



INFLUENCE OF MOLARITY ON PHYSICAL PROPERTIES OF SPRAY PYROLYSED TRANSPARENT CONDUCTING CdO THIN FILMS

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ABSTRACT

Transparent highly conducting CdO thin films were coated on glass substrates by homemade Chemical Spray Pyrolysis technique (CSPT). The X-ray diffraction studies were carried out the CdO films was found to be cubic polycrystalline structure with preferential reflection of (111) plane. The crystallite size was determined by Scherer formula and is in the range of 6-23 nm. The SEM analysis indicated the film prepared at higher molarity with two different magnification exhibited porous nature of the surface and nano clusters are interconnected to form a nanorod of CdO. From UV-VIS-NIR studies, the absorption coefficient was found and connected with the photon energy in order to value the direct band gap energy (2.17 eV-1.99 eV). Depending on the molarity, Hall measurement showed the electrical resistivity and mobility at 300K varied in the range $16.5 \times 10^{-3} \Omega\text{cm}$ to $1.23 \times 10^{-3} \Omega\text{cm}$ and $11.7 \text{ cm}^2/\text{Vs}$ to $34.2 \text{ cm}^2/\text{Vs}$.

Keywords: thin film, spray pyrolysis, X-ray diffraction, optical properties, electrical properties, oxide material.

1. INTRODUCTION

Most optically transparent conducting oxides (TCO) are binary or ternary compounds, containing one or two metallic elements. Their resistivity could be as low as 10^{-4} cm , and their extinction coefficient k in the optical visible range (VIS) could be lower than 10^{-4} , owing to their wide optical band gap (E_g) that could be greater than 3 eV. This remarkable combination of conductivity and transparency is usually impossible in intrinsic stoichiometric oxides; however, it is achieved by producing them with a non-stoichiometric composition or by introducing appropriate dopants. Badeker discovered that thin CdO films possess such characteristics [1]. Later, it was recognized that thin films of ZnO, SnO₂, In₂O₃ and their alloys were also TCOs [2]. The actual and potential applications of TCO thin films include: transparent electrodes for flat panel displays, transparent electrodes for photovoltaic cells, low emissive windows, window defrosters, transparent thin films transistors, light emitting diodes, and semiconductor lasers. TCO thin films are essential part of technologies that require both large area electrical contact and optical access in the visible portion of the light spectrum. The various TCOs include the oxides of Sn, In, Zn, Cd and their alloys.

CdO is one the promising transparent conducting oxides from II to VI group of semiconductors having high absorption and emission capacity of radiation in the energy gap. CdO has special features such as high conductivity, high transmission and low band gap made it applicable in photodiodes [3], phototransistors [4], photovoltaic cells [5], transparent electrodes [6], liquid crystal displays, IR detectors and anti reflection coatings [7]. CdO thin films have been obtained by different techniques such as chemical bath deposition [8], SILAR [9], sol-gel [10], electrodeposition [11], dc reactive sputtering [12], reactive vacuum evaporation process [13],

metal organic vapor-phase epitaxy [14] and spray pyrolysis [15] techniques. Among these techniques spray pyrolysis technique is simple, amendable to large growth, conformal coverage, non line of sight and wide range materials. This work is to study the effect of molarity on the structural, optical and surface morphological characteristics of CdO thin films prepared at 230 °C by using spray pyrolysis technique.

2. EXPERIMENTAL DETAILS

The precursor solution used to form CdO thin films was obtained by dissolving the salts of Cadmium acetate [$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ 99.99%] in the three different molar (0.025M, 0.05M and 0.1M) in double distilled water. The amount of solution was made together as 50ml and optically plane cleaned glass plates ($7.5 \text{ cm} \times 2.5 \text{ cm}$) was placed over the hot plate. The aqueous solution was then sprayed on the preheated glass substrate maintained at $230^\circ\text{C} \pm 2^\circ\text{C}$. Compressed dry air at a pressure of 2 kg/cm^2 from an air compressor via an air filter cum regulator was used as the carrier gas and spray rate of the solution was maintained at 3 ml/min.

The flow rate of the solution is kept minimum due to the fact that at lower flow rates the spray will get sufficient time to react endothermically at the heated substrate surface to give the final film in the near stoichiometric phase of CdO. The distance between the spray nozzle and the substrate is 35 cm. Film obtained due to endothermic thermal decomposition that takes place at the hot surface of the substrate? The overall reaction process can be expressed as decomposition of cadmium acetate to form cadmium oxide onto the substrate as a strongly adherent film and they appeared in yellowish in colour. The deposited film was subsequently annealed in air at 300 °C for 1 hour. Film thickness of CdO was determined by gravimetric weighing method [16]. The



film thickness was determined to be ranged between 330 nm to 680 nm for the solution molarity of 0.025M, 0.05M and 0.1M. This was consequently verified by the cross sectional studies of the film using Scanning Electron Microscope. Here, the film is mounted vertically to measure the thickness directly [17].

The structural study was determined by X-ray diffractometer (Rigaku Model RAD II A) with $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The surface morphologies of the films were determined by using Scanning Electron Microscope (TESCAN -VEGA 3 SEM). Optical transmittance and band gap energy was measured by UV-VIS single beam spectrophotometer (ELICO-159). The experimental accuracy for absorbance is ± 0.005 abs and of wavelength is ± 0.05 nm. The resistivity (ρ) and Hall coefficient (R_H) were measured by a standard four-probe technique (ECOPIA HMS5000 Hall system) and silver contacts were used for all electrical measurements.

3. RESULTS AND DISCUSSIONS

3.1. XRD and surface morphology studies

The molarity had a significant effect on the X-ray diffraction structural analysis of CdO thin films as shown in Figure-1. Observation of film shows smooth surface and well adhesive with substrate. The peaks observed in the diffractograms confirm the polycrystalline nature of the CdO film. XRD pattern showed that the films have mainly preferential orientation with the cubic face-centered structure along the c-axis, (111) perpendicular to the substrate plane. No other impurities peaks are observed. Also the intense peak oriented along (111) lattice plane indicates that the growth of the grains is parallel to the substrate.

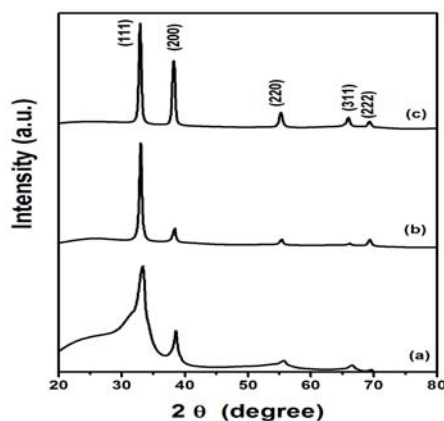


Figure-1. X-ray diffraction pattern for (a) 0.025M (b) 0.05M (c) 0.1M CdO thin films.

It was found to be polycrystalline nature with five peaks at $2\theta = 33.08^\circ, 38.57^\circ, 55.67^\circ, 66.57^\circ$ and 69.58° were identified for the film deposited in 0.025M. The corresponding peaks are good in agreement with JCPDS data (65-2908) which are attributed to (111), (200), (220),

(311) and (222) planes. However, the peak position of the preferential (111) orientation is close to the JCPDS (65-2908) file data for the films grown from 0.025M to 0.1M of precursor solution as in Figure-2.

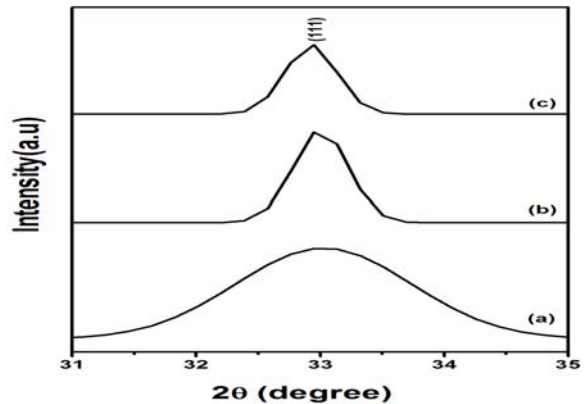


Figure-2. X-ray diffraction pattern close to (111) plane for (a) 0.025M (b) 0.05M (c) 0.1M CdO thin films.

For the films grown from concentrations 0.025 M to 0.1M, the peak position shifted to lower angles indicating increase of 'd' value and hence the bond length. While comparing the shapes of the peak of higher and lower molarity it is found that (111) peak of lower molarity is broad confirms the presence of nanostructures. It is due to the atomic density increase in the planes attributed to higher molarity of the precursor and thickness [18]. The (111) plane of CdO film grew more predominantly than the other plane and its intensity increased with increasing as the molarity of cadmium acetate. While comparing the diffraction pattern of 0.025M to 0.1M of as deposited film, it is concluded that a clear improvement in crystallinity for higher solution concentration. Even though the crystallinity increases with higher solution molarity presence of nano structures is confirmed for the SEM analysis. Thus the structural studies confirmed that the spray technique CdO films on glass substrate can be easily prepared at higher concentration than other conventional solid state reaction method. The crystallite size D of as deposited film is determined by Scherer's Equation (1) [19, 20],

$$D = \frac{0.9 \lambda}{\beta_{hkl} \cos \theta_{hkl}} \quad (1)$$

Where, D is the crystallite size (nm), β_{hkl} is the FWHM of the observed peak (radians), λ is the wavelength of the X-ray diffraction ($=1.54056 \text{ \AA}$) and θ is the Bragg angle of diffraction. The average crystallite size determined was 6-23 nm for 0.025M to 0.1M of CdO films.

This small crystallite size is due to the evaporation of individual fine droplets during the spray



process [21]. It may be attributed to the presence of large number oxygen fault. The dislocation density δ for preferential reflection (111) is determined using the Equation (2) [22],

$$\delta = \frac{1}{D^2} \quad (2)$$

The strain ε is calculated from the Equation (3) [22],

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (3)$$

Texture Coefficient (TC) of CdO thin film is found to be the following Equation (4) [23],

$$Tc_{hkl} = \frac{\frac{I_{hkl}}{I_{0hkl}}}{N^{-1} \sum \frac{I_{hkl}}{I_{0hkl}}} \quad (4)$$

Where I is a measured intensity, I_0 is standard intensity, N is number of diffraction peaks. The number of crystallites n of CdO thin film is determined from the Equation (5),

$$n = \frac{t}{D^3} \quad (5)$$

Where t is the film thickness and D is the crystallite size. Table-1 gives the micro structural parameters of CdO film as deposited from various molarities.

Table-1. Micro structural parameters of CdO thin films at (111) plane.

Sample	Lattice constant (a) (Å)	InterPlanar distance (d) (Å)	Crystallite size (D) (nm)	Dislocation density (δ) (10^{15}) lines/m ²	Strain (ε) (10^{-3}) lines ² m ⁻⁴	Texture coefficient (TC)	No. of crystallites (n) (10^{16} /Unit/area)
0.025M	4.65	2.704	6	28.9	5.6	1.99	162
0.05M	4.695	2.711	19	2.71	1.8	3.25	7
0.10M	4.711	2.718	23	1.87	1.5	2.42	5

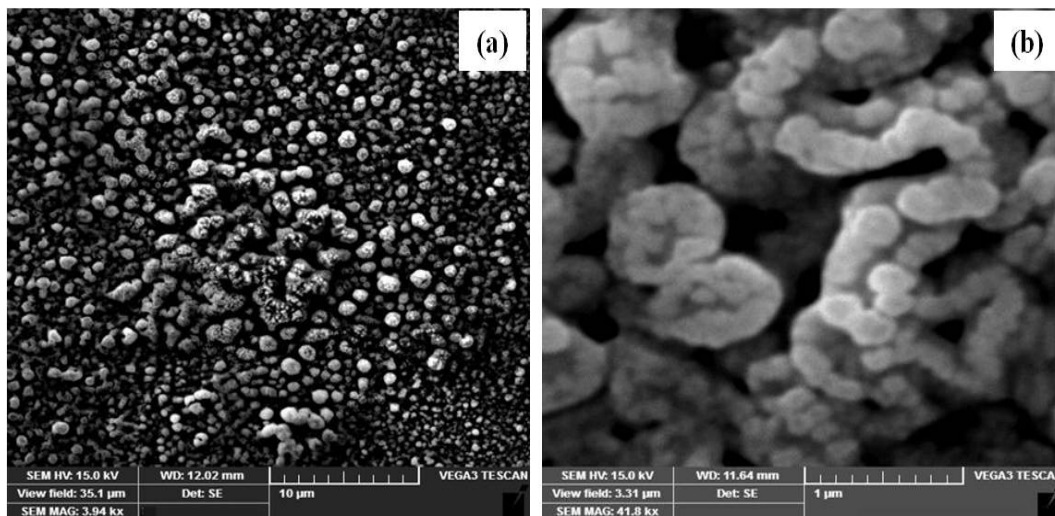


Figure-3. SEM image of CdO thin film prepared at 0.1M for magnifications (a) 10 μ m (b) 1 μ m.

Figures 3a and 3b show that the SE micrograph of CdO thin films prepared at 230 °C in 0.1M with two different magnifications. It shows that the CdO films were smooth and heterogeneous having porosity with some pinholes. XRD analysis confirms the presence of nano structures in the thin film prepared with increasing the

solution concentration. SE micrographs also implies in lower magnification it appears as nanoclusters as in Figure-3a. As the magnification increases the clear structure of the nanocluster is visible shown in Figure-3b. And it is found that nano clusters are interconnected to form a nanorod of CdO.



3.2. Optical studies

The absorption spectra of CdO thin films prepared at 230 °C on glass substrate were recorded as a function of wavelength range 200 nm-1100 nm with glass as reference is shown in Figure-4.

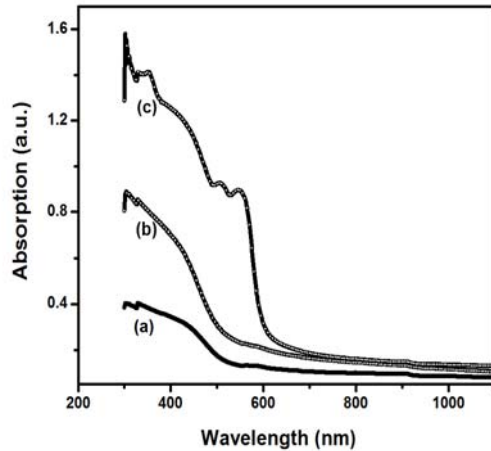


Figure-4. Absorption Vs Wavelength for (a) 0.025M (b) 0.05M (c) 0.1M CdO thin films.

It shows the representatives of optical absorbance which reveals that the absorbance of the film decreases gradually with increase in wavelength. It is clear from the graph that, in the visible region there is no significant change in band edge by increasing the molarity of the solution from 0.025M to 0.1M. This implies that the basic crystal structure is not changed [24]. It also shows that as the solution concentration of the film increases from 0.025M - 0.1M there is a drastic increase in absorbance. The overall increase in absorbance with increase in solution concentration may be associated with the increase in film thickness. This is because in the thicker films more atoms are present in the film so more states will be available for the photons to be absorbed [25].

Sample of CdO thin films of 0.025M, 0.05M and 0.1M showed a peak absorbance in the visible region at 310 nm with maximum value of 0.42, 0.94 and 1.92 respectively. The film deposited with higher concentration of cadmium acetate showed highly increasing of absorption then decreases up to 560 nm and attaining saturation. So, the higher concentration of precursor solution is more preferable in the preparation of CdO films for better quality on glass substrate. The optical absorption values are in line with XRD and SEM results, the nano crystallite sizes could be obtained in the films deposited higher concentration, that produce higher absorption results.

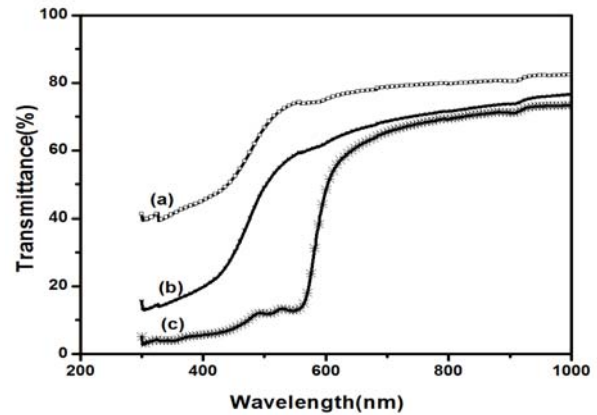


Figure-5. Transmittance Vs Wavelength for (a) 0.025M (b) 0.05M (c) 0.1M CdO thin films.

Figure-5 shows the optical transmittance pattern of the films in the wavelength region range from 200 to 1100 nm. The results indicate the transmission over the whole spectral range investigated, is lowered with increasing solution concentration. This is due to the higher film absorption associated with stress in the film produced by structural defect. It is observed that the increase in transmittance with increase in wavelength is not sharp. Films prepared with concentration of precursor 0.1M, show the transmission exceeding 70% over the spectral range investigated with a well defined absorption edge lying in the UV region.

Transmission spectra reveal that CdO films exhibits transmittance in the range of 80% in visible region of 0.025M of solution concentration. The similar results were also reported for CdO films prepared by thermal evaporation [26], Spray pyrolysis [27], and vacuum evaporation [28]. The absorption coefficient α is calculated using Lambert's law [29] and it is found to be in the order of 10^6 cm^{-1} . The optical direct band gap of the films were calculated by the Equation (6),

$$\alpha = A (h\nu - E_g)^{1/2} \quad (6)$$

Where A is a constant, E_g is Energy band gap, ν is the frequency of the incident light, h is the Plank's constant. The typical plots of $(\alpha h\nu)^2$ versus $h\nu$ for CdO thin films deposited on glass substrate is shown in Figure-6.

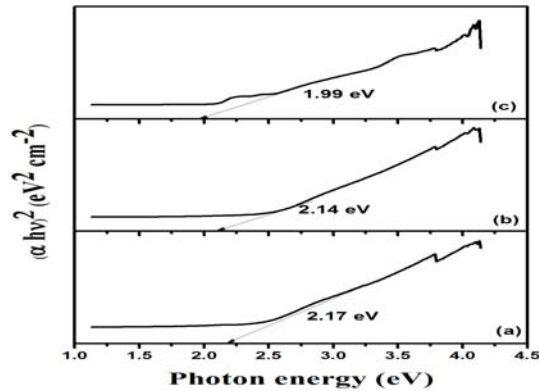


Figure-6. Band gap energy for (a) 0.025M (b) 0.05M (c) 0.1M CdO thin films.

It was observed that increase in concentration of the precursor solution yields slight shrinkage in optical band gap (2.17 eV-1.99 eV). This shrinkage was generally attributed to Moss-Burstein shift [30, 31]. These values are good agreement for previous literature [32].

3.3. Electrical studies

At room temperature, Hall Effect was measured with the magnetic field applied perpendicular to film surface in the Van der Pauw configuration [33]. The film resistivity has been determined by taking the product of resistance and film thickness. The carrier concentration

N_d and the Hall mobility μ were calculated from the electrical resistivity ρ and the Hall coefficient R_H by using the following Equation (7) and Equation (8) [34].

$$N_d = \frac{1}{eR_H} \quad (7)$$

$$\mu = \frac{1}{ne\rho} \quad (8)$$

The changes in electrical parameters as a function of various solution concentration of CdO thin film are presented in Table-2 and Figure-7. It was noted that the molarity of solution concentration increases the resistivity decreases. The minimum resistivity $1.23 \times 10^{-3} \Omega\text{cm}$ obtained from the present work is comparable with the value of $1.5 \times 10^{-3} \Omega\text{cm}$ reported by Reddy *et al.* [35] for reactive evaporation method. The maximum resistivity $16.5 \times 10^{-3} \Omega\text{cm}$ obtained from this work is comparable with the value of $20.1 \times 10^{-3} \Omega\text{cm}$ reported by Zhao *et al.* [36]. Thus higher molarity is taken as the most suited molarity for preparing CdO films using chemical spray pyrolysis technique. On the other hand, carrier concentration of as deposited films also increases with increasing of molarity.

Table-2. Measured electrical parameters for CdO thin films at (111) plane.

Sample	ρ ($\times 10^{-3} \Omega\text{cm}$)	μ (cm^2/Vs)	N_d (10^{19}cm^{-3})
0.025M	16.5	11.7	0.322
0.05M	5.71	13.7	7.96
0.1M	1.23	34.2	14.9

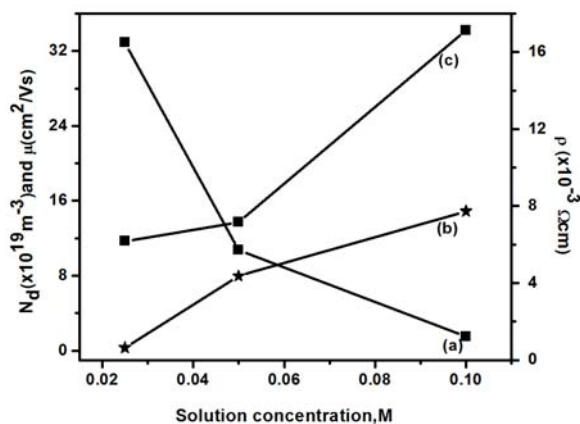


Figure-7. Electrical parameters of CdO thin films (a) Electrical resistivity (ρ) (b) Carrier concentration (N_d) (c) Hall mobility (μ) with different solution concentration.

This result is consistent with the observation from XRD and SEM studies shows that the grain size increases up to 0.1M. Thus as the molarity increases the crystallinity and grain size improve is attributed to reduce the scattering of grain boundary. It is connected with mobility and conductivity to improve the nanocrystalline nature of the as deposited film. At higher molarity, the mobility value has high and it may be due to low grain boundary scattering.

4. CONCLUSIONS

The highly conducting CdO thin films were obtained by using chemical spray pyrolysis method on glass substrates at 230°C . The XRD studies have confirmed that the films are nanocrystalline in nature and CdO crystallites have cubic structure of (111) preferable orientation. The structural parameters like crystallite size, dislocation density, number of crystallites per unit area, texture coefficient and strain were calculated from XRD pattern. The 0.1M of SE micrographs indicated for lower



magnification appears as nanoclusters and higher magnification is found that the nano clusters are interconnected to form a nanorod of CdO. Transmission of CdO thin films is found to be 80% in visible and near infrared region. Energy band gap of thin films is found to be in the range of 2.17–1.99 eV. The carrier concentration of $14.9 \times 10^{19} \text{ cm}^{-3}$ and resistivity $1.23 \times 10^{-3} \Omega\text{cm}$ are obtained for the 0.1M of CdO thin film.

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