

Zakia Fekkai

Department of Physics, Al Imam Mohammad Ibn Saud Islamic University, Riyadh 11623, Saudi Arabia

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Abstract: Due to its high electrical conductivity and high transparency in the visible light wavelength range, transparent conductive oxide thin films are able to be used as semiconductor materials on electronic devices. Among these films/materials, zinc oxides (ZnO), indium oxides (In_2O_3) and tin oxide thin films (SnO_2) which are particularly attractive due to their optical, electrical and mechanical properties. In this investigation, the metal oxide films were prepared by pulsed laser deposition technique (PLD) using the same deposition parameters. The electrical, structural, and optical properties of these films were examined. The resistivity of the films were calculated based on the sheet resistance R_s measured by the standard four-point probe technique at room temperature. Concerning the structural properties, all films presented uniform, dense and smooth surface. The films were annealed for 1 hour at different temperatures (200-600 °C) in an argon atmosphere. Annealing greatly decreased the resistivity of the films. Atomic Force microscopy (AFM) measurements revealed an increase in surface roughness of the annealed films with temperature. Improvement to the crystallinity was observed from the double layers (SnO_2)/(ZnO) annealed at 300-400 °C and above with a slight decrease in the optical transmittance above (85%) in the visible region was exhibited by the films annealed at 400 °C and above. A lower resistivity and better spectra selectivity is a measurement of the quality and potential use of indium/tin oxides onto intrinsic zinc oxide deposited on cleaned glass substrates, for the application as transparent electrodes of electronic devices such as solar cells and organic light- emitting diodes.

Key words: Transparent conducting oxides, optical properties, annealing, pulsed laser deposition, optoelectronic devices.

1. Introduction

Among various functional thin film materials, metal oxides are particularly attractive due to their unique properties covering all aspects of material science and solid state physics. Tin oxide (SnO₂) is one of the most important metal oxides. SnO₂ is a transparent n-type semiconductor having a wide optical band gap of 3.8 eV.

Due to various properties, tin oxide is suitable for a number of applications such as transparent electrodes for solar cells, liquid crystal displays, highly active catalysts, anodes for lithium ion batteries, transistors, nano & ultra filtration membranes, gas sensors, anti corrosion coatings, etc..

In recent years, there has been an increase in the number of applications of (ZnO), indium oxides (In₂O₃) and tin oxide thin films (SnO₂) thin films, due to their unique optical, electrical and mechanical properties which are different to those of bulk material. All these metal oxides are n-type transparent semiconductors with a wide optical band gap in the range ($E_g = 3.8-4$ 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 [1-3].

Interest in transparent films with an oxide layer such as (ZnO), (In_2O_3) and (SnO_2) thin films has increased

Corresponding author: Zakia Fekkai, assistant professor, research fields: polymer physics, OLED and applied materials. E-mail: zakiafekkai@hotmail.co.uk.

due to its excellent electrical and optical properties for a wide range of applications including heat-reflecting mirrors [4], the field of flat panel displays [3] antireflection coatings [4], organic light-emitting diodes [5], and gas sensors [6], and as transparent electrodes in solar cells [7].

The major concerns for transparent metal oxide films transparent conducting oxides (TCO) deposition are as follows:

- low specific resistivity (< $1.50 \times 10^{-6} \Omega \cdot cm$);
- high uniformity across the substrate;
- low particle contamination;
- low manufacturing costs.

There are several deposition techniques to grow TCO thin films including chemical vapor deposition [11], magnetron sputtering [12, 13], evaporation [6, 14], spray pyrolysis [15], sol-gel [16] and pulsed laser ablation [10, 17]. The resulting TCO thin films exhibit low resistivity (ca. $4.2 \times 10^{-4} \ \Omega \cdot cm$) and high optical transmittance in the visible region (ca. 85%); and band gap of (3.87-4.78 eV), deposited on a glass substrates.

2. Experiments

Pulsed laser deposition (PLD) was used in the preparation of pure ZnO, In_2O_3 and SnO_2 thin films onto glass substrates at 400 °C. The films were grown in a typical PLD system that uses an excimer laser beam (KrF, $\lambda = 248$ nm, laser energy 2 J/cm², repetition rate 5 Hz) [1, 2]. The materials of deposition targets were commercially available of 99.999% pure In_2O_3 , SnO₂ and ZnO. The targets employed during

thin film growth were sintered and pressed locally. Prior to film deposition, the (0.7 mm thick) glass substrates were cleaned by sonication with detergent (acetone, methanol), rinsed with deionised water for 20 min, blown dry by nitrogen gas and finally dried in the oven at 120 °C for outgassing. Fig. 1 shows a schematic diagram of the pulsed laser deposition process (PLD).

Immediately after drying, the substrates were transferred to the PLD system for the deposition of zinc oxide materials (70 nm thick) and then indium or tin oxide layers (30 nm). The base pressure pressure prior to deposition was approximately 2×10^{-6} Torr. Substrate to target distance was 32 mm and was maintained at the same value for all experiments. Film growth was performed at a temperature of 300 °C in an oxygen pressure of 10 mTorr for 20 min.

After deposition, the samples were divided into two sets: one for characterization as-deposited and one set to be annealed in an argon atmosphere for 1 h at various temperatures (200, 300, 400, 500, and 600 °C), and then charaterized in order to investigate the changes in microstucture or properties if any. Resistivities of the films were measured using a four-point probe configuration/method at room temperature for as-deposited and annealed films. The surface morphology and roughness of the films before and after annealing were observed using atomic force microscopy (AFM) in tapping mode. The structural properties and grain sizes of the grown films were investigated using an AFM.



Fig. 1 A schematic diagram of the Pulsed Laser Deposition process.



Fig. 2 A cross-sectional view of metal oxide physical interface structure used as an electrode in optoelectronic devices.



Fig. 3 The TRansmission spectra of the ZnO/In_2O_3 thin films: (a) for different annealing temperatures; (b) for selective annealing temperatures as a function of wavelength.



Fig. 4 The transmission spectra of the ZnO/SnO_2 thin films for different annealing temperatures as a function of wavelength.

The optical transmittance and absorption measurements were performed with an UV/V is spectrophotometer. A typical proposed physical interface structure used in our investigation is shown in Fig. 2.

After all the film depositions and during characterization, the nano-structured layers were kept in a nitrogen-filled box to protect them from oxygen and water vapors.

Finally, energy dispersive X-ray spectroscopy (EDX) was used for the elemental analysis or chemical characterization of transparent conducting oxide samples.

3. Results and Discussion

3.1 Optical Properties

Fig. 3 represents the transmittance in the visible wavelength range from 300 nm to 800 nm of a 75 nm thick $ZnO:In_2O_3$ thin films. All deposited films showed high transmittance more than 80%. Furthermore, the TCO films show an increase of transmittance with annealing temperature which probably indicates that the annealing treatment improved the crystallinity.

The optical transmission characteristics of ZnO/SnO_2 thin films deposited on glass substrates are shown in Fig. 4. The annealed films showed an increase in the transmission with increased annealing temperatures.

3.2 Resistivity

The sheet resistance R_s of the TCO 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

Resistivity (Ω ·cm) ×10 ⁻⁴ for SnO ₂ :ZnO films	Annealing temperature (°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	400	3.86	
2.2	500	3.91	
1.98	600	4.10	

Table 1 Resistivities and band gap values for SnO₂:ZnO annealed at various temperatures.



Fig. 5 Plot of $(EA)^2$ versus photon energy for ZnO/In₂O₃ films fabricated by annealed at 500 °C.

calculated from the simple equation $\rho = R_s d$, where *d* is the TCO film thickness. A low resistivity of 2.25×10^{-4} $\Omega \cdot cm$ was measured for the 100 nm thick SnO₂/In₂O₃:ZnO films at ambient temperature.

Annealed films had lower resistivity than the as -deposited TCO ones ranging from $20 \times 10^{-4} \Omega \cdot \text{cm}$ to $2.2 \times 10^{-4} \Omega \cdot \text{cm}$. Probably due to increase in carrier concentration with the indium/tin oxides entering into the ZnO lattice caused a shift in absorption edge and the average transmittance increased to 85% in the visible region. Resistivities and band gap values for SnO₂:ZnO annealed at various temperatures are shown in Table 1.

The absorption spectra (EA) of the ZnO: In_2O_3 films in the band gap edge region have been obtained from the optical transmission and reflection measurements at room temperature, the energy gap was found to be very similar for the as-deposited and annealed films ($E_g =$ 3.25 eV).

3.3 Atomic Force Microscopy

AFM was also used to find surface roughness and

grain sizes of the deposited TCO (ZnO/In₂O₃) films used as anodes in the optoelectronic devices. Images are provided (Fig. 6) at 20 μ m magnification for transparent oxide films. The deposited film surfaces were mainly smooth and dense for all the films used, and showed fine crystalline structure, with grain sizes at 300 °C temperature in the range of 5-6 nm. Smooth and dense anode would enhance its chemical stability, especially when used in long term operation of optoelectronic devices. Fig. 6 shows the AFM images of the surface roughness and morphology of In₂O₃:ZnO films.

Fig. 7 shows the morphology of SnO₂:ZnO thin films with small grain sizes of 5-7 nm. It shows a surface roughness of approximately 15 nm. The surface roughness and work function of transparent conducting oxide films are very important to enhance the stability and efficiency of optoelectronic devices such as solar cells and light emitting diodes. All functional active layers of the devices which act as injection, transportation and emission layers are deposited on TCO, so surface morphology of TCO film is directly transferred to them and uneven interface is not desirable for the efficiency and stability of these devices.

3.4 Energy Dispersive X-Ray Spectroscopy (EDX)

EDX was used for the elemental analysis or chemical characterization of transparent conducting oxide samples. The EDX characterization results are presented in Fig. 8.

EDX analyses show that Zn, O and In elements in the sample In_2O_3/ZnO present in the solid film. The Si



Fig. 6 AFM images of (a) the Surface of In_2O_3 : ZnO thin film annealed at 300 °C for 60 minutes with small grains and (b) and roughness of the film.



Fig. 7 AFM images of: (a) the Surface of SnO_2 : ZnO thin film annealed at 300 °C for 60 minutes with small grains and (b) and roughness of the film. It shows a surface roughness of approximately 15 nm.



Fig. 8 EDX spectra of the films: (a) In₂O₃: ZnO and (b) SnO₂: ZnO.

Table 2	represents	the	elemental	weights in	the	deposited	films.
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	Zinc (wt%)	Oxygen (wt%)	Indium (wt%)	Tin (wt%)
In ₂ O ₃ /ZnO	3.8	6	0.85	-
SnO ₂ /ZnO	3.8	0.85	-	0.85

Mg, and Ca elements that are not expected to be in solid films may probably result from the glass substrates. Elemental weights (wt. %) of Zn, O and Sn elements in the SnO2/ZnO thin films are listed in Table 2. These spectra show that the expected elements exist in the solid films.

4. Conclusions

In summary, this paper presents the fabrication of a nano-structured electrode with highly transparent and conducting oxide (TCO) thin films. It has been proved that TCO thin film with low resistivity (ca. 2.2×10^{-4} $\Omega \cdot cm$) and high visible-light-transmittance (ca. 80%-85%, band gap, 3.71 eV) can be achieved on glass substrate using a pulsed laser deposition process. The super-smooth TCO films obtained here are applicable to various optoelectronic devices such as solar cells and organic light emitting diodes.

Annealing the nano-structured film would improve the adhesion of the physical interfaces between the PLD deposited films and the substrate. The atomic force microscopy (AFM) showed an increase in the surface roughness of the annealed films while maintaining high transmittance in the range 80-85% for the visible region (300-800 nm). Resistivity decreased rapidly for the annealed films.

Highly transparency, good conductivity and super smooth properties of transparent conducting oxide (TCO) thin films are particularly desirable in optoelectronic devices.

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