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SYNTHESIS AND ELECTRICAL CHARACTERIZATION OF ALUMINIUM DOPED ZINC OXIDE THIN FILMS

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Al doped ZnO (AZO) thin films for different compositions were deposited by using sol-gel technique. Thin film preparation, structural, optical and electrical properties have been studied. Investigations on the effect of structural, optical and electrical properties revealed the relationship that exists between these properties and the film lattice defect distribution. XRD studies showed that AZO thin films a preferred orientation (002) direction, and decrease in the lattice distance indicating a less defected structure. The electrical and optical properties of AZO films have reached a good level. Films with electrical resistivity as low as 1.84×10^{-3} Ω cm and 90 % optical transmittance in the visible region, which is suitable for gas sensing applications. It is found that electrical resistivity was due to increase in concentration of donor atoms.

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1. Introduction

Transparent conductive films (TCF) were fabricated from transparent conductive oxides (TCO) such as tin-doped indium oxide (ITO) [1]. Now a day's TCFs are widely used in existing optoelectronic devices such as light-emitting diodes, solar cells and flat panel displays [2, 3]. The performances of these devices were influenced by the properties of TCF. Hence, it has great importance in the electrical and optical devices. In order to improve the device performance, fabrication and properties need to be controlled. A conductive transparent cadmium oxide thin film by sputtering and thermal oxidation of cadmium on glass reported good electrical properties [4]. Currently for mass production, Tin-doped indium-oxide (ITO) has been used in the TCO preparation, considering the cost and shortage of ITO [5] in near future. Literatures reveal that the zinc oxide (ZnO) stands out as a potential alternate for ITO due to its wide range of electrical and optical properties obtained by doping and controlled processing [2].

ZnO-based thin films were doped with various elements, i.e., aluminum (Al), indium (In), tin (Sn), gallium (Ga) and manganese (Mn) [6-8]. Among these dopants, Al presence significantly influenced the crystalline size and film thickness. Doping Al up to 1 at% decreased the resistivity of intrinsic ZnO thin films [9], which has high chemical and mechanical stability. It stands out as a promising application in such as gas sensors, memory devices, UV-light emitting diodes, photodiodes, photodetectors, solar cells, piezoelectric transducers, transparent conductive oxides, and biomedical [10–15]. The desired characteristics need to be balanced with the processing costs for the practical industrial applications. Hence, in order to study the suitability of ZnO candidature, it was processed through various techniques such as chemical vapour deposition [16], pulsed laser deposition [17], sputtering [18], and sol-gel process [19]. Out of these various techniques sol-gel

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process stands as a promising method for controlled chemical composition with low cost and processing temperature to obtain consistently chemically homogenous thin films [20]. Parameters that affect the characteristics of TCO are viscosity, composition, pH, substrate/film interaction and coating technique (dip or spin). The other important factors that influence TCO are furnace atmosphere, drying and annealing time [21]. This technique holds good for both large and small-sized substrates which can be employed for advanced applications [21, 22]. The major criteria for preserving the c-axis orientation in doped ZnO are achieved possibly by sol-gel technique. Annealing at high temperature reported low resistivity [7].

In this paper, an attempt have been made to fabricate cost effective thin film deposition using aluminum-doped zinc oxide (AZO) with different concentrations on the glass substrates by using sol-gel process . Investigations on AZO thin films were carried out to study the effect of structural, optical and electrical properties.

2. Experimental Procedure

Zinc acetate dehydrate [$Al(NO_3)3{\cdot}9H_2O$] (Sigma-Aldrich, assay ≥98 %) was dissolved in 2-methoxyethanol [$C_3H_8O_2$] (Sigma-Aldrich, assay ≥99.5 %) to prepare AZO solutions with different concentrations (1-5 at%). The magnetic stirrer was used to refluxed at 80°C for 30 min. Ethanolamine was added to prevent precipitation in the solution. Molar ratio 1:1 was followed for ethanolamine/zinc. The refluxing was carried out for 1h 45min, maintaining the same temperature; aluminium nitrate nonahydrate (($Al(NO_3)3\ 9H_2O$) was added and stirred for 1 hour and the obtained solution was stable and clean. Glass substrates were cleaned ultrasonically in acetone for 10 min prior to deposition and dried with hot air. In Spin coating deposition technique, the substrates were rotated at speed 2500 rpm. 180 µl of solution was dropped on the rotating substrates. AZO coated substrates were heated at 220- 250 °C (drying) for 10 min after each coating. By repeating this procedure seven times the films with different thickness were obtained. The obtained thin films were annealed between 400 - 500 °C in Ar for 1h. Heating from 25 to 500 °C was performed with rate of 5 °C per min.

The as deposited samples were characterized by using XRD [SEIFERT Diffractometer with Cu-K_α radiation] to identify the phase. Peaks measured by XRD analysis were identified by comparing with those of JCPDS data. Ellipsometric measurements were performed, under 70 ° incidence angles, between 350 and 800 nm by using spectroscopic ellipsometer (Horiba Jobin Yvon Uvisel) with rotating polarizer. Transmission spectra taken on UV–vis spectrometer (Perkin Elmer) in the wavelength range 300–800 nm to measure the transmittance. The electrical resistivity was measured at room temperature by using the four probe technique

3. Results and Discussion

3.1 XRD

Figure 1 shows the XRD diffraction patterns of Al doped ZnO (Al -1 at%) films. The AZO exhibits a hexagonal wurzite structure, while the Al dopants replace the Zn lattice sites in AZO. These sol-gel prepared samples were annealed at various pre-heating temperatures of 400–500 ºC and then heated at 500 ºC. XRD diffraction peaks at 31.8, 34.4 and 36.2º, correspond to (100), (002) and (101) planes in the AZO films, respectively. Hexagonal wurzite structure was preserved with (002) preferred crystal orientation on the glass substrates. The slightly higher diffraction angles were due to the smaller ionic radius of Al than Zn. Thermal treatment process affected the crystallinity of the AZO films, with crystalline quality being improved at 500 ºC.

3.2 Optical properties

Transmittance spectra of the sol-gel deposited AZO thin film are presented in Fig. 2 for the wavelength range of 300–800 nm. Transmittance spectra for the non-annealed and annealed sample AZO (Al - 1 at%), the optical transmittance is found in the visible range is 80–90%. The highest transmittance was obtained at around 90% for the lowest (500 ºC) heat temperature. The reduction in optical transmittance at high annealing temperature was likely to be caused by the segregated Al_2O_3 and micropores that could be formed in the AZO films during the post-deposition heating.

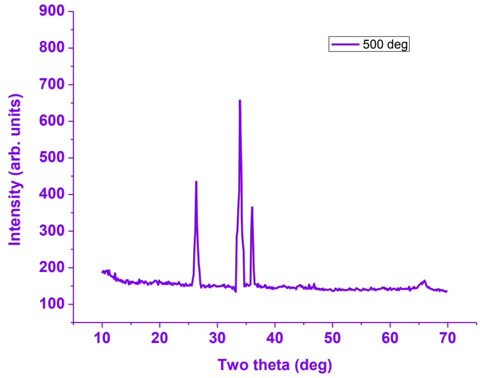

Fig. 1 XRD pattern for aluminum-doped ZnO (Al- 1 at.%) thin film

3.3 Film thickness

The average film thickness of AZO thin films was measured by using ellipsometer. All glass samples were deposited with Al-doped ZnO thin films under similar conditions besides varying aluminum doping level. The significant difference in thickness was observed by varying aluminum content in sol solution. AZO film with Al -1 at% doping was found to have maximum thickness (14.3 µm) than other samples. It was also evaluated that after first dipping and drying cycle, the film structure was porous and had uneven surface thickness. The successive second and third dipping cycles eliminated pores and defects due to penetration of sol solution, hence making the film more compact and uniform.

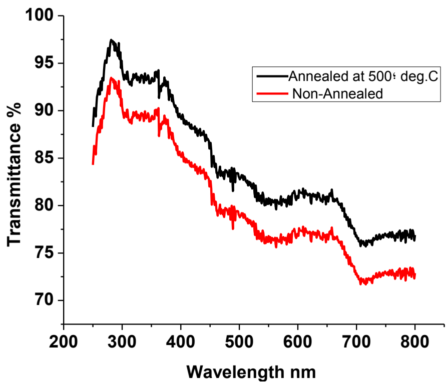

Fig. 2 The optical transmittance spectra of the aluminum-doped ZnO (Al-1 at.%) thin films in the wavelength range 300–900 nm

3.4 Electrical properties

The sheet resistivity of the AZO thin films with different pre-heating temperatures was analyzed by the Mitsubishi MCP-T600 four point probes at room temperature. The data obtained shown in fig 3 is analyzed. Electrical conductivity of ZnO thin film is influenced by the oxygen vacancies and Zn interstitials. Both structural defects provide extra electrons as carriers, thus making great n-type materials. The resistivity decreases with the increasing pre-heating temperature, with a clear critical temperature of 420ºC. The AZO thin film sample (Al-1 at%) that was heated at 500ºC measured sheet resistivity of 1.84×10^{-3} Ω cm, exhibited low electrical resistivity. The gradual increase in resistivity is depicted by the increased lattice distortion caused by the additional N and NO that occupy oxygen vacancies.

On the other hand in the AZO thin films, some Al atoms replace oxygen vacancies and even deplete the formation of Zn interstitials. The electrical charge is balanced between N_{3-} and O_{2-} by creating electron holes. Thus makes it possible for the AZO films to become p-type materials.

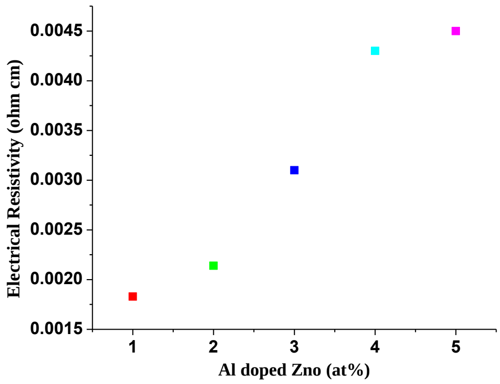

Fig. 3. Electrical resistivity of the deposited Al doped ZnO thin films on Al concentration

4. Conclusions

AZO thin films on glass substrates were successfully prepared by sol-gel processing. The samples were analyzed and drawn the following conclusions are:

XRD results showed clear (002)-oriented polycrystalline films on the glass substrates.

AZO (1 at%) thin film heated at 500ºC exhibited the lowest sheet resistivity of 1.84×10^{-3} Ω cm. The characteristics were depicted by the gradual increase in N and NO that occupy the oxygen vacancies.

Optical transmittance in the visible range was high at 80–90%.

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