Effect of Cd Dopant Concentration on the Properties of ZnO Thin Films Prepared by Spray Pyrolysis

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Abstract: ***ZnO and Cd doped ZnO thin films were obtained by spray pyrolysis technique characterized by XRD, SEM, EDAX and Optical measurements. The XRD pattern of the film showed polycrystalline nature and they have hexagonal wurtzite crystallographic phase with (0 0 2) preferred orientation. SEM analysis indicates decrease in crystallite size with increase of Cd content. Through UV analysis it was found that band gap decreases from 3.29 to 3.10eV with increase Cd content.***

Keywords: Cd doped ZnO films,Spray pyrolysis, XRD, SEM, EDAX and UV-Vis.

1. Introduction

In recent years, there has been great demand for low cost transparent conducting films (e.g., ZnO, SnO2, Cd2SnO4, CuAlO2, etc.) [1]. From all the transparent conducting oxide (TCO) materials studied, in last year's, Zinc Oxide (ZnO) has emerged as one of the most promising material [2] due to its optical and electrical properties, high chemical and mechanical stability together with its abundance in nature, which makes it a low cost material when compared with the most currently used TCO materials, such as indium tin oxide. ZnO films of this nature find application in various fields such as solar cells, displays, OLED's, heat mirrors, piezoelectric devices, gas sensors and optoelectronic devices [3]. Moreover, zinc oxide can be prepared by different techniques, such as magnetron sputtering, reactive evaporation, chemical vapour deposition, pulsed laser deposition and spray pyrolysis. The addition of Cd into theZnO lattice results in an improvement of the characteristics of the ternary CdZnO to be used as TCO, due to its better transmittance and lower resistivity of the films.

The incorporation of Al into ZnO is very useful for the fabrication of ZnO/CdZnO hetero junctions and super lattices, which are key elements in ZnO based light emitters and detectors. Several techniques have been used to prepare CdO-ZnO alloy films like electro deposition, molecular beam epitaxy, Sol-gel and Spray pyrolysis. Among these methods, the Spray pyrolysis technique – in the form of spray chemical vapour deposition (CVD) – has several advantages, such as, simplicity, safety and low cost of the apparatus. The critical operation for the spray pyrolysis technique is the preparation of uniform fine droplets and the controlled thermal decomposition of these droplets in terms of environment, location and time. Generally commercialized nozzle atomizers are used to spray solutions for thin film preparation. In conventional spray pyrolysis technique, a spray gun assembly, compressed air container and a solution reservoir are generally used. We have reported the structural, morphological, optical and electrical properties of medical jet nebulizer atomizer spray deposited ZnO and Cd doped ZnO thin films by varying the percentage of the dopant[4].

2. Experimental Technique

For ZnO thin film, zinc acetate salt was thoroughly mixed with deionized water and few drops of conc. hydrochloric acid were added. This is done, so that insoluble salts in solution also get dissolved. Similarly for Cd doped ZnO thin film, zinc acetate and cadmium acetate salts were mixed with deionised water and along with it few drops of conc. hydrochloric acid was added. By varying the percentage of zinc and cadmium in the solution such as 100:0, 95:5, 90:10, 85:15 ZnO and Cd doped ZnO films were coated.The solution was sprayed on to heated glass substrates held at constant temperature 450°C. Thin films are also prepared by varying the percentage of the dopant and keeping all other parameters under optimum conditions.

3. Results and Discussions

Zinc Oxide and Cd doped Zinc Oxide thin films at different dopent concentrations (0 to 15 % by a step of 5 %) deposited on glass substrate at 450°C by using spray pyrolysis technique. The structural, surface morphological, compositional analysis and optical characterizations of deposited films were investigated.

3.1. Structural Characterization

The XRD patterns of the zinc oxide and Cd doped zinc oxide at various concentrations of the dopant deposited on glass substrate at 450°C is shown in the Fig 1.

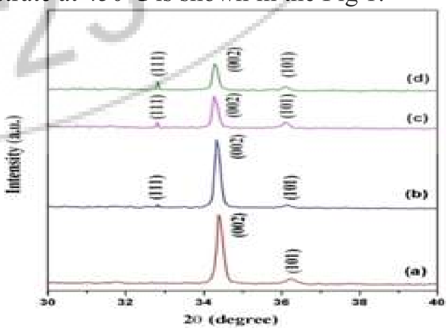
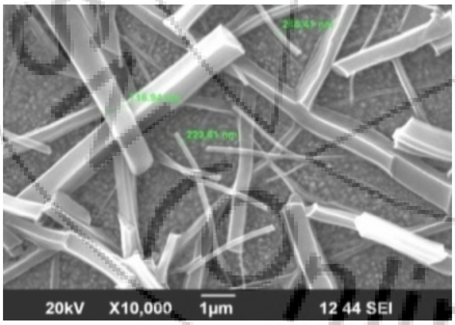


Figure 1: XRD pattern of ZnO and Cd doped ZnO thin films(a)Undoped, (b) 5% at Cd,(c) 10% at Cd, (d) 15% at Cd.

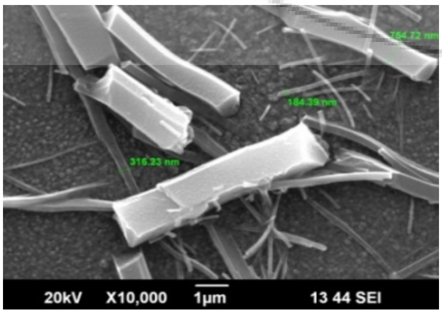
It is seen that all the films are polycrystalline in nature having wurtzite crystal structure with a preferential oriented growth along (0 0 2) and (1 0 1) plane. All the films show single ZnO phase (without significant detection of Cd or CdO phase) with two typical (0 0 2) and (1 0 1) peaks. The XRD pattern shows the peak position of (1 0 1) plane and intensities of peaks decreases greatly with broadening full-width at half-maximum (FWHM) varying as a function of Cd concentration which suggests that the crystallinity and c-axis orientation are reduced dramatically for Cd doped ZnO films with a nominal Cd content of 15%. The preferred growth along (1 0 1) is found to be remaining predominant irrespective of thin films of Cd doping concentration [5, 6]. For 5% doping of Cd, a peak related to (1 1 1) plane of the hexagonal structure is observed. As the composition of Cd increases as 10% and 15%, the peak related to (1 1 1) plane increases. This shows about the recrystallization and the formation of mixed oxides.

Lattice parameter values 'a' and 'c' were calculated using the XRD data and the values are found to be in the range of 3.245 – 3.253 Å and 5.221 – 5.239 Å respectively,which is in agreement with the standard JCPDS data (JCPDS cardno. 36-1451).There is no significant variation between lattice parameters for the Cd doped ZnO films prepared with different Cd concentrations. This clearly suggests that there is no lattice strain in the deposited films. The variation of crystallite size is determined for the ZnO and Cd doped ZnO films using the FWHM along (0 0 2) plane. Crystallite size of the doped ZnO films decreases with increase in Cd from 42nm to 24nm. This may be explained as crystallinity decreases with increase in Cd doping. Higher the doping results in the films losing their polycrystallinity and tending towards less crystalline. Moreover, the increase of the FWHM as Cd content increases, show that the increase of lattice defects and grain boundary defects is due to the doping of Cd[7,8].

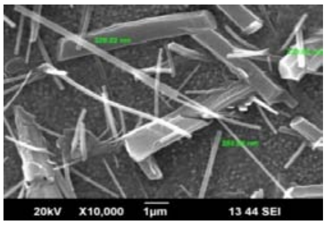
3.2. Surface Morphology



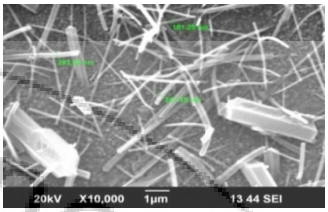
(a). Undoped ZnO



(b). 5 %at Cd doped ZnO



(c). 10 % at Cd doped ZnO



(d). 15%at Cd doped ZnO

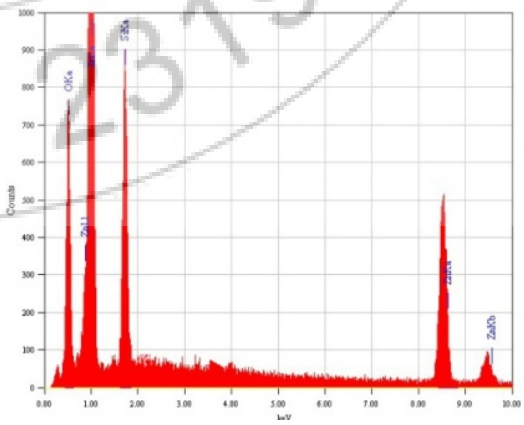
Figure 2: (a),(b),(c) and (d) are SEM images of Undoped and Cd doped ZnO thin films.

The surface morphology of the doped and undoped ZnO films were analysed by scanning electron microscopy (SEM). SEM images of the films are shown in Fig.2 (a), (b), (c) and (d). The surfaces of the films are found to be uniform and homogeneous. In the present case, all Cd doped films are highly oriented along (0 0 2) direction which shows needle shaped morphology at magnification of 10000. [9].

It shows a large variety of nano structures randomly distributed over the film surface. Fig. 2(a) shows undoped ZnO particles which had smooth and the formation of rod shapes of different sizes aligned horizontaly and distributed over the film surface [10], which agrees well with the XRD data. The types of nano-structures have potential use as gas sensor, dye synthesized solar cells and energy storage device etc. Fig. 2(b) shows that increase of Cd doping, the size of the rods become small.As the Cd doping increases with decrease in grain size values. Film deposited with the Cd ratio 15% has a smooth surface structure composed of crystallites in the rod like grains of approximately 161 nm in size. Fig.2(d).

4. Elemental Analysis

The EDAX spectrum of ZnO and Cd doped ZnO thin films are shown in fig.3 (a) and (b).


(a) Undoped ZnO

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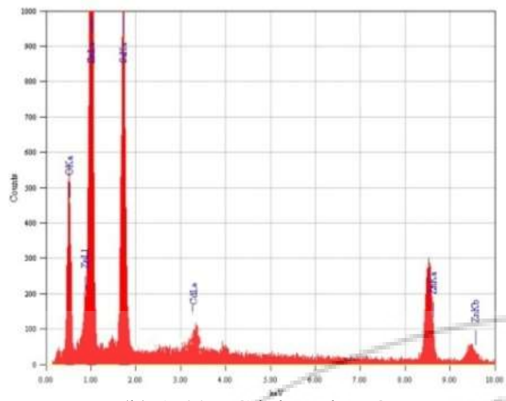

(b) 15% atCd doped ZnO

Figure 3: (a),(b): EDAX images of ZnO and Al doped ZnO thin films

The EDAXspectra reveal that the films contain the Cd, Zn and O as expected. The compositional analysis of the undoped ZnO film indicates that the atomic percentage ratio of Zn : O is 36.05 : 22.35. The atomic percentage ratio of 15 at % Cd doped ZnO film is 18.7 : 4.33 : 29.75. It reveals that Cd is incorporated in ZnO films and it is not present in undoped ZnO films and also that the atomic percentage ratio of Cd is less than the nominal composition in the solution.

5. Optical Characterization

UV-Vis Analysis

Transmission was recorded for the range of 300-1000 nm of incident beam. The Fig. 4 shows the Optical transmission spectra of the ZnO and Cd doped ZnO films in the wavelength range from 350 to 1000 nm with optimum substrate temperature of 450°C.

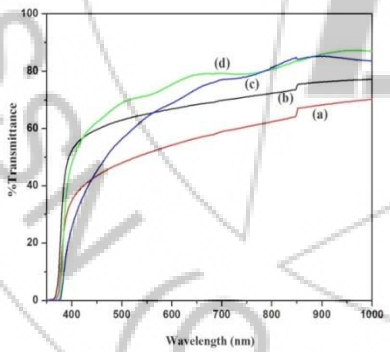

Figure 4: The Variation of % of Transmittance with Wavelength (a) Undoped (b) 5 at % Cd (c) 10 at % Cd (d) 15 at % Cd

The transmittance spectra reveal that the maximum transmission of 80 % for the undoped film. The percentage of transmission increases with increasing in Cd dopant concentration.

In order to determine the optical band gap energy Eg from the absorption spectra we used the variation of the absorption coefficient (α) with photon energy, using the relation;

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

Where Eg is the optical band gap of the films and A is a constant. Fig. 5 shows the plots of $(\alpha h\nu)^2$ versus (hν) for the various ZnO samples. Extrapolation of the linear portion of $(\alpha h\nu)^2$ gives the direct allowed band gap values for the spray deposited films.

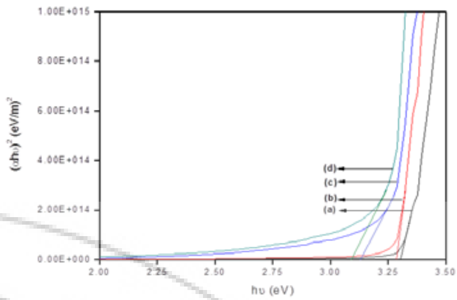

Figure 5: Determination of Band gap Energy (a) Undoped (b) 5 at % Cd (c) 10 at % Cd (d) 15 at % Cd

The calculated direct bandgap value for the as-deposited film is 3.30, 3.29, and 3.12, 3.10eV for the undoped ZnO, 5% at Cd, 10% at Cd, and 15% at Cd-doped ZnO films respectively. It shows that the band gap decreases from 3.29, 3.12, 3.10 eV with increase of Cd content from 5% to 15%. CdO is an n-type semiconductor, with the direct band gap of approximately 2.5eV which is lower than that of ZnO(~3.3eV) however CdO thin films show low resistivity due the defect of oxygen vacancies and Cadmium interstitials. This systematic decrease in band gap with the increasing Cd concentration might arise from the doping defect [11, 12]. The band gap variation is also due to the influence of the free carrier electrons on the fundamental absorption edge in the near ultra-violet (UV) region.

6. Conclusion

Various Cd doped zinc oxide thin films have been prepared on glass substrates under the optimized conditions. All the films showed polycrystalline nature and they havehexagonal wurtzite structure. An interesting orientation modification has been observed that the preferential orientation of the crystalline lattice changes for (0 0 2) and (1 0 1) planes at Cd doping concentrations. At the same time the plane (1 1 1) corresponding to Cd increases with increase in Cd concentrations. The grain size of CdZnO film decreases as the Cd content increases. The band gap energy of deposited films was decreased from3.29, 3.12, 3.10 eV with increase of Cd content from 5% to 15%.

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