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Preparation of Nanostructure ZnO-SnO_2 Thin Films for Optoelectronic Properties and Post Annealing Influence

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***Abstract*—**ZnO-SnO_2 i.e. Zinc-Tin-Oxide (ZTO) thin films were deposited on glass substrate with varying concentrations (ZnO:SnO_2 - 100:0, 90:10, 70:30 and 50:50 wt.%) at room temperature by flash evaporation technique. These deposited ZTO film were annealed at 450 0C in vacuum. These films were characterized to study the effect of annealing on the structural, electrical, and optical properties. Atomic force microscopy (AFM) and Scanning electron microscopy (SEM) images manifest the surface morphology of these ZTO thin films. The apparent growth of surface features revealed the formation of nanostructure ZTO thin films. The small value of surface roughness (root mean square RRMS) ensures the usefulness in optical coatings. The sheet resistance was also found to be decreased for both types of films with increasing concentration of SnO_2. The optical transmittance found to be decreased however blue shift has been observed after annealing.

***Keywords*—**ZTO thin film, AFM, SEM, Optical transmittance, Sheet resistance.

I. Introduction

TRANSPARENT conducting oxide (TCO) films have been widely used in the field of optoelectronics such as flat panel displays, solar cell, IR reflectors, light emitting diode (LED) etc. Therefore, there has been a rapidly growing demand for TCO films in recent years [1]. At present indium tin oxide (ITO) is used as TCO films because of its low resistivity and high transmittance in the visible region. However, ITO contains the rare and expensive indium element and thus it is necessary to develop new TCO materials that are composed of abundant and inexpensive elements [2, 3]. Apart from other TCO thin films, ZTO thin films show high visible transmittance and n-type electrical conductivity therefore they are able to show their promising applications as an alternative TCO material due to their low cost as the constituents ZnO and SnO_2 are much cheaper [4]. J.H. Ko et al [4] studied the Zn-Sn-O (ZTO) film with continuous compositional gradient of Sn (16-89 at.%). The optical transmittance of ZTO films were between 75 and 90% in the visible region. The shift of absorption edge towards shorter wavelength upon annealing at 450 0C was attributed to the Burstein-Moss effect. E. Cetinorgu et al [5] studied the effect of deposition conditions on the characteristics of ZnO-SnO_2 films. The high transmission (70-90%) has been measured in the visible region. In this paper, transparent ZnO-SnO_2 i.e. Zinc-Tin-Oxide (ZTO) thin films were investigated with the aim of fabricating new cost effective transparent conducting oxide films having structural, electrical, and optical properties in comparison to expensive TCOs materials like ITO.

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II. Experimental Detail

ZTO thin films were deposited on glass substrates by flash evaporation technique [6, 7] using HINDHI Vacuum coating unit at a pressure of 10-6 torr. High purity ZnO (99.99%) and SnO_2 (99.9%) powders at different concentrations (100:0, 90:10, 70:30 and 50:50 wt. %) were mixed with the help of steel balls for one hour using ball milling (Retsch-TM100, Germany). The spacing between target i.e. boat shaped tantalum filament and substrate was fixed at 10 cm. The thickness of the prepared films was measured by a quartz crystal thickness monitor. Thickness of all the films was observed in the range 1000±25Å. Substrate was kept at room temperature. Deposition rate was kept in the range of 20 ±2 Å/sec. The current and power supplied in the boat type filament were in range of 4-5 ampere and 240-350 watt respectively. Deposition conditions were maintained carefully stable during the growth of ZIO films. Surface morphology of the films was investigated by AFM (Digital Instruments NanoScope IIIa) and SEM (LEO-435VP scanning electron microscope). The I-V characteristics of the films were determined using the four-probe van der Pauw technique. The absorption spectra of as prepared ZTO thin films were taken in the range 300-800 nm with the help of spectrophotometer (Hitachi-330). Further, these ZTO thin films were annealed in vacuum at the temperature 450 0C for 1 h. The heating rate was kept at 10 0C/min. The annealed films were also characterized by AFM, SEM, electrical, and optical measurements with the same instruments.

III. Results and Discussion

The surface morphology of the films has been studied by atomic force microscopy (AFM). Fig. 1 shows the surface morphology of as-prepared and annealed ZTO (50:50 wt. %) thin films as a specimen. The apparent growth of surface features in both types of ZTO films is evident from three

dimensional AFM images. The AFM data showed that the ZTO thin films were homogeneous and uniform with regard to surface topography and thickness. The average grain size calculated was 44 nm. The grain size increased after annealing and approached to 100 nm. Surface roughness of thin films plays a vital role for developing optical coatings especially in the UV region for application such as lithographic uses [8]. The root mean square roughness not only describes the light scattering but also gives an idea about the quality of the surface under investigation. The measured surface roughness (root mean square RRMS) for as-prepared film was 7 nm. The surface roughness was increased to 13 nm after annealing. The improvement of the surface roughness after annealing can be attributed to increase in crystalline nature due to which rough surface developed Units

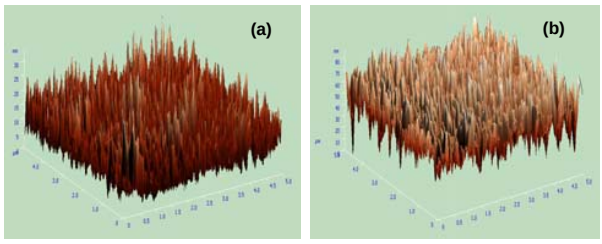

Fig. 1 3D-AFM of (a) as-prepared and (b) annealed ZTO (50:50 wt. %) thin films

The surface morphology of the films has been also studied by Scanning electron microscopy (SEM). Figs. 2 (a and b) and 3 (a and b) show SEM image of as-prepared and annealed ZTO (100:0 wt. %) and ZTO (50:50 wt. %) films respectively. The micrograph indicates that films were crack-free. It was revealed from as-prepared ZTO films of both compositions that the films were composed of roughly spherical grains of varying size. Absence of apparent grains on the surface of as-prepared ZTO (100:0) film can be interpreted as amorphous nature of film. The grains were appeared in films after addition of SnO_2 and post annealing. The average grain size calculated was 48 nm for as- prepared ZTO (50:50 wt. %). Further, the average size of grains approached to 37 nm for annealed ZTO (100:0) film and 115 nm for annealed ZTO (50:50 wt. %) film. Therefore, the grain size increased after annealing. The higher grain sizes in annealed ZTO films, as esteemed from SEM images, indicate that there may be agglomeration of the particles resulting in increased size. The similar trend of increasing grain size was also observed in AFM results.

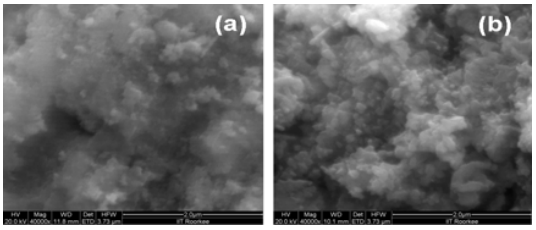

Fig. 2 SEM image of (a) as-prepared (b) annealed ZTO (100:0 wt. %) thin films

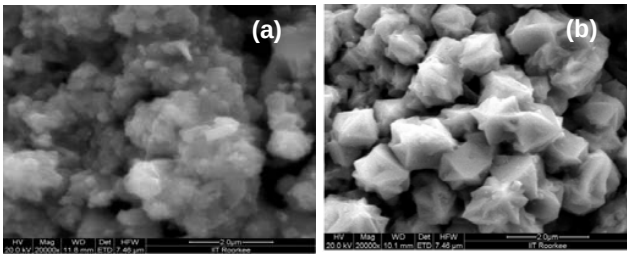

Fig. 3 SEM image of (a) as-prepared (b) annealed ZTO (50:50 wt. %) thin films

The I-V characteristics of as-prepared and annealed ZTO thin films with varying concentration of SnO_2, are shown in Fig. 4(a) and Fig. 4(b) respectively. It can be noticed that the I-V curves show ohmic behavior.

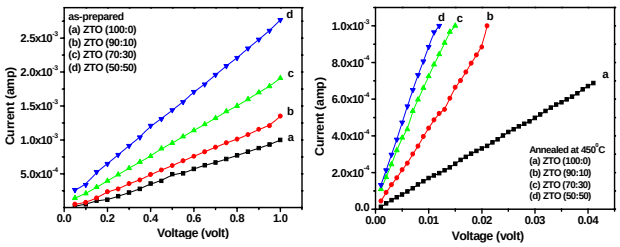

Fig. 4 I-V characteristics of (a) as-prepared and (b) annealed ZTO thin films

Table II shows that the sheet resistance are found to be decreased as concentration of SnO_2 increased from 0 to 50 wt.%. This behavior of sheet resistance could be understood as the tin atoms may diffuse into ZnO matrix in ZTO thin films. Due to difference in their grain sizes, diffusion of SnO_2 in ZnO matrix causes an increase in free interstitial lattice spaces. The annealing process causes a greater possibility of diffusion of SnO_2 from grain boundaries and interstitial lattice locations to regular ZnO lattice locations [10]. After annealing the grain growth results in less grain boundary and, consequently, there is less grain-boundary scattering and thus the mobility of the charge carriers enhanced.

TABLE II
SHEET RESISTANCE OF AS-PREPARED AND ANNEALED ZTO THIN FILMS

Specimen	Sheet resistance R_s (Ω/cm^2)	
	as-prepared	annealed at 450 ^{0}C
ZTO (100:0)	10430	641
ZTO (90:10)	8259	232
ZTO (70:30)	5453	140
ZTO (50:50)	3693	112

Transmittance of as-prepared and annealed ZTO thin films with varying concentration of SnO_2, are shown in Fig. 5 over the wavelength range from 300 nm to 800 nm. For as-prepared films, the transmittance is decreased from ~95% to 70% where as it has been decreased from ~90% to 50% for annealed films as concentration of SnO_2 increased from 0 to 50 wt.%.

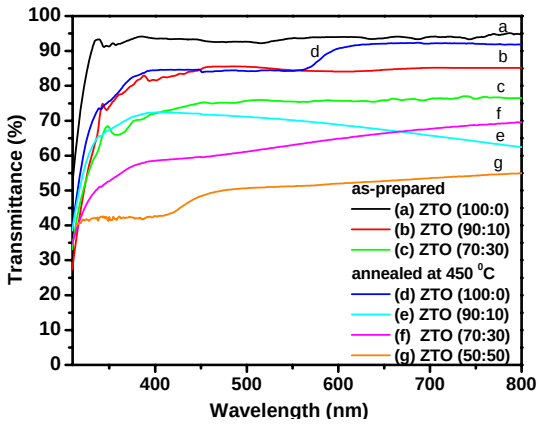

Fig. 5 Optical transmission spectra of ZTO thin film

It is also observed from figure that the transmittance of the annealed films is smaller than that of the as-prepared films. D. Beena et al [9] represented a general phenomenon of decreasing the transmittance of the film due to the many factors like (i) presence of mixed phases (ii) increase in thickness (iii) presence of defects and oxygen vacancies (iv) large rms surface roughness (v) porous nature of the films and (vi) grain boundary scattering, etc. but in the present case it seems that the decrease of the transmittance is caused by the rough surface developed during grain growth of the annealed films. AFM and SEM images show the enrichment of average grain size and surface roughness after annealing as well as increasing the concentration of SnO_2. A rough surface scatters light and reduces transmittance. After annealing, there is a possibility of oxygen desorption which leads to oxygen vacancies. Oxygen vacancies like defects are the source of charge carriers. Hence, scattering of light by the charge carriers and oxygen vacancies like defects may be the reason for the reduction in transmittance exhibited by the annealed film. S. Kaleemulla et al [6], D. Beena et al [9] and Wen-Fa Wu et al [10] were also observed that transmittance decreases at higher substrate temperature and after annealing respectively. The absorption edge of the ZTO films moved towards the higher wavelength with increasing concentration of SnO_2. The shifting of absorption edge toward the lower wavelength upon annealing at 450 ^{0}C can be attributed to the Burstein-Moss effect resulting from the increase of the carrier concentration.

IV. Conclusion

In summary, we have studied the structural and optical properties of cost effective ZTO thin films with varying concentrations with the effect of annealing. The AFM and SEM images showed improvement in grain size and surface roughness of nanostructured ZTO films. The ZTO thin films have been shown ohmic behavior in nature. The reduction of sheet resistance with the increasing concentration of SnO_2 and after annealing may be attributed to increase in mobility due to diffusion process, less grain-boundary scattering etc. The optical transmittance of films decreases while blue shift has been observed after annealing due to BM effect. The ZTO films exhibit high transmittance (~95-70%) in visible region.

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