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FABRICATION & CHARACTERIZATION OF NANOSTRUCTURED ZINC OXIDE THIN FILMS

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Thin film of Zinc Oxide (ZnO) have been obtained from ZnS films by annealing process in air at temperatures 450ºC & 750ºC. The ZnS films have been fabricated onto glass substrates using simple & inexpensive chemical bath deposition technique (CBDT). The optical & structural characterization of obtained materials was performed. The x-ray diffraction (XRD) study has confirmed the formation of ZnO with nano-size scale whereas the scanning electron microscopy (SEM) studies showed that all the films were polycrystalline in nature. The films were found to exhibit high transmittance (>80 %), low absorbance and low reflectance in the visible regions. The optical energy bandgaps of the films were evaluated. The nano-crystalline materials exhibiting small particle size & large surface area may be applied for gas sensors.

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1. Introduction

In recent years, the international research community shows strong interest in realizing inexpensive oxide thin films such as ZnO, SnO_2, In_2O_3, CdO etc. due to their unique & versatile properties of optical sensing [1], gas sensing [2] and piezoelectric sensing[3] for various applications. ZnO is a wide band gap semiconductor, useful for other possible applications in the field of optoelectronic devices such as ultraviolet light emitting diodes, blue luminescent devices, solar cells & photo catalysts [4].

ZnO thin films have been fabricated by variety of techniques such as spray pyrolysis, sputtering, molecular beam epitaxy, electrodeposition, chemical deposition, etc. Among these, CBDT from aqueous solutions is the simplest and most economical also the films can be fabricated on different kinds, shapes and sizes of substrates [5].

In this work, we present a new approach to fabricate nanostructured ZnO thin films by post thermal annealing treatment over ZnS thin films prepared by using controlled chemical reaction bath and their physical properties have been investigated.

2. Experimental

To prepare ZnO films, aqueous solutions of 0.08 M zinc acetate Zn $(CH_3COO)_2$, 0.15 M thiourea SC $(NH_2)_2$ was added in 100-120 ml of de-ionized water. Complexing agent ammonia was added slowly to adjust the pH (between 9 and 10). The solution was stirred and transferred to another container containing substrate. The resulting solution was kept at 70±2ºC for 1 hour. Zinc

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acetate used as zinc precursors, which slowly releases the Zn^{2+} ions. Thiourea releases s^{2-} ions by means of an alkaline hydrolysis process. The substrate used is commercial glass slide. Cleaning of substrate is important in fabrication of thin films, cleaning steps and growth procedure is reported elsewhere [6-9]. After 20-30 minutes the bath solution in beaker turned white, thus indicating the onset ZnS deposition on the glass slide. After a reaction time of 1 hour the glass slides were taken out and dried in air for 15 minutes. Then for the post annealing treatment in air, the prepared ZnS films were kept in the oven at 450ºC and 750ºC for 10 hours. The ZnS films get oxidized in the oven to form thin films of ZnO.

The crystallographic structure of films was analyzed with x-ray diffractometer (EXPERT-PRO) by using Cu-Kα lines (λ= 1.54Å). The average grain size in the fabricated films was obtained from a Debye-Scherrer’s formula. Surface morphology was examined by JEOL model JSM-6400 scanning electron microscope (SEM). The optical transmission spectra for a range of samples of ZnO thin films of various annealing temperatures were obtained in UV-VIS-NIR region using Perklin-Elmer UV-VIS lambda-35 spectrometer in the wavelength range 100-1000nm with uncoated glass slide as the reference[9].

3. Results and discussion

3.1 XRD analysis

Fig. 1 shows the X-ray diffraction pattern of ZnO thin film obtained from post annealing treatment over ZnS films at 450°C and 750°C. The XRD pattern confirms that the ZnS films get oxidized in the oven to form ZnO thin films. It was found that the ZnS is not completely oxidized at 450°C and showing a weak reflection peak at 2θ=28.35 with cubic phase. However at 750°C the film shows reflections from (002), (102) and (110) planes, indicating the formation of ZnO nano particles having pure hexagonal structure (matches with JCPDF card no 36-1451). The lattice parameters have been calculated for c-axis which is 0.5209nm.

The average size of grain (g) have been obtained from the XRD patterns using Debye-Scherrer’s formula, [9-12]

$$g = K\lambda / \beta \cos\theta$$

Where,

K = constant taken to be 0.94,
λ = wavelength of X-ray used (1.542Å),
β = FWHM of the peak and
θ = Bragg’s angle.

The grain sizes from the (002) peak width were found to be within the range from 9 to 14nm. This confirms the good crystallinity of the samples.

3.2 SEM analysis

Figure 2 shows scanning electron micrographs (SEM) of ZnO nano-crystalline films at different magnifications. It is an excellent technique for the study of surface morphology of thin

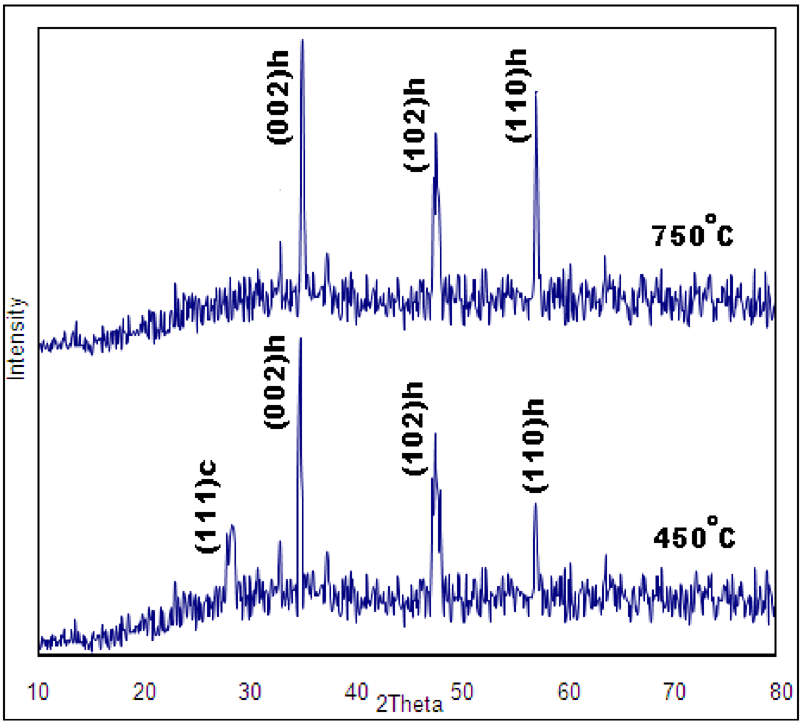

Fig.1. XRD patterns of ZnO thin films fabricated at 450^{o}C & 750^{o}C

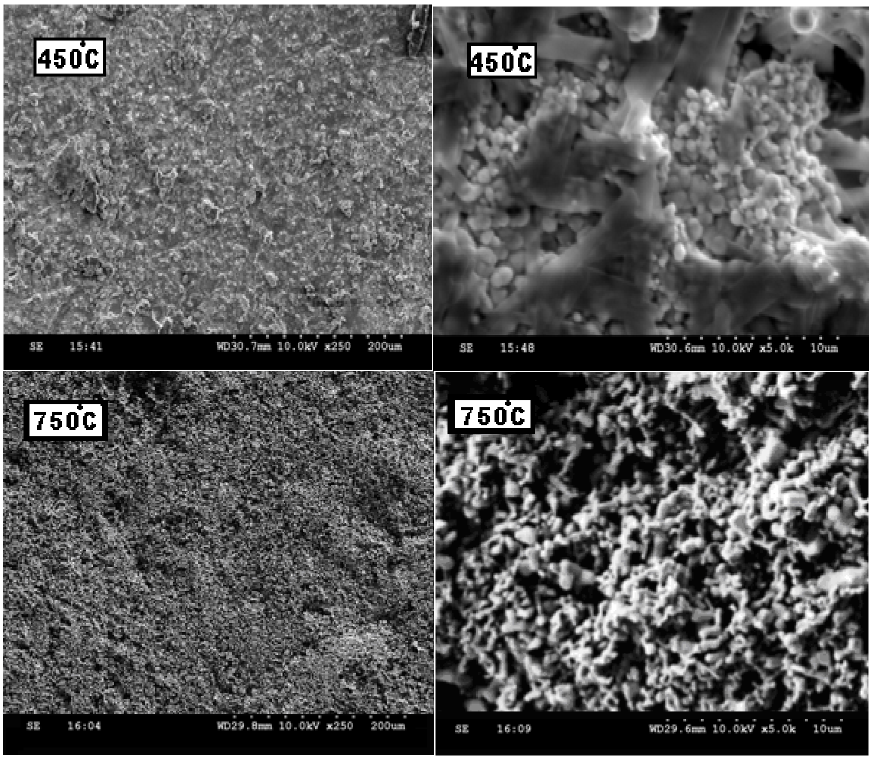

Fig.2.SEM images of ZnO thin films fabricated at 450^{o}C & 750^{o}C

films. From the SEM images, it is observed that the grains are more densely packed due to which the films are uniform throughout without any cracks and the substrate is well covered. It is also observed that the grain size slightly decreases at higher annealing temperature. The grain size obtained from SEM matches with the grain size obtained from XRD.

3.3 Optical analysis

Figure 3 shows the optical transmission spectra of ZnO thin films in the wavelength range from 200 to 1000nm for various annealing treatment. All the films are highly transparent in the visible region with an average transmittance of 81%. The sharp rise in transmission is an identification of good crystallinity of films. It is observed that the films obtained at higher annealing temperature shows slightly less transmittance in visible region as compared to the films obtained at lower annealing temperature. These results slightly increase in optical band-gap of ZnO films and it may be due to the small grain size of the polycrystalline ZnO films.

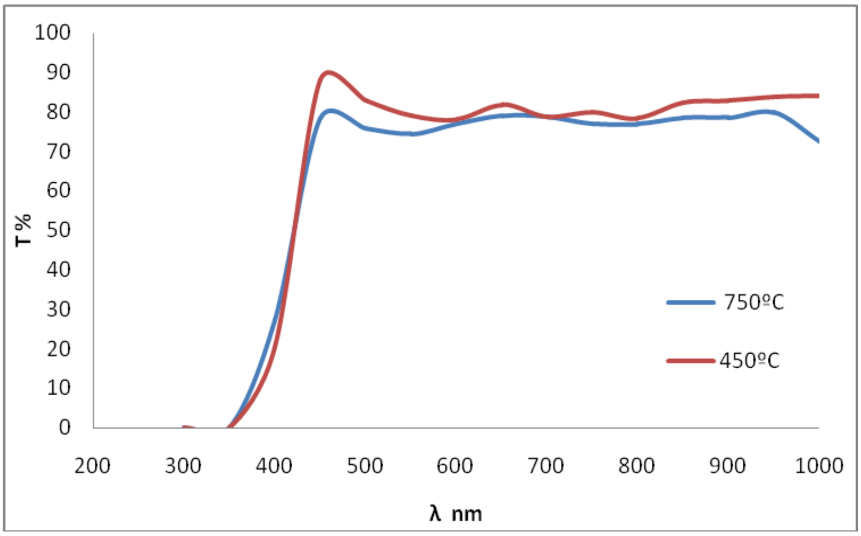

Fig.3. Optical transmission spectra of ZnO thin films fabricated at 450ºC & 750ºC

From the transmittance data, the absorption co-efficient α was calculated using Lamberts law [11-12],

$$\ln (I_0/I_t) = 2.303\ A = 2.303 \log 1/T = \alpha\ t$$

Where, I_0 and I_t are the intensity of incident and transmitted light respectively. A the absorbance, T the optical transmission and t the film thickness.

The absorption co-efficient α was found to follow the relation, [12-13]

$$\alpha h\nu = A\ (h\nu - Eg)^{1/2}$$

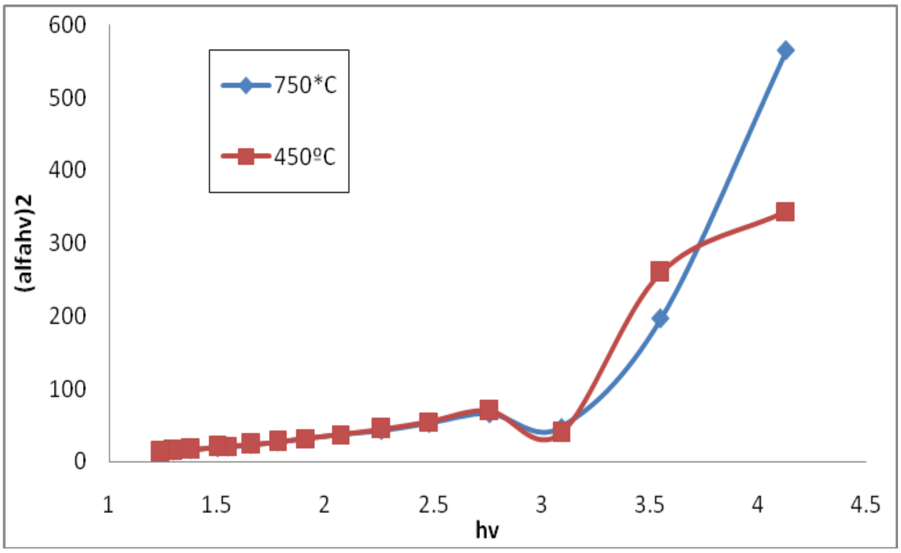

Fig.4. Plot of $(\alpha h\nu)^2$ vs hν for ZnO thin films fabricated at 450ºC & 750ºC

The band gap (Eg) was determined from each film by plotting $(\alpha h\nu)^2$ versus hν and then extrapolating the straight line portion to the energy axis at α =0. The band gap energy Eg obtained for each film is different. It was observed that the band gap of the film obtained at higher annealing temperature is 3.21eV whereas it is 3.03eV for the films obtained at lower annealing temperature. This difference (0.18eV) in optical band-gap of ZnO films may be due to the difference in grain size. Fig.4 shows band gap values observed for the ZnO thin films obtained at various annealing temperatures.

4. Conclusion

Highly transparent nano-structured ZnO thin films were successfully fabricated by post annealing treatment over ZnS thin films prepared by CBDT. The X-ray diffraction analysis showed that film is polycrystalline in nature. The grain size estimated is in the range of 9 to 14nm. This small grain size makes the films applicable for the gas sensors. The film has a direct band gap with an optical value of 3.21eV which is in good agreement with the standard value. The optical characterization shows, all the films exhibit high transmittance, low absorbance and low reflectance in the visible region. This makes the films suitable for use as an antireflection coating for hetero-junction solar cells and optoelectronic applications.

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