mass flow controller. A schematic diagram of the PLD system is shown in Figure 1.2.

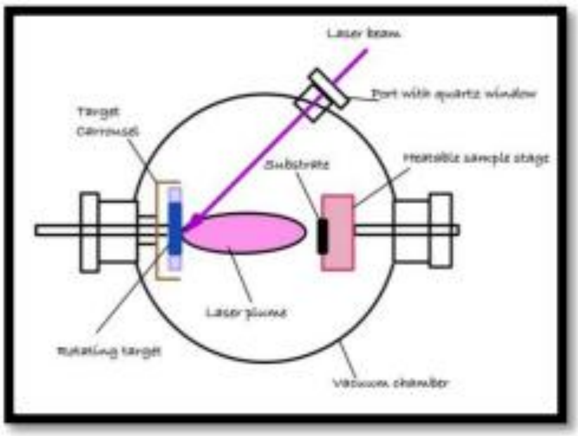


Figure 1.2: A schematic diagram of a pulsed laser deposition.

Chapter 2
Experimental details
2.1 Commercial ITO

Commercial ITO thin films deposited on polished soda-lime glass substrates by sputtering process were purchased from [MTI,USA] The 150 nm thick films (ITO) were deposited on glass substrates (0.7 mm thick) and 1”×1’’ size were used for the deposition of the oxide films.

Optical properties such as Transmission (T), Reflectance (R), and Absorption (A), were measured with UV-Vis spectrophotometer. The surface morphology were examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Prior to characterization, the ITO films were annealed at various Temperature 300, and 450 °C in oven for 60 minutes. Energy-dispersive X-ray spectroscopy (EDX) was performed to find the Chemical composition of ITO film. Figure 2.1 shows the oven used for annealing the substrates.

2.2 Drying oven

Drying ovens can be used in laboratory or industrial settings for a variety of tasks including evaporation, sterilization, temperature testing, and for incubating temperature sensitive experiments.

Figure 2.1: A photo of the Oven used.

2.3 Scanning Electron Microscopy (SEM)

The surface morphology of as-deposited and annealed ITO samples on glass substrates were investigated using Scanning Electron Microscopy (SEM) JEOL JSM-7600F. The scanning electron microscope used is shown in figure 2.2.

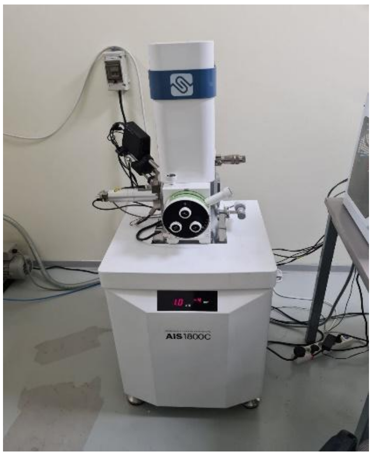


Figure 2.2: Scanning Electron Microscopy (SEM)

2.4. Atomic force microscopy (AFM)

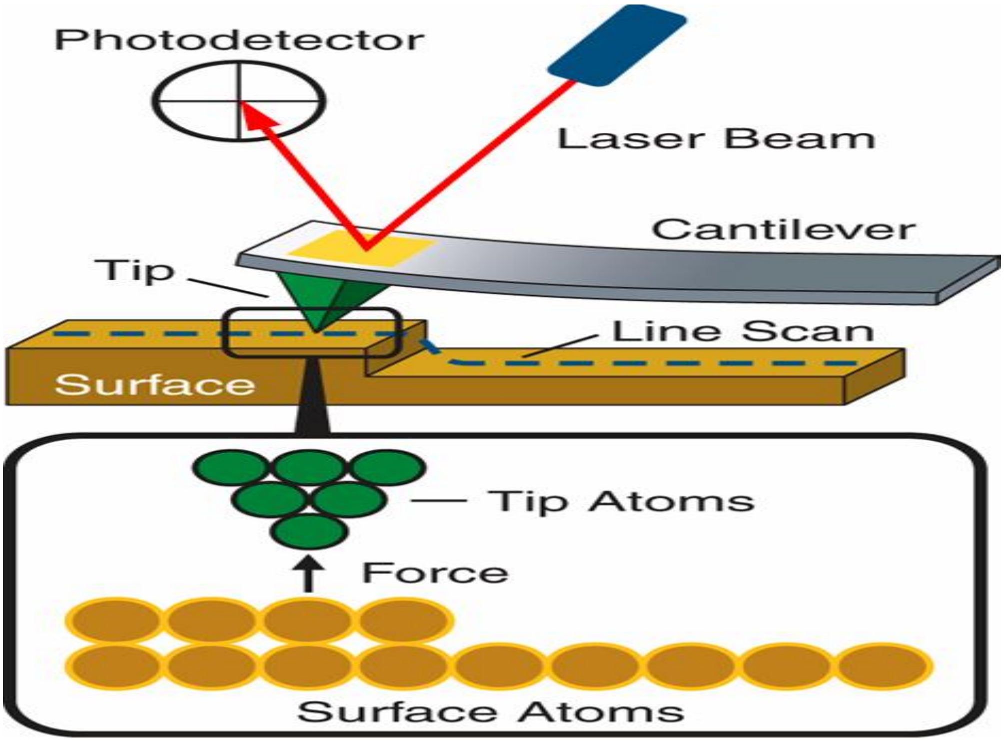


Figure 2.3: Schematic diagram of Atomic Force Microscopy (AFM) used.

Atomic force microscopy (AFM) was used to evaluate the morphology and surface roughness of the ITO films. The instrument type is an (AFM) Multi-Mode8-Bruker. Fig. 2.3 shows a schematic diagram of the Atomic Force Microscopy.

2.5 UV-visible spectrophotometer

The optical properties such as transmission, reflectance and absorption of the oxide films deposited on glass substrates were measured using a Perkin Elmer Lambda 950 UV-VIS spectrophotometer shown in figure 2.4, over the range from 350 to 800 nm.

Figure 2.4: UV-visible spectrophotometer used.

2.6 Energy-dispersive X-ray spectroscopy (EDX)

The chemical composition of the samples were obtained using an energy-dispersive X-ray spectroscopy (EDX) to examine the Indium (In), tin (Sn) , and oxygen O_2 concentration of the ITO films.

Chapter 3

Results and discussions

The morphology and composition of the ITO films were obtained through examination with SEM and EDX, respectively.

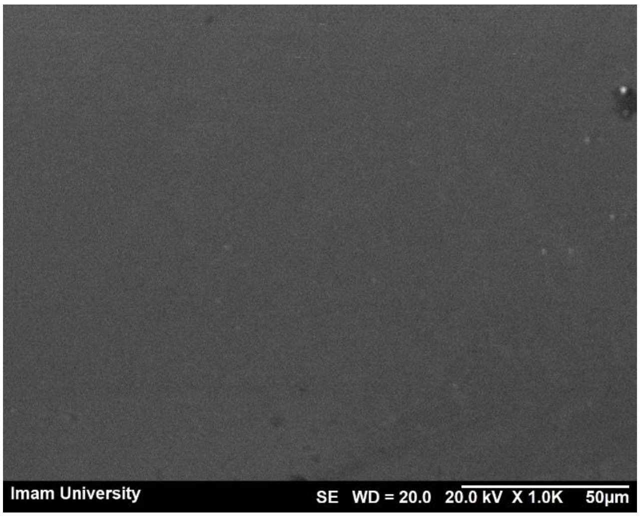
The results of morphological characterization were obtained by SEM using a magnification of 1000 and 5000× for the ITO surface layers. A considerable smooth and dense surface can be observed. Likewise, the space between particles (pores) also indicates that the particle fabrication process has not been fully homogeneous [5]. This causes particle contact to be not maximal so the layer resistance is large [6].

3.1 Surface morphology

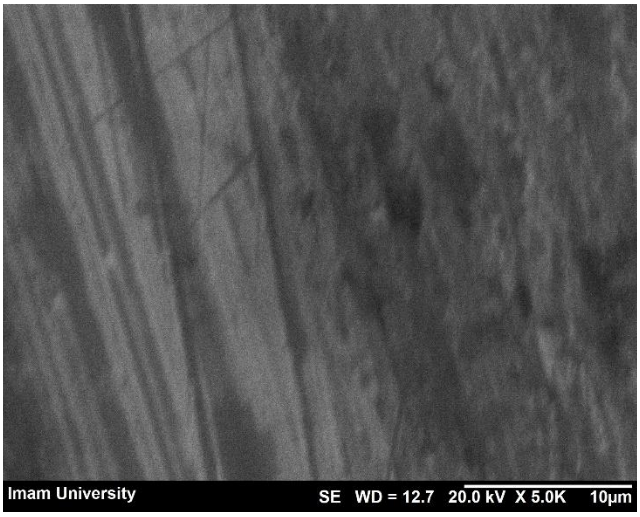
Figures 3.1, 3.2 and 3.3 represent the micrograph images of the as-deposited, and annealed ITO films at 300°C and 450°C degrees respectively.

The magnification of the SEM instrument used was not sufficient to show the details of the grain sizes of ITO, therefore we used AFM apparatus at KACST to obtain better details of the atomic structure.

3.1.1 Scanning Electron Microscopy (SEM)

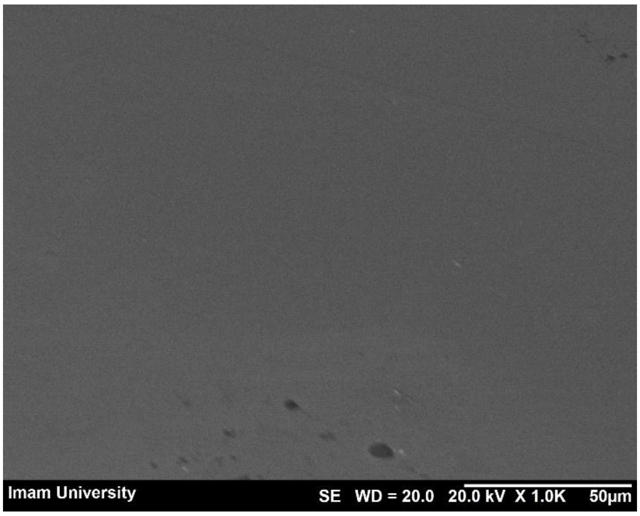


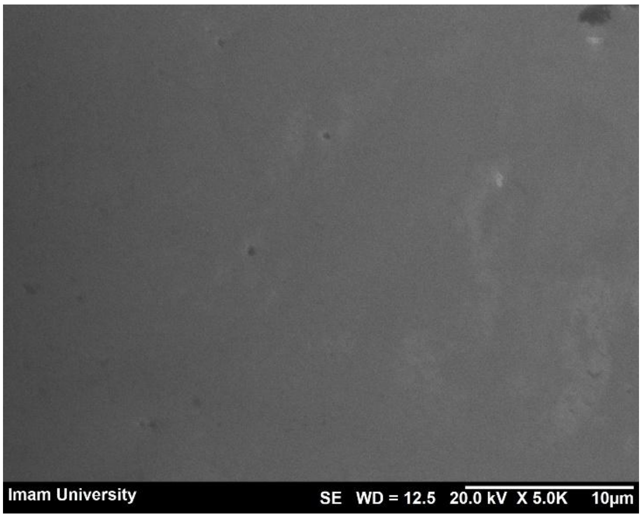
(a) 1K



(b) 5K

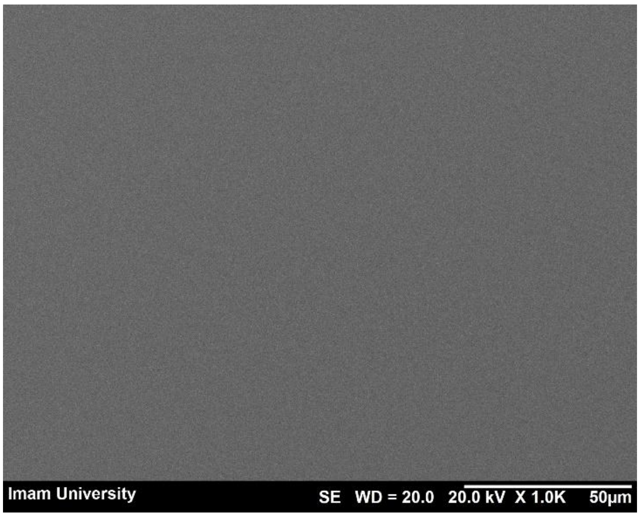
Figure 3.1. as-deposited ITO surface morphology images with magnification: (a) 1K (b) 5K.

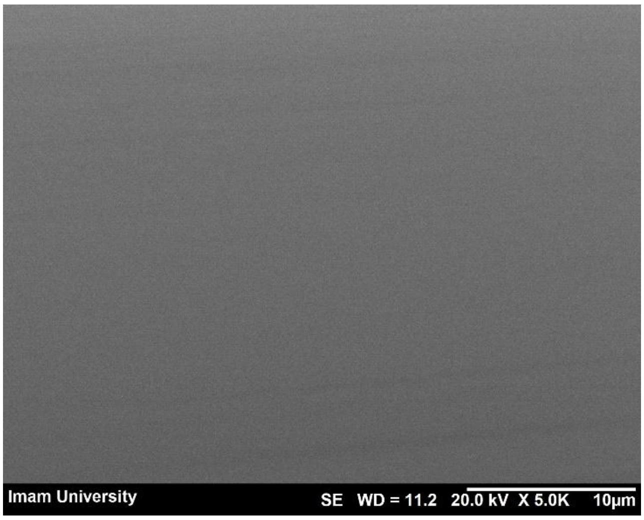




(a) 1K **(b) 5K**

Figure 3.2. 300°C ITO surface morphology images with magnification: (a) 1K (b) 5K.





(a) 1K **(b) 5K**

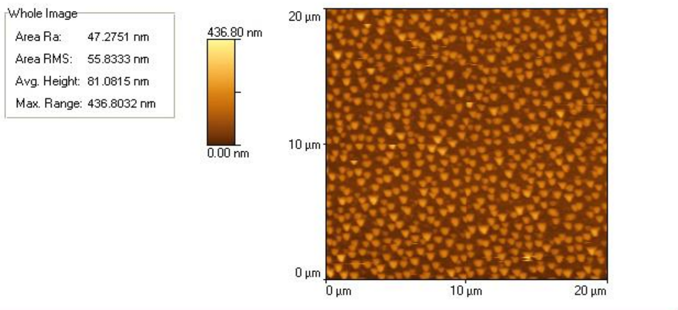
Figure 3.3 450°C ITO surface morphology images with magnification: (a) 1K (b) 5K.

3.2 Atomic force microscopy (AFM)

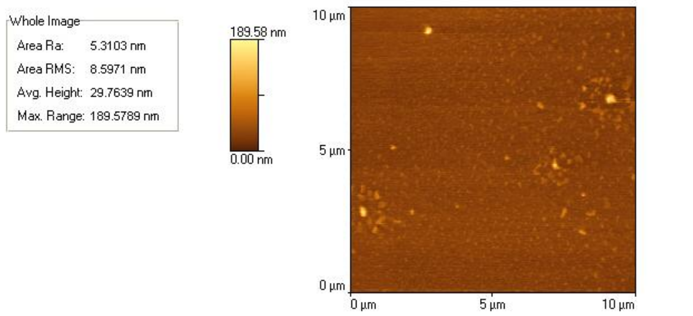
Figures3.4 a b c d shows the AFM images of Ito thin films, as-deposited and after annealing at 450 C, respectively. As can be seen, two typical morphological features are identified readily by visual inspection of the figures.

The first feature is that the granules with different scales exist in all the thin films and are distributed evenly in some ranges. Also, the granules possess different sizes, irregular shapes, and separations. The second feature is that the evolution of the RMS

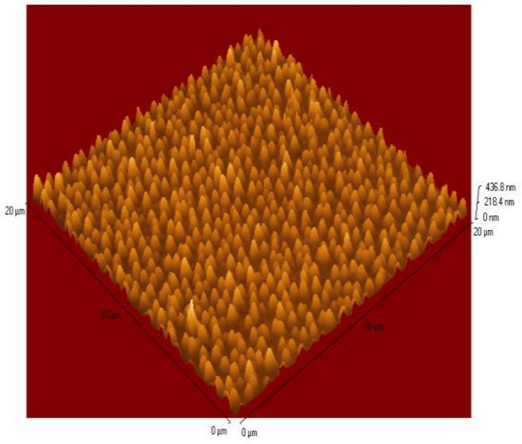
AFM images of ITO films are shown in figure 3.4.



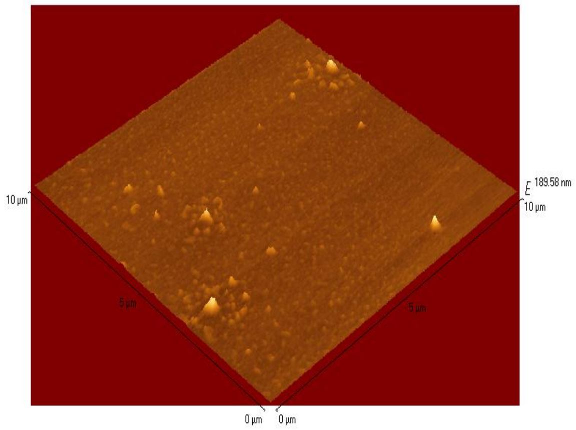
a) Surface morphology as-deposited



b) Annealed at 450°C



c) Surface roughness as-deposited



d) Annealed at 450°C

3.3 Optical Properties

3.3.1: Transmission

Transmission was measured at wavelengths range (350 - 800) nm. Transmission is a fundamental property of thin films, determining their ability to allow light to pass through. In this study, the transmission of ITO was measured at wavelengths ranging from 350 to 800 nm, reflecting the film's efficiency in utilizing solar energy. The results indicate that ITO exhibits a high transmission rate of 89% at a wavelength of 550 nm shown in figure 3.1, making it suitable for optical applications such as solar cells. It is also important to note that increasing the film thickness may negatively impact transmission, necessitating a balance between thickness and optical performance.

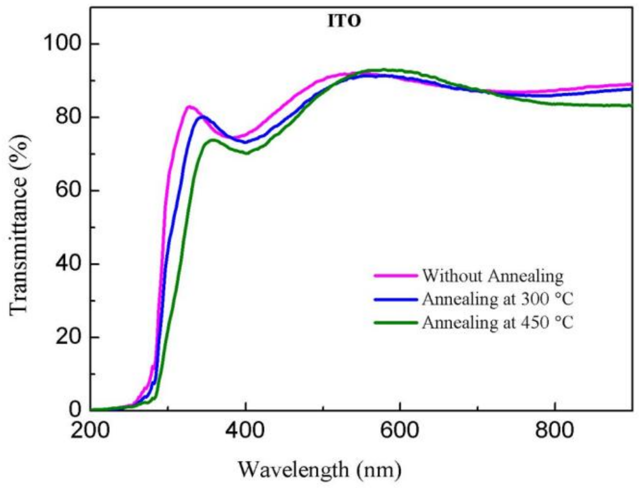


Figure 3.3: graph showing Transmission in all 3 samples

3.3.2: Reflection

Reflection of ITO films was measured at wavelengths range (350 - 800) nm. Reflection measures the extent to which the film can reflect incident light, a crucial factor in optical applications.

In the study, the reflection percentage was measured at 8.8% at a wavelength of 550 nm shown in figure 3.2. This low reflection rate enhances the film's transmission efficiency, allowing maximum light to reach the active layers in solar cells. The low reflection is attributed to the structural and physical properties of the film, indicating a good compatibility between optical and morphological characteristics.

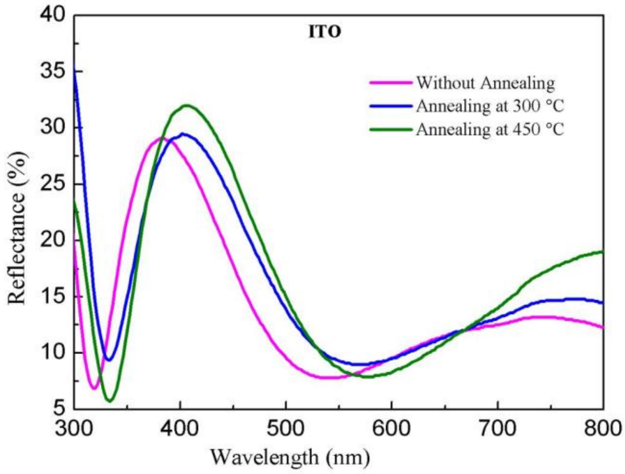


Figure 3.4: graph showing Reflection in all 3 samples

3.3.3: Absorption

Absorption was calculated using the relation (T + R + A = 1), which is essential for understanding how the material interacts with light. In this research, the absorption was reported to be 2.2% at a wavelength of 500 nm shown in figure 3.3. This low absorption indicates that the film has a high capacity for transmitting light, a significant advantage in applications requiring light to reach active layers. The structural properties of the film can influence the absorption rate, thereby affecting overall performance in optical applications.

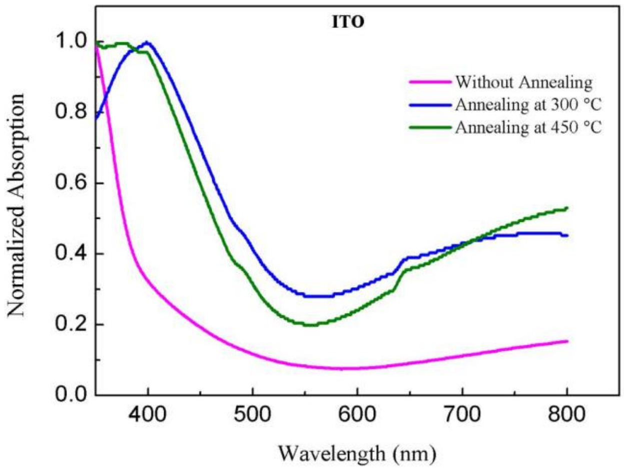


Figure 3.5: graph showing Absorption in all 3 samples

3.4: Energy Band Gap

The optical band gap energy E_g of each film was deduced from the absorption spectra by using the Tauc model.

The Tauc relation is written in equation (1) as:

$$(\alpha h\nu)^2 = C(h\nu - E_g) \qquad (1)$$

where (α) the absorbance coefficient, ($h\nu$) is the photon energy, C is a characteristic Constant of the materials and E_g is the optical band gap energy between the valence and conduction bands.

Figures 3.8: Display the optical band gap relation of the films with photon values ,which serves as a key indicator of the material's electron transport capability, aiding in assessing its suitability for applications in optical devices such as light-emitting diodes and solar cells.

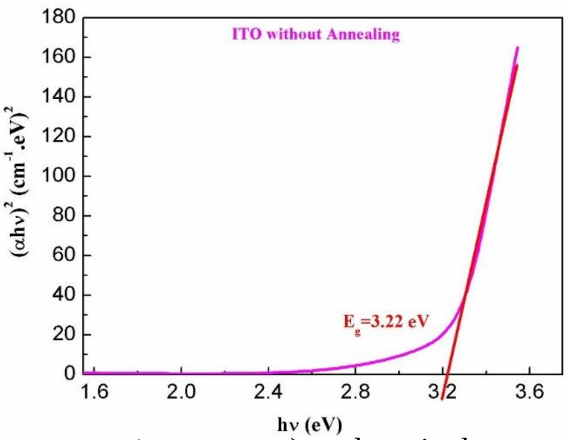


Figure 3.8a: a) as-deposited

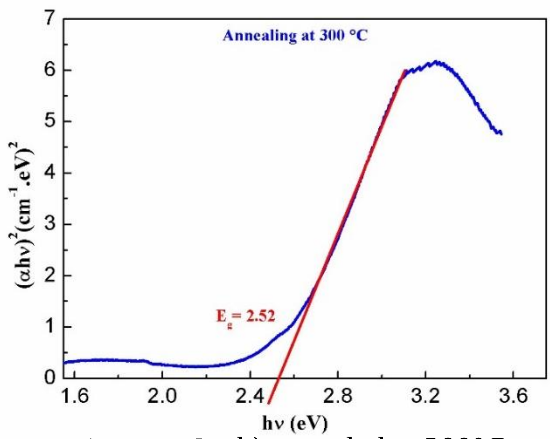


Figure 3.8b: b) annealed at 300°C

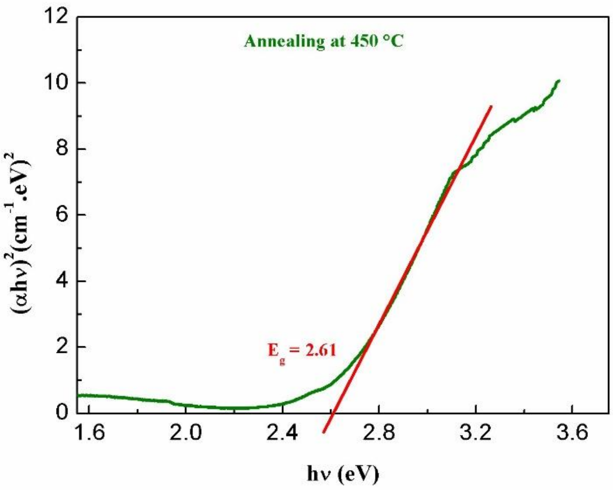


Figure 3.8c: c) annealed at 450°C

Figures 3.8: Direct optical band gap corresponding to $(\alpha h\nu)^2$versus $h\nu$ of the ITO films on glass substrate.

Table 3.1: summary of the optical properties of ITO films with calculated Energy gaps (Eg)

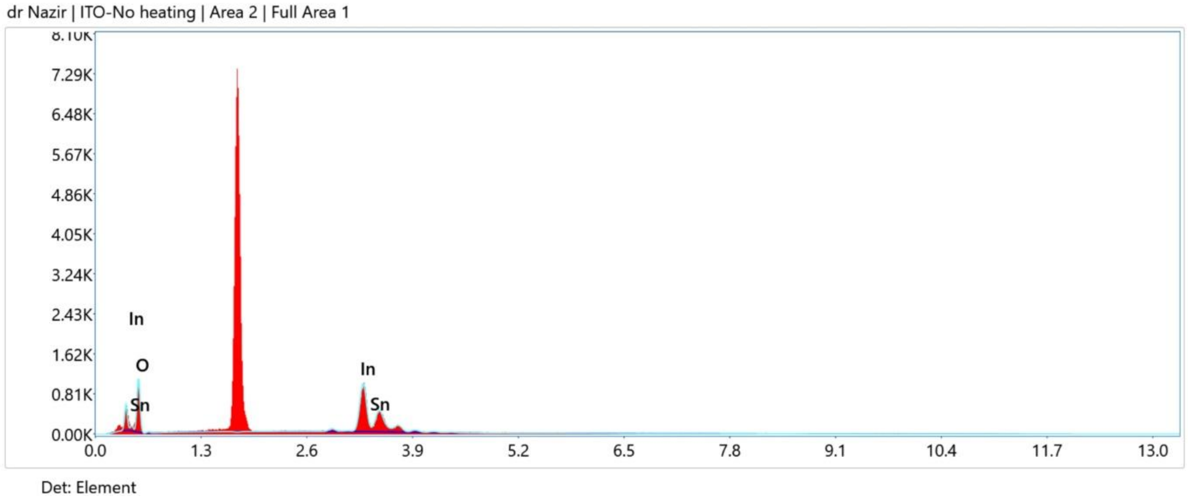
ITO	T (%)	R (%)	A (%)	Eg (eV)
as-deposited	89	8.8	2.2	3.22
300°C	90.7	8.9	0.4	2.52
450°C	90.9	9	0.1	2.61

N.B: T, R and A measured at wavelength 550 nm.

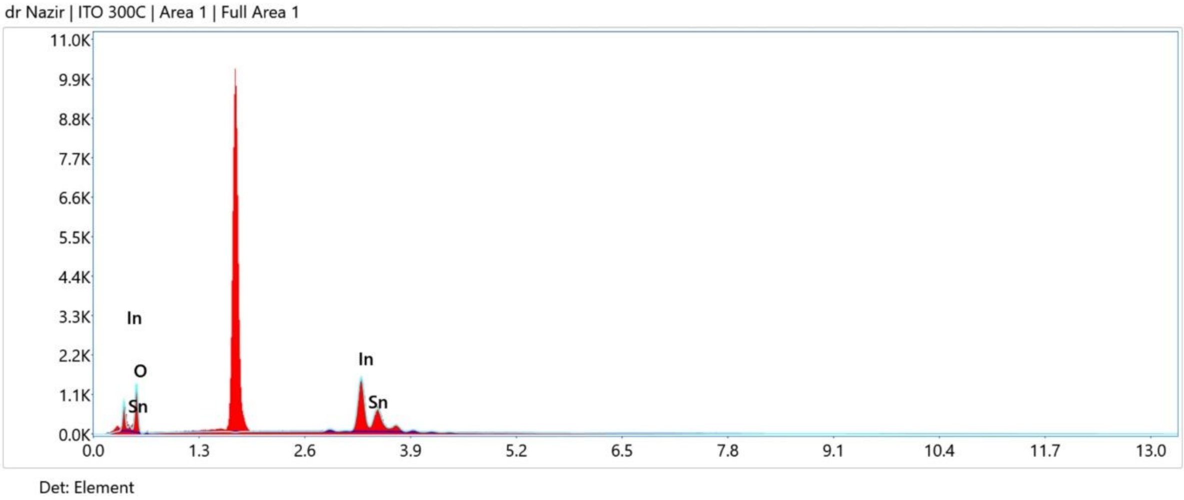
3.5 Energy Dispersive EDX

EDX is a vital technique for analyzing the chemical composition of thin films. Through energy spectrum analysis, precise information regarding the percentage of elements in the ITO films was obtained, revealing 58.7 oxygen, 3.7 tin, and 37.6 Indium. These percentages reflect the ideal composition of the film and contribute to understanding how chemical composition affects the optical and electrical properties. Additionally, these results provide insights into how to optimize the preparation process to achieve better characteristics for use in optoelectronic applications.

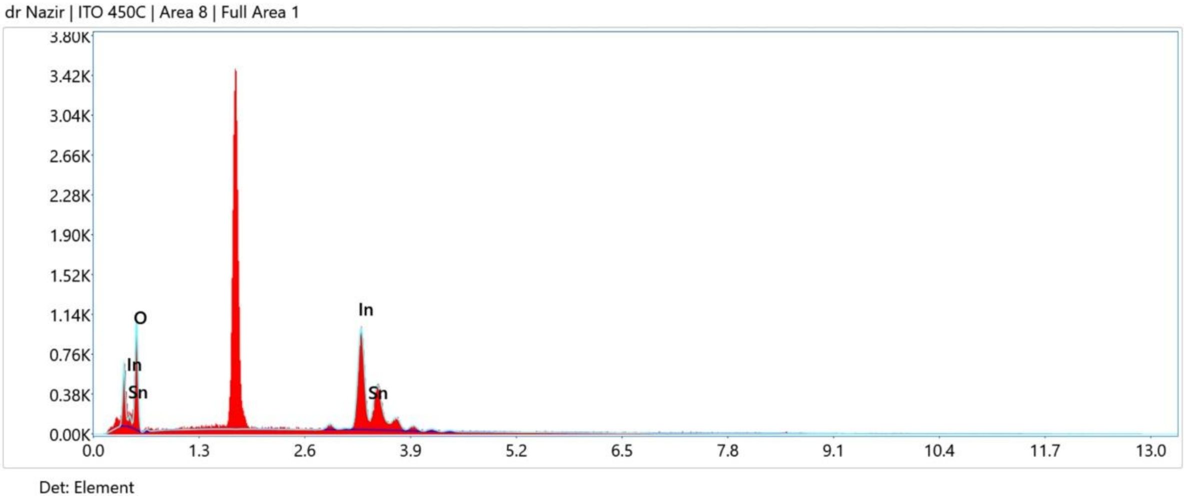
Figures 3.9-3.11: Shows The Energy-Dispersive X-ray Spectroscopy (EDX) results for the ITO layer, providing information on the chemical composition of the thin films. The percentage of key elements such as Oxygen, Tin, Indium is displayed, which enhances the film's properties for optical applications.



Figures 3.9: EDX of as-deposited ITO film.



Figures 3.10: EDX of 300°C ITO film.



Figures 3.11: EDX of 450°C ITO film.

Chemical composition of the ITO film is shown in table 3.2

Element	**Weight %**			**Atomic %**		
ITO Samples	as-deposited	300°C	450°C	as-deposited	300°C	450°C
oxygen	50.9	47.2	50	88.2	86.6	82.8
indium	44.7	48.3	45.4	10.8	12.3	11.1
Tin	4.4	4.5	4.6	1.0	1.1	1.1
Total			100			

Table 3.2: EDX results of the ITO films

Conclusions

The good optical and morphological properties of ITO films deposited onto glass substrates indicate that the oxide films studied in this research are suitable as protective coatings and for opto-electronic devices such as anode for solar cells and light emitting diodes. Our results showed that the post-deposition annealing has an influence on the properties of ITO films examined. High values of optical transmittance (more than 85%) were maintained at high annealing temperatures. Generally, the transmittance in the range 380–780 nm of all films on glass substrates slightly decreased with increasing annealing temperatures. AFM images for all samples showed an increase in the grain sizes and roughness of the films. Band gaps were reduced for the annealed samples, which is a sign of improvement in the conductivity of the films. Further investigations may be necessary of the influence of post-deposition annealing on the thin film oxide properties.

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