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Effect of Zinc Doping on Cdo Thin Films Prepared by Spray Pyrolysis Technique

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Abstract: ***Pure (undoped) and Zinc doped CdO thin films were prepared using spray pyrolysis technique with various dopant concentrations of Zn such as 3, 5, 7, 10 and 15% on glass substrates. Influence of Zn doping on the structural, optical and electrical properties of CdO thin films is reported. XRD analysis reveals that as prepared pure and Zn doped CdO films show polycrystalline nature with face centered cubic structure. Also, Zn doping significantly increases the crystallinity and changes the crystallite size. SEM images shows grains which are uniform and agglomerated grain size increasing with increase in dopant concentration. The transmittance of the prepared CdO films recorded in the UV visible spectra show 50 to 70% in the visible region. However, the higher dopant concentration of Zn (10 and 15%) in CdO diminishes the transmittance value. The estimated optical bandgap varies from 2.59 to 2.65 eV for various dopant concentrations. Hall measurement shows that the films are n-type semiconductor. Also, it is observed that when the doping level is increased, the electrical resistivity also increases in the spray pyrolysed CdO thin film.***

Keywords: Spray pyrolysis, concentrations, Optical, Electrical and Band gap.

1. Introduction

Nowadays, thin film technology is considered as a promising application in solar cell, which harnesses the energy of the solar radiation into useful electrical energy. Transparent conducting oxide thin films such as tin oxide, indium oxide, zinc oxide, cadmium oxide etc., have great importance in the fabrication of solar cells due to their excellent optical and electrical properties. Among the above mentioned conducting oxides, cadmium oxide has been considered as a suitable II – IV n-type semiconductor material because of high transmittance in the visible and UV regions of the electromagnetic spectrum coupled with high ohmic conductivity. Here, we report the characterization of undoped and doped CdO thin films prepared by easy and simple spray pyrolysis technique. Literature shows that materials like Al, In, F, Mn were used as dopant materials for the preparation of CdO thin film but, there are few reports seen on Zinc doped CdO thin films. CdO and ZnO are both important materials for the use of window materials in photovoltaic industry. Hence, it is expected that the homogenous composition of these two materials may change the optical and electrical properties of both CdO and ZnO to form a few material which is useful for various applications such as buffer layer in solar cells. The present work focuses on the influence of Zn on the structural, morphological, optical and electrical properties of CdO thin films deposited by spray pyrolysis technique on glass substrate with various doping concentrations.

2. Experimental Details

In spray pyrolysis method, film formation takes place by the condensation of atoms or molecules onto a heated substrate. Many parameters like substrate temperature, solution flow rate, spraying distance and molarities play important roles in the formation of high quality thin films. The spray solution consists of cadmium acetate dihydrate (Sigma Aldrich) dissolved in water and methanol in the ratio 1:1. To investigate the doping effect of zinc on CdO films, we have used zinc acetate dihydrate as the source material for zinc which was added in different weight percentage such as 3, 5, 7, 10 and 15%. The carrier gas used was compressed air and the nozzle to substrate distance was maintained as 18 cm. We maintained the solution flow rate of 3ml/min and cadmium ion concentration was taken as 0.1M. All the films were prepared at 400°C substrate temperature. An X- Ray diffractometer (Pananalytical Xper pro X) was used to study the structural properties and the surface morphology was taken using scanning electron microscope. Optical properties have been studied using UV-VIS spectrophotometer (UV Vis NIR Jasco V-670) in the wavelength range of 300 - 1000 nm. Electrical properties of thin films were measured by Hall measurement instrument (ECOPIA Hall Effect Measurement System HMS 3000).

3. Results and Discussion

3.1 XRD Analysis

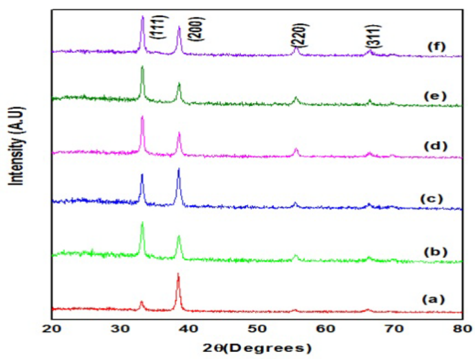

Figure 1: XRD patterns of Zn doped CdO thin films (a) 0%, (b) 3% (c) 5% (d) 7% (e) 10% and (f) 15%

XRD patterns of undoped and Zn doped CdO thin films are shown in figure 1. The prepared films exhibit polycrystalline nature with cubic structure. The peaks observed at 33.14, 38.5, 56 and 66° are consistent with the standard peaks of CdO thin films (JCPDS Card No. 65-2908). It is observed that the intensity of the peak at $2\theta \sim 33°$ corresponding to (111) plane increases with the increase in Zn dopant concentration. The lower angle shift in the preferential orientation of the (111) plane may be attributed to the imperfection in crystalline structure by the excess of Zn incorporation into the CdO lattice structure. Incidentally, the crystallite size gets increased up to 3% of zinc doping, beyond which there is no significant variation in the crystallite size. This tendency suggests that Zn dopant creates newer nucleation centers, which in turn would vary the nucleation type from homogenous to heterogeneous, and deteriorate the crystalline structure with higher doping contents [1]. The grain size D values were determined by using the Scherrer's formula using,

$$D = \frac{0.9\,\lambda}{\beta \cos \theta}$$

where D is grain size, λ is the X-ray wavelength, β is the angular line width of half maximum intensity, and θ is the Bragg's angle. Table 1 shows the values of structural parameters deduced from XRD patterns of CdO thin films for various Zn concentrations.

Table 1: Structural properties of Zn doped CdO thin films

Doping (%)	2θ (deg) (111)	Lattice constant Å	FWHM (deg)	Crystallite size (nm)	Microstrain ($x10^{-3}$)
0	33.3	4.692	0.4	22	1.422
3	33.14	4.678	0.5	41	8.359
5	33.1	4.682	0.4	21	1.672
7	33.16	4.675	0.37	22	1.546
10	33.16	4.699	0.34	24	1.421
15	33.16	4.675	0.41	20	1.714

3.2 Morphological Studies

SEM images of undoped and Zn doped CdO thin films are shown in figure 2. Chain like structures interconnected on the surface of pure CdO films is seen from SEM images. It is observed that as the Zn dopant concentration increases, the grains gets agglomerated and bigger grains of spherical shape are formed. SEM images suggest that the films are showing crystalline nature for lower zinc doping and the films become amorphous for higher concentration of Zn doping.

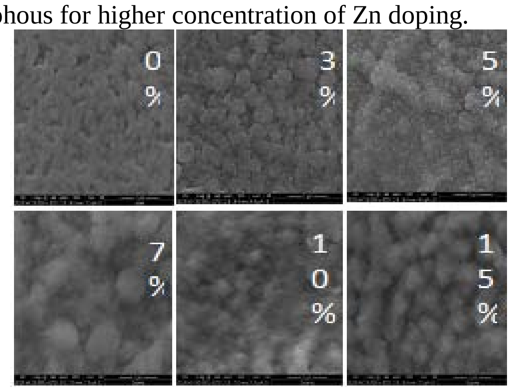

Figure 2: SEM images of pure and Zn doped CdO thin films (a) 0%, (b) 3% (c) 5% (d) 7% (e) 10% and (f) 15%

3.3 Optical Properties

Generally, the energy bandgap value depends on crystal structure of the films and the arrangement and distribution of atoms in the crystal lattice. The absorption coefficient and the incident photon energy are related by the equation

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

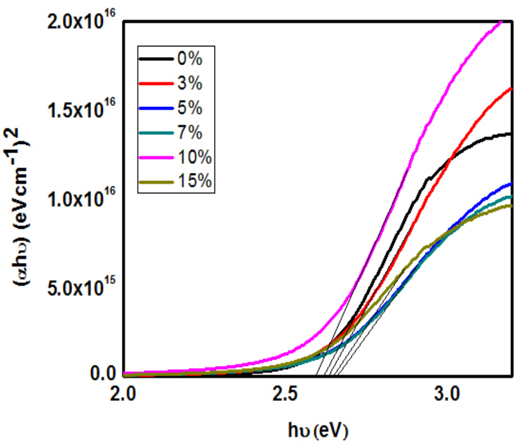

Figure 3: Energy bandgap of undoped and Zn doped CdO thin films

where α is absorption coefficient, A is constant, E_g is the band gap of the material and the exponent N depends on the type of transition, N = 1/2, 2, 3/2, and 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect respectively [2]. The determination of E_g was carried out by extrapolating the linear portion of the curves until they intercept the photon energy axis. The allowed direct transition bandgap values vary from 2.59 to 2.65 eV in fig 3. E_g values are the highest for undoped CdO thin film and lowest for 10% Zn doped thin films. This reveals Zn doping causes decrease in bandgap energy values for CdO films.

3.4 Electrical Studies

I-V Characteristics

I-V characteristics of Zn doped CdO thin films are shown in figure 4.

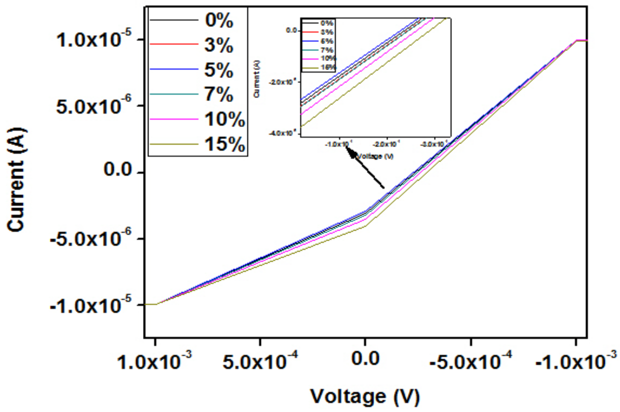

Figure 4: I-V of undoped and Zn doped CdO thin films

The figure shows all the films have linear response showing the ohmic behaviour. The results are consistent with the values of mobility and free charge carrier concentration of Zn doped CdO thin films.

4. Conclusion

Pure and Zn doped CdO thin films were prepared by spray pyrolysis technique. Changes in the structural, optical and electrical properties were studied. XRD analysis shows that the films are polycrystalline nature with cubic structure. Zinc dopant causes the lower angle shift in (111) plane. SEM images show that the grains are agglomerated and uniformly spread over the substrate. Optical study reveals that Zn doping decreases the optical bandgap. Electrical studies show that the films have linear relationship between current and voltage confirming the ohmic behaviour of the films.

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