



EFFECT OF THE SOLUTION CONCENTRATION ON THE STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF SILAR DEPOSITED CdO THIN FILMS

A.R. Balu ^{a,*}, V.S. Nagarethinam ^a, M. Suganya ^a, N. Arunkumar ^b, G. Selvan ^c

^a Department of Physics, A.V.V.M Sri Pushpam College, Poondi, India

^b Department of Physics, Bharath College of Arts and Science, Thanjavur, India

^c Department of Physics, Thanthai Hans Roever College, Perambalur, India

rajavelubalu@yahoo.com

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ABSTRACT

Cadmium oxide (CdO) thin films were grown on glass substrates by the successive ionic layer adsorption and reaction (SILAR) technique. The effect of solution concentration on the structural, morphological, optical and electrical properties of the as deposited samples was analyzed. The structural studies reveal that the films are polycrystalline with preferred orientation along the (2 0 0) plane. The lattice parameter was found to be equal to 4.690 Å. Grain size increases from 15.96 nm to 21 nm as the solution concentration increases. Optical absorption measurements showed that films coated with 0.05 M showed a maximum transmittance of 84 %. Band gap energy of the coated films decreases with the increase in solution concentration. The sheet resistance increases from $14 \times 10^2 \Omega/\square$ to $17.5 \times 10^2 \Omega/\square$ as the solution concentration increases from 0.05 M to 0.2 M. Films coated with 0.1 M has low temperature coefficient of resistance ($-1.75 \times 10^{-3} / K$).

Keywords: Thin films CdO; Semiconductors; Orientation; Thickness; Resistivity.

I. INTRODUCTION

Transparent conducting oxide (TCO) films have high technological potentials in the field of optoelectronic and other solid state devices. TCOs 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. Cadmium oxide is one of the promising transparent conducting oxides from II to VI group of semiconductors having high absorption and emission capacity of radiation in the energy gap [1]. The CdO compound is

reddish brown in colour and is formed by burning of Cd in air. The oxide is insoluble in water, absorbs CO₂ from air and can be reduced to the conducting oxides which have received very little attention; though it is one of the promising candidates for optoelectronic field [2 - 4]. Cadmium oxide have special features such as high conductivity, high transmission and low band gap made it applicable in photodiodes [5], phototransistors [6], photovoltaic cell [7], transparent electrodes [8], liquid crystal displays, IR detectors and anti reflection coatings [9]. A plethora of deposition techniques viz. dc magnetron sputtering [10, 11],

reactive evaporation [12], sol-gel [13] and spray pyrolysis [14 – 17] have been employed to make thin layers of CdO.

The Successive Ionic Layer Adsorption and Reaction (SILAR) method also known as modified version of chemical bath deposition is a promising technique for the preparation of thin films from aqueous solution because of its simplicity and cost effectiveness. The SILAR technique involves multiple dipping of a substrate in cationic and anionic precursors. In spite of its simplicity, SILAR has a number of advantages: i) it offers extremely easy way to dope film with virtually any element in any proportion by merely adding it in some form of the cationic solution, ii) unlike closed vapour deposition method, SILAR does not require high quality target and/or substrates nor does it require vacuum at any stage, iii) the deposition rate and the thickness of the film can be easily controlled over a wide range by changing the deposition cycles, iv) operating at room temperature can produce films on less robust materials, v) unlike high power methods such as radio frequency magnetron sputtering (RFMS), it does not cause local over heating than can be detrimental for materials to be deposited and vi) there are virtually no restrictions on substrate material, dimensions or its surface profile. Moreover, it is relatively inexpensive, simple and convenient for large area deposition. Stoichiometric deposit is easily obtained. Since the basic building blocks are ions instead of atoms, the preparative parameters are easily controllable and better orientation and improved grain structure can be obtained.

The SILAR method is mainly based on the adsorption and reaction of

the ions from the solution and rinsing between every immersion with deionized water to avoid homogeneous precipitation in the solution. The SILAR is based on sequential reaction at the substrate surface. In general, the SILAR growth cycle contains four different steps: adsorption, rinsing, reaction and rinsing. Rinsing follows each reaction, which enables heterogeneous reaction between the solid phase and the solvated ions in the solution.

The present study deals with the preparation of CdO thin films onto glass substrates by SILAR method. The coated films have been characterized by different techniques such as X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), optical absorption and electrical resistivity for further investigation, which is essential to make full use of their active properties.

II. EXPERIMENTAL

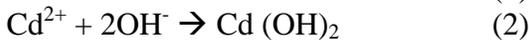
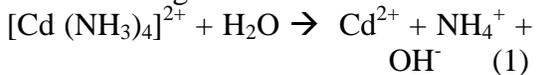
Cadmium Oxide thin films was prepared by successive immersion of ultrasonically cleaned glass substrates in an aqueous solution of cadmium acetate [$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ 99.99%] (cation) with different molarities (0.05, 0.1 and 0.2 M) and 6ml/100ml 13M aqueous ammonia solution. The complexing agent ammonium hydroxide was used to stabilize the crystallite size. The pH of the prepared solution was maintained as 7 throughout the deposition process. The thickness of the coated films was measured using the surfstest SJ – 301 stylus type surface roughness and thickness measuring instrument. X-ray diffraction analyses were obtained using the model X'pert PRO (Analytical) X-ray powder diffractometer with Ni filtered CuK_α (1.54056 Å) radiation. The

surface morphology and homogeneity of the deposited films were studied by SEM model JSM 35 CF JEOL. Optical absorption measurement in the range 350 – 1100 nm was carried out by using a Hitachi – 3400 UV-Vis-NIR Spectrophotometer. The electrical resistivity (ρ) of the films was measured by the Vander Pauw four point probe method.

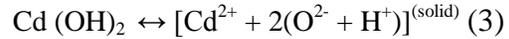
III. RESULTS AND DISCUSSION

III.1 Film formation

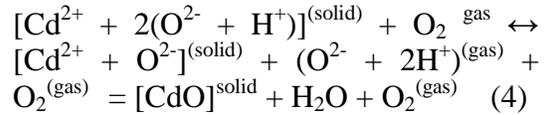
The deposition of CdO thin films takes place by introducing the glass substrates in a beaker containing cadmium acetate and liquid ammonia for 30s, where Cd^{2+} with ammonia formed cadmium ammonia complex $[\text{Cd}(\text{NH}_3)_4]^{2+}$. The cadmium ammonia adsorbed substrate was then immersed into a beaker containing distilled water for 30s, where the adsorbed cadmium ammonia complex was converted into cadmium hydroxide ($\text{Cd}(\text{OH})_2$). The immersion of glass substrates in cadmium acetate and liquid ammonia solution followed by an immersion in distilled water corresponds to one complete dipping. In this work 40 dipping were adopted to get uniformly coated CdO films. After 40 dipping, the substrates were annealed at 350°C for 1 hr to get dark yellow colored CdO thin films. The detailed chemical reactions involved are given as follows:



In order to consider the transformation of the hydroxide phase during the heat treatment, $\text{Cd}(\text{OH})_2$ could be written in an equivalent form, in the Kofstadt notation [18, 19]



At higher temperature in air atmosphere, the hydroxide phase (Eq. 3) is transformed into oxide phase,



After deposition, the peel-off test was conducted to confirm the adhesivity of the coated films on glass substrates which showed that well adherent CdO films were formed. The thickness of the films measured by the weight difference-density consideration method was found to be equal to $0.76 \mu\text{m}$, $1.25 \mu\text{m}$ and $1.98 \mu\text{m}$ for the films coated with 0.05 M, 0.1 M and 0.2 M respectively. A check of these thicknesses were made by measuring the thicknesses using the surfstest SJ-301 stylus type surface roughness and thickness measuring instrument. The results showed that the thicknesses are on the average comparable for the two measurement methods at a factor of 10%. It is observed that film thickness increases with increase in molarity of the solution. The variation of film resistivity with solution concentration is shown in Fig. 1.

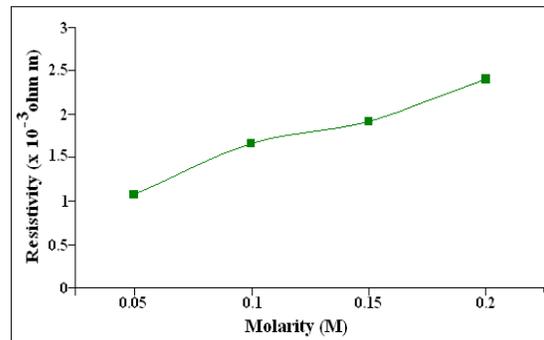


Fig. 1

Figure 1: Variation of film resistivity with solution concentration.

It is observed that films became more resistive at higher solution concentration, which may be due to large terminal thickness. Increase in solution concentration results into increment in the amount of mass being deposited on the substrates with lower layers of CdO and upper layers with precursor salt deposited without complete thermal decomposition.

III.2 X-ray diffraction

Figure 2(a-c) shows the X-ray diffraction patterns of the CdO films deposited with different solution concentrations.

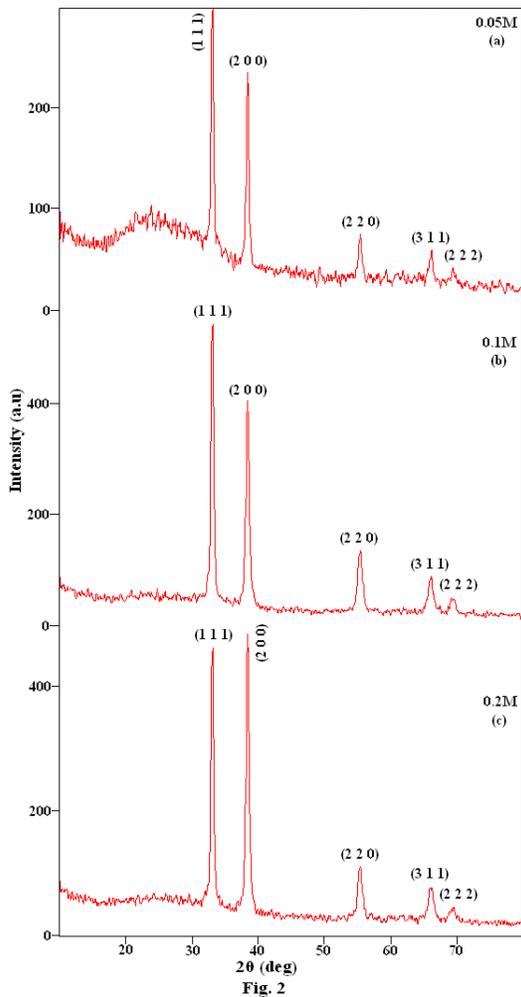


Figure 2[a-c]: XRD patterns of CdO thin films deposited with different solution concentrations.

The presence of many peaks indicates the polycrystalline structure of the films. Three prominent diffraction peaks observed in the patterns can be indexed to (1 1 1), (2 0 0) and (2 2 0) planes by using the ASTM standards [20]. Also peaks corresponding to (3 1 1) and (2 2 2) planes were also observed. The crystallites in a polycrystalline material normally have a crystallographic orientation different from that of its neighbours. This orientation of the crystallites, called the preferential orientation, may be randomly distributed with respect to some selected frame of reference. In the present investigation, the films exhibit a preferential orientation along the (1 1 1) diffraction plane. To describe this orientation, the texture coefficient TC (hkl) for all the planes was calculated using the expression [21]:

$$TC(hkl) = \frac{I(hkl) / I_s(hkl)}{N_r^{-1} \sum_r I(hkl) / I_s(hkl)} \quad (1)$$

where I is the measured intensity, I_o is the standard intensity of the corresponding powder data and N_r is the reflection number.

From the definition, it is clear that the deviation of the texture coefficient from unity implies the preferred orientation of the growth. The preferred orientation of a film will be (hkl) plane for the higher value of TC.

Figure (3) shows the variation of TC(hkl) with solution concentration for the diffraction planes (1 1 1), (2 0 0) and (3 1 1).

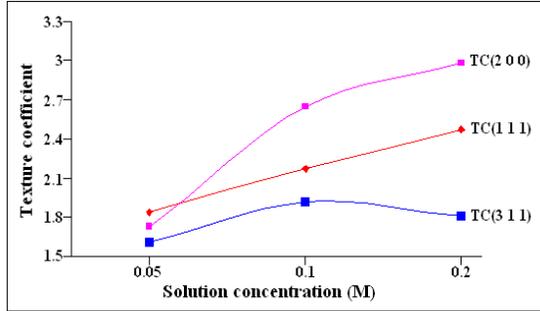


Fig. 3

Figure 3: Variation of TC(h k l) with solution concentration for the diffraction planes (1 1 1), (2 0 0), (3 1 1) and (2 2 2) of the as-deposited CdO thin films .

TC(1 1 1) gradually increases with molarity whereas TC(2 0 0) varies linearly. The TC(3 1 1) increases upto 0.1 M and then decreases for higher molar concentration. The value of TC(2 0 0) indicates the maximum preferred orientation of the coated films along the (2 0 0) diffraction plane meaning that the increase in preferred orientation is associated with the increased number of grains along that plane.

The preferential orientation

Standard 'd' values (Å)	Observed 'd' values (Å)			(hkl) planes
	0.05 M	0.1 M	0.2 M	
2.71	2.708	2.708	2.709	(1 1 1)
2.34	2.345	2.344	2.344	(2 0 0)
1.65	1.658	1.659	1.659	(2 2 0)
1.41	1.413	1.415	1.414	(3 1 1)
1.35	1.355	1.355	1.356	(2 2 2)

Table 1: Comparison of d values (Å) and hkl planes for the CdO films.

factor for the (1 1 1) and (2 0 0) planes relative to the other observed peaks are calculated by evaluating the fraction of the intensity of that particular plane over the sum of the intensities of all the peaks within the 2θ range 10 - 80°. The variation in preferential orientation

factor f(hkl) for (1 1 1) and (2 0 0) planes as a function of precursor solution concentration is shown in Fig. 4, which shows that f(2 0 0) increases as the solution concentration increases with solution concentration.

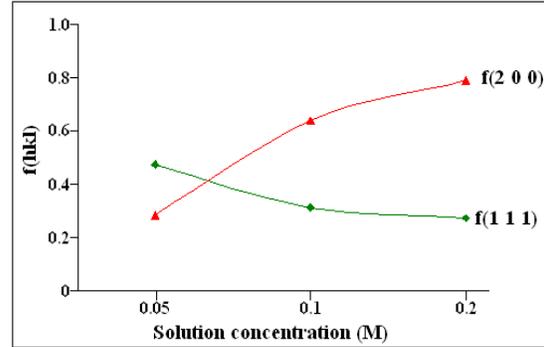


Fig. 4

Figure 4: Variation in preferential orientation factor of (1 1 1) and (2 0 0) planes as a function of solution concentration.

The above discussed structural details clearly reveal that the films have preferred orientation along the (2 0 0) plane.

The comparison of observed and standard 'd' values for the CdO films prepared with different molarities is given in Table. 1.

The lattice parameter 'a' for cubic structure for each diffraction plane has been found from the well known Bragg formula and it is found to be equal to 4.690 Å with ± 0.002 Å. The lattice parameters evaluated from various crystallographic planes have the following systematic observations:

$(a_{111})_{0.05\text{ M}} = (a_{111})_{0.1\text{ M}} < (a_{111})_{0.2\text{ M}}$,
 $(a_{200})_{0.05\text{ M}} = (a_{200})_{0.1\text{ M}} = (a_{200})_{0.2\text{ M}}$,
 $(a_{220})_{0.05\text{ M}} < (a_{220})_{0.1\text{ M}} = (a_{220})_{0.2\text{ M}}$
 The lattice parameter for the (2 0 0) plane remains the same for all the films. The lattice parameter obtained in the present investigation is smaller when compared to the corresponding bulk material which may be attributed to lattice contraction.

The crystallite size D has been calculated from the Scherer formula [22]:

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (2)$$

where β is the full-width at half-maximum (FWHM) and θ is the corresponding Bragg's angle.

The crystallite size was found to be in the nano range (15.6 - 21 nm) as the solution concentration increases from 0.05 M to 0.2 M. With the increase in solution concentration, the diffraction lines become more and more sharp, thus apparently showing an increase in the size of the crystallites. These results are confirmed by SEM images (Fig. 5).

The dislocation density (δ), defined as the length of dislocation lines per unit volume, has been estimated using the equation [23]:

$$\delta = \frac{1}{D^2} \quad (3)$$

δ is the measure of the amount of defects in a crystal. The lesser values of δ obtained (1.095×10^{15} and 0.5586×10^{15} lines/m²) for the films coated with 0.1 M and 0.2 M indicate that the degree of crystallization is higher for the films with higher molarity. Also using crystallite size ' D ' and film thickness ' t ', number of crystallites per unit area (N) of the films is estimated using the relation:

$$N = \frac{t}{D^3} / \text{unit area} \quad (4)$$

The calculated structural parameters are presented in Table. 2.

Table 2: Micro structural parameters of the CdO films calculated for the (2 0 0) plane.

Micro-structural parameters	Solution concentration		
	0.05 M	0.1 M	0.2 M
Lattice parameter 'a' (Å)	4.179	4.180	4.181
Crystallite size, D (nm)	14.23	30.22	42.31
Dislocation density, δ ($\times 10^{15}$ lines/m ²)	1.938	1.095	0.5586
Number of crystallites, N ($\times 10^{17}$ /unit area)	0.0692	0.2004	0.1087

III.3 Surface morphological studies

Figure (5) shows the SEM micrographs of the surface of CdO films prepared with different molarities of cadmium acetate.

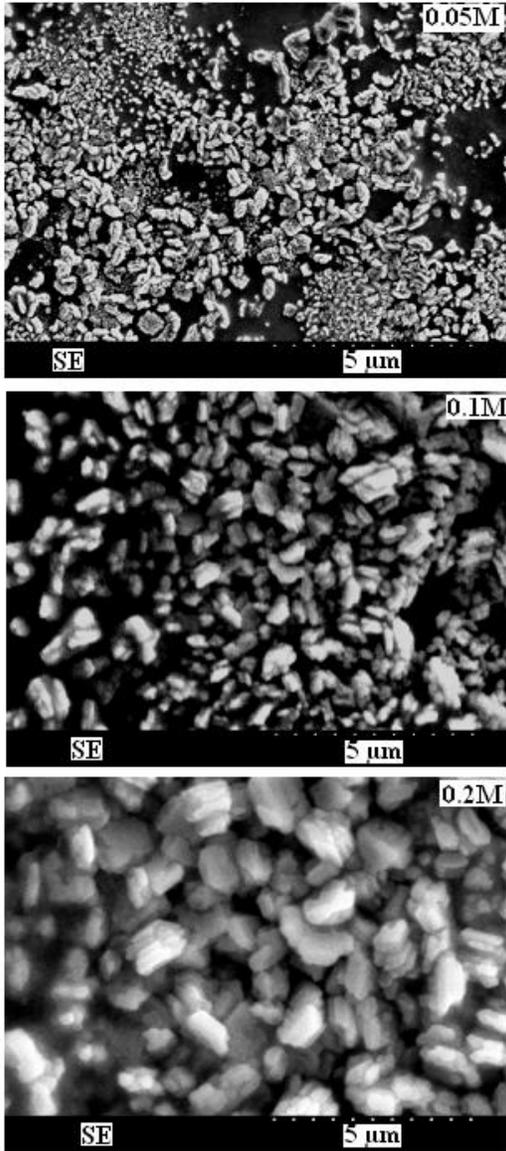


Fig. 5

Figure 5: SEM Images of CdO films prepared with different molarities of precursors.

The film prepared with 0.05 M of solution concentration has small grains of size equal to 13.6 nm distributed throughout the surface with some uncoated areas near the edges of the substrate. However films coated with 0.1 M shows uniform distribution of grains with size larger than the size coated with 0.05 M. The grain size was found to be equal to 22.73 nm. The films coated with 0.2 M shows large sized

grains clustered together throughout the surface. The grain size was found to be equal to 36.4 nm. It is observed that the grain size increases with molarity which is evident from the XRD results.

III.4 Optical absorption studies

Figure (6) shows the optical transmission spectra of the CdO thin films coated with 0.05 M, 0.1 M and 0.2 M aqueous solution of cadmium acetate.

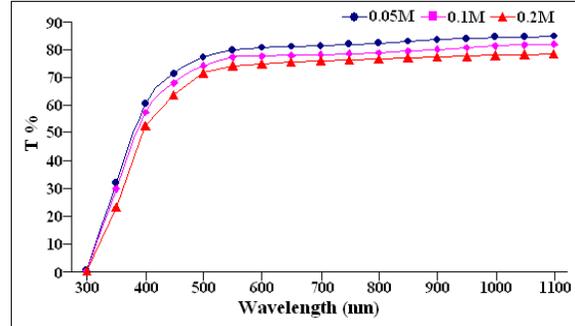


Fig. 6

Figure 6: Transmission spectra of the CdO thin films.

The maximum transmittance values obtained in the wavelength range 350 nm to 1100 nm was found to be equal to 84 %, 81 % and 79 % for the films coated with 0.05 M, 0.1 M and 0.2 M respectively. The spectra of all the films show a sharp fall in transmission near the fundamental absorption, which is an identification of the good crystallinity of these films. Also a shift of the absorption tail towards long wavelengths is observed. The transmittance decreases with increase in the solution concentration which might be due to the increased thickness of the films coated with higher molarity as evident from the XRD and SEM analyses. From the absorbance data, the absorption coefficient (α) was calculated using Lambert law [24]:

$$\ln(I_0/I) = 2.303A = \alpha t \quad (5)$$

where I_0 and I are the intensities of the

incident and transmitted light respectively,

A is the optical absorbance and t is the film thickness.

The absorption coefficient (α) values calculated from the transmittance data are about 10^6 cm^{-1} . The variation of the absorption coefficient (α) with wavelength for the coated films is shown in Fig. 7.

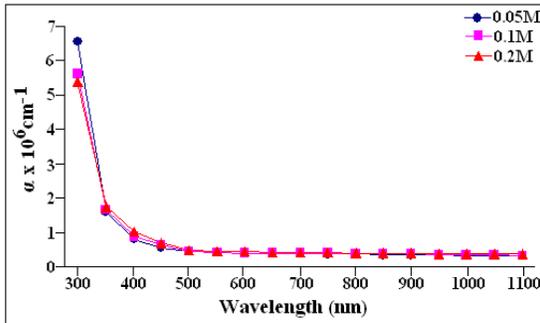


Fig. 7

Figure 7: Variation of the absorption coefficient (α) of the CdO thin films with wavelength.

It is seen that at short wavelengths, a steep decrease occurs in the absorption coefficient around the absorption edge (at E_g). The value of α decrease as the solution concentration increases. This decrease in α might be due to the increase in surface smoothness which might be due to the improved crystallinity of the film coated with higher solution concentration. The absorption coefficient was found to follow the relation [24, 25]:

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

where A is a constant which is related to the effective masses associated with the bands and E_g is the band gap energy.

Plots of $(\alpha h\nu)^2$ vs the photon energy ($h\nu$) for the as-deposited samples is shown in Fig. 8.

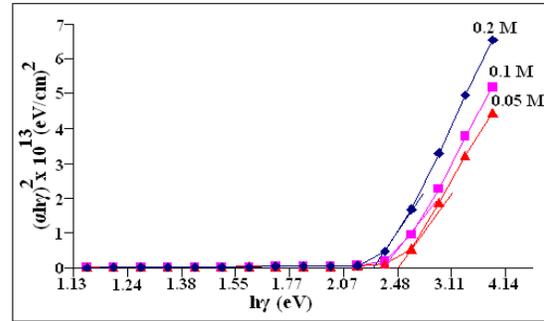


Fig. 8

Figure 8: Plots of $(\alpha h\nu)^2$ vs $h\nu$ for the CdO thin films.

Linearity of the plots indicates that the material is of direct band gap nature. Extrapolation of linear portion of the graph to the energy axis at $\alpha = 0$ gives the band gap energy E_g values, which are found to be equal 2.48 eV, 2.36 eV and 2.27 eV for the films coated with 0.05 M, 0.1 M and 0.2 M respectively. These values are in good agreement with the values reported by others [16, 3]. This decrease in E_g is attributed to the incorporation of some impurity energy levels in the forbidden energy gap of the CdO caused by the incomplete thermal decomposition of $\text{Cd}(\text{OH})_2$ precipitates collected on the surface of the substrate for the films coated with higher solution concentration.

The variation of extinction coefficient as a function of photon energy is shown in Fig. 9.

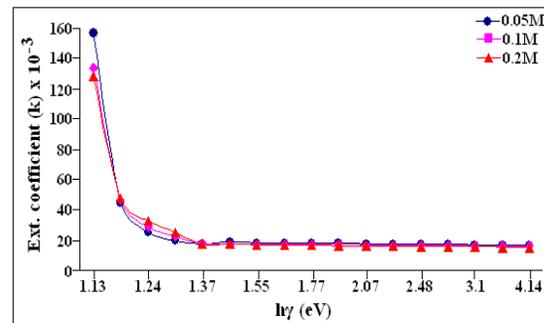


Fig. 9

Figure 9: Variation of extinction coefficient of the CdO films as a function of photon energy.

The variation of the extinction coefficient is directly related to the absorption of light. In the case of polycrystalline films, extra absorption of light occurs at the grain boundaries. This leads to non-zero value of k for photon energies smaller than the fundamental absorption edge.

III.5 Electrical resistivity

The electrical resistivity of the coated CdO films were measured in the temperature range of 303 K to 503 K by the Vander Pauw four point probe method [26] with the appropriate correction factor. Fig. 10 shows the variation of sheet resistance with temperature for the as deposited samples.

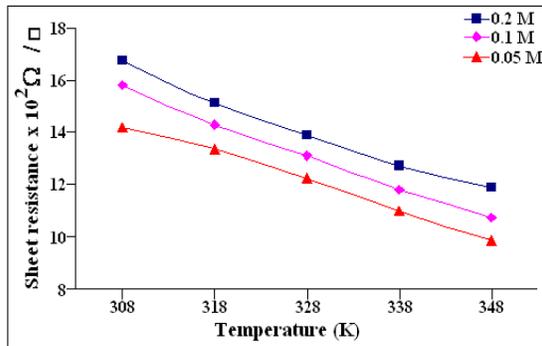


Figure 10: Variation in sheet resistance of the CdO films.

It is observed that as the temperature increases the resistivity decreases, indicating the semi conducting behavior of the material. The film coated with 0.2 M of solution concentration has the high resistivity compared to the film coated with 0.05 M. This increase in resistivity may be due to increased grain size for the film with higher solution concentration, as evident from the XRD and SEM analyses. All the films have resistivity values in the range of $0.668 - 1.98 \times 10^{-3}$ ohm-m. The low resistivity

value obtained makes the films coated with this technique applicable for solar cell applications. From the resistance values recorded at different temperatures, the temperature coefficient of resistance (TCR) of the films is evaluated. The variation of TCR as a function of solution concentration is given in Fig. 11.

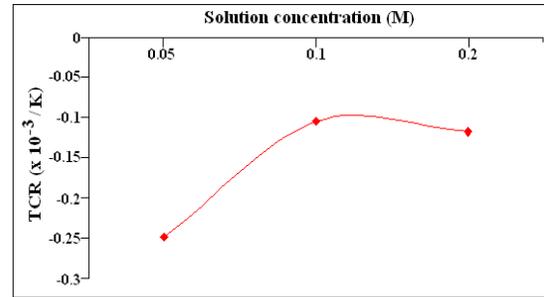


Figure 11: Variation in temperature coefficient of resistance CdO films with different solution concentrations.

The figure reveals that the magnitude of TCR decreases with solution concentration up to 0.1 M and then it starts slightly increasing for the films with higher molarity, indicating that films coated up to 0.1 M of solution concentration have heat resistant property which is one of the desirable qualities for solar cell TCO layers. The magnitude of the TCR for the films coated with 0.1 M are remarkably lesser than that of the films coated with 0.05 M and 0.2 M respectively. Therefore it can be concluded that films coated with 0.1 M have higher thermal stability.

IV. CONCLUSION

Transparent conducting CdO thin films with good thermal stability were fabricated by cost effective SILAR method. XRD studies show that all the films are polycrystalline in nature with cubic structure having preferential

orientation along (2 0 0) plane. Micro structural parameters have been calculated for all the samples. The lattice parameter 'a' is found to be equal to 4.690 Å with ± 0.002 Å. Grain size increases from 15.9 nm to 21 nm as the solution concentration increases. The optical transmittance in the visible range is greater than 83%. The optical band gap of the coated CdO films decreases with the increase in solution concentration. Extinction coefficient has been evaluated using reflectance and absorbance data. Electrical resistivity measurements showed that all the films have resistivity values in the range of $0.668 - 1.98 \times 10^{-3}$ ohm-m. The TCR is very small of the order of -1.75×10^{-3} K. The films were found to have good physical properties desirable for solar cell and other opto-electronic applications.

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