Influence of Lead Substitution in Zinc Oxide Thin Films†

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Abstract: Lead substituted zinc oxide thin films were deposited onto the glass substrates at 400 ^{o}C by spray pyrolysis technique. The influence of lead substitution concentration (0–25 wt. %) on the structural, morphological and optical properties of zinc oxide thin films were studied. X-ray diffraction (XRD) analysis confirms that all the films have a typical hexagonal wurtzite structure having high preferred orientation along (002) crystallographic direction. The Scanning Electron Microscopy (SEM) reveals the deterioration of crystallinity as we increase the substitution percentage. The average transmittance is maximum for 25 wt. % ZnO:Pb ~93% in the visible region (400–800 nm). Optical band gap energy has a slight increase from 3.21 eV to 3.36 eV.

Keywords: Thin films, Spray pyrolysis, Optical transmittance

Introduction

Zinc oxide (ZnO) is highly interesting and widely studied transparent conducting oxide which has numerous applications. Some of its distinguishing properties are high transmittance range[1], large exiton binding energy (~60 meV)[2] and large band gap (3.2 eV)[3]. The properties of ZnO thin film depend on the non-stoichiometry of the film resulting from the presence of oxygen vacancies and interstitial zinc. However stoichiometric zinc oxide is an insulator that crystallizes with wurtzite structure to form transparent needle-shaped crystal[4]. The structure contains large voids which can easily accommodate interstitial atoms. Thus the substitution in ZnO can be easily achieved, because of this property. A lot of researches have been done by varying the dopant material in ZnO thin films. However literature review reveal that there are only a very few reports on lead (Pb) substituted zinc oxide thin film. In this work the aim was to prepare Pb substituted zinc oxide thin films by low cost spray pyrolysis technique and to analyze the influence of Pb substitution on the structural, morphological and optical properties of ZnO thin films.

†Presented to the National Conference on Chemistry Solutions at SRM University, India

Experimental

A simple homemade spray pyrolysis experimental setup[5] was employed to prepare Pb substituted ZnO thin films on ultrasonically cleaned microscopic glass substrate. 0.2 M solution of zinc acetate was prepared in double distilled water and lead substitution was achieved from the source material of lead acetate. The Pb concentration was varied from 0 wt. % to 25 wt. % and dissolved in double distilled water along with Zinc acetate solution. Hereafter, the substitution concentration refers to the concentration of lead acetate in the spray solution. The solution was sprayed on the preheated glass substrates at 400 °C. Spray parameters were kept constant. Dry air was used as the carrier gas.

Thickness of the films was measured by Filmetrics F20. The structural properties were analyzed by the XRD technique using a Philips X'Pert Pro X-Ray Diffraction System. The surface morphology was observed by using the ZEISS-XIGMA Field emission scanning electron microscope. The optical transmittance spectra were recorded in the range from 300 to 1100 nm with a Shimadzu (UV-1601) UV- Visible spectrometer.

Results and Discussion

Structural study

The XRD patterns were obtained for pure ZnO and Pb substituted ZnO thin films are shown in Figure 1. The XRD studies clearly reveal that all the films are polycrystalline in nature. The XRD pattern of the film shows that the film is crystallized in the wurtzite phase and for these samples, the diffraction peaks were compared with the hexagonal wurtzite ZnO (JCPDS No. 36-1451). It is perceptible from the Figure 1 that the unsubstituted films grow along the (002) and (101) directions. As the substitution is increased one of the predominant (101) peak disappears. From these data it is evident that as the substitution concentration is increased, the 002 peak become very strong, while the other peak almost vanishes.
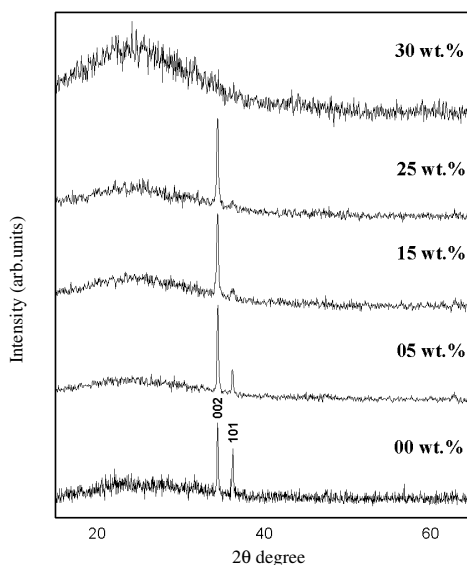

Figure 1. X-Ray diffraction pattern of ZnO and Pb substituted ZnO films with different concentration

It also shows that there is an increase in the surface migration of adatoms and thus it makes us attain films having highly preferred orientation. The crystalline quality of film is found to deteriorate with the increase of Pb substitution attains amorphous state for 30 wt. % of Pb thereby reducing the intensity of ZnO (0 0 2) plane. A similar behaviour has also been reported[6] for Zr doped ZnO films and found that interstitial inclusion of dopant atoms deteriorate the film structure and lead to the amorphization of film. Hence it is worth to conclude that increasing the Pb concentration in the solution increases the occupation of Pb^{4+} in the interstitial position rather than substitution of Zn^{2+} site which degrades the crystalline quality of the films and thus resulting amorphization for higher Pb substitution levels. The mean crystallite size calculated by using Sherrer's formula,

$$L= (0.9\lambda) / (\beta cos\theta) \text{ (nm)}$$

Where, λ is the wavelength of the X-Rays used (λ =1.5408 Å), β is the full width at half maximum (FWHM) value in radians and θ is the Bragg's diffraction angle[7]. For 0 – 25 wt. % Pb substituted ZnO thin films the mean crystallite size are 46 nm, 38 nm, 32 nm and 33 nm respectively.

Morphological Study

The SEM images for the pure ZnO, 5 wt. %, 15 wt. % and 25 wt. % Pb substituted ZnO thin films sample are shown in Figure 2. When we increase the substitution percentage dark spots were observed in the images, these are the irregular arrangement or the unequal spread of the molecules which results in the amorphization of the film and the area of these dark spots increases as the substitution concentration is increased it shows the crystallinity of the film decreases as the substitution concentration is increased and it resemble the XRD pattern.
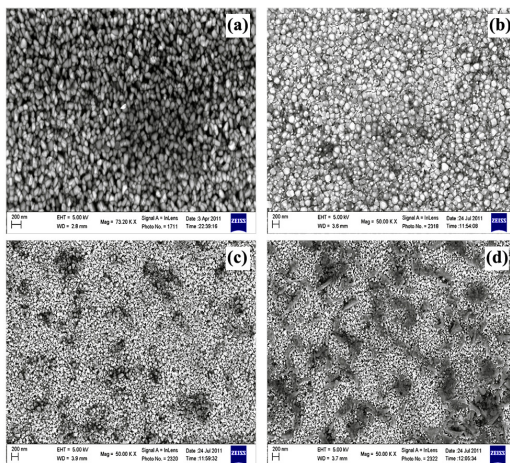

Figure 2. SEM images for pure ZnO (a), 5 wt. % Pb substituted ZnO (b), 15 wt. % Pb substituted ZnO (c) and 25 wt. % Pb substituted ZnO (d) respectively

Optical study

Figure 3 shows the transmittance spectra of the pure ZnO, 5 wt. %, 15 wt. % and 25 wt. % Pb substituted ZnO thin films samples. The transmittance spectra clearly reveal that the transmittance % of the film increases as the lead substitution concentration is increased in the ZnO thin films. It shows that the increase in lead concentration increases the transmittance

of the film. The tabulation is made for determining the Average Visible Transmittance (AVT) is given in Table 1. The AVT in the wavelength ranging 400-800 nm for pure ZnO film is about 78% which nearly coincides with the results obtained by Gokulakrishnan *et al*[8]. The AVT increases gradually as the substitution concentration is increased from 00 wt. % (pure ZnO) to 25 wt. % Pb substitution in the ZnO thin films. The optical bandgap value E_g can be obtained by extrapolating the linear region of "Tauc" plot of "$(\alpha h\nu)^2$" drawn as the function of hν, is presented in Figure 4.

Table 1, Average visible transmittance as a function of substitution concentrations

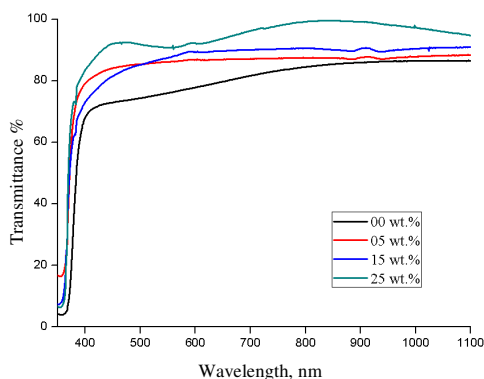| Substitution Concentration Wt. %	Average visible Transmittance % AVT, 400-800 nm
00%	77.85
05%	85.95
15%	87.02
25%	93.32

Figure 3. Transmittance spectra of ZnO: Pb thin films as a function of wavelength for different Pb substitution concentration (wt. %)
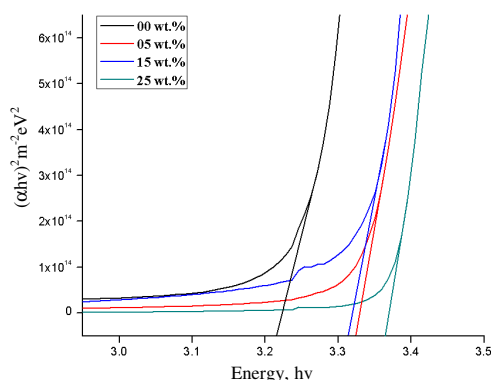
Figure 4. Plots of $(\alpha h\nu)^2$ *vs*. hν of ZnO:Pb films for various concentrations of Lead (Pb)

From the plot it is noted that the direct band gap for ZnO is found to be 3.27 eV and as the substitution concentration is increased it is noted that the band gap value increases to 3.36 eV. This could be due to quantum confinement effect. According to quantum confinement theory, the energy band gap of a semiconductor increase with a decrease in crystallite size[9]. In our case, the crystallite size for pure ZnO films is 46 nm and decreases to 33 nm for 25 wt.% Pb substituted ZnO film. Therefore the increase in bandgap energy is probably due to the quantum confinement effect.

Conclusion

Lead substituted zinc oxide thin films were prepared using the spray pyrolysis technique. The structural, optical and the morphological properties based on the substitution dependence for the films are studied. The XRD studies clearly reveal that the thin films prepared are polycrystalline in nature and the increase in substitution concentration makes us attain films having highly preferred orientation along (002) plane. The crystallinity of film is found to deteriorate with the increase of lead substitution concentration. The Scanning

electron microscope images reveals that the crystalline quality of the film decreases as the substitution concentration is increased, which is similar to the results obtained from the XRD studies. The films were transparent in the wavelength range of 300-1100 nm. The AVT (400 – 800 nm) of the film was ~93 % for 25 wt. %. The direct energy band gap value for pure ZnO is 3.27 eV and increases to 3.36 eV for 25 wt. % Pb substituted ZnO. Thus the properties of ZnO are influenced by the Pb substitution. They could therefore offer opportunities for further fundamental research and technological application.

Acknowledgement

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