Kingdom of Saudi Arabia
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Optical Properties and morphology of FTO Thin Films deposited on glass Substrates

A graduation project submitted to the Department of Physics in partial fulfillment of the requirements for the degree of Bachelor of Science in Physics

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Transparent Conductive Oxide (TCO)
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Acknowledgment شكر و تقدير

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شكراً لكل من ساهم في نجاح هذا العمل ولو بشكل بسيط .

والحمد لله رب العالمين

Abstract

Optical and morphological properties of the films are highly sensitive to the deposition method and processing parameters used. The aim of this project is to study the properties of Fluorine tin Oxide (500 nm thick) deposited commercially by a spray pyrolysis process on glass substrates. Prior to characterisation of the thin films, FTO-coated substrates were cleaned using detergent then ethanol and dried in oven. The optical properties such as transmittance, reflectance and absorption were measured, energy gap was calculated from the absorption spectrum and morphology of FTO thin film was also investigated. The research was aimed to assess the possibility to use the films as anodes in optoelectronic devices such as solar cells and light emitting diodes.

الملخص

تتأثر الخواص البصرية والمورفولوجية والبنيوية للأغشية الرقيقة الشفافة بشكل كبير بطريقة التحضير وبالظروف المستخدمة لتحضير تلك الاغشية.

الهدف من المشروع هو دراسة الخواص البصرية والبنيوية والمورفولوجية لطبقات الأغشية الرقيقة (بسماكة ٥٠٠ نانومتر) والمكونة من طبقة أكسيد القصدير المطعم بالفلور محضرة بواسطة إحدى الشركات التجارية فوق شرائح زجاجية بالرش بجهاز التحلل الحراري. قبل دراسة الخواص لتلك الاغشية تم غسلها بواسطة مادة منظفة والايثانول وبعدها تم التجفيف داخل الفرن الكهربائي. بعد ذلك تم قياس الخواص البصرية مثل نفاذية الضوء والانعكاس والامتصاص ومن ثم حساب فجوة الطاقة للاغشية والمورفولوجي لمعاينة سطح مادة الاكسيد المستخدمة.

البحث يهدف لبحث إمكانية استخدام تلك الأغشية كطبقة أنود في الأجهزة الالكتروبصرية مثل الصمام الثنائي المضيء والخلايا الشمسية.

Introduction

Transparent conducting oxide (TCO) thin films of Fluorine doped Tin Oxide (FTO) are finding wide ranges of optoelectronic device applications due of their specific electrical, structural and optical properties [1-2]. FTO generally exists as an n-type and wide band gap semiconductor with high transmittance in the visible region [2]. FTO has been recognized as a very promising material for a number of optoelectronic applications because of its stable nature at atmospheric conditions, mechanical hardness, chemical inertness, and high temperature durability. It also has excellent electrical conductivity, greater mobility and good mechanical stability [1-3]. Due to these distinctive characteristics, it is used in solar cells as transparent and protective electrodes and in flat plate collectors as spectral selective windows for light to pass through to the active material where carrier generation occurs as an ohmic contact for carrier transport out of the photovoltaic [2,3]. It is also used in gas detecting sensors, photo thermal converters, and for providing thermal insulation for houses [1-4]. Another advantage of FTO is that it is easy to fabricate using low cost materials. The structure, surface morphology and electrical and optical properties of the FTO films strongly depend on the method of preparation and growth parameters. Thin films of FTO can be prepared by several deposition techniques such as dip coating[5], inkjet printing [6], magnetron sputtering [7], spray pyrolysis, etc [8-11].

Several physical and chemical deposition techniques are commonly used to produce high-quality FTO films. These techniques include sputtering (both Radio Frequency (RF) and Direct Current (DC)), electron beam evaporation (E-beam), pulsed laser deposition (PLD), and spray pyrolysis [12].

In this project, we characterized commercial transparent conducting FTO thin films prepared by spray pyrolysis deposition technique on glass substrates. The optical properties, such as transmission, reflectance and absorption were measured. Also the optical band gap, morphology, and chemical composition of the FTO films were investigated. Our aim was to assess the possibility to use the films as anodes in optoelectronic devices such as organic light emitting diodes and even organic solar cells.

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 is achieved by producing them with a non-stoichiometric composition or by introducing appropriate dopants [8].

1.2 Fluorine Tin Oxide (FTO)

Fluorine Tin Oxide FTO is a ternary composition of Fluorine**,** 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 FTO. It is 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.

Fluorine 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 decrease its transparency [9].

1.3 Physical Vapor Deposition (PVD)

1.3.1 Sputtering

Magnetron sputtering is a dominant technique for the production of 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 shown in figure 1.1

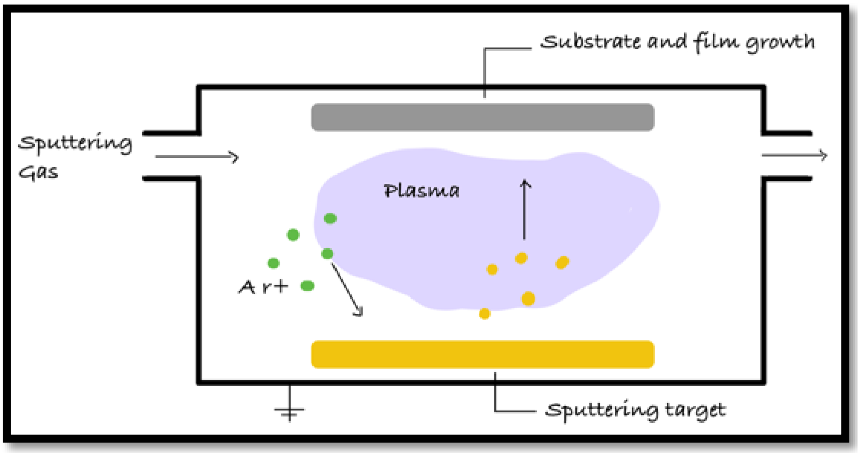


Figure 1.1: A schematic of a sputtering process system

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 [11].

1.3.2 Evaporation process

Evaporation is a common method for deposition of thin film from their source materials in a vacuum as a physical vapor deposition (PVD) technique. The source materials are evaporated using evaporation source such as metal boat or coiled wire [13]. It normally uses a resistive heat source to evaporate a source material within a chamber. The evaporated material rises in the chamber via thermal energy, ultimately coating a substrate with a thin film. This process can be used for metals or nonmetals and is a good choice for electrical contacts [14] shown in Figure 1.2.

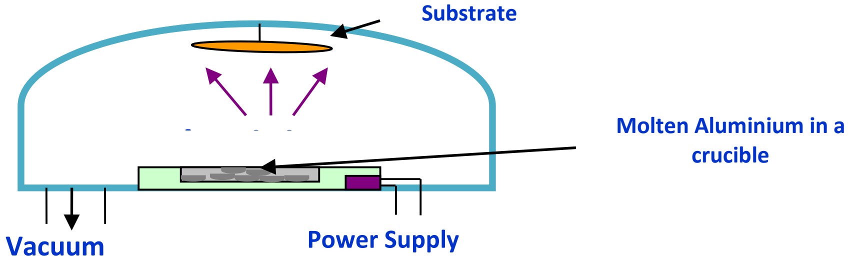


Figure 1.2: A schematic of an evaporation process system.

1.4 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 a ArF excimer laser. The targets and collector substrate are mounted in the chamber in a vertical position, at variable distance. The angle of incidence of the laser beam was set at 45°. The substrates were fixed on a heating system. During deposition, the targets were rotated and the laser beam was translated on surface of the targets. The film deposition was performed in a dynamic ambient background gas (O_2, N_2, etc.) and the flow rates of gases were precisely controlled through a mass flow controller shown in Figure 1.3

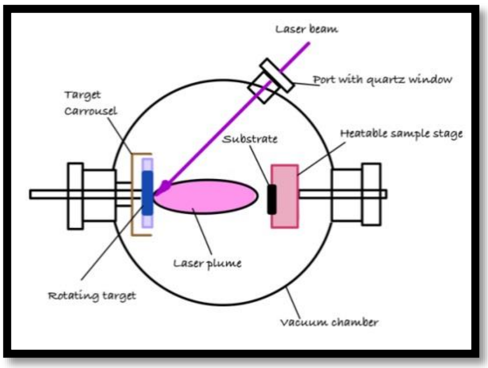


Figure 1.3: A schematic of a Pulsed laser deposition

1.5 Spray Pyrolysis:

Spray pyrolysis was the method of fabricating FTO glass. FTO itself comes from materials in the form of the chemicals Tin(II) Chloride Dihydrate ($SnCl_2.2H_2O$, Sigma Aldrich Germany) and Ammonium Fluoride ($NH4F$, Sigma Aldrich Germany) were dissolved in Ethanol 96%. These materials were then deposited on a glass substrate using the OMRON NE-C28 nebulizer as shown in Figure 1(a) [13]. Particle formation on the substrate was depicted in Figure 1(b).

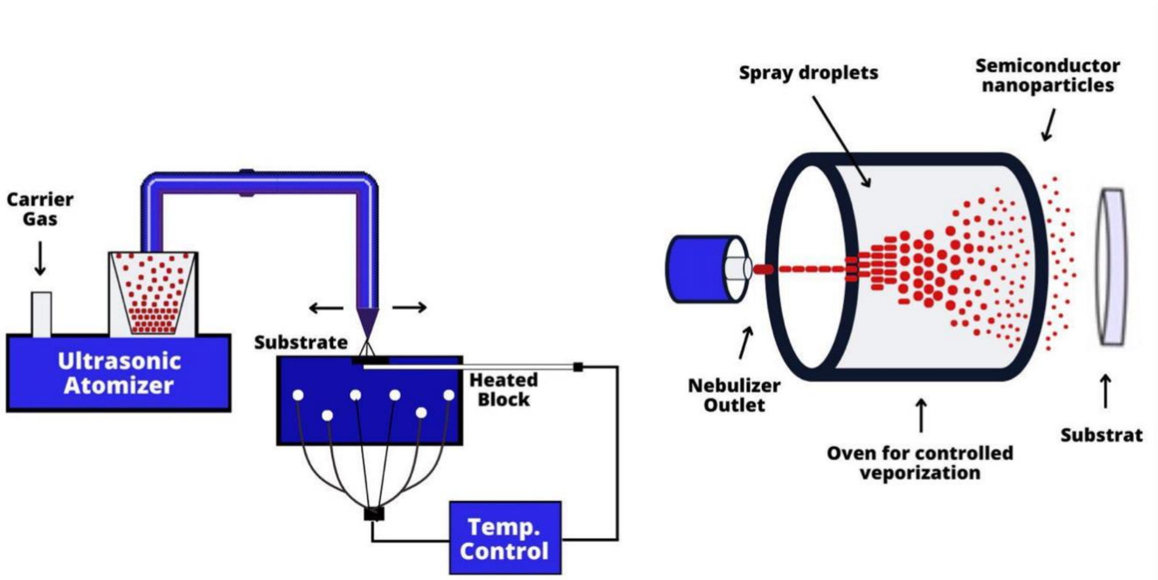


Figure 1.4: A Schematic diagram of the spray Pyrolysis process for Fabricating FTO layers: (a) Spray Pyrolysis Methods; (b) Inset deposition process on the substrate [13]

Chapter 2

Experimental details

2.1 Commercial FTO

Commercial FTO thin films deposited on glass substrates by a spray pyrolysis process were purchased from [Solaronix]. The 500 nm thick films (FTO) were deposited on glass substrates (2.2 mm thick) and 1"×1" size were used for the deposition of the oxide films.

Optical properties were measured with a UV-Vis spectrophotometer. The surface morphology were examined by scanning electron microscopy (SEM).

Prior to characterization, the FTO films were cleaned usingdetergent and washed with ethanol using an ultrasonic bath for 15 minutes. The films were then dried in oven at 100 0C for 30 minutes. Figure 2.1 shows the oven used for drying 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 Drying Oven used.

2.3 Scanning Electron Microscopy

The surface morphology of freshly cleaned samples (to avoid the effects of humidity) were investigated using Scanning Electron Microscopy (SEM) JEOL JSM-7600F. As shown in figure 2.2.

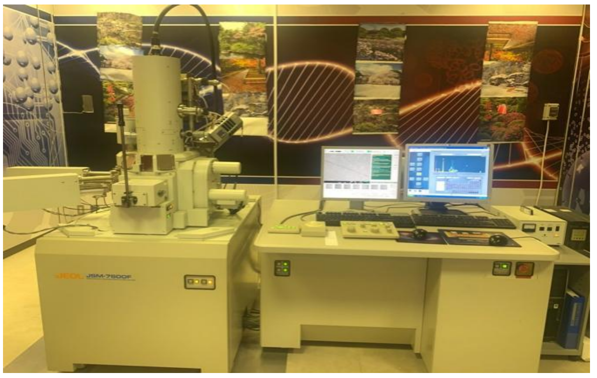


Figure 2.2: Scanning Electron Microscopy (SEM).

2.4 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 2.3 , over the range from 300 to 800 nm .

Figure 2.3 : UV-visible spectrophotometer

2.5 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 fluorine (F), tin (Sn) , and oxygen O_2 concentration of the FTO films.

Chapter 3

Results and discussions

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

The results of morphological characterization were obtained by SEM using a magnification of 100,000× for the FTO surface layer. A considerable number of pyramid-shaped SnO_2: F particles can be observed. Likewise, the space between particles (pores) also indicates that the particle fabrication process has not been fully homogeneous [15]. This causes particle contact to be not maximal so the layer resistance is large [14].

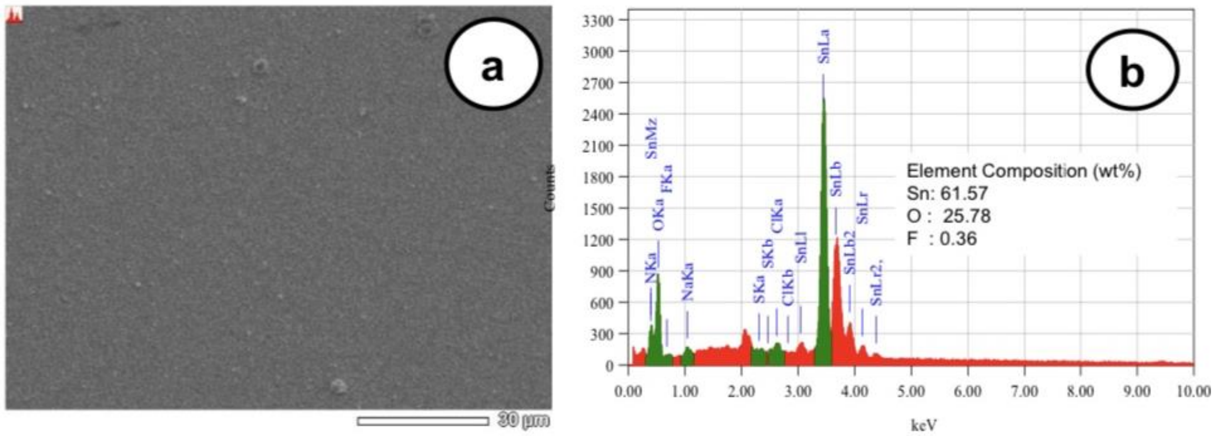


Figure 3.1: (a) The morphology and EDX results of FTO films obtained from references [16] [17].

3.1 Optical Properties

3.1.1:Transmission

Transmission was measured at wavelengths range (300 - 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 FTO was measured at wavelengths ranging from 300 to 800 nm, reflecting the film's efficiency in utilizing solar energy. The results indicate that FTO exhibits a high transmission rate of 80% at a wavelength of 500 nm, 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.

3.1.2: Reflection

Reflection of FTO films was measured at wavelengths range (300 - 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 11% at a wavelength of 500 nm. 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.

3.1.3: 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 9% at a wavelength of 500 nm. 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.

3.2: 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:

$$(\alpha h v)^2 = C\left(h v - E_g\right) \qquad (1)$$

where α the absorbance coefficient, hv 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.

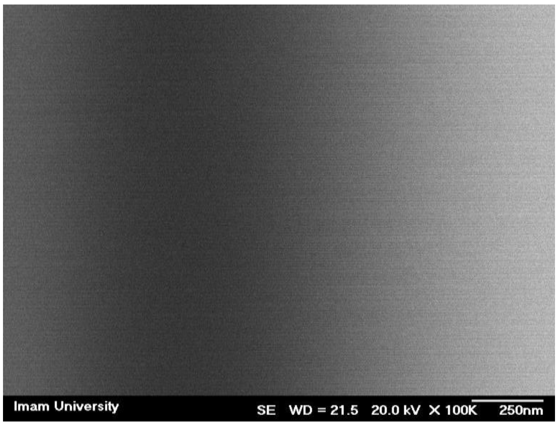
3.3 Energy Dispersive EDX

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 FTO film was obtained, revealing 71.9% oxygen, 24.2% tin, and 3.8% fluorine. These percentages reflect the ideal composition of the film and contribute to understanding how chemical composition affects the optical and electrical properties.

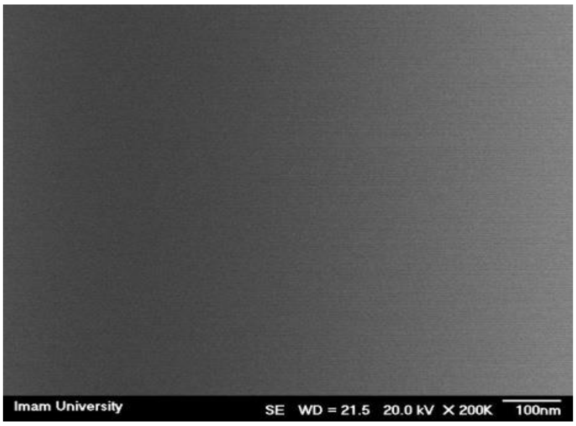
Additionally, these results provide insights into how to optimize the preparation process to achieve better characteristics for use in optoelectronic applications.

Our Result:

Figure 3.2. (a) and (b) of the FTO surface morphology with various magnifications. Even with high magnification 200k, the FTO film shows no features, this may be due to the small grain size of the film in the range of several nanometers. It is also clear that the FTO film consists of two parallel layers: top layer exposed to air and second layer on glass substrate side. That would result by an interference and fringes (due to varying thickness through the film and small grain size) in the reflectance and transmittance spectra, such kind of interference only appears between two parallel layers.



(a)100k



(b)200k

Figure 3.2: SEM micrographs of FTO films: (a) magnification 100k, (b) magnification 200k

Figure (3.3) shows the cross-sectional image of the FTO film on the glass substrate. The bright part of the image predicts that there is a good adhesion of the film with the glass substrate. It was difficult to predict the film thickness since the viewing angle was not known. Therefore, a cross-sectional view at an angle of 30^0 only, FTO thickness will be between 400-500 nm as mentioned by the supplier.

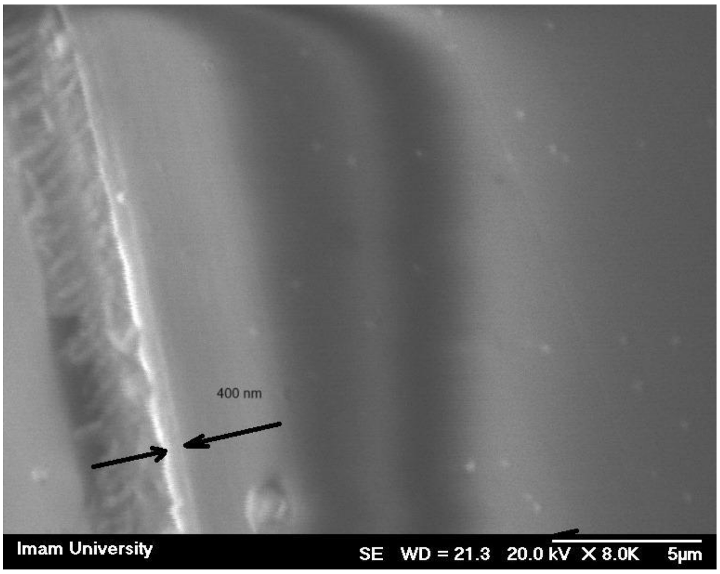


Figure (3.3) shows the cross-sectional image of the FTO film on the glass substrate.

Figure 3.4: Shows the Energy-Dispersive X-ray Spectroscopy (EDX) results for the FTO layer, providing information on the chemical composition of the thin film. The percentage of key elements such as oxygen, tin, and fluorine is displayed, which enhances the film's properties for optical applications.

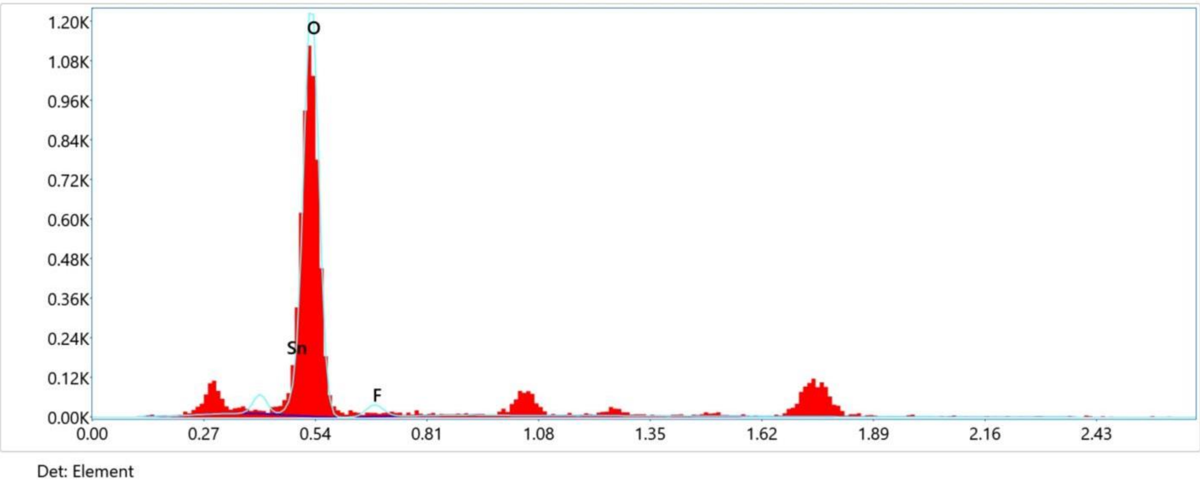


Figure 3.4: EDX of the FTO film.

A summary for the chemical composition of the FTO film is shown in table 3.1

Table 3.1: EDX results of the FTO film.

Element	Weight %	Atomic %
O K	71.9	91.7
F K	3.8	4.1
Sn M	24.2	4.2
Total	100.00	

Figure 3.5: Depicts a graph of the transmittance of the film across wavelengths ranging from 300 to 800 nm, demonstrating the film's capability to transmit light in this range, making it suitable for optical applications such as solar cells.

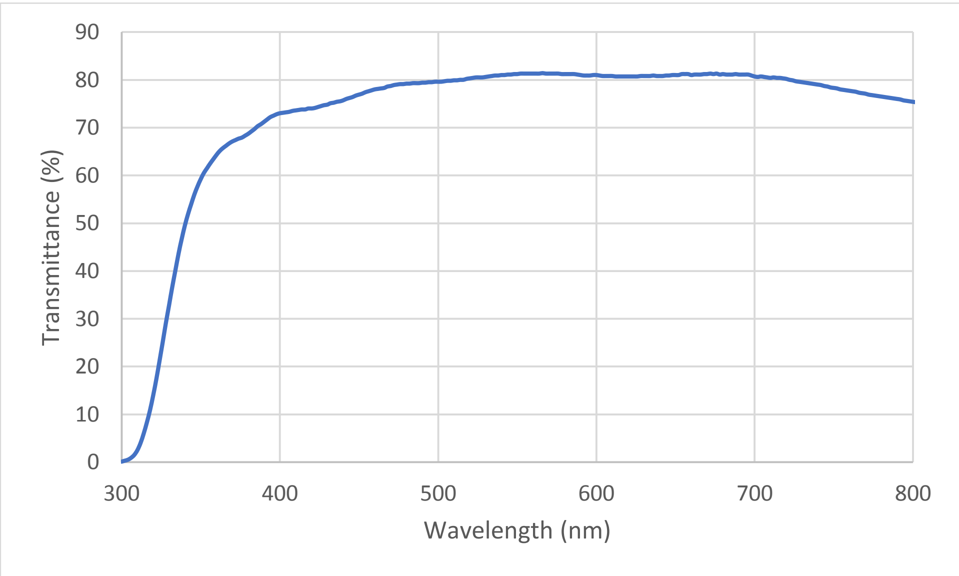


Figure 3.5: The transmittance versus wavelength of FTO film in range 300-800 nm

Figure 3.6: Shows a reflectance graph across the same wavelength range, indicating that the low reflectance at a particular wavelength enhances the film's efficiency in transmitting light by minimizing reflection, which boosts the device's optical efficiency.

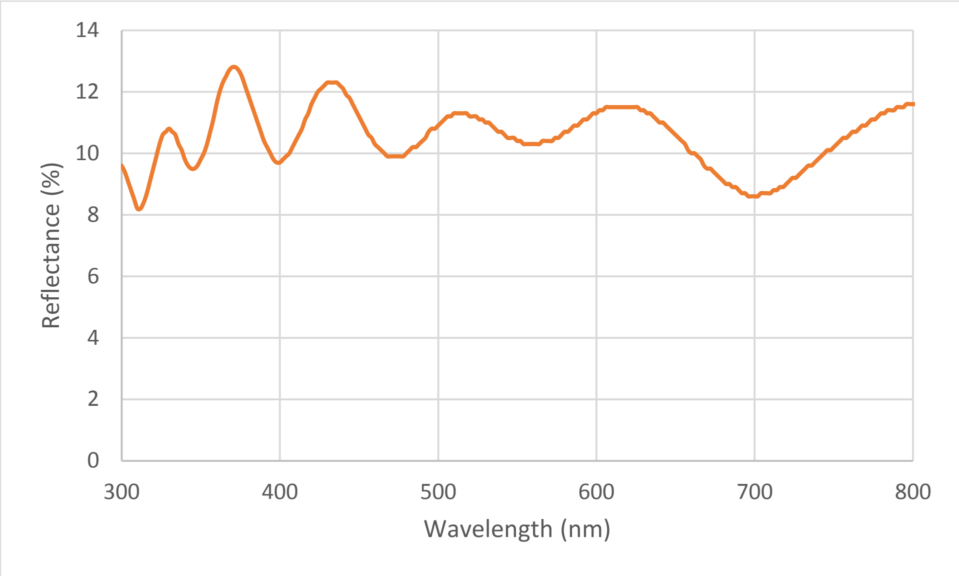


Figure 3.6: The reflectance versus wavelength of FTO film in range 300-800 nm

Figure 3.7: Displays the optical band gap relation of the film 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.

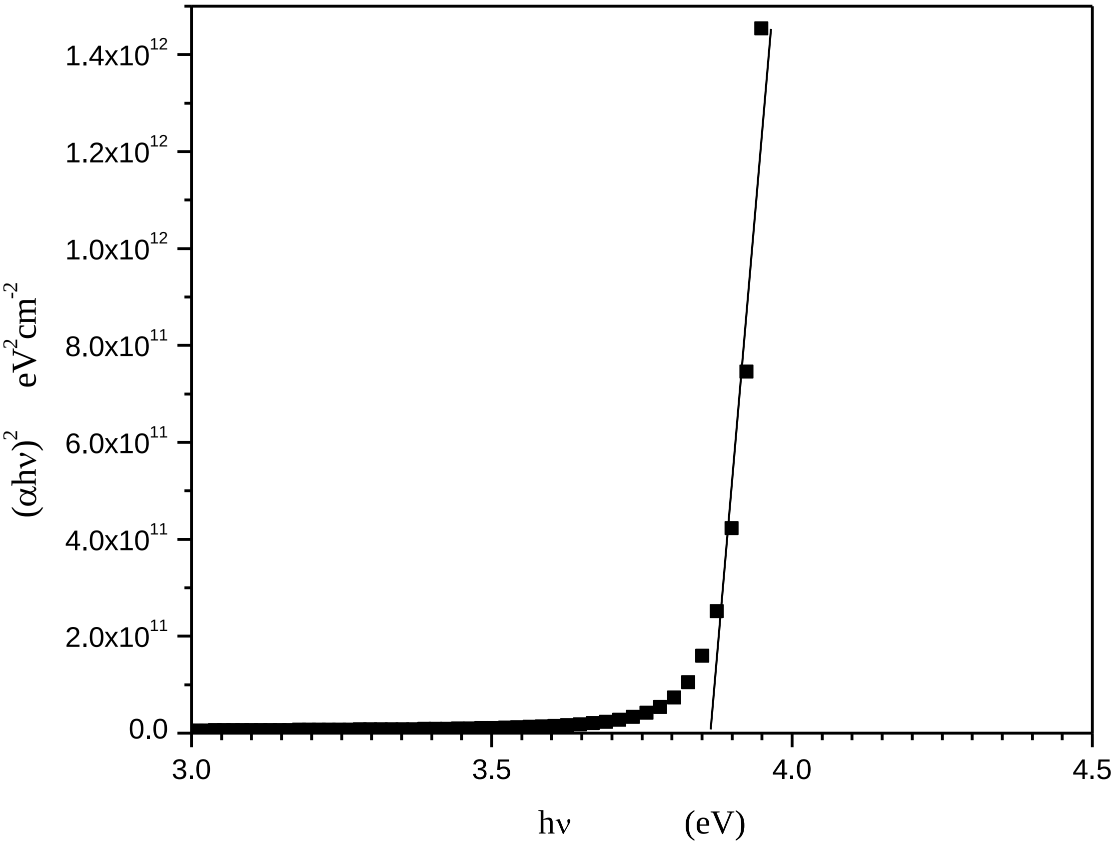


Figure 3.7: Direct optical band gap corresponding to $(\alpha h v)^2$ versus hv of the FTO film.

Table3.2: Summary of the optical properties with calculated Energy gap (Eg)

Sample	T%	R%	A%	Eg (ev)
FTO	80	11	9	3.86

N.B: T, R and A measured at wavelength 500 nm.

Conclusion

The good optical and structural properties of FTO films deposited onto glass substrates indicate that the oxide films studied in this research are suitable for opto-electronic devices such as anode for light emitting diodes and solar cells. High Optical transparency was maintained > 78% @ 555nm.

The conclusion serves as a critical synthesis of the research findings, emphasizing the significance of the optical and morphological properties of FTO thin films. The study successfully demonstrated that FTO, with its high transmission (80%), low reflection (11%), and minimal absorption (9%), is a promising candidate for use in optoelectronic applications, particularly in solar cells and light-emitting diodes. The analysis using EDX confirmed the favorable chemical composition of the films, which is essential for optimizing their performance in practical applications. Overall, the results indicate that careful control of deposition methods and parameters can lead to the fabrication of high-quality FTO films, paving the way for advancements in the field of transparent conductive oxides. Future work should focus on exploring different deposition techniques and their effects on the film properties to further enhance performance and applicability.

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