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Study of Transparent Conducting Oxide (ZnO:Al) Thin Film at 723k by Nebulized Spray Pyrolysis Technique

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Abstract: Transparent Conducting oxide (ZnO:Al), thin film was deposited by nebulized spray pyrolysis technique starting from zinc acetate dehydrate and aluminium chloride hexahydrate. The structural, morphological, optical and electrical characterization on the TCO thin film such as X ray diffraction, SEM, UV-visible spectrometer and four-probe studies are taken respectively. From the X-ray diffraction, the TCO thin film is polycrystalline in nature with hexagonal structure and the average crystallite size is 25 nm. The most prominent X-ray diffraction peaks corresponding to [100], [002] and [101] planes are found. The surface morphology of the prepared film shows smooth and uniform spherical grains without creaks or pinholes and well covered to the glass substrate. High transmittance and low resistivity value is presence of the TCO thin film. The direct band gap value is 3.31eV. The calculated value of activation energy Ea is 0.16eV for 0.1 M concentration. This technique is very simple and low cost to producing transparent conducting oxide thin film.

Key words: Al doped ZnO, Nebulized Spray Pyrolysis, Structural, morphological, Optical and electrical measurements.

1. Introduction

Transparent conducting oxide (TCO) thin films are materials with numerous applications in electronic and optoelectronic devices as well as some other applications such as protective coatings, heat mirrors, and catalysis [1]. ZnO can also be used as a transparent conducting material in solar cells, transparent transistors and in so many consumer products [2]. Its property as a TCO material can still be improved by doping. Doping leads to increase carrier concentration and provides conducting electrons to reduce resistivity. In recent various metals are doped with zinc oxide such as, indium [3], gallium [4] and aluminium [5]. Al doped ZnO thin films have high transmittance in the visible region, and low electrical resistivity. Doping of Al improved the electrical conductivityand thermal stability of ZnO films and the optical band gap of ZnO can be controlled by using Al doping amount [6]. Various techniques such as chemical vapourdeposition (CVD) [7], thermal evaporation [8], magnetron sputtering [9], sol–gel method [10] and spray pyrolysis method [11] are used to produce doped ZnO thin films. Recently, Al doped ZnO films have been deposited by nebulized spray pyrolysis (NSP) method [12]. In the present work, we prepared transparent conducting oxide ZnO:Al thin film using nebulized spray pyrolysis technique.

2. Materials and method

The TCO thin film were prepared using 0.1M Zinc acetate dehydrate [Zn (CH3COO)2.2H2O] and 3% of aluminium chloride [AlCl3.6H2O] Hexahydrate, were dissolved in 10 ml of distilled water and two drops of acetic acid were added for solution transparency. The cleaned glass substrate was kept onto the hot plate and the substrate temperature was maintained at 723k using temperature controller with k-type thermocuple. The distance between the substrate and spray nozzle is 50mm and the carrier pressure was maintained 1.0 kg/cm^2. The solution was sprayed onto the hot substrate of an effective area of 25×25 mm^2. After deposition the TCO

thin film was allowed to cool at room temperature and finally we got a good transparent thin film.

3. Results and discussion

3.1 Structural Studies

X-ray diffraction spectrum of the prepared film was recorded using XPERT with CuKá (ë=1.5406 nm) at 2è from 0 degree to 80 degrees. Fig.1 shows that the XRD pattern of TCO thin film deposited at 723k under with 0.1M concentration. The 2Θ value and d-spacing value are well match with compared JCPDS File No.89-0510. The peaks were identified to (100), (002), (101), (102), (110), (103) and (112) plane of reflections for a single phase wurtzite structure of ZnO. The presence of these peaks indicates that the film was found to be polycrystalline nature [13]. The most intense peak was observed in XRD at (101) plane for this thin film. Apart from ZnO characteristic peaks, no phase corresponding to aluminium or other aluminium compounds was observed in the XRD pattern. The diffraction pattern show the deposited TCO thin film exhibit a hexagonal structure, which indicates that Al^{3+} ions substituting Zn^{2+} ions did not change the hexagonal wurtzite structure in TCO thin film.

The quantity of the crystallinity can be studied from the calculation of crystallite size. The crystallite size D is determined from the Full Width at Half Maximum (FWHM) value using Debye Scherer formula. [14]

$$D = \frac{0.9\lambda}{\beta \cos\theta} \text{ -------- (1)}$$

Where, λ is the X-ray wavelength (1.5406 Å), β is the full width half maxima in radians of the (101) diffraction peak and θ is the Bragg diffraction angle. The average crystallite size is 25nm at 0.1 M concentration.

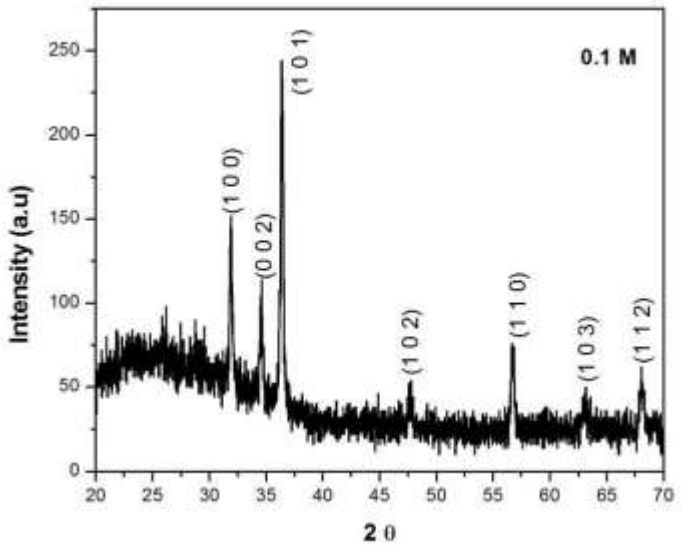

Fig.1 XRD pattern of TCO thin film at 0.1 M

3.2 Morphological Studies

Surface morphology and surface roughness of the film were studied by means of (SEM) scanning electron microscopy and (AFM) atomic force microscopy using ZEISS system at the range of 1 and 2.0 μmrespectively. SEM and AFM images of TCO thin film at 0.1 M concentration are presented in Fig.2 (a)

and (b). SEM and AFM results indicate that the average grain size and the surface roughness of the TCO thin film. The SEM image is found relatively well uniform with smaller spherically shaped grains. The average grains size of the TCO thin film was found to be 56 nm. The AFM image is randomly distributed and the formation of different height and width for this film. This film shows spinous and granulous structure. In general, the regular and dense film structure rendered the film with more compact and smooth morphology. The average surface roughness value of the TCO thin film was found to be 21 nm.

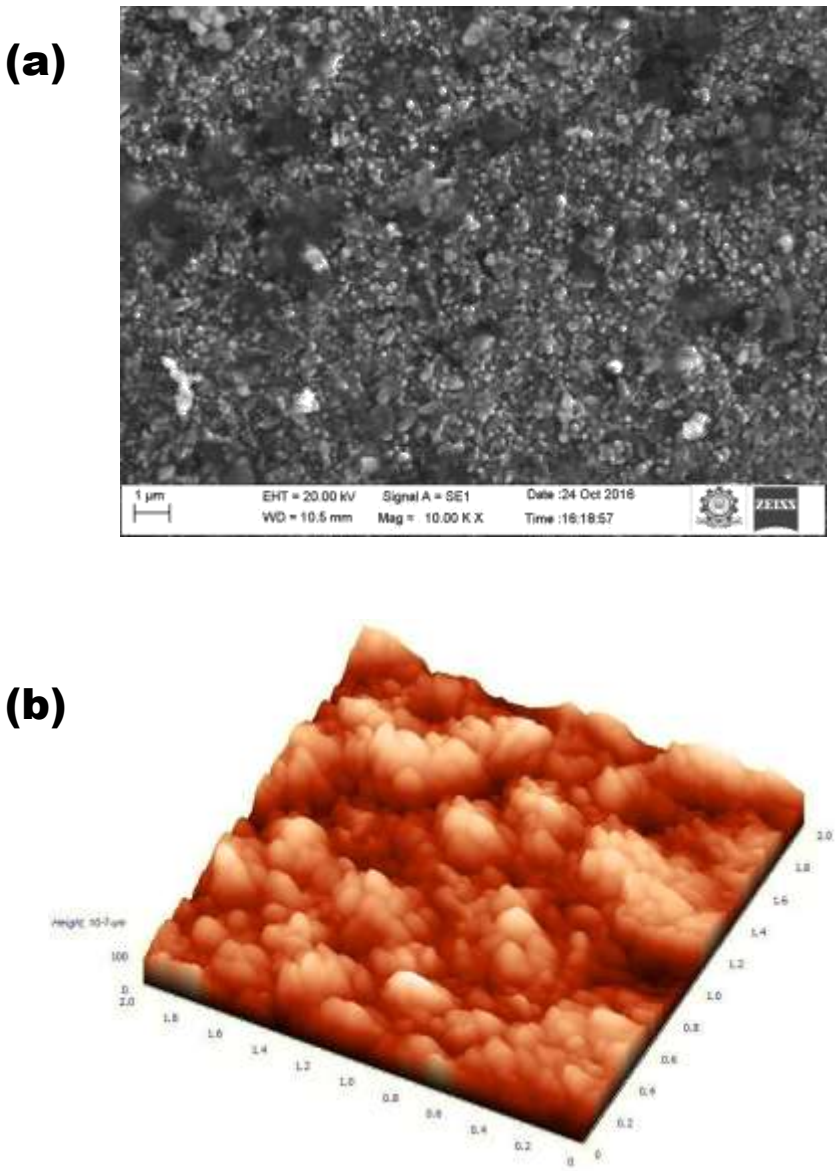

Fig.2 Morphology images ofTCO thin film (a) SEM and (b) AFM

3.3 Optical studies

The optical transparency study of TCO thin film were performed in the wavelength range (350-1200nm) using SHIMADZU 1800 (UV- visible spectrophotometer. The optical transmittance of the film clearly shows the multiple interference at the wavelength range of 400-700nm is shown in fig.3. Generally, thin films optical transmittances 65-85% in the 500-800 nm wavelength ranges which is high enough for solar cell applications.

In this TCO thin film deposited at 0.1M concentration shows an highest optical transmittance of 83 % in the visible region which is good agreement with AchourRahal et.al.[15]. This is can be explained by a

less light scattering of this film due to its smoothest surface and relatively a better crystallinity.

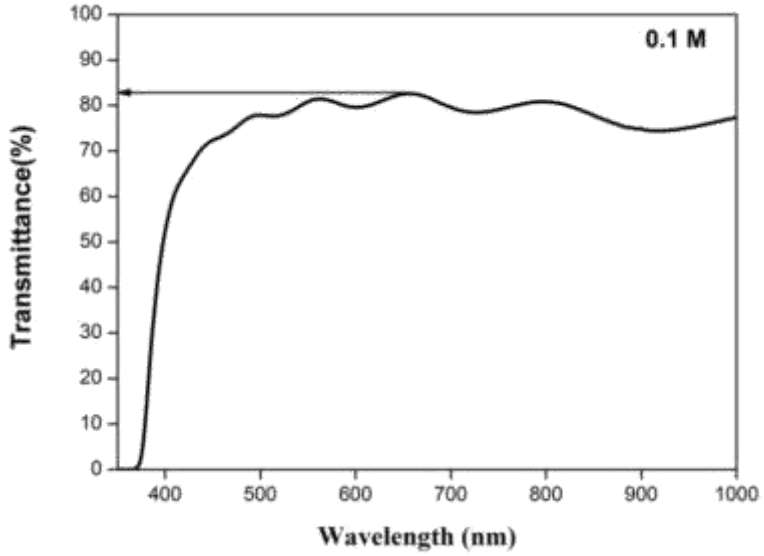

Fig.3 Transmittance spectrum of TCO thin film at 0.1M

The fundamental absorption edge of the films corresponds to electron transitions from valence band to conduction band and this edge can be used to calculate the optical band gap of the films. The direct allowed optical band gap of TCO thin film has been determined from following equation [16].

$$\alpha h\nu = B(h\nu - E_g)^n \qquad \text{-------- (2)}$$

Where, *B* and *E*g are constant and optical band gap, respectively. The optical band gap of the TCO thin film is shown in fig.4. It is seen that the direct optical band gap (*E*g) is 3.31eV. The calculated value is very close to the previously reported value [17].

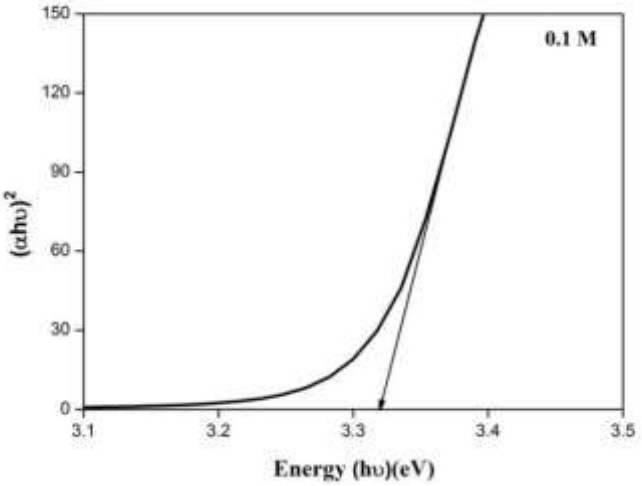

Fig.4 Band gap value of TCO thin film at 0.1M

3.4 Electrical studies

Fig.5 shows the electrical resistivity for TCO thin film was measured by four-probe measurement with different temperature. This result show that the film were n-type semiconductor due to the presence of oxygen vacancies and interstitial Zn atoms. The TCO thin film observed that the resistivity decreases with increase in temperature, it confirming the semiconducting nature of the film. The interstitial incorporation of Zn^{2+} into the ZnO matrix, this is one of the main reasons of observed low resistivity. The calculated value of activation energy Ea is 0.16eV for 0.1 M concentration.

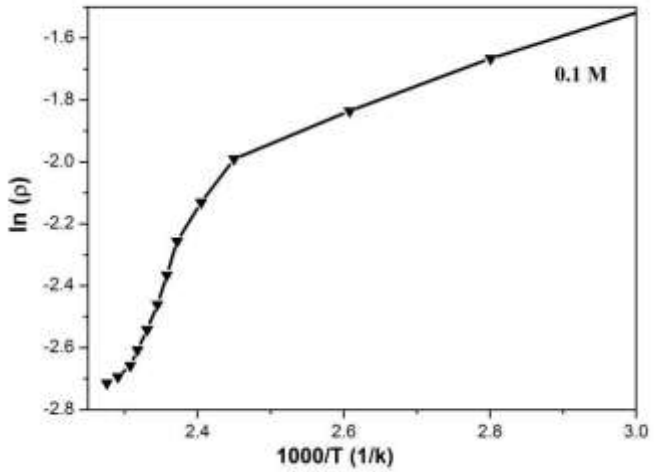

Fig.5 Resistivity ln(ñ) Vs temperature value of TCO thin film at 0.1M

Conclusion

Transparent conducting oxide thin film has been successfully deposited onto glass substrate from nebulized spray pyrolysis technique with 0.1 M concentration. In our experiment, XRD studies the formation of hexagonal structure is identified. The morphological studies SEM and AFM is found relatively uniform with smaller spherically shaped grains and granulous structure respectively. High transparency and low resistivity values are obtained from the optical and electrical studies, of the TCO thin film. The calculated activation energy Ea is 0.16eV. This is the method of very low cost of producing TCO (ZnO:Al) thin film, which is very important for many applications in industry.

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