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Synthesis of Low Resistive Transparent Nano-crystalline Cadmium Oxide Thin Films by Chemical Route

V.P. Deshpande[1], S. D. Sartale[2], A.U. Ubale[1*]

[1]Thin Film Physics Laboratory, Department of Physics, Govt. Vidarbha Institute of Science and Humanities, India
[2]Thin Film and Nanomaterial Laboratory, Department of Physics, University of Pune, India

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ABSTRACT

In the present investigation, low resistive transparent Nano-crystalline cadmium oxide chemical spray pyrolysis technique deposited thin films. The effect of deposition temperature on structural, electrical, and optical properties is studied. The X-ray diffraction patterns revealed that, the CdO films are Nano-crystalline in nature having cubic structure and highly oriented along (111) plane. Scanning electron micrograph images of films showed smooth and dense spherical grains of CdO deposited onto entire glass substrate. The XRD and SEM results showed that the film grown on 3500C exhibits better crystallinity with well-defined grains. The optical band gap energy of CdO varied between 2.46 to 2.71 eV depending on deposition temperature. The resistivity measurement showed that films are semiconducting in nature with very low resistivity of the order of 10-4 to 10-5 ohm-cm. The estimated activation energy was in the range of 0.07 to 0.03 eV.

Keywords: Cadmium Oxide, Thin films, Chemical spray pyrolysis technique.

INTRODUCTION

Amongst transparent conducting oxides CdO is one of the outstanding material. However, the concentrated research on CdO started progressively about 1907 with the investigation of testing its ability as TCO by Badekar [1]. It is now well convinced that the CdO displays excellent properties, which makes it suitable as TCO. CdO not only possess high electrical conductivity [2] but also exhibits high optical transparency in the visible region of the spectrum [3]. CdO is known to be an n-type semiconductor with nonstoichiometric composition due to the presence of either interstitial cadmium or oxygen vacancies, which act as doubly charged donors [4]. Consequently, thin films of CdO have been used in wide variety of applications such as photo detectors, solar cells, gas sensors, antireflection coatings, etc.[5-8]. In the last decade, various techniques such as thermal evaporation [9], sputtering [10], solution growth [11], pulsed laser sputtering [12], activated reactive evaporation [13] and spray pyrolysis deposition (SPD) [14] were employed to prepare thin films of CdO. Spray pyrolysis has been evolved as one of the potential technique to deposit CdO thin films. It is well known that the preparation conditions, the nature of the precursor and solvents influence film properties profoundly. Ma and Bube [15] have studied the effect of these preparative parameters on the properties of CdS films. Uplane et al. [14] studied CdO thin films by spray pyrolysis technique. They reported the electrical resistivity of the order of 10-2 ohm-cm. Flores-Mendoza et al. [16] reported that the electrical conductivity and optical transparency of CdO thin films depend on the nature, number, atomic arrangements of metal cations, morphology and on the presence of intrinsic or intentionally produced defects. Lamb et al. [17]

reported a temperature dependent crystal orientation transition of cadmium oxide films deposited by metal organic chemical vapor deposition. They found that films were highly conducting with resistivity of 10 -4 ohm-cm. The concentration of oxygen vacancies plays a vital role as far as the resistivity of undopped CdO film is concerned, which is usually difficult to control and too much oxygen vacancies can also deteriorate the quality of the film.

Specifically, this chapter looks at a temperature dependent structural, optical, and electrical properties of CdO thin films. In present investigation, we have focused on achieving a low resistivity and wide band gap of CdO, by varying the deposition temperature.

EXPERIMENTAL DETAILS

Cadmium oxide thin films were deposited by means of chemical spray pyrolysis technique at different substrate temperature that varies from 1500C to 4000C in the step of 500C. (Here after, the samples deposited at 150, 200, 250, 300, 350 and 4000C are referred as A1, A2, A3, A4, A5 and A6 respectively). Prior to the deposition, the glass substrates were initially boiled in chromic acid for 15 min, washed with double distilled water and dipped in detergent and again washed with double distilled water, followed by ultrasonic cleaning for 10 min. For deposition of CdO films, 0.1M cadmium acetate ((CH3COO)2 Cd. 2H2O) (AR grade) was used. The pH of the solution was increased to 10 by adding ammonia drop by drop with constant stirring. In the beginning ammonia, white precipitate was formed, however with further addition of ammonia, it was completely redissolved in the solution at pH 10. After adding access ammonia, solution became completely colorless and transparent. The resulting solution was sprayed on to preheated substrate. The atomization of the solution into a spray of fine droplets was carried out by spray nozzle, with the help of compressed air as carrier gas. During spray, the substrate temperature was monitored using a chromel alumel thermocouple. After doing several trials preparative parameters were optimized (table 1).

Table1: Preparative parameters

Spray parameter	Optimum value
Concentration of Cadmium Acetate	0.1M
Solvent	Double distilled water
Carrier gas	Compressed air
Solution flow rate	7.5 ml/min
Nozzle substrate distance	30 cm

RESULTS AND DISCUSSION

XRD analysis

XRD is a very convenient and non-destructive analytical technique which gives information about the crystallographic structure of a material. Figure (1) shows the XRD patterns of CdO thin films deposited at different temperatures. It reveals that CdO thin films are nanocrystalline in nature with cubic structure, which is confirmed from JCPDS Card No.005-0640 data [18]. Comparison of standard JCPDS data and observed data is presented in table 4.2. The spray deposited CdO films shows preferred orientation along (111). The existence of the characteristic diffraction lines corresponding to the (111), (200), (220) and (311) planes for CdO thin films are clearly observed in the pattern. The increment in the peak intensities indicates the improvement in crystallinity. Moreover, the intensity of all the peaks increases with deposition temperature upto 3500C. The decrease in the intensity for sample A6 (deposited at 4000C) might be due to relatively lower thickness of the film caused by evaporation of primary ingredients before reaching the surface of the substrate.

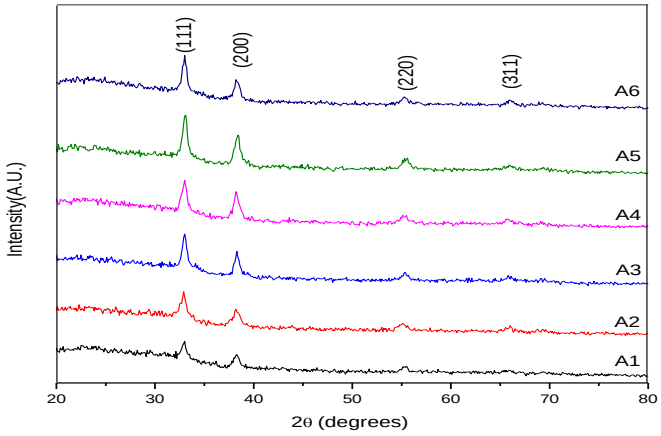


Figure 1: XRD patterns of CdO thin films deposited at A1) 150, A2) 200, A3) 250, A4) 300, A5) 350 and A6)4000C.

This similar trend of decrease in intensity at higher deposition temperature is also reported for CdO: Ga thin films [19]. The average crystallite size was calculated by using Debye Scherrer's formula [20]. It is found of the order of 50-68 nm. The grain size of CdO decreases with substrate temperature upto 3500C and then again increases. The variation of grain size of CdO films with deposition temperature is shown in figure (2).

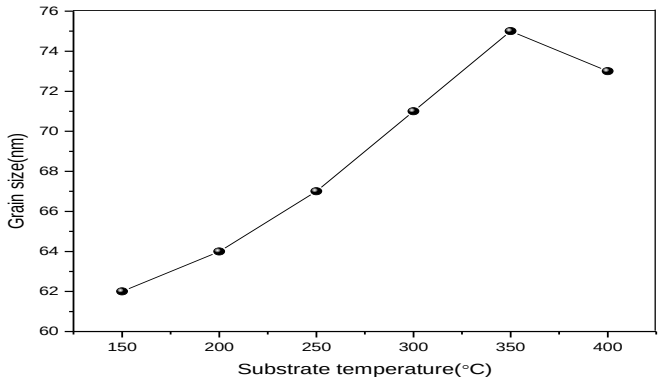


Figure 2: Variation of grain size of CdO thin film with substrate temperatures.

The dislocation density 'δ 'is calculated by using relation,

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

Where D is the grain size. The relation can calculate this lattice strain,

$$\varepsilon = \frac{\beta Cos\theta}{4} \quad (2)$$

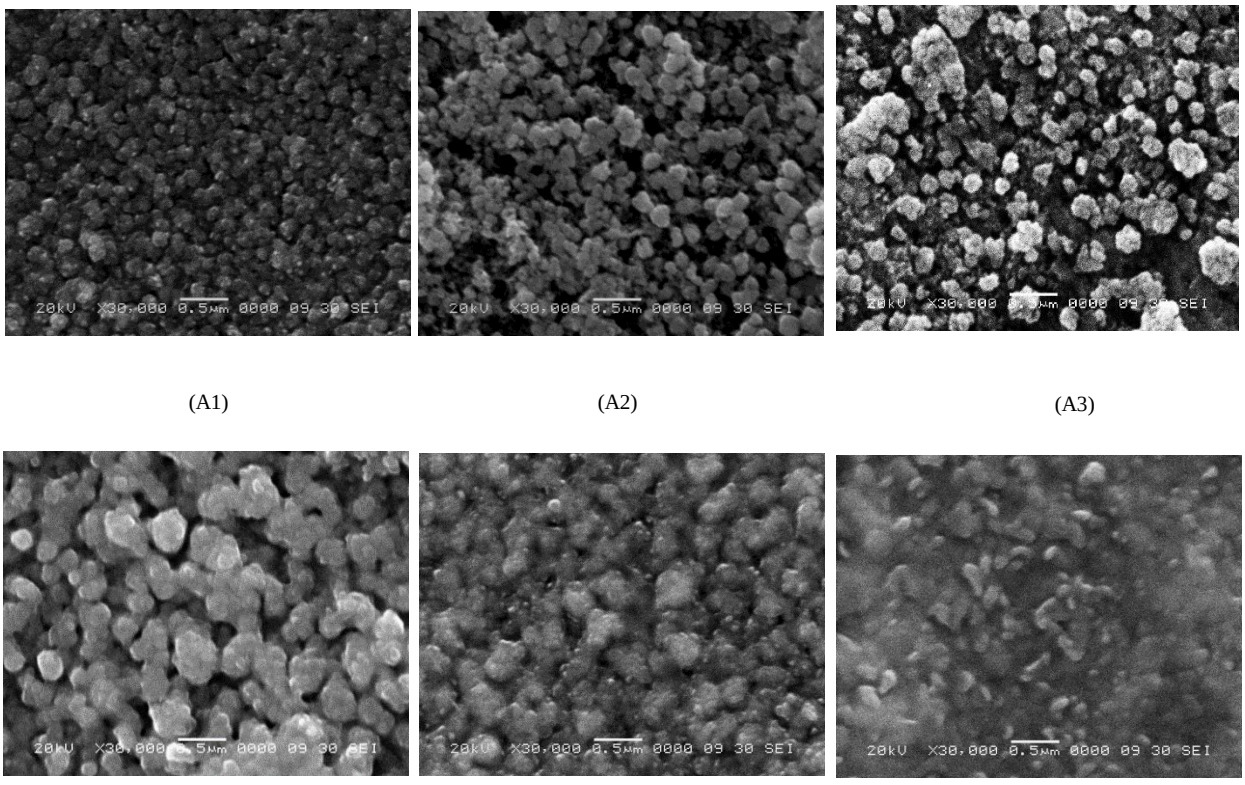
The estimated values of dislocation density and micro strain values are listed in table 3. Both these values decrease with increase in substrate temperature. Basically, the properties of nanostructured thin films differ from the properties of the bulk phase of a material mainly due to the difference in their environment at interfaces. For the film having lower grain sizes (Sample A1) the number of inter-grain boundaries i.e. interfaces can contain different types of defects as single vacancies, vacancy agglomeration or pores formed at triple junctions of crystallites or in the place of a missing crystallite which naturally increases the dislocation density.

Table 2: Comparison of observed crystallographic data of CdO thin films with standard JCPDS (005-0640) card.

Sample	hkl	Standard 2θ (degrees)	d- values standard (A^0)	Observed 2θ (degrees)	d- values observed (A^0)
A1	(111)	33.0	32.90	2.71	2.67
	(200)	38.28	38.20	2.34	2.30
	(220)	55.25	55.15	1.66	1.60
A2	(111)	33.0	32.90	2.71	2.67
	(200)	38.28	38.20	2.34	2.30
	(220)	55.25	55.15	1.66	1.60
	(311)	65.90	65.87	1.41	1.33
A3	(111)	33.0	32.89	2.71	2.68
	(200)	38.28	38.23	2.34	2.29
	(220)	55.25	55.12	1.66	1.59
	(311)	65.90	65.86	1.41	1.31
A4	(111)	33.0	32.91	2.71	2.67
	(200)	38.28	38.25	2.34	2.31
	(220)	55.25	55.17	1.66	1.61
	(311)	65.90	65.87	1.41	1.33
A5	(111)	33.0	32.91	2.71	2.67
	(200)	38.28	38.25	2.34	2.31
	(220)	55.25	55.17	1.66	1.61
	(311)	65.90	65.87	1.41	1.33
A6	(111)	33.0	32.91	2.71	2.67
	(200)	38.28	38.24	2.34	2.30
	(220)	55.25	55.18	1.66	1.60
	(311)	65.90	65.87	1.41	1.33

SEM studies

The scanning electron microscopy (SEM) provides morphological information about the surface of the solid that is necessary in understanding the behaviour of surface and various other physical properties. Figure (3) shows the scanning electron micrograph of CdO thin films prepared at various temperatures.



(A1) (A2) (A3)

(A4) (A5) (A6)

Figure 3: SEM of CdO thin films deposited at A1) 150, A2) 200, A3) 250, A4) 300, A5) 350 and A6)4000C

As evident from the spectra, film prepared at low temperature showed agglomeration of particles. However, as the temperature increases the particles form smooth and uniform surface. Film prepared at 3500C shows more dense structure and optimum growth of particles. Above 3500C particles does not remain spherical in shape this may be due to melting at higher temperature. Energy dispersive analysis showed the chemical composition of CdO thin films.

EDAX spectra of CdO films deposited at deposited at 200 and 3500C is shown in figure 4(a) and 4(b) respectively. The ratio of Cd: O for film deposited at 200 and 3500C is 54.80: 45.20 and 64.82: 35.18 respectively. Film deposited at higher temperature has more oxygen vacancies / Cd interstitials, which is responsible for decrease in resistivity of film.

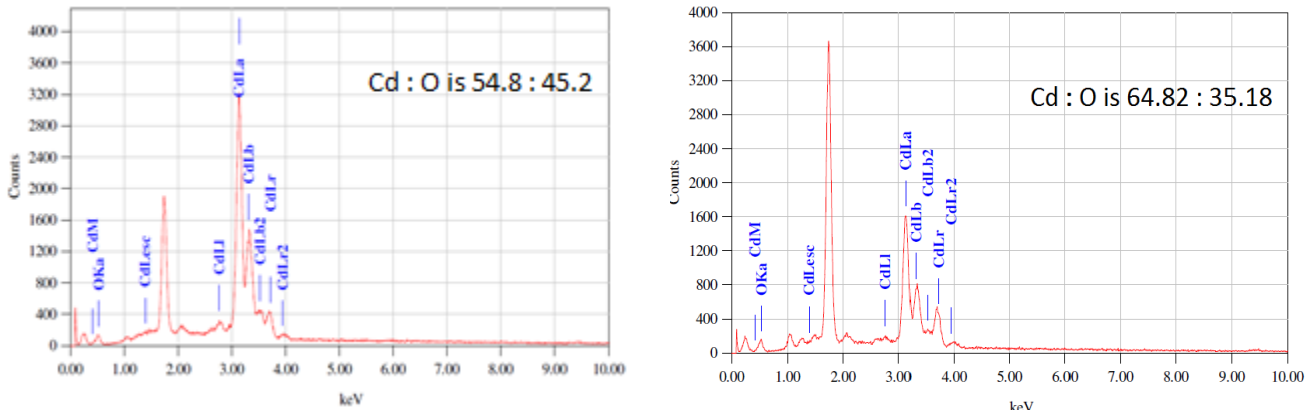


Figure 4: EDAX of CdO thin film deposited at 3500C

Optical studies

The optical absorption of CdO thin films was studied in the wavelength range 330–850 nm shown in figure (5). All films show higher absorbance on shorter wavelength side with presence of absorption edge. The nature of the transition (direct or indirect) was determined by using the relation

$$\alpha = \frac{A(h\nu - Eg)^n}{h\nu} \qquad (3)$$

where hν is the photon energy, Eg is the band gap energy, A and n are constants. For allowed direct transitions n = 1/2 and for allowed indirect transitions n = 2. The plots of (αhν)2 versus hν are shown in figure (6). The variation of (αhν)2 with hν is a straight line, indicating that the involved transition is direct one. Band gap energy, Eg was determined by extrapolating the straight-line portion to the energy axis for zero adsorption coefficient (α). It is found that the band gap value ranged between 2.46 eV to 2.71 eV as deposition temperature varied from150 to 4000C which are in good agreement with the values obtained for bulk CdO crystal [21,22]. Figure (7) shows variation of band gap CdO films with substrate temperatures.

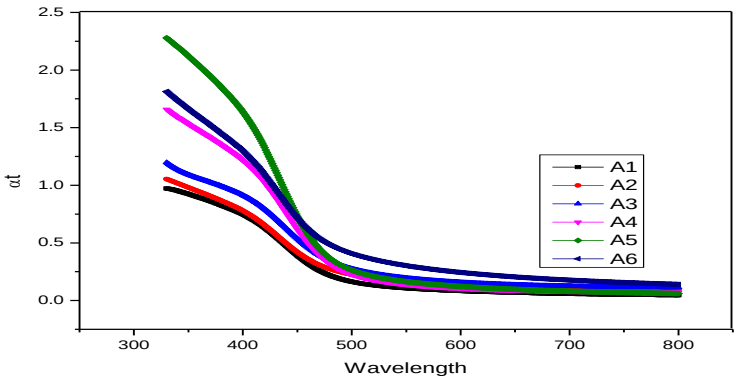


Figure 5: Plot of optical absorption (□t) with wavelength for CdO thin films deposited at

A1)150, A2) 200, A3) 250, A4) 300, A5) 350 and A6) 4000C temperature.

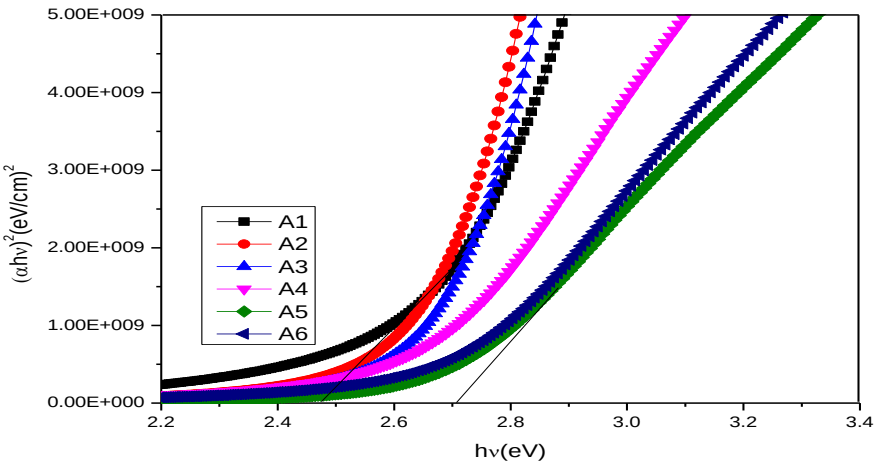


Figure 6: Variation of (□h□)2 with h□ for CdO thin films deposited at A1) 150, A2) 200, A3) 250, A4) 300, A5) 350 and A6)4000C

The value of band gap increases as the substrate temperature increases. This blue shift in band gap of CdO films can be attributed to the increase in carrier concentration. With increase in carrier concentration, blocking of the lowest states in the conduction band takes place, a phenomenon known as the Burstein–Moss effect [23]. According to this theory the lifting of the fermi level up to the conduction band of the degenerate semiconductor leads to the energy band broadening effect. The following equation can express this shift:

$$E_g = E_o + \Delta E_{BM} \qquad (4)$$

So, the measured optical gap Eg is the sum of the optical gap of the lightly doped material E0, and that due to filling of the conduction band because of donors ΔE_BM.

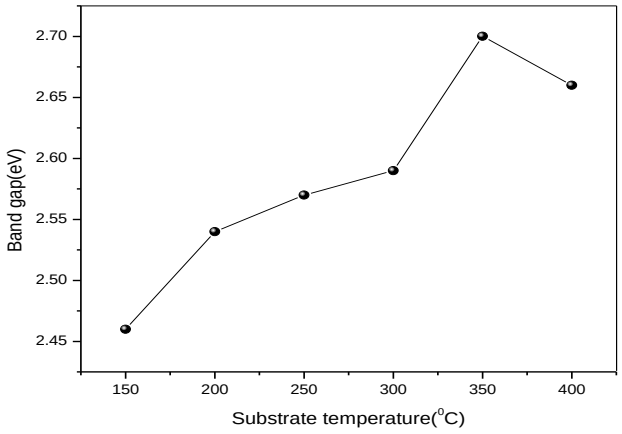


Figure 7: Variation of band gap of CdO thin film with substrate temperature

Photoluminescence studies

Figure (8) shows the deconvolution of room temperature PL spectra of CdO thin film deposited at 3500C. Spectrum was recorded in the wavelength ranged between 460 to 800 nm with excitation wavelength 480 nm. PL spectra consisted of peak centered around 520 nm which corresponds to near band edge transition. Wu reported similar result et al. [24]. The peak found at 530 nm due to near band-gap radiative combination. The peak around 562 nm

belongs to yellow emission band that arises due to donar to valence band transition causes by interstitial position occupied by Cd [25].

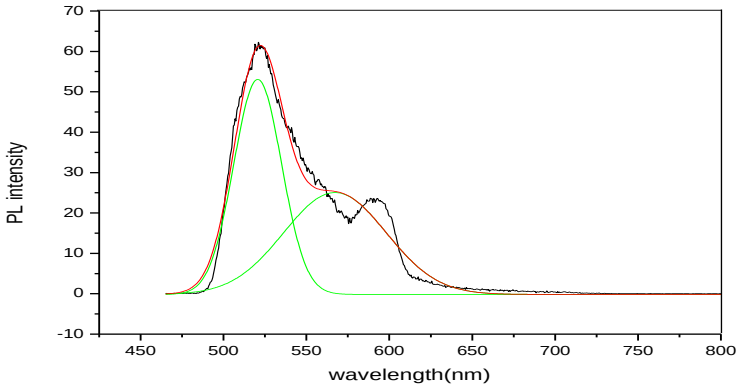


Figure 8: Deconvolution of PL spectra of CdO thin film.

Electrical Resistivity

Figure (9) shows the variation of the dark resistivity with temperature. It was observed that the resistivity of CdO thin films decreases with increase in temperature, indicating a semiconducting electrical behaviour. It is of the order of 10-4 to 10-5 ohm-cm. The resistivity of CdO films decreases from 2.3 ×10−4 to 9.6 ×10−5 ohm-cm as the deposition temperature increases from 150 to 3500C. Above 3500C, the resistivity starts to increase therefore

of stoichiometric deviations, which signify the decrease of dislocations and grain boundaries.

The thermal activation energy was calculated using the relation,

$$\rho = \rho_0 \exp\left(\frac{Ea}{KT}\right) \qquad (5)$$

where, ρ is resistivity at temperature T, ρ_ (0) is a constant, K is Boltzmann's constant and is Ea the activation energy required for conduction. Figure (10) shows variation of activation energy of CdO thin film with substrate temperature. The estimated activation energy was found to be low that earlier reports. [17, 26]. It is found that activation energy is lowest for the films deposited at 3500C substrate temperature. This decrease in Ea. with increase in substrate temperature may be attributed to change in intercrystallite barrier height caused by the grain size variation.

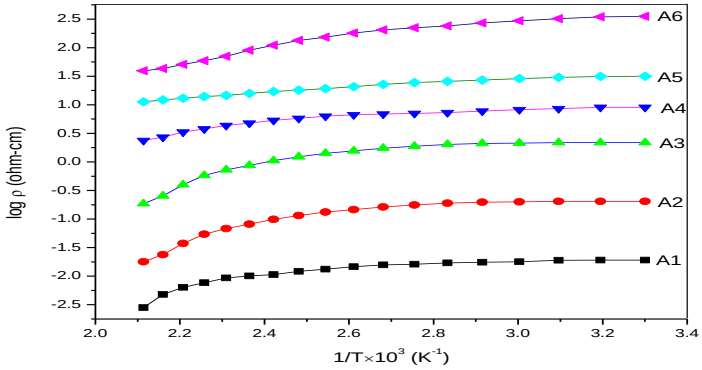


Figure 9: Variation of log ρ Vs 1/T×103 (K−1) for CdO thin films deposited at A1) 150, A2) 200, A3) 250, A4) 300, A5) 350 and A6)4000C

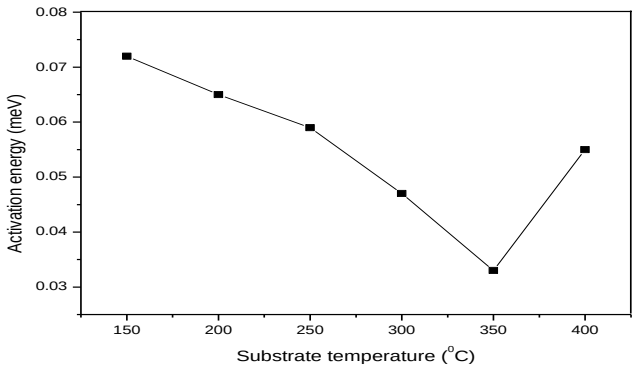


Figure 10: Variation of activation energy of CdO thin film with substrate temperature.

Thermoelectric power studies

The temperature difference between the ends of sample causes transport of carriers from hot to cold end and thus create field which gives thermal voltage. The variation of thermo emf with temperature difference for CdO films is shown in figure (11). From thermo emf measurement it was observed that the polarity of thermally generated voltage at the hot end is positive indicating that films are of n-type. The Seeback's coefficient α is calculated from the slope of graph. It is of the order of 16 to 59 μV/K which is in well agreement of reported value [26].

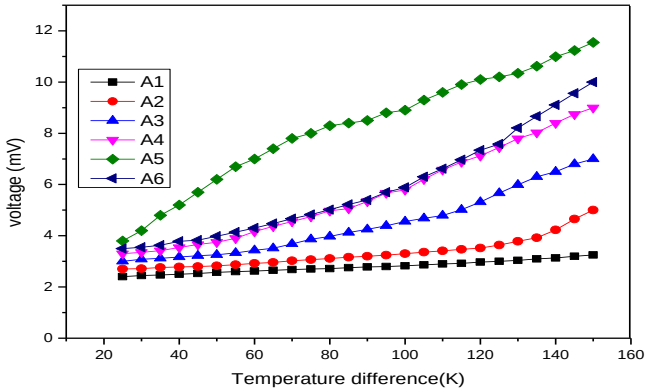


Figure 11: Variation of thermo emf with temperature difference for CdO thin films deposited at A1) 150, A2) 200, A3) 250, A4) 300, A5) 350 and A6) 4000C temperature.

CONCLUSIONS

In the present work nanocrystalline n-type high quality CdO thin films were successfully deposited at various substrate temperatures by spray pyrolysis technique. The optimum substrate temperature for deposition of CdO thin film was found to be 350□C. The XRD studies confirmed the cubic structure of CdO thin films. The SEM studies revealed that the deposited CdO films are dense and uniform in nature. The optical investigation showed that, the optical band gap energy of CdO varies from of 2.46 to 2.71 eV depending upon substrate temperature. The resistivity measurement showed that the resistivity of CdO thin films is very low. It is of the order of 10-4 to 10-5 ohm-cm. The activation energy decreases from 0.07 to 0.033 eV nm for substrate temperature 150 to 3500C and then again increases to 0.055eV for 4000C. Seeback's coefficient is calculated from thermo emf graph. It is found

that the value of coefficient α increases from 16 to 59 μV/K with substrate temperature from 150 to 4000C. Thus, we can conclude that the CdO films with low resistivity, wide band gap has significant commercial relevance. Moreover, by varying the substrate temperature of CdO thin films, its physical properties can be transformed as per requirement. All the results are summarized in table 3.

Table.3: Values of grain size, dislocation density, micro strain, optical band gap, activation energy and Seeback coefficient of CdO thin films.

Sample (CdO Deposited at)	Grain size, D (nm)	Dislocation density, 10^{14} lines/m^2	Strain, $\varepsilon 10^{-3}$	Optical band gap (eV)	Activation energy (eV)	Seeback's coefficient (μVK^{-1})
A1 (150^0C)	62	2.60	0.1287	2.46	0.072	16
A2 (200^0C)	64	2.44	0.1226	2.54	0.065	31
A3 (250^0C)	67	2.22	0.1127	2.57	0.059	43
A4 (300^0C)	71	1.98	0.1093	2.59	0.047	52
A5 (350^0C)	75	1.77	0.1068	2.71	0.033	59
A6 (400^0C)	73	1.87	0.1088	2.66	0.055	54

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