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OPTICAL STUDIES ON AMORPHOUS ZnO FILM

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The present work reports the structural and optical properties of amorphous ZnO film prepared by physical vapour condensation method. In this method, Zinc metal (99.99% pure) is used as the source material, which is evaporated in the oxygen atmosphere to deposit the ZnO film on glass substrate. XRD spectrum does not show any significant peak, thereby suggesting that the nature of this film is amorphous. Field Emission Scanning Electron Microscopy (FESEM) investigation suggests the formation of spherical amorphous ZnO nanoparticle of size varying from 50-100 nm. The absorption, reflection and transmission data of this film are recorded in the wavelength range (300-600 nm). The absorption coefficient is calculated from the recorded absorption data and it is best fitted for direct band gap. The direct optical band gap for this sample comes out to be 3.75 eV. Using reflection and transmission data, various other optical parameters such as refractive index and extinction coefficient of as-grown a-ZnO film are calculated.

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1. Introduction

Zinc oxide (ZnO) is one of the most competent materials for the fabrication of the next generation of optoelectronic devices in the UV region and optical or display devices. ZnO is a wide-band gap semiconductor having band gap of about 3.3 eV. As a matter of fact, simultaneous occurrence of both high optical transmittance in the visible range, and low resistivity make it an important material in the manufacture of heat mirrors used in gas stoves, conducting coatings in aircrafts glass avoiding surface icing, and as thin film electrodes in amorphous silicon solar cells. ZnO is a member of the hexagonal wurtzite class; it is a semiconducting, piezoelectric and optical waveguide material and has a variety of potential applications such as gas sensors [1], surface acoustic devices [2], transparent electrodes [3] and solar cells [4, 5]. Some of these applications are based on the simultaneous occurrence of low resistivity and high transmittance in the visible spectrum, when ZnO is manufactured in the form of thin solid films. For many of these applications, it is very important to control its physical properties. Various deposition techniques have been extensively used to produce thin films. However, seeking the most reliable and economic deposition technique is the main goal. The most intensively studied techniques include: RF magnetron sputtering [6], metal organic chemical vapour deposition [7], sol-gel method [8] and spray pyrolysis [9, 10]. These techniques have been employed intensively in the last three decades due to their simplicity and economy. The chemical bath deposition, chemical spray pyrolysis and sol-gel techniques are well known methods of preparation of thin films. The spray pyrolysis is an excellent method for the deposition of thin films of metallic oxides, as is the case for the ZnO material. Out of which the physical vapour condensation method is most reliable for the preparation of ZnO thin films. In this method, we can simply placed the material inside the boat

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and evaporates the materials by passing current. The thin film prepared by the physical vapour condensation method is quite uniformly grown on the substrate. Optical characterization of thin films gives information about other physical properties, e.g. band gap energy and band structure, optically active defects etc., and therefore may be of permanent interest for several different applications. Considerable differences between optical constants of bulk material and thin films or those of films prepared under varying growth characteristics are often reported. Therefore, determination of optical constants for each individual film by a non-destructive method is highly recommended. Generally, the optical band gap (E_g) could be evaluated from transmittance or absorbance spectra.

2. Experimental

Thin film of ZnO is deposited by physical vapour condensation method. In this method, the starting material is Zn powder (99.999 % pure), which is heated at a temperature of 400^{o}C in presence of oxygen and argon gases in the chamber. Initially, small quantity of Zn powder was kept in a molybdenum boat and the chamber was evacuated to a vacuum of the order of 10^{-6} Torr. After attaining this vacuum, the gases (oxygen and argon) are purged in to the chamber. The pressure of these gases is kept fixed at 4 mbar and 3 mbar respectively. The substrate is kept at room temperature and this evaporated material is deposited on glass substrate pasted on this substrate. The nanoparticles of ZnO are deposited on the glass substrate and also collected in the powder form by scratching from the substrate. The crystal structure of the film is determined by X-ray-diffraction (XRD) measurements. The film is measured at $\theta/2\theta$ configuration. Powder X-ray diffraction (XRD) is performed using a X-ray diffractometer (Panalytical, model PW 1830/40) using Cu K_α radiations (λ = 1.5412Å). The morphology of this amorphous ZnO film is studied using a Joel field emission scanning electron microscope (FESEM 7500f). UV–VIS absorption spectrum is recorded using Camspec spectrophotometer (model M-550). The scanning wavelength range is 300–600 nm.

3. Results and discussion

The typical X-ray diffraction (XRD) pattern of as-deposited ZnO film is presented in Fig. 1. This XRD spectrum does not show any significant peak, thereby showing amorphous nature. FESEM images of the as grown a-ZnO film are as shown in Fig 2 (a&b). From these images, it is observed that spherical nanoparticles of size vary from 50-100 nm are formed on surface of the film. This process involves the effusion of atoms from the source material and these atoms will rapidly lose their energy by colliding with gas atoms. As the collision mean free path is very short, the nucleation process is performed homogenously in the vapor phase. The nucleation begins abruptly and proceeds at a very high rate as the difference between the evaporation temperature and the gas phase is very high.

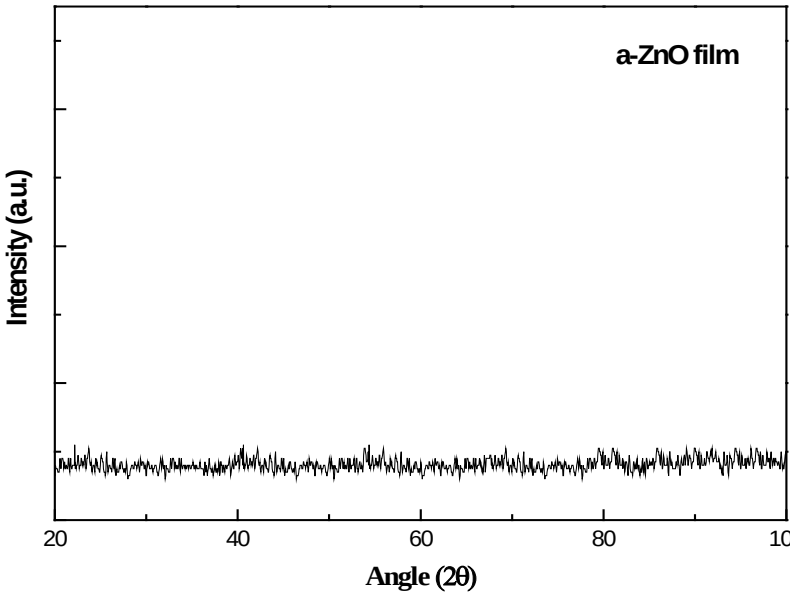

Fig. 1; XRD pattern of as-deposited a-ZnO film.

A Camspec spectrophotometer (model M-550) is used to measure the optical absorption, reflection and transmission of the as-deposited a-ZnO film in the wavelength range of 300–600 nm. The absorption is measured in terms of optical density. Thin film of a-ZnO deposited glass substrate and reference (glass) is kept inside the appropriate film holder. The optical absorption is measured as a function of incidence wavelength.

The absorption coefficient (α) is calculated using the following relation;

$$\alpha = \frac{OD}{t} \tag{1}$$

where OD is the optical density measured at a given film thickness (t).

In case of semiconductors, the fundamental absorption edge follows an exponential law. Above the exponential tail, the absorption coefficient has been reported [11] to obey the following equation:

$$(\alpha h\gamma)^{1/n} = B\left(h\gamma - E_g\right) \tag{2}$$

where ν is the frequency of the incident beam ($\omega=2\pi\nu$) , B is a constant, E_g is optical band gap, n is an exponent and it can have any value e.g. 1/2, 3/2, 2 and 3 depending on the nature of electronic transition responsible for the absorption. For allowed direct transition, n can have value either ½ or 3/2 and for forbidden indirect transition, n can have value either 2 or 3 [12]. Here, the direct and indirect transitions are optical transitions that occur in both the crystalline and non-crystalline semiconductors. It is well known that direct transition across the band gap is feasible between the valence and the conduction band edges in k space. In the transition process, the total energy and momentum of the electron–photon system must be conserved.

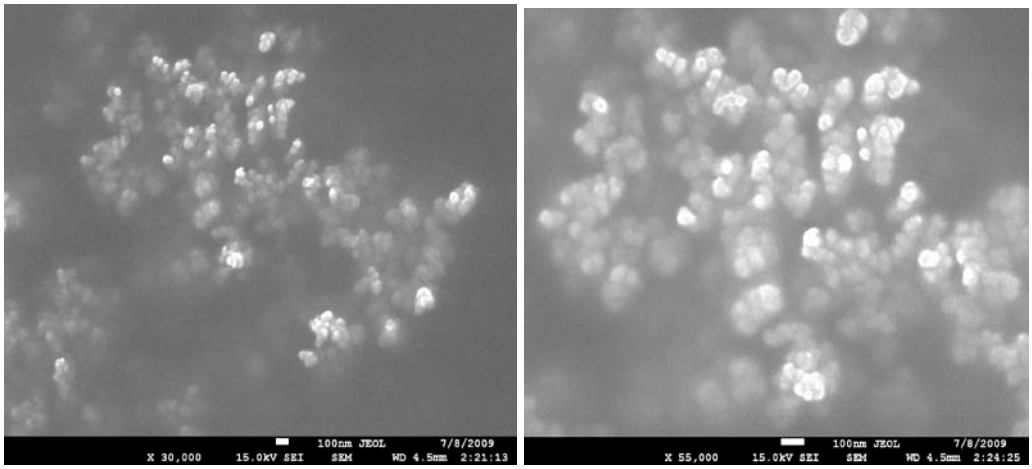

Fig. 2; FESEM images of as-deposited a-ZnO film.

The experimental data for the present sample of a-ZnO film gives a best fit with n = 1/2 using equation (2), which suggests that the absorption in this a-ZnO film is due to direct transition. Therefore, the experimental data is re-plotted as $(\alpha.h\nu)^2$ Vs photon energy ($h\nu$) for direct transition. Fig. 3 shows the variation of $(\alpha.h\nu)^2$ with photon energy ($h\nu$) for ZnO film. The value of direct optical band gap (E_g) is calculated by taking the intercept on the X-axis. The calculated value of E_g for the present a-ZnO film is found to be 3.75 eV, which is slightly higher than the standard value of the ZnO. Anthony et al [13] reported the growth of ZnO film on ITO substrate using electrochemical deposition from aqueous solution at low temperature (70^{o}C), under the SEM investigation they found the film contains nanowires. They calculated a direct optical band gap of 3.55 eV of ZnO film prepared by the electrochemical deposition. Li et al [14] calculated the band gap 3.77 eV of the ZnO film prepared by the chemical bath deposition method (CBD). Khan et al [15] reported the growth of ZnO film on glass substrate using physical vapor condensation. Under the FESEM investigation, they found the film contains nanocluster on the surface of the ZnO film. They calculated a direct optical band gap of 3.54 eV of ZnO film prepared by the physical vapor condensation method.

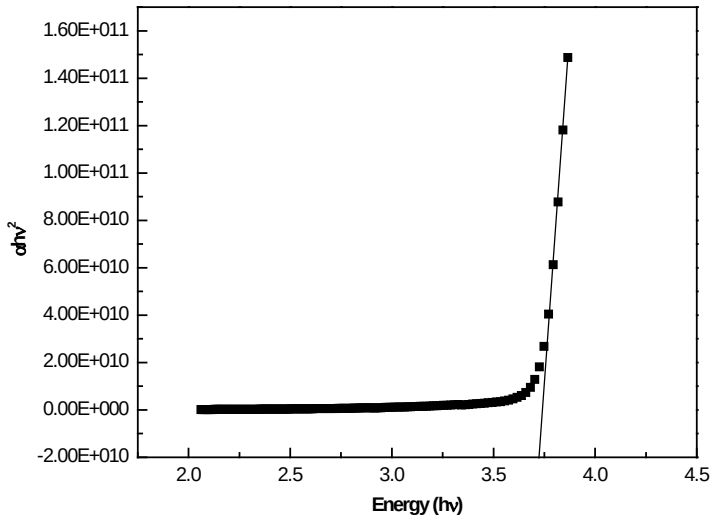

Fig. 3; Variation of $(\alpha h\gamma)^2$ Vs.photon energy ($h\gamma$) for as-deposited a-ZnO film.

The values of refractive index (n) and extinction coefficient (k) have been calculated using the theory of relativity. According to this theory, the reflectance (R) of light from the thin films can be expressed in terms of Fresenel's coefficients. The reflectivity (R) of an interface can be given by

$$R = [(n-1)^2 + k^2]/ [(n+1)^2 + k^2] \quad (3)$$

And

$$\alpha = 4\pi k/\lambda \quad (4)$$

where n is the refractive index, k is extinction coefficient and λ is the wavelength. The spectral dependence of the refractive index (n) and extinction coefficient (k) for the ZnO film are shown in Figs. 4 and 5 respectively. We have observed an overall decreasing trend for the refractive index with the photon energy shifting to the higher value. Whereas for the extinction coefficient, an overall increasing trend with the increase in photon energy is observed. Shakti et al [16] prepared the ZnO film by sol gel spin coating process on the quartz substrate by post annealing of the film. They found an exponential variation of extinction coefficient k in the range of 0 to 0.4 with the photon energy of range 1 to 3.5 eV. Cheng et al [17] deposited the ZnO by dc reactive magnetron sputtering using the Zinc metal target on the different substrate like Pt, Ti, SiO_2 and Si. They also found the exponential variation of k within the range of 0 to 4 with the photon energy ranging from 0.5 to 4.5 eV. In our case, the similar rend is observed and the values of extinction coefficient (k) are comparable with the reported values (Fig. 4). For the present sample of amorphous ZnO film, the values of n and k at a wavelength of 374 nm are estimated to be 3.30 and 3.66 respectively. Struk et al [18] deposited the ZnO film using reactive cathode magnetron sputtering technique for the application in planer optical waveguide. They found the value of refractive index as 2.08. Heideman et al [19] deposited the ZnO film using RF magnetron sputtering on quartz as well as silicon substrate. They found two different values of the refractive index i.e. 1.99 and 2.00 for the ZnO film deposited on different substrate. Sun et al [20] reported a value of 2.4 for the refractive index of ZnO film deposited on the glass substrate using pulsed laser deposition technique. For the present sample of amorphous ZnO film, the values of optical band gap, refractive index and extinction coefficient are slightly higher than the reported values. These large values of optical band gap and optical constants may be due to the presence of high disorderedness in this sample of amorphous ZnO film.

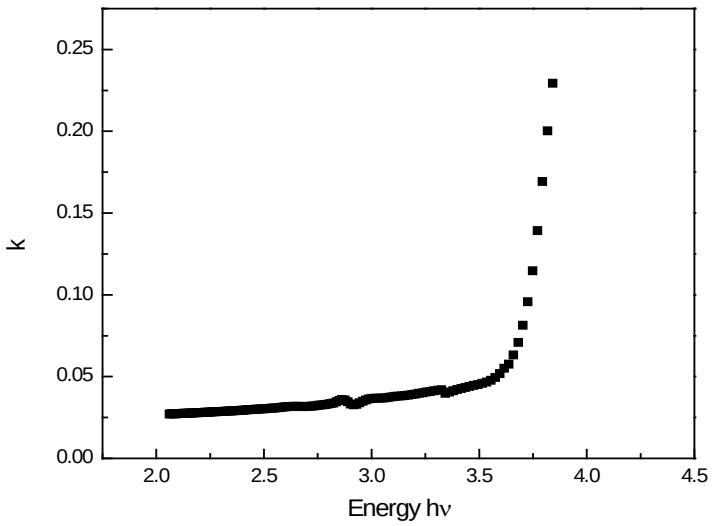

Fig. 4; Variation of extinction coefficient (k) Vs.photon energy (hγ) for as-deposited a-ZnO film.

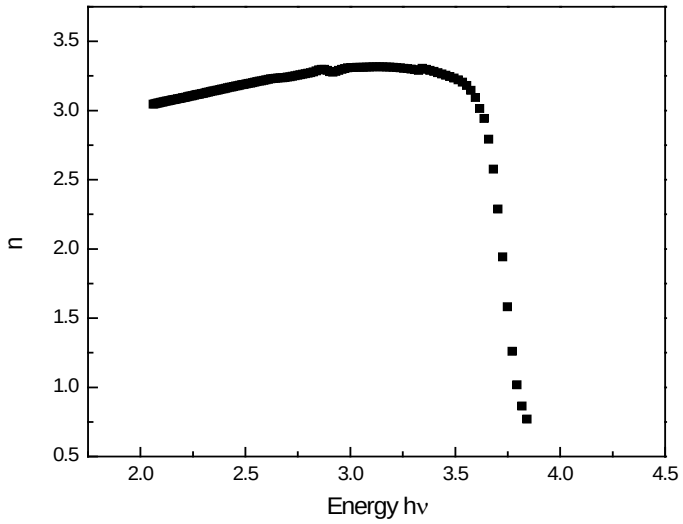

Fig. 5; Variation of refractive index (n) Vs.photon energy (hγ) for as-deposited a-ZnO film.

4. Conclusion

Amorphous ZnO film has been deosited on glass substrate using the physical vapour condensation method. The surface morphological investigation confirms the size of the ZnO spherical nanoparticles varies in the range of 50-100 nm on the surface of the film. XRD spectrum doesn't show any characteristics peaks of ZnO, which confirms the amorphous nature of this ZnO film. The calculated value of E_g for the present a-ZnO film is found to be 3.75 eV. The values of n and k at a wavelength of 374 nm are estimated to be 3.30 and 3.66 respectively. The values of optical band gap, refractive index and extinction coefficient are slightly higher than the reported values. These large values of optical band gap and optical constants may be due to the presence of high disorderedness in this sample of amorphous ZnO film.

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