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Study of Structural and Optical Properties of Cd Doped ZnO Thinfilms

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Abstract:
Transparent conducting Zinc oxide and Cadmium doped Zinc oxide thin films have been prepared on glass substrates using sol-gel spin coating technique. The effects of Cd addition on the structural and optical properties of ZnO thin film were investigated. The crystalline behavior of the Zinc oxide thin film was studied by X-ray diffraction (XRD). It has been found that the crystalline behavior of ZnO film reduced after the addition of Cadmium in ZnO lattice. The optical properties of Zinc Oxide thin film have been investigated by Photoluminescence spectrum. PL spectrum observed the violet and blue-green emissions of undoped and Cd-doped ZnO thin film.

Keywords*: Spin coating, XRD, PL*

1. Introduction

Transparent conducting Zinc Oxide films have been extensively studied in recent years. ZnO is an II-VI semiconductor with a wide and direct band gap about 3.3eV. ZnO is a technologically important material exhibiting multifunctional properties for various applications in optoelectronic devices such as solar cell transparent conducting electrodes and heat mirror. In order to improve the electrical and optical properties of the ZnO thin film, introduce the dopants. Because of the low cost among those elements Cd was added into ZnO.

Several techniques have been used to prepare ZnO films such as spray pyrolysis, chemical bath deposition, chemical vapor deposition, sputtering, dip coating, spin coating and pulsed laser deposition **[1]**. Among the different techniques, the Sol-gel technique has the advantage of coating on large areas with easy control of the doping level, solution concentration and homogeneity without using expensive and complicated equipment compared with the other methods.

2. Experimental Details

The undoped and Cd doped ZnO thin films were prepared by sol-gel method on glass substrate. For preparing undoped ZnO thin film, Zinc acetate dehydrate was dissolved in a solution of ethanol and diethanolamine (DEA). The molar ratio of DEA to zinc acetate was maintained as 1.0 and the concentration of zinc acetate was 0.5M. For Cd doped ZnO film, Cadmium chloride was used as a dopant in the precursor ZnO solution. The concentration of dopant is varied about 0.5at%, 1at%, 1.5at%, 2at% respectively. The prepared solutions were stirred for 1hour at 50^0C by a magnetic stirrer to yield a clear homogeneous solution. The obtained solution was allowed for aging at room temperature for 24 hours before used for coating process. The final sol was used to prepare films by spin coating technique. First, glass substrates were immersed in Chromic acid and then cleaned with soap solution followed by distilled water. The prepared sol was dropped onto glass substrate which was rotated at a constant speed of 2500 rpm for 30 seconds using a spin coater. After each deposition, the film was dried at 150^0C for 10 minutes to remove the organic residuals. The process was repeated eight times to get the film of desired thickness. Finally, the film was annealed in air at 500^0C for 1hour.

3. Result and Discussion

3.1. Structural Properties

The X-ray diffraction patterns of all the films prepared by using spin coating technique and annealed in air at 500^0C are shown in Fig.1. All the films have polycrystalline nature. The undoped ZnO thin film has the diffraction peaks at the 2θ values of 34.60, 36.4 which are assigned to the corresponding planes of (002) and (101) respectively. These observed principal orientations indicated an hexagonal wurtzite structure for the ZnO and Cd-doped ZnO. All the Cd doped thin films had the highest (002) diffraction peak intensity indicating that (002) plane is the preferential orientations. The preferential peak intensity sharply rises for ZnO film doped with 0.5at% of Cd and suddenly decreases when the doping concentration is increased to 1at%. Further increase of doping concentration of Cd from 1.5at% to 2at%, the intensity increases. This reveals that the crystallinity of the film enhances initially and then deteriorates. This result may be due to deformation and formation of stresses by the difference in the ion size between Zinc and dopant [2].

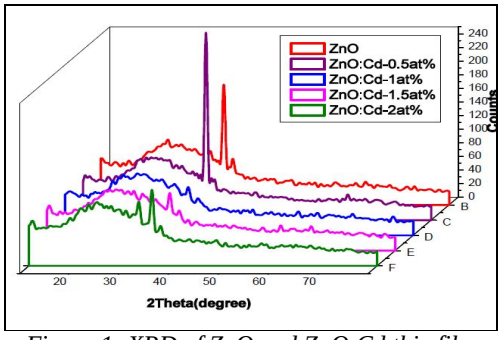

Figure 1: XRD of ZnO and ZnO:Cd thin film

The concentration of 1at% Cadmium doped film which had preferential orientation along (202) plane. This revealed that doping of 1at% Cadmium has induced a structural change in ZnO film as it causes a loss of preferential orientation (002). The increase of peak intensities against the increase of Cd concentration indicates that incorporation of Cd greatly improves the crystallization quality of ZnO thin film, which may be due to the fact that a lot of Cd ions are not substituted in the Zn sites, but as interstitials exist in the vicinity of the oxygen vacancies(V_o^+). They prevent lattice distortion by the V_o, which enhances crystallization quality**[3]**. The crystallite size D is calculated using the Scherrer's formula

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where k is a constant and in our case k = 0.9, λ is the wavelength of the incident X-ray (λ =1.54060Å), β is the corrected FWHM for instrumental broadening of the maximum intensity peak and θ is the angle at which the maximum peak occurs.

Sample	Cadmium doping concentration (at %)	Grain size D (nm)	Dislocation density δ X10^{-4} (nm)$^{-2}$
ZnO	0.0	75.6808	1.7459
	0.5	61.8304	2.6157
	1.0	55.6413	3.2300
	1.5	83.4710	1.4352
	2.0	166.969	0.3587

Table 1

The grain size for Cd doped films is less than the bare ZnO film. This may be attributed to the nucleation mechanism of ZnO. As Cadmium is doped ,the number of nucleations of ZnO enhances and results in a smaller grain size as a consequence**[4]**. It is suppressed at higher concentration of Cd(2at%) and results in a larger grain size.
The dislocation density δ which represents the amount of defects in the film is determined using the formula

$$\delta = \frac{1}{D^2}$$

The Lattice constants,

$$a = \frac{\sqrt{1}}{3}\frac{\lambda}{\sin\theta} \qquad c = \frac{\lambda}{\sin\theta}$$

The calculated values of lattice parameters a and c are well agreed with the JCPDS data.
While the grain size D decreases due to doping, the dislocation density increases. This confirms that all Cd ions are not substituted into the Zn sites but exist as interstitials in the vicinity of the oxygen vacancies and thus have prevented the lattice distortion of bare ZnO film.

3.2. Optical Properties

3.2.1. Photoluminescence Spectra

Photoluminescence spectra of bare and Cd doped ZnO thin film annealed at 500^{o}C with different Cd concentrations ranging from 0.5at% to 2at% is shown in Fig.4.

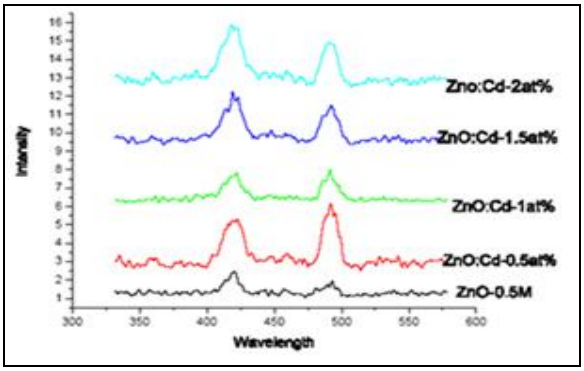

Figure 2: Photoluminescence Spectrum for ZnO and Cd doped ZnO

From the spectra, it can be seen that there is violet emission in the range 400-430nm centered at 420nm and blue-green emission ranging from 475-500 nm centred at 493nm. The violet dominant emission of undoped bare ZnO thin film is subjected to red shift for 0.5at% Cd doped ZnO thin films followed by a blue shift at 1at% Cd doping. The shift was feeble for the other doping concentrations. The blue-green emission of undoped ZnO thin film observed at 493nm has shown a significant blue shift (490nm) only at 1.5at% of Cd doping concentration. This result may be connected with the defects of the Oxygen vacancy(V_o), Zinc vacancy(V_{Zn}), interstitial Zinc(Zn_i), interstitial oxygen(O_i) and anti-site oxygen(O_{Zn})**.**

The violet dominant emission for bare undoped ZnO thin film observed at 420 nm is shifted to 423 nm when 0.5at% of Cd is doped. The shift is to 421 nm for 1at%, 419 nm for 1.5at% and to 421 nm for 2at%. The initial red shift may be due to the higher Cd interstitials than Cd substitutions and hence Zn interstitial is larger than Zn vacancy which would have led to the defect level ZnO grain boundaries. The blue shift observed at 1.5at% of Cd may be ascribed to the change in the ratio of zinc vacancy and zinc interstitial

Upon increasing the Cd concentration in the sol-gel, the initially observed red shift at 0.5at% of Cd indicated the narrowing of band gap and the followed blue shift above 0.5at% indicated the widening of the band gap due to Cd incorporation. This implies the degradation of the grains as well as the crystalline quality with increasing Cd concentration. Absolute intensities of the defect related deep level emission (blue green) band in the visible region and the violet emission band are all increases initially against Cd concentration and decreases and then increases. This may be due to the change of the ratio of Zinc vacancy to Zinc interstitial due to the increased Cd interstitials and hence to the structural defects [**5**].

4. Conclusion

The effect of Cd addition on the Structural and optical properties of ZnO have been investigated. The nucleation mechanism of ZnO has been influenced due to the Cd doping. The red shift and blue shift of dominant emission was due to the changing radiative centre between Zinc vacancy and Zinc interstitial.

5. References

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