The Role Of Annealing Temperature On Optical Properties Of ZnO Thin Films Prepared By Spray Pyrolysis Techniques

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Abstract—In this research work the role of annealing temperature on optical properties of ZnO thin films prepared by spray pyrolysis method at a substrate temperature of 573K has been studied. The optical properties of as-deposited samples and samples annealed at 573K and 673K were investigated in the wavelength range of 380-750nm using a double beam UV-VIS-NIR spectrophotometer. The results showed that all the films have direct optical transition and showed the larger values of optical transparency (greater than 80%) with increase in annealing temperatures. The optical band gap energy was found to be in the range of 3.2-3.85 eV with increasing annealing temperature. Similarly other optical parameters were found to improve appreciably with increase in annealing temperature.

Keywords— Spray pyrolysis, Substrate temperature, Annealing, ZnO, Band gap.

I. INTRODUCTION

Transparent conducting oxides (TCOs) such as In_2O_3, SnO_2, ITO, etc have been used in several applications such as transparent electrodes in optoelectronic devices, solar cells, flat panel displays and other future devices. TCO's low electrical resistivity (10^{-3} - 10^{-4} Ω cm) is exploited in front-surface electrodes for solar cells and flat-panel displays. Other properties of TCO films includes large band gap (>3 eV) and a very good optical transmittance (80 - 90%) in the visible range [1]. Despite all these tracking properties, TCOs have some problems such as high cost, low stability to H_2 plasma and toxicity. Recently, Zinc Oxide (ZnO) thin films have attracted much attention as a transparent and conductive film material because it exhibits a wide band gap, high transparency and low resistivity. ZnO has a wide band gap of 3.37 eV at room temperature, which makes it potential in blue and ultraviolet (UV) photoelectric applications, such as transparent high power electronics, UV detectors, and short wavelength devices. Its large exciton binding energy of about 60 MeV makes it a good choice for fabrication of exciton-related devices, such as short-wave light emitters. Zinc oxide has some advantages over GaN such as higher radiation hardness, simplified processing due to amenability to conventional chemical wet etching and the availability of large area substrates at relatively low material costs, non-toxicity and relatively low deposition temperature [2]. Zinc oxide thin films have been prepared by various deposition methods such as thermal oxidation [3], Spin coating [4] vacuum evaporation [5], electron beam evaporation [6], sputtering [7] - [10] Spray pyrolysis [11] - [14], chemical bath deposition [15] etc. In this paper, we reported the role of annealing temperature on Optical properties of ZnO thin films grown by Spray pyrolysis technique. Spray pyrolysis technique is convenient for deposition of thin films and has the several advantages in comparison with other deposition techniques such as low cost of the source materials, high quality films, simple deposition equipment, moderate substrate temperatures, deposition scaled for large area and uniform deposition with very thin layers with good adhesion between the deposited films.

II. MATERIALS AND METHOD

Graded chemicals (Aldrich) were used for the deposition of ZnO thin films, soda lime glass was used as substrate, and film thickness was measured using Profilometer (STYLUS TAYLOR HOBSON MODEL). Zinc oxide thin films were prepared on soda lime glass substrates using KM 150 spray pyrolysis deposition machine. Before deposition the substrates, the beakers and measuring cylinders were washed first with detergent and rinsed with distilled water, then washed with acetic acid and finally rinsed with ethanol, dried and rubbed gently with cotton. A 1.10g of Zinc Acetate was dissolved in 15ml of H_2O. 50ml of Acetone, 30ml of Ethanol and few drop of Acetic Acid precisely 5ml were poured in the same beaker containing the Zinc Acetate making a total volume of 100ml. 1ml of the mixture was placed in a syringe which is attached to the spray chamber. The nozzle to substrate distance was set at 11.0cm. Zinc sulphide thin films were deposited on the substrate at a flow rate of 0.8ml/min. After deposition, samples were removed from the spray Chamber. One sample was kept as deposited and two samples were subjected to a thermal annealing by inserting them into a horizontal Carbolite oven one after the other at temperatures 573K and 673K respectively under nitrogen atmosphere for one hour at the ramp rate of 6℃/sec. The samples were allowed to cool at room temperature before they are taken out for characterization.

To investigate the optical properties of the prepared ZnO thin films, AVANTES AVASPEC-2048 UV-VIS-NIR Spectrophotometer was used in the wavelength range of 180nm-1200nm.

III.RESULTS AND DISCUSSION

Optical transmittance

Fig.1 shows plot of optical transmittance as a function of wavelength in respect of as-deposited ZnO thin films and ZnO thin films annealed at 573K and 673K respectively. For all the samples the transmittance is high at UV-VIS region. It can be seen from the figure that films annealed at 573K and 673K, exhibited a transmittance of 85% and 90% respectively where as for as deposited sample the transmittance was 80%. This trend shows that transmittance increases with increase in annealing temperature. These may be due to complete evaporation of the parent residual of organic compound and water molecules at increased temperature, uniform oxidation and improvement in lattice orientation (Nehru et al. 2012). It may also be attributed to increase in grain size, structural homogeneity and crystallinity [15].

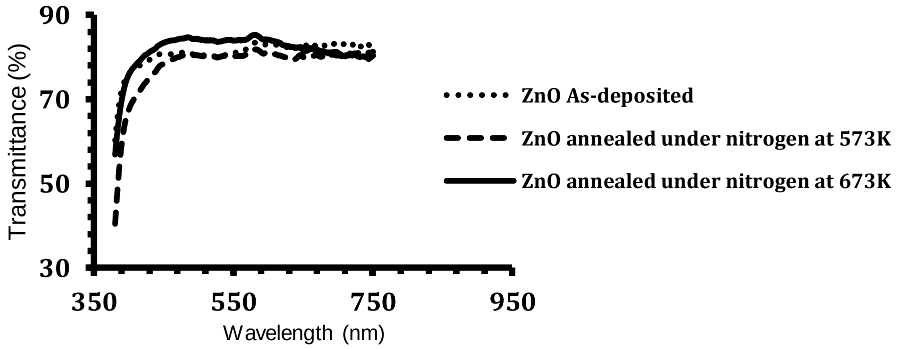

Fig. 1. Transmittance (%) as a function of wavelength (nm).

Optical band-gap energy

The optical band-gaps of the Zinc oxide thin films (ZnO) had been calculated using equation (1)

$$(\alpha hv) = A (hv - Eg)^m \qquad (1)$$

The optical band gap was obtained by plotting $(\alpha hv)^2$ as a function of photon energy (hv). The intercept of the extrapolation to zero absorption with photon energy axis gave the values of the direct energy gap E_g. Typical plot of $(\alpha hv)^2$ as a function of (hv) for ZnO thin films fabricated by spray pyrolysis method and annealed at two different temperatures at 573K and 673K respectively is shown in Fig. 2. The band gap energy of 3.2, 3.6 and 3.85eV were observed for as deposited, and films annealed at 573K and 673K respectively. These values are close to the value of 3.3 eV for bulk ZnO. The value also clearly indicates the blue shift of band gap energy as annealing temperature increase. The shift may be due to the fact that the quality of the ZnO film improves when the sample is annealed at a higher annealing temperature. It may also be attributed to the rising of the Fermi-level into the conduction band of a degenerate semiconductor which leads to optical energy band-gap widening. Similar observations were made in [16].

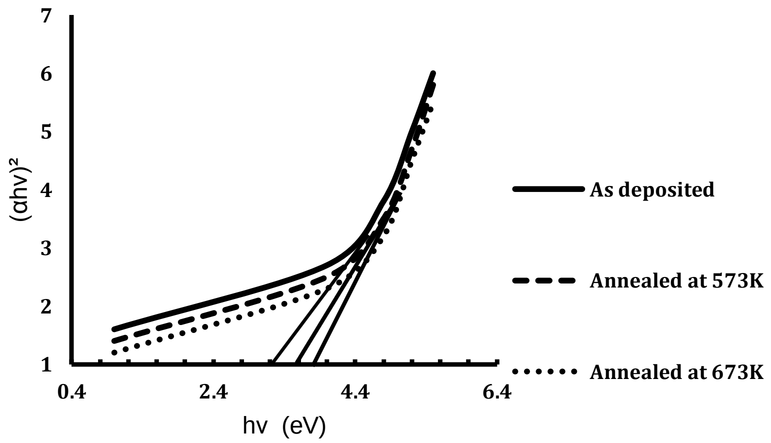

Fig. 2. $(\alpha hv)^2$ versus photon energy for Zinc Oxide thin films.

Extinction coefficient

Fig. 4 shows the extinction coefficient of Zinc oxide thin films. The extinction coefficient is determined using equation (2) [4],

$$k = \frac{\alpha\lambda}{4\pi} \qquad (2)$$

Where α is the absorption coefficient and λ is the wavelength. It can be observed that for all the samples, the extinction coefficient is high at the high ultraviolet region, but the value tends to fall at low visible region. However at high visible region the value of k for all the samples rises again.

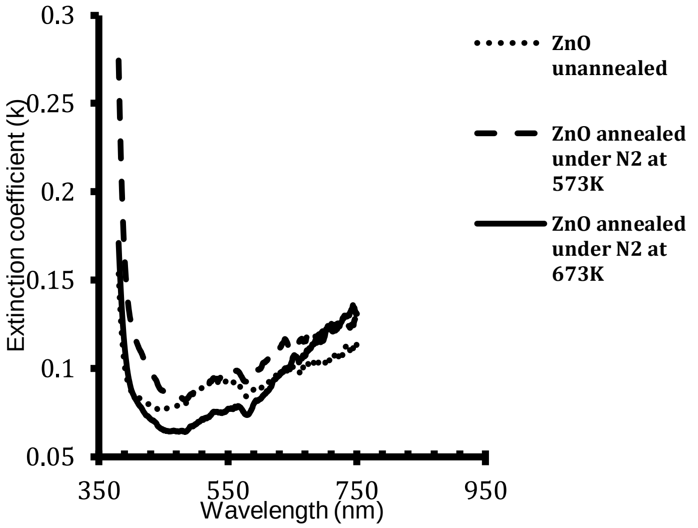

Fig. 3. Extinction coefficient versus wavelength (nm).

Refractive index

Fig. 4, shows the optical refractive index n of the Zinc oxide thin film (ZnO) for as deposited, annealed at 573K and annealed at 673K under nitrogen atmosphere. It was calculated from the following equation (3) [5].

$$n = \left[\frac{4R}{(R-1)^{\frac{1}{2}}} - 1\right]^{\frac{1}{2}} - \frac{R+1}{R-2} \qquad (3)$$

Where R is the reflectance, k is the extinction coefficient. It can be seen that it displayed a kind of sinusoidal shape which falls totally at the wavelength of about 750nm, implying that as temperature increases the refractive index decreases. This decrease in refractive index may be attributed to the surface morphological arrangement of thin films or the structural ordering of the thin films. Our observation agrees with those in [17].

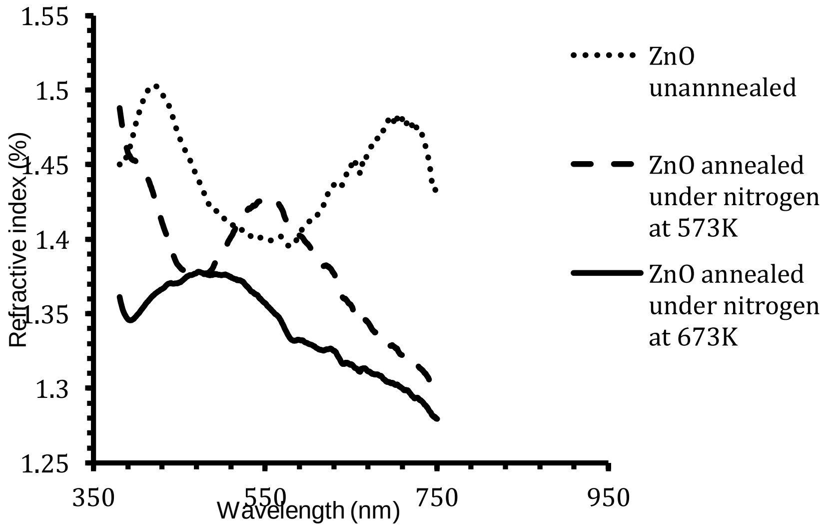

Fig. 4. Refractive index of Zinc Oxide thin film versus wavelength.

Dielectric constant

Fig. 5, shows the dielectric constant of as deposited as well as thin films annealed at 573K and 673K respectively. The dielectric constant ε of the thin films has been calculated by employing equation (4) [3].

$$\varepsilon = n^2 - k^2 \quad (4)$$

where n is the refractive index and k is extinction coefficient. It should be observed that dielectric constant decreases with increasing wavelength at the visible region. These behaviors may be attributed to the enhancement of grain size, compactness and the structural quality of the material. These observations are in conformity with those made in [18 -20].

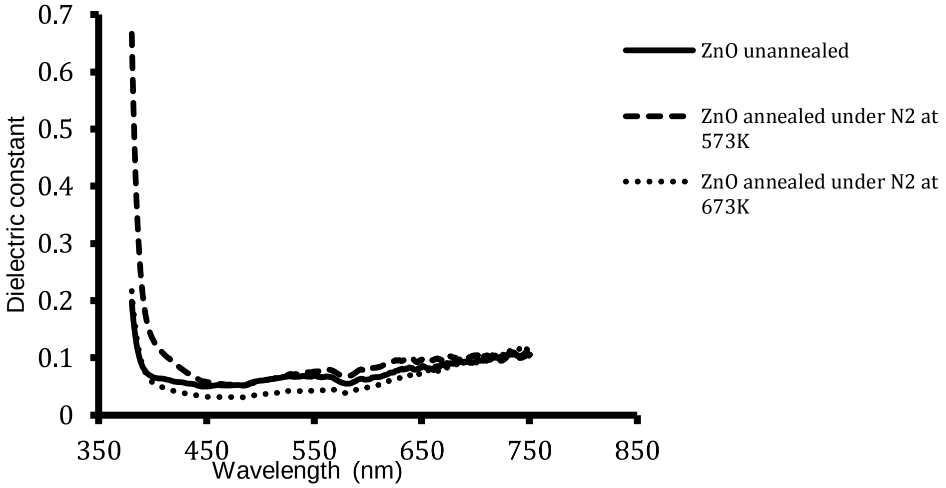

Fig. 5. Dielectric constant versus wavelength.

IV. CONCLUSION

Zinc Oxide thin films were prepared by low cost spray pyrolysis technique. The role of annealing temperature on optical properties of Zinc Oxide thin films have been studied, it has been found that the annealing temperature plays an important role in the optical properties of Zinc Oxide thin films. The values of optical band gap energy, transmittance and other optical constants of ZnO thin films improved significantly with increase in annealing temperature. The good optical properties exhibited by Zinc Oxide thin films in this research would be attractive for applications in fabrication of optoelectronic devices, solar cells, light-emitting diodes, laser diodes and other devices.

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