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RESEARCH ARTICLE

EFFECT OF CONCENTRATION OF Cd ON STRUCTURAL AND OPTICAL PROPERTIES OF  
ZNO:Cd THIN FILMS PREPARED BY SOL-GEL METHOD

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ABSTRACT

Cadmium doped zinc oxide polycrystalline thin films were prepared by sol-gel process. The sol was prepared from zinc acetate dehydrate and cadmium acetate was used to it. Methoxyethanol and monoethanolamine were used as solvent and stabilizer, respectively. The quantity of cadmium in the sol was 0, 1, 5 and 10 at % Cd. Structural investigation including microstructure was carried out by X-ray diffraction (XRD) analysis. The films give a hexagonal wurtzite structure with diffraction peaks at (100), (002) and (101). It is found that the particle size of the films change with Cd doping. Optical properties of the thin films were determined by using UV-VIS-NIR spectrometer. It was found that the band gap of the thin films decreased from 3.16 eV to 2.6 eV as the concentration of Cd was increased. Such films can be applied on silicon solar cells as the changes in the band gap are acceptable as a requirement for good anti-reflecting coating element.

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INTRODUCTION

Zinc oxide is an inexpensive n-type semiconductor having direct band gap of 3.3 eV which crystallizes in hexagonal Wurtzite structure ( $c = 5.025$  and  $a = 3.249$ ) [1]. Due to large exciton binding energy of 60 meV, they have potential applications in Optoelectronic devices such as in solar cells, Optical wave guide, Light emitting diodes (LED). Various gas, chemical and biological sensors were based on ZnO thin film. Thin films of Zinc oxide can be prepared by various techniques; among them are Sputtering, Chemical Vapor Deposition (CVD), Laser ablation, Sol- gel methods [2- 4]. Properties of ZnO thin films show dependence on the technique used. Apart from doping, to increase the functionality of ZnO thin film, the effect of preparation conditions on the properties have to be considered for its effective technological applications. In the present work we have used sol-gel methods to prepare ZnO liquid and spin coating process for film preparation. Zinc acetate dihydrate was used as the precursor material. The Sol-gel process has the advantages of controllability of compositions, simplicity in processing and is cost effective [5]. We have studied the effect of concentration of Cd on the structural and optical properties of ZnO thin films. X-ray diffraction (XRD) was used for structural characterization. UV-Vis spectrometry was used for optical characterization.

Experimental details

Zinc acetate dehydrate ( $Zn(CH_3COO)_2 \cdot 2H_2O$ ) and cadmium hexahydrate were dissolved in a solution of isopropanol and monoethanolamine. The molar ratio of MEA to zinc acetate was 1.0 and the concentration of zinc acetate was 0.7 mol/l.

The quantity of cadmium in the sol was 0, 1, 5 and 10 at % Cd. The resultant solution was stirred at 50 °C for 1 h to yield a clear and homogeneous solution. The solution was finally aged at room temperature for 24 h. Cd-doped ZnO (AZO) films were prepared on glass substrate by repeated coating. Spin coating was performed at room temperature, with a rate of 3000 rpm for 30 s. After depositing each times, the films were preheated in air at 275 °C for 10 min. After repeating the coating procedure five times for the final film thickness of approximately 200 nm, the films were finally postheated at 500 °C for 1 h in air using an electronic furnace. For measuring the optical absorption of thin films, a double beam UV/VIS/NIR Spectrophotometer (Camspec-M550) was used. The XRD measurements were carried out using an X-Ray Diffractometer PW 1830 PANalytical which has tube anode; copper using the wavelength 1.54056 Å.

RESULTS AND DISCUSSION

Structural Properties

The structure of ZnO: Cd thin films were studied using high resolution X-ray diffraction (XRD). XRD spectra of the thin films were showed in Fig. 1. The XRD peaks of 31.48°, 35.26° and 37.17° were correspond to ZnO (100), (002) and (101) respectively in Fig. 1 A. These peaks confirmed that the film was polycrystalline in nature and the type of structural was a hexagonal wurzite[5]. The crystallite size (D) of the crystallites can be determined using the Scherrer's formula from the full width at half maximum (FWHM)  $\beta$  [6, 7];

$$D = 0.94\lambda/\beta\cos\theta \quad (1)$$

where  $\lambda$  is the wavelength of the X-ray used,  $\beta$  is the FWHM and  $\theta$  is the angle between the incident and scattered X-ray. The crystallite size of ZnO was 32.01 nm.

Fig. 1 B, C and D show XRD of ZnO: Cd thin film when concentration of Cd are 1%, 5% and 10%. The structural of ZnO: Cd thin films were a hexagonal wurzite. The full width at half maximum (FWHM) of the thin films increased after Cd doping. The crystallite size of ZnO: Cd thin films were 13.65, 13.65 and 18.42 nm.

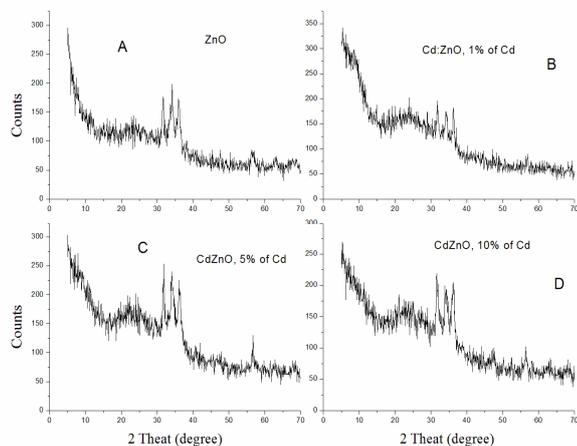


Figure 1 XRD of ZnO: Cd thin films before and after Cd doping

The changed in crystallite size in not systematic due to the value of it is depends on the crystallographic axes as well as the doping concentration and also related to a large number of physical parameters therefore it is difficult to maintain a uniform crystallite size.

**Optical properties**

The optical absorption spectra of ZnO and ZnO: Cd thin films, Cd concentration 1%, 5% and 10%. The thin films deposited onto a glass substrate were studied at room temperature in the range of wavelengths 300–750 nm. Figure 2 shows the variation of absorption spectra with wavelength ( $\lambda$ ).

The value of optical band gap ' $E_g$ ' is calculated using the following relation [8,9];

$$\alpha = A (h\nu - E_g)^n / h\nu \tag{2}$$

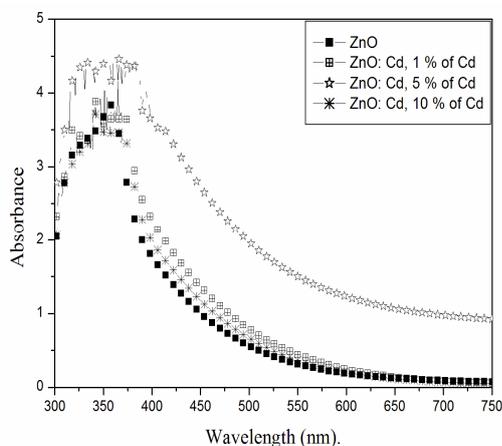


Figure 2 Absorbance spectra with wavelength ( $\lambda$ ). For ZnO: Cd system films

Where A is a constant and n is equal to 1/2 for direct band gap semiconductors. The plots of  $(\alpha h\nu)^2$  versus  $h\nu$  are shown in

Fig. 3 for ZnO and ZnO: Cd system films. We find the optical band gap decreased with Cd content. The decrease in the optical band gap on the addition of Cd in the ZnO system films may be explained on the basis of the model of density of states in amorphous semiconductor proposed by Mott and Davis [10]. According to this model, the width of localized states near the mobility edges depends on the degree of disorder and defects presented in the amorphous structure. In particular, it is known that unsaturated bonds together with some saturated bonds [11] are produced as a result of insufficient number of atoms deposited in the amorphous films [12]. The unsaturated bonds are responsible for the formation of some defects in the films. Such defects produce localized states in the amorphous solids.

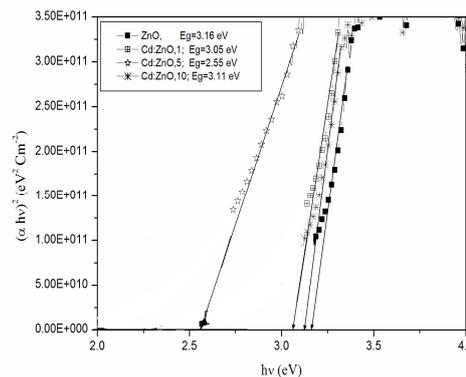


Figure 3 Optical band gap of ZnO: Cd thin films.

Many of authors have reported that optical band gap of semiconductors decreased with metal doping due to increase in the free carriers with doping, enhance the electric screening between holes and electrons and reduce the intensity of the oscillator strength of the discrete exciton state [13-15].

**CONCLUSION**

We have instigated the optical and structure properties of the ZnO thin films. In spite of the insignificant change in the structure with the variation of (Cd) content the grain size decreased for thin films variation of Cd increase, it is found that the optical band gap decrease with increasing (Cd) content, a result has been attributed to the increase in the localized tail states.

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