
Chapter III

PREPARATION AND CHARACTERISATION OF CdO THIN FILMS

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Preparation and characterization of CdO thin films

3.1 Introduction

The demand for low-cost and high performance optoelectronic devices leads to the development of better transparent and conductive oxide thin films. Cadmium oxide (CdO) is one of the promising transparent conducting oxides (TCO) from II to VI group of semiconductors having high absorption and emission capacity of radiation in the energy gap [1]. Initial investigations on CdO were done in view of testing its ability as TCO. It is now well conceived that the CdO displays excellent properties, which make them suitable as TCO. Consequently, thin films of CdO have been used in wide variety of applications such as photodiodes [2], phototransistors [3], photovoltaic cell [4], transparent electrodes [5], liquid crystal displays, IR detectors and anti reflection coatings [6]. A plethora of deposition techniques viz. dc magnetron sputtering [7, 8], reactive evaporation [9], sol-gel [10], chemical bath [11] and spray pyrolysis [12–15] have been employed to make thin layers of CdO. Spray pyrolysis has been evolved as one of the potential technique to deposit CdO thin films. The present chapter deals with the preparation of CdO films employing spray pyrolysis of an aqueous cadmium acetate solution and studies on their structural, surface morphological, electrical and optical properties. Different preparative parameters, such as substrate temperature, spray rate, concentration of spray solution, quantity of spray solution etc were optimized to get well adherent films.

3.2 Experimental

Deposition of CdO films using spray method includes the substrate cleaning, solution preparation etc. The preparative parameters were optimized in order to get well

adherent films. The CdO films were characterized using various techniques in order to get information about the structural, surface morphological, electrical and optical properties.

3.2.1 Experimental set up of spray pyrolysis technique

In this method, the starting material required to form the desired thin film is taken in the solution form and then sprayed onto the preheated glass substrates maintained at a desired temperature, resulting in the formation of the film. By spraying the mixture of metallic chlorides, nitrides or oxides with particular doping concentration, semi-conducting films can be prepared. The constituent ions form a complex in the solution and do not precipitate on coming in to contact with the hot substrates. The complex in the fine spray dissociates and the desired film results.

Vertical and slanted spray deposition arrangements with stationary or linearly moving spray nozzle have been frequently used in this technique. The thickness of the film depends upon the distance between the spray nozzle and substrate, substrate temperature, the concentration of the starting solution and the total quantity of solution sprayed. The schematic diagram of the spray pyrolysis technique is shown in Fig. 3.1. It mainly consists of (a) spray nozzle, (b) rotor for spray nozzle, (c) liquid level monitor, (d) hot plate with temperature controller, (e) air flow meter and (f) air tight fiber chamber (g) Speed controller.

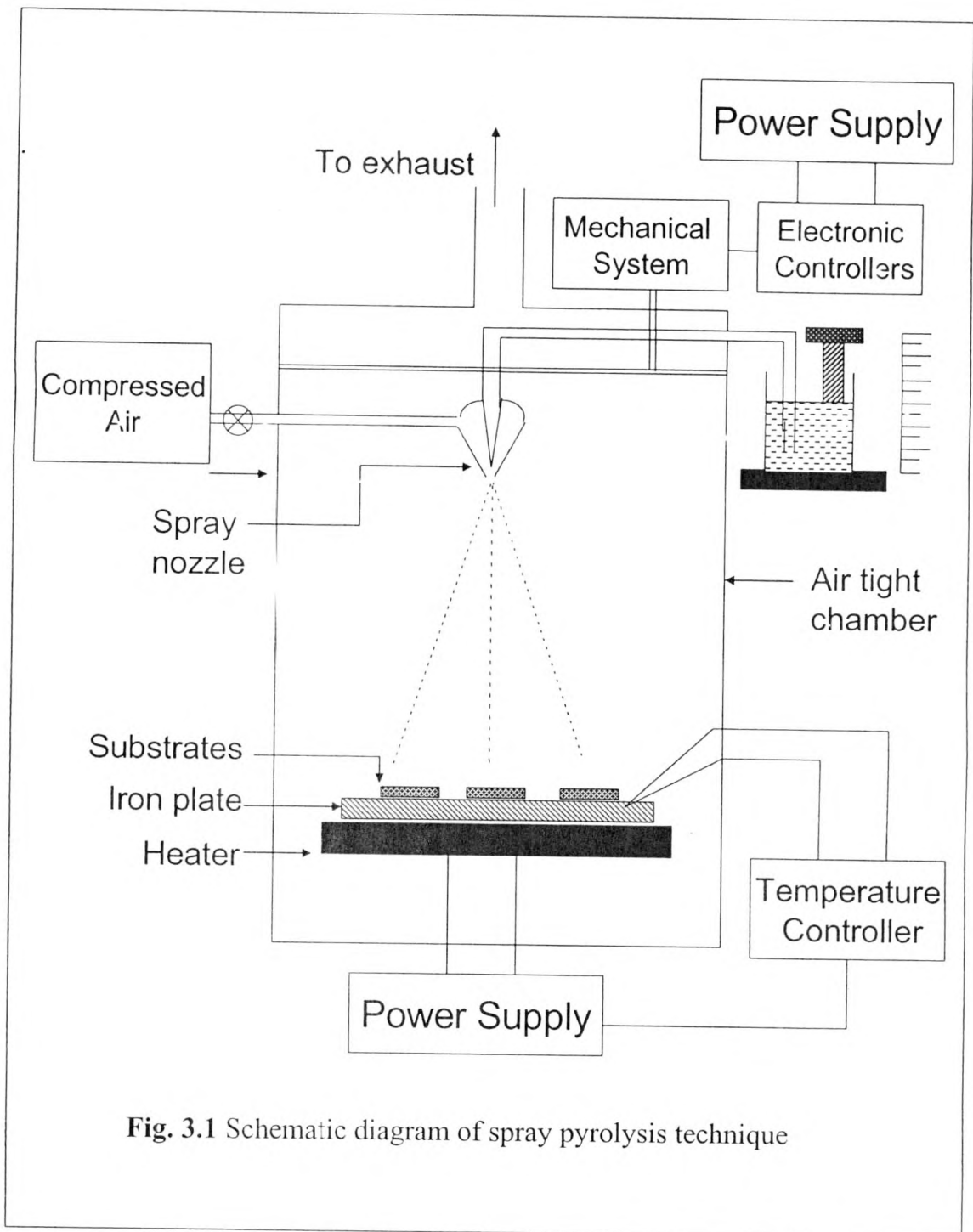


Fig. 3.1 Schematic diagram of spray pyrolysis technique

a) Spray nozzle

It is made up of corning glass and consists of the solution tube surrounded by the glass bulb. With the application of pressure to the carrier gas, the vacuum is created at the tip of the nozzle and the solution is automatically sucked in the solution tube and the spray starts.

b) Rotor for spray nozzle

Stepper motor based microprocessor controller is used to control the linear simple harmonic motion of the spray nozzle over the required length of the substrates.

c) Liquid level monitor

The spray rate at a fixed air pressure depends upon the height of solution measured with respect to the tip of the nozzle. The arrangement for the change in height of the solution forms the liquid level monitor

d) Hot plate

A round, cast-iron plate placed on 2000 Watt heating coil is used as a heating means. Maximum temperature of 600 °C can be obtained with this arrangement. The chromel-alumel (26 gauge) thermocouple is used to measure the temperature of the substrates and is fixed at the center of the front side of the iron plate. The temperature of the hot plate is monitored with the help of temperature controller.

e) Gas regulator valve / Air flow meter

The gas regulator valve is used to control the pressure of the carrier gas flowing through the gas tube of the spray nozzle. A corning glass tube of length 25 cm and of diameter 1.5 cm is converted into gas flow meter. Since air pressure depends upon the size of the air flow meter, the air flow meter should be calibrated from nozzle to nozzle.

f) Air tight metallic chamber

Since number of toxic gases, are evolved during the thermal decomposition of sprayed solution, it is necessary to install the spraying system inside an airtight chamber. An airtight metallic chamber of the size, 60 x 60 x 60 cm³ was fabricated. Inside surface of the chamber is painted with liquid epoxy in order to avoid the corrosion of the chamber. The outlet of chamber is fitted to an exhaust fan to remove the gases involved during thermal decomposition.

g) Speed controller

It contains the rectifying circuit and complementary emitter follower circuit. The output voltage varies from 0-12V with the help of resistance. The current sourcing capacity of the controller is 2A.

3.2.2 Mechanism of thin film formation

The scheme of pyrolysis and formation of thin films by the spray pyrolysis technique is described in detail [23] as shown in fig. 3.2. In spray pyrolysis technique thin film formation is based on a thermally stimulated chemical reaction between clusters of liquid or vapor atoms of different chemical species. In this process the precursor solution is atomized through a glass nozzle. The nozzle converts the solution into small droplets, known as aerosols. These aerosols are allowed to incident onto the preheated glass substrates. The pyrolytic decomposition of aerosols and formation of thin films with desired properties depends upon optimum substrate temperature. Various steps during pyrolysis of aerosols are summarized below.

- 1) Precursor solution is converted into aerosols by spray nozzle.

- 2) Solvent evaporation takes place.
- 3) Vaporization of solvent leads to precipitate formation as droplets / aerosols reaches the substrates.
- 4) Pyrolysis of the precipitate occurs in succession before the precipitate reaches the substrates.
- 5) When precipitate reaches the substrates, nucleation and growth of thin film on the substrate takes place.
- 6) Finally, growth of the nuclei leads to the formation of continuous thin layer of films.

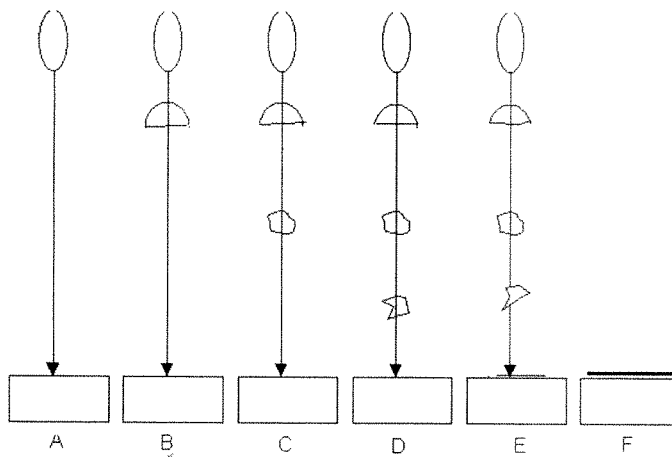


Fig. 3.2 Mechanism of thin film formation by pyrolytic decomposition.

3.2.3 Substrate cleaning

In thin film deposition process, substrate cleaning is an important factor as it affects the smoothness, uniformity, adherence and porosity of the films. The substrate cleaning process depends upon the nature of the substrate. The common contaminants are grease, adsorbed water, air borne dust, lint, oil particles, etc. The micro-slides supplied by 'Blue Star' of dimensions 7.5 cm x 2.5 cm x 0.1cm have been used as the substrates. The following process has been adopted for cleaning the substrates.

- 1) The substrates were washed with detergent solution 'Labolene' and then with water.
- 2) These substrates were then cleaned with distilled water.
- 3) Then substrates were boiled in 0.5M chromic acid for about few minutes.
- 4) Further substrates were cleaned with distilled water.
- 5) Then substrates were kept in sodium hydroxide solution to remove the acidic contaminations.
- 6) The substrates were again washed with distilled water and cleaned ultrasonically.
- 7) Finally substrates were dried in alcohol vapors.

3.2.4 Solution preparation

Initial ingredients used to deposit CdO thin films in aqueous medium are as follows

- i) A. R. grade Cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), supplied by s. d. fine chem. limited, Boisar, Mumbai.
- ii) Double distilled water

Initial ingredients used to deposit CdO thin films in nonaqueous medium are as follows

- i) A. R. grade Cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), supplied by s. d. fine chem. limited, Boisar, Mumbai.
- ii) Methyl alcohol (CH_3OH)

3.2.5 Films deposition procedure

The following experimental steps were involved in the deposition of thin films using a chemical spray pyrolysis technique.

- i) Firstly, the nozzle was washed using diluted hydrochloric acid.
- ii) The cleaned substrates were placed in the uniform temperature region of hot plate. Obtain desired temperature and control it with temperature controller.
- iii) Pass the air as a carrier gas through glass nozzle and again obtain the desired temperature.
- iv) Mix the appropriate quantities of solutions.
- v) Set the motion of the glass nozzle with the help of rotor and speed controller.
- vi) By adjusting the constant spray rate, spraying was started onto the hot glass substrates maintained at desired substrate temperature.
- vii) After completion of deposition, heater is made off and films were allowed to cool to room temperature and taken out of the deposition chamber to preserve them in dark desiccators.

The cadmium oxide thin films were deposited on glass substrate using the chemical spray pyrolysis technique. The spraying solution consisted of cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), in a de-ionized double distilled water. For nonaqueous medium, cadmium acetate dissolved in methanol is used as spraying solution. Compressed air was used as the carrier gas. 50cc of this solution was sprayed on preheated substrates.

Depositions are taken for 250 °C, 275 °C, 300 °C, 325 °C and 350 °C substrate temperatures with different concentrations of solutions (0.05M, 0.075M, 0.1M) When the droplets of the sprayed solution, reach the hot substrates, then owing to the pyrolytic decomposition of the solutions; results in uniform, pinhole-free and well- adhesive films of CdO.

3.3 Results and discussion

The structural, surface morphological, optical and electrical characterization of the films deposited at optimized preparative parameters was carried out by means of X-ray diffraction, scanning electron microscopy (SEM), optical absorption, electrical resistivity.

3.3.1 Thickness measurement

Thickness of CdO film was measured by the gravimetric weight difference method, using the density of CdO in bulk form ($\rho = 8.125 \text{ g/cm}^3$ for CdO) [16].

a) Thickness variation with temperature

The graph of thickness of cadmium oxide film with substrate temperature is shown in Fig.3.3. The concentration of solution was kept constant (0.05 M). It is observed from the figure that, the film thickness is increased with the temperature up to 300 °C and then decreased afterwards. At 300 °C, the heat supplied is optimum for decomposition of initial ingredients. Above 300 °C, film thickness decreases due to more evaporation of initial ingredients.

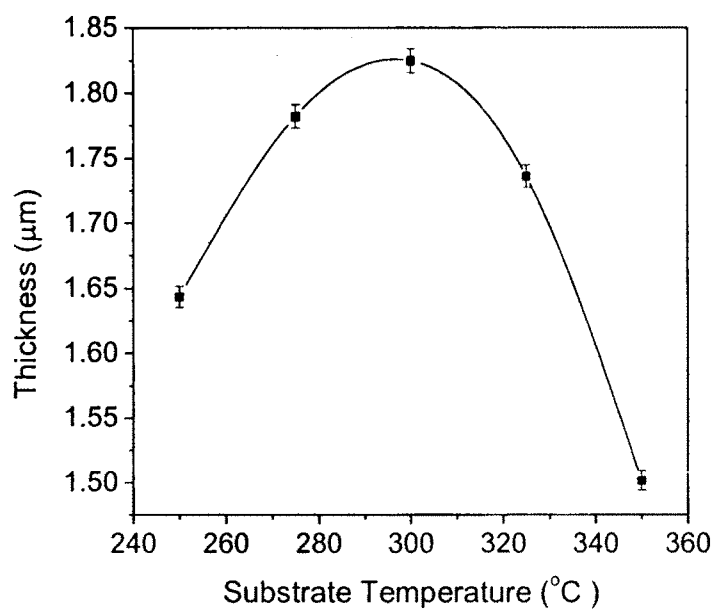


Fig. 3.3 Variation of film thickness of CdO thin film with substrate temperatures

b) Thickness variation with concentration

After optimization of temperature (300 °C), the films were deposited at different concentrations 0.05M, 0.075M and 0.1M. The variation of film thickness with concentration is shown in Fig.3.4

Initially the thickness increases with concentration, it attains maximum value (2.6 μm) at 0.075 M, and then decreases with further increases in concentration. After 0.075 M concentration of solution, film thickness decreases due to formation of porous, non uniform and powdery films.

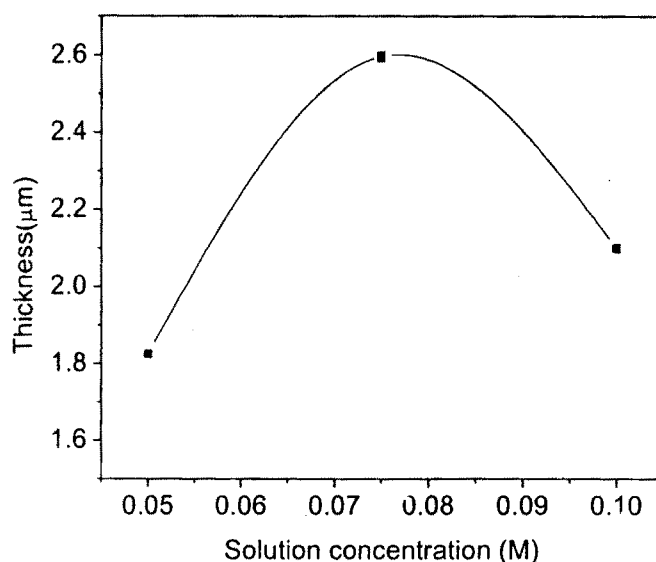


Fig. 3.4 Variation of film thickness of CdO thin film with concentration

c) Thickness variation with quantity of solution

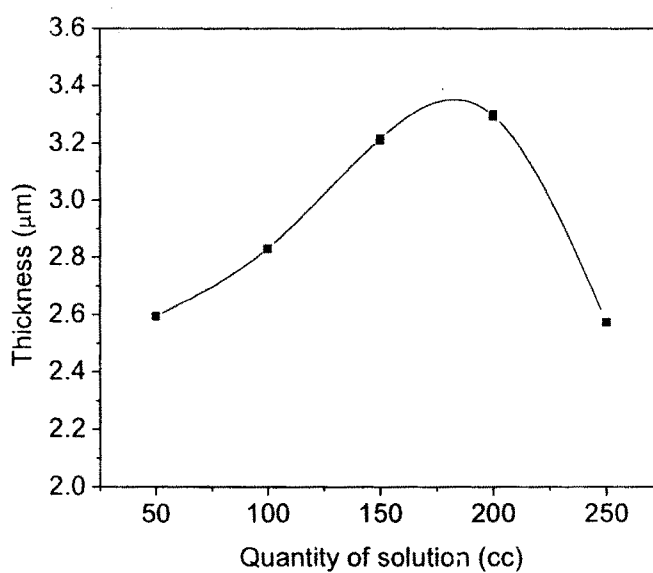


Fig. 3.5 Variation of film thickness of CdO thin film with quantity of solution.

The graph of thickness of cadmium oxide film with quantity of the solutions sprayed is shown in Fig. 3.5. It is observed from the figure that, the film thickness is increased with the quantity of the spray solution up to 200 cc of solution and then decreased afterwards.

This behavior can be attributed to the formation of powdery film at higher solution quantity, analogous to Shinde et al. [17].

3.3.2 X-ray diffraction studies

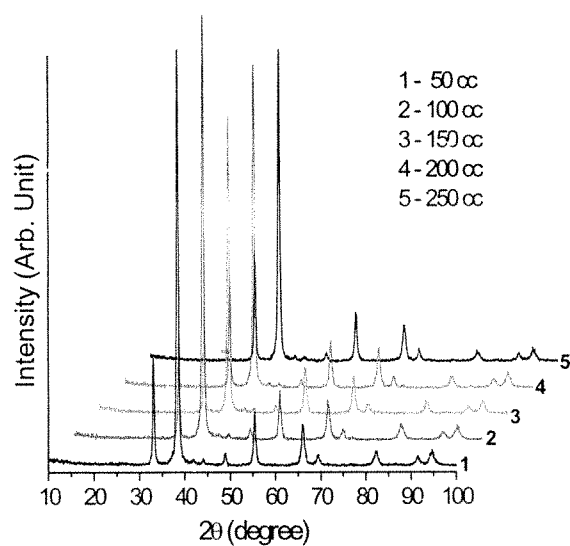


Fig.3.6 Superposed X-ray diagram of CdO thin films deposited at optimized substrate temperature of 300°C and concentration of 0.075 M cadmium acetate for different quantity of solution [JCPDS Card No.65-2908].

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Table 3.1 observed and standard d values for the CdO thin film deposited at optimized preparative parameters on amorphous glass substrate.

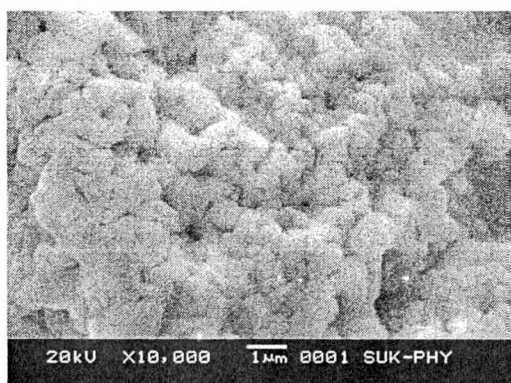
Sr. No.	Standard d value Å	Observed d value Å	(hkl) planes
1	2.7112	2.7057	(111)
2	2.3480	2.3513	(200)
3	1.6602	1.6630	(220)
4	1.4158	1.4205	(311)
5	1.3556	1.3585	(222)
6	1.1740	1.1743	(400)

Fig. 3.6 shows the X-ray diffraction patterns of cadmium oxide films deposited at optimized temperature and optimized concentration with different quantity of spraying solution. All the peaks in the pattern correspond to polycrystalline cubic structure of cadmium oxide; peaks are indexed on the basis of JCPDS card number 03-065-2908. The lattice parameter value 'a' for cubic structure, calculated for the deposited films are found to be in good agreement with the reported values. The diffractograms shows characteristics CdO orientations along the preferred direction (200). The presence of other peaks such as (111), (220), (311), (222), and (400) have also been detected but with substantially lower intensities. The absence of impurity peaks suggests the high purity of the nanocrystallites. The crystallite size was determined by the broadening of the (200) diffraction peak, using a well-known Scherrer's formula and FWHM values. The average crystallite size was calculated and was found to have average value 16.4 nm.

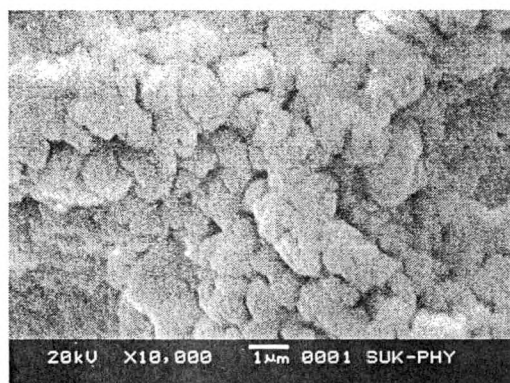
3.3.3 Scanning electron microscopy

The two dimensional surface morphological studies of the CdO films have been carried out from images taken by using scanning electron microscope, JEOL JSM-6360 (Japan) equipped with an energy-dispersive X-ray analysis (EDAX) to measure the composition quantitatively. Fig. 3.7 (A), (B) and (C) shows SEM image of as-deposited cadmium oxide thin film onto the glass substrate at optimized substrate temperature of 300°C , optimized concentration of 0.075 M and optimized quantity of solution 200 cc.

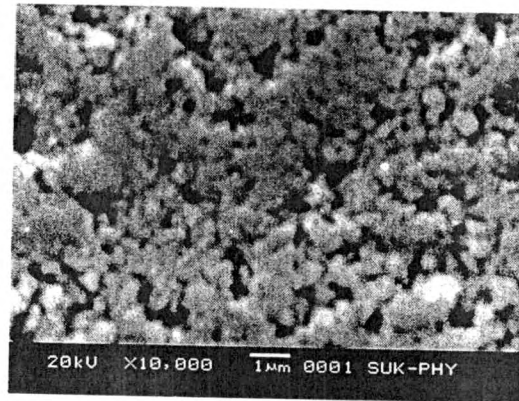
The micrographs (A) and (B) show spongy morphology of the material deposited on the substrate. The micrograph(C) reveals that the substrate is well covered with large number of fine grains and film surface is uniform, porous with compact growth. Fig.3.8 shows a typical EDAX pattern for as-deposited CdO film at optimized deposition conditions. The films prepared at these conditions are almost stoichiometric.



(A)



(B)



(C)

Fig.3.7 SEM micrographs of as deposited CdO thin films at X 10,000 magnification:

(A) SEM image of CdO thin film for optimized substrate temperature of 300 °C,

(B) SEM image of CdO thin film for optimized concentration of 0.075 M,

(C) SEM image of CdO thin film for optimized quantity of solution 200 cc.

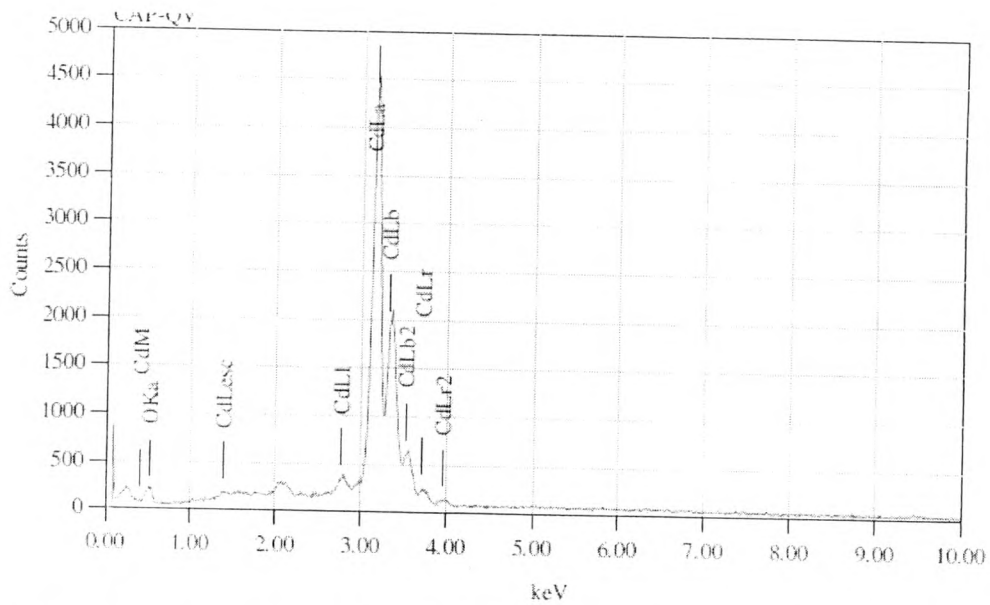


Fig. 3.8 Energy dispersive X-ray analysis of pure CdO thin film deposited with optimized deposition conditions.

3.3.4 Optical absorption and transmission

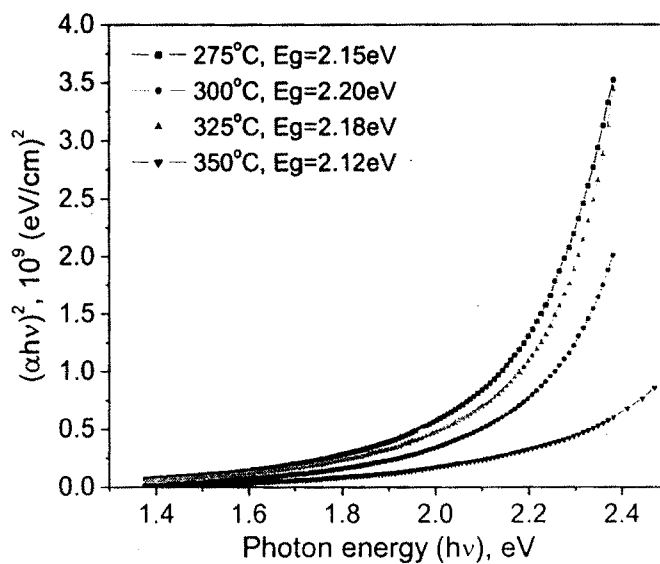


Fig. 3.9 Variation of $(\alpha h\nu)^2$ versus $h\nu$ for spray deposited CdO thin films for different deposition temperatures.

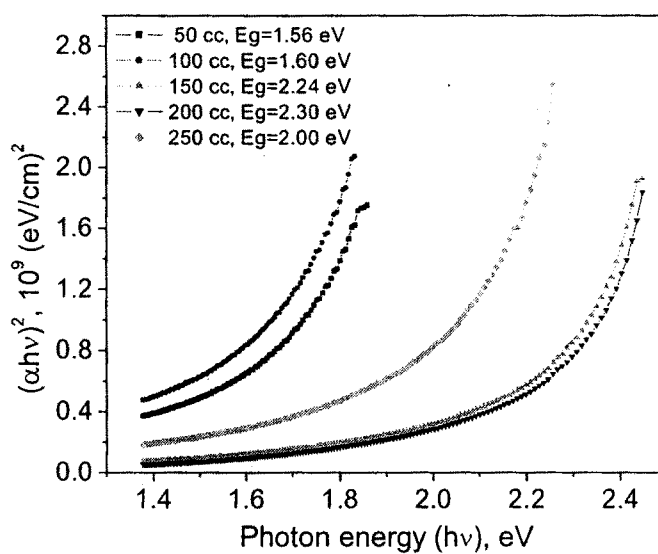


Fig. 3.10 Variation of $(\alpha h\nu)^2$ versus $h\nu$ for spray deposited CdO thin films for different quantity of spraying solution.

Fig. 3.9 and 3.10 show variation of $(\alpha h\nu)^2$ versus $h\nu$ for the films deposited at different temperatures and different quantity of solution respectively. Extrapolation of linear portion of the plot to the energy axis at $\alpha = 0$ gives the band gap energy of the material. The graph clearly shows significant change in bandgap energy. With the variation of temperature, the bandgap increases to 2.2 eV for 300 °C and thereafter decreases. The increase in solution quantity finds the same effect. Maximum bandgap of 2.3 eV is obtained for 200 cc spraying solution. The increase of optical band gap with increasing temperatures and quantity of solution may be due to the decrease of carrier concentration [18].

3.3.5 Electrical resistivity

The surface transport phenomena have a strong influence on the electronic properties of semiconductor. This phenomenon plays an important role in the transport properties of semiconducting thin films. Electrical resistivity measurements were carried out using van der pauw method.

a) Resistivity variation with temperature

The resistivity of thin film strongly depends on deposition temperature. Generally the films deposited at high temperature have less concentration of oxygen vacancies as compared to the films deposited at low temperature. The electrical properties of the oxide films depend on oxidation state of metal component.

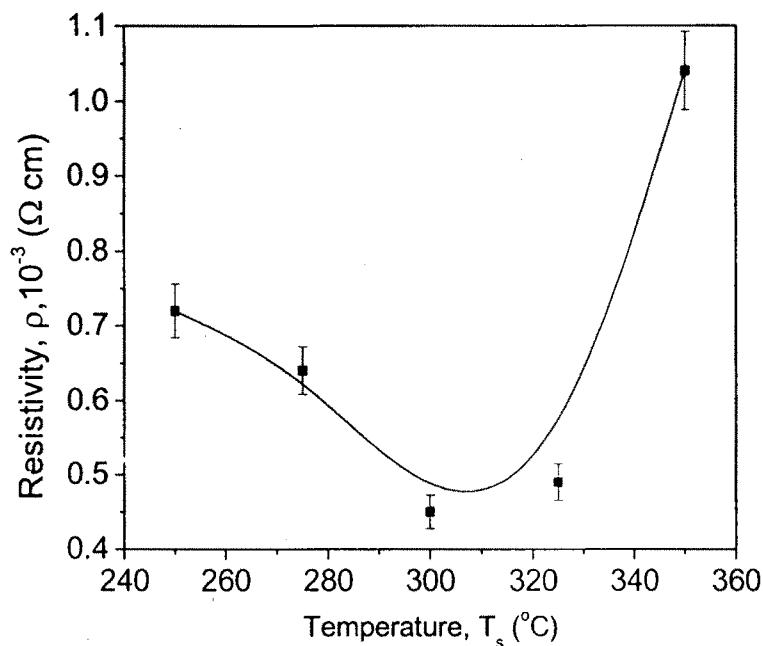


Fig.3.11 Variation of resistivity of CdO thin film with substrate temperatures

Fig. 3.11 shows that the resistivity of CdO thin film initially decreases with increasing temperature. It attains minimum value of $4.7 \times 10^{-4} \Omega$ cm at 300 °C and then increases at higher temperature.

b) Resistivity variation with concentration of solution

The dependence of resistivity on solution concentration of cadmium acetate is shown in Fig.3.12. Up to 0.075 M solution concentration, the resistivity has decreasing trend but after that it starts to increase. The initial decrease in resistivity with concentration is attributed to increase of mobility which is found to increase due to the improvement of the crystalline structure.

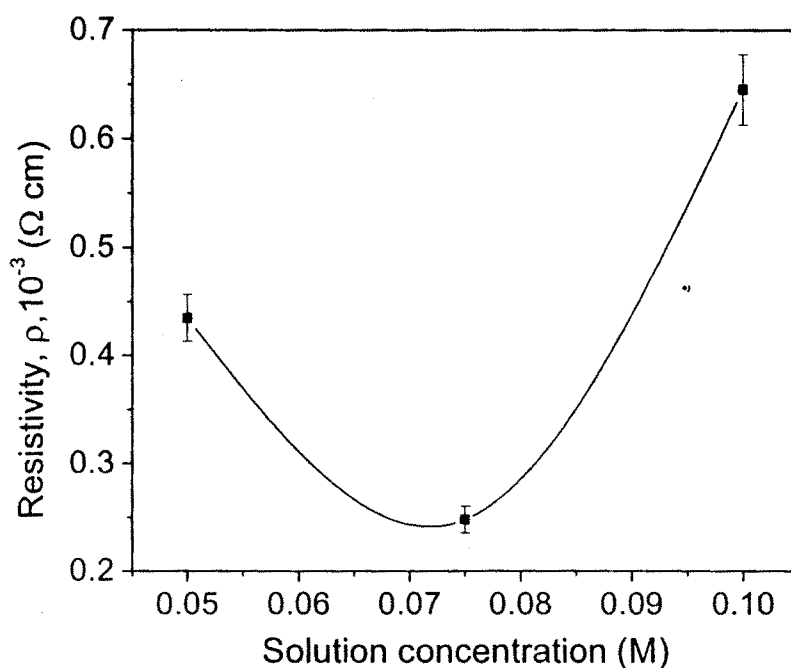


Fig. 3.12 Variation of resistivity of CdO thin film with concentration

c) Resistivity variation with quantity of solution

The thickness of film also plays crucial role to change its resistivity. Film thickness can be changed by varying the quantity of spraying solution. The variation of resistivity with quantity of spraying solution is shown in Fig. 3.13. Resistivity decreases up to 200 cc of solution ($1.75 \times 10^{-4} \Omega \text{ cm}$) and afterward increases.

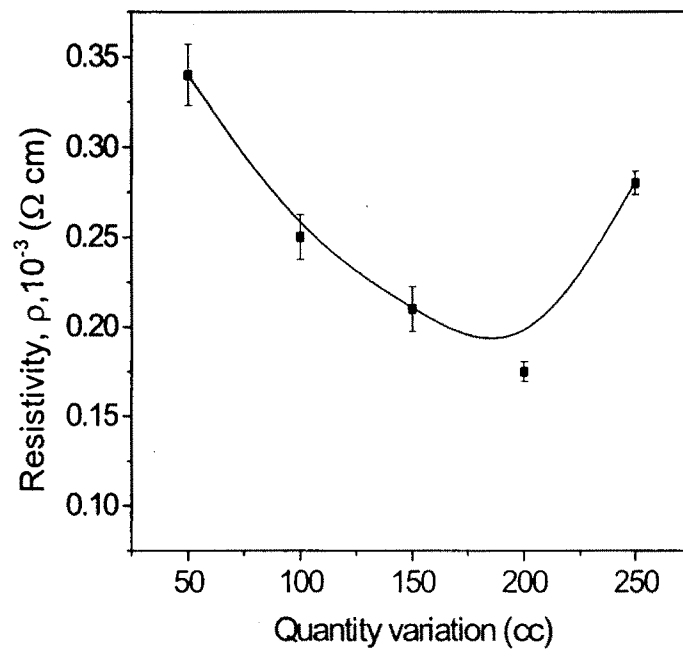


Fig. 3.13 Variation of resistivity of CdO thin film with quantity of solution

3.4 Effect of solvent variation on properties of CdO

3.4.1. Introduction

The materials exhibiting high electrical conductivity and optical transparency are being used extensively for several of applications including architectural windows, thin film photovoltaic and photo-electronic devices [19, 20]. Transparent conducting oxides (TCOs) such as SnO₂, ZnO, CdO, Cd₂SnO₄ etc. have great technological interest due to their high quality electrical and optical properties. Among these, CdO is emerging as one of the best TCO because of its low-cost precursor requirement. CdO thin films have been synthesized by various techniques such as sputtering; T.K. Lakshmanan et al. prepared the indium and copper doped CdO thin films by sputtering technique and studied optical and electrical properties. [21-24], spray pyrolysis; K. Gurumurugan et al. deposited CdO thin films by spray pyrolysis technique. They used solution of cadmium nitrate containing definite proportions of distilled water and isopropyl alcohol. They studied structural, optical and electrical properties. [25], reactive evaporation; C. Sravani et al prepared CdO thin films by reactive evaporation method. They studied optical and electrical properties. [8,9], sol-gel [26], chemical vapor deposition; Zhiyong Zhao et al. prepared tin doped CdO thin films with metal organic chemical vapour deposition technique by using dimethylcadmium (DMCd), tetramethyltin (TMT) and O₂. They studied structural, optical and electrical properties of the film. [27], and pulsed laser deposition [28]. Among these, spray pyrolysis is well-suited technique because of its simplicity and inexpensive experimental arrangement, reproducibility, high growth rate and mass production capability for uniform large area coatings [29].

Recently, CdO thin films are deposited by spray pyrolytic deposition using cadmium acetate and ammonium fluoride as precursors [30]. These films have been deposited at different substrate temperatures and different amounts of fluorine doping, and obtained device quality n-type F: CdO films at a substrate temperatures of 275°C with 4% F doping. It is quite well known that properties of TCO films strongly depend on the deposition conditions. Therefore, to gain a better control over all the physical properties of such films, systematic investigations over each process parameters are necessary. Most of the TCOs which had been in applications use organic solvents like methanol, ethanol or propanol for their preparation [31, 32] However, there are very sparse reports on the synthesis of TCOs, especially CdO thin films wherein water/methanol (volume ratio) is varied. It would be quite interesting to see the effect of solvent ratio on the properties and quality of CdO thin films. Although, very interesting results have been obtained by varying water to propane-2-ol solvent ratio in case of fluorine doped tin oxide (F:SnO₂) thin films [31], no reports are available on variation of solvent ratio for sprayed CdO thin films. For F:SnO₂ films, the increased water content in the solvent ratio is found to affect the structural, morphological and electrical properties, in that the crystallite size increases with decrease in water content in the ratio. Moreover, there is increase in figure of merit and carrier concentration.

In the present investigation, CdO thin films have been deposited by varying water to methanol solvent ratio. The composition of solvent has been changed in volumetric proportions of water to methanol. The effect of solvent ratio on the structural, optical, morphological and electrical properties has been discussed

3.4.2. Experimental details

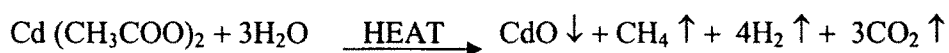
CdO thin films were deposited onto the preheated ultrasonically cleaned glass substrates at a fixed substrate temperature of 275 °C and concentration of 0.05M. The spraying solution 50 cc of cadmium acetate [$\text{Cd}(\text{CH}_3\text{COO})_2$, 99.9% pure] in a mixture of solvent consisting of varying proportions of water and methanol. The water to methanol ratio in the spraying solution (volumetric proportions) was varied as 50:00, 40:10, 30:20, 25:25, 20:30, 10:40 and 00:50. The nozzle to substrate distance was kept 30 cm and the solution was sprayed at constant spray rate of 2 cc min⁻¹. When droplets of sprayed solution reach a hot substrate, the pyrolytic decomposition of the sprayed solution occurs and well adherent, pin-hole free, uniform, yellowish coloured CdO films are formed on the substrate. The structural properties were studied by Philips X-ray diffractometer model PW-i710 using Cu-K α radiation ($\lambda=1.54056\text{\AA}$). X-ray diffraction patterns of CdO films grown on the glass substrates were scanned in 2θ range of 10 to 100°. Surface morphology of the films was studied by JEOL; Japan make scanning electron microscope (model JSM-6360). Optical absorption study is carried out in the wavelength range of 350-850 nm using Systronics model-119 spectrophotometer. Resistivity, carrier concentration, and mobility of the films were measured by van der Pauw method and Hall Effect at room temperature [33, 34].

3.4.3. Results and discussion

3.4.3.1 CdO thin film formation

In the spray pyrolysis technique, starting material required to form the desired semiconducting compound is in the form of solution, which is then sprayed onto preheated

substrates, resulting in the formation of thin film on the upper surface of substrate. Aqueous solution of cadmium acetate with water and methanol as solvent, when sprayed over hot substrate, pyrolytic decomposition of solution takes place and results in well adherent, dark yellow films of cadmium oxide. The possible chemical reaction that takes place is as follows;



3.4.3.2 X-ray diffraction (XRD) studies

Fig.3.14. shows the X-ray diffraction patterns of spray deposited CdO thin films on glass substrates at different ratios of water to methanol in the solvent.

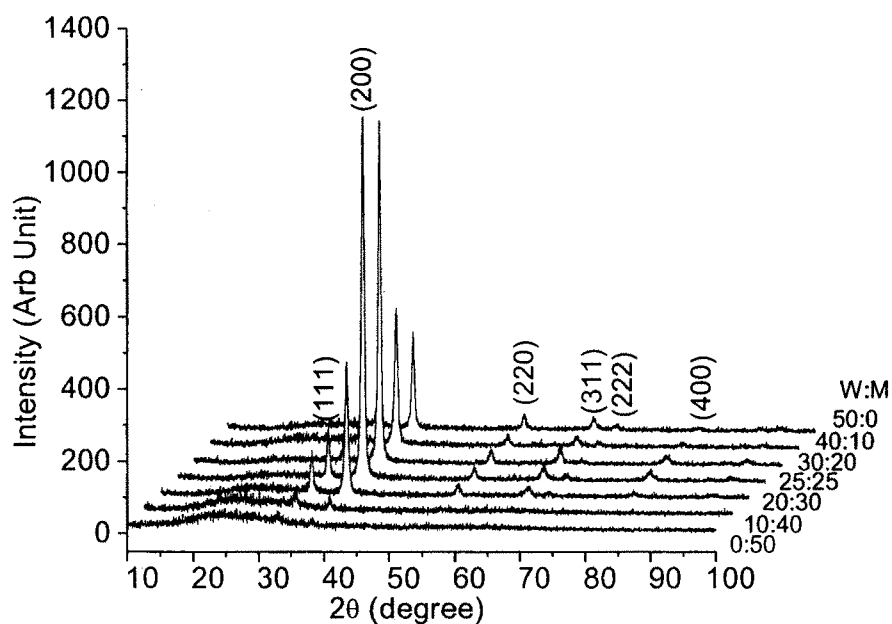


Fig.3.14. Superposed X-ray diagram of CdO thin films deposited at optimized substrate temperature of 275°C and concentration of 0.05M cadmium acetate for different water to methanol solvent ratios [JCPDS Card No.65-2908].

The matching of observed and standard 'd' values confirms that the deposited material is CdO film having cubic crystal structure. The average value of lattice parameter for optimized film (4.69Å) for cubic structure is found to be in good agreement with the reported standard value in JCPDS card number 65-2908. It is observed that, by varying the ratios of solvents in spraying solution, the lattice parameter does not get altered significantly. The unique feature of all the diffractograms is that they contain the characteristics CdO orientations along the preferred direction (200). The presence of other peaks such as (111), (220), (311), (222), and (400) have also been detected but with substantially lower intensities. The intensity increases with methanol. It becomes optimum for 25:25 water to methanol solvent ratio (200) peak increases as quantity, and then decrease with increase of methanol proportion in the solvent. In order to understand the growth mechanism involved in the spray deposited CdO films, the values of standard deviation were estimated using following relation [35],

$$\sigma = \sqrt{\frac{\sum I^2(hkl) - \frac{(\sum I(hkl))^2}{N}}{N}} \quad (3.1)$$

where, I stand for relative intensity of a (hkl) plane. The standard deviation varies between 35.10 and 37.13. The preferred orientation of the films was studied by calculating texture coefficient T.C. (hkl) using the relation [36],

$$TC(hkl) = \frac{\frac{I(hkl)}{I_0(hkl)}}{\frac{1}{N} \sum_N \frac{I(hkl)}{I_0(hkl)}} \quad (3.2)$$

where, $I(hkl)$ is measured intensity and $I_0(hkl)$ is ASTM standard intensity of (hkl) plane, N is number of reflections observed in X-ray diffraction pattern. The texture coefficients for (200) plane are plotted in Fig.3.15.

The plot clearly indicates that the texture coefficient for (200) increases with increase in quantity of methanol in solvent, becomes maximum (3.6) at 25:25 water to methanol ratio and then decreases with further increase in quantity of methanol. The value of TC (200) at 25:25 water to methanol solvent ratio indicates the maximum preferred orientation of the films along (200) diffraction plane. This may be attributed to the increase in grain size for water to methanol solvent ratio of 25:25 in the solution. The grain size obtained for 50:00 volumetric proportions of water to methanol in the spraying solution is 64.30 nm. For 25:25 it is 260.33 nm and for 00:50 it is found to decrease up to 177.09 nm. Variation of coefficients shown in Fig.3.15 may be attributed to the variation in grain size with different proportions of water to methanol ratio in the spraying solution.

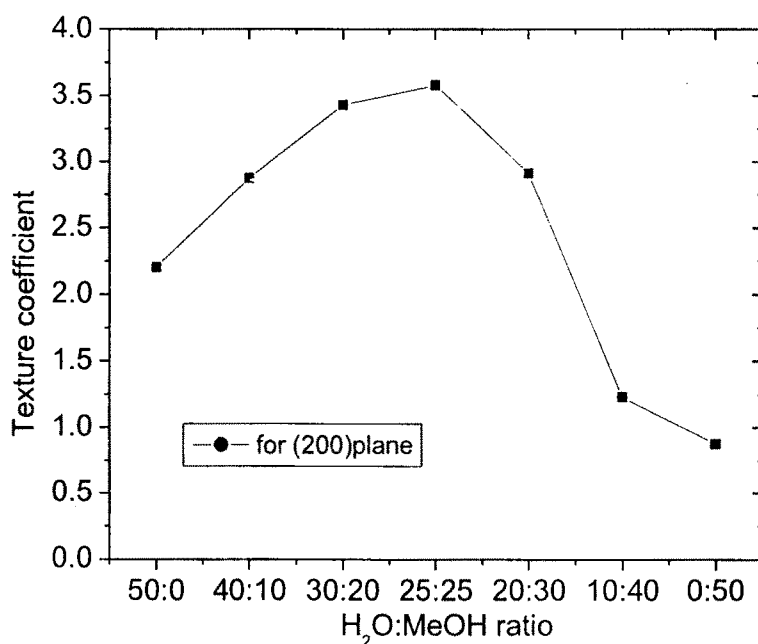


Fig.3.15 Variation of texture coefficient for (200) plane of CdO films prepared with different water to methanol ratio at optimized substrate temperature of 275°C and concentration of 0.05M cadmium acetate.

The lattice parameters determined from the Bragg equation are found to vary in the range 4.694 to 4.723 Å. To find true value of lattice constant, we use an extrapolation technique by plotting the calculated lattice constants against the Nelson-Riley function (NRF) .fig. 3.16

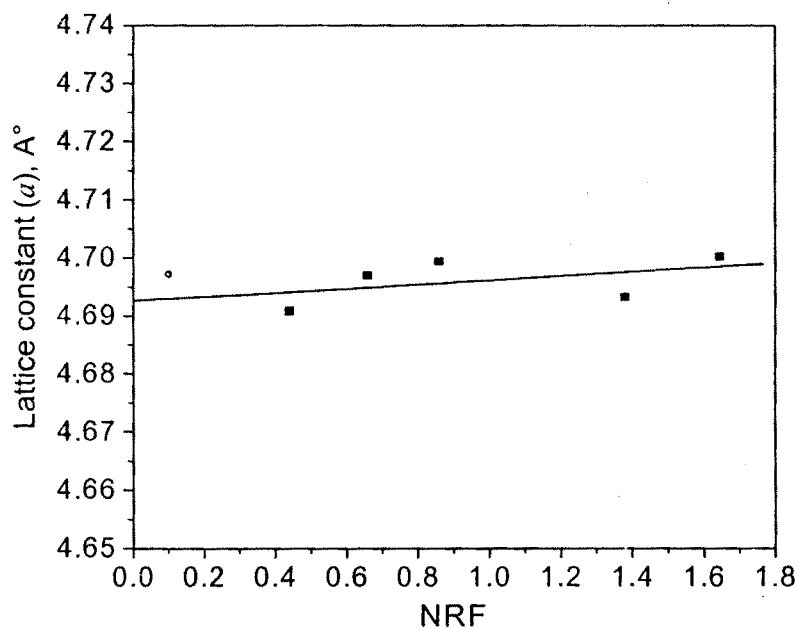


Fig.3.16 Plot of lattice parameters versus Nelson-Riley function for optimized sample.

$$NRF = \frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right) \quad (3.3)$$

Where, θ is the Bragg angle.

The true value of lattice parameter is found to be $a=4.692 \text{ \AA}$. The material deposited is an unstrained poly-crystalline material. This is confirmed by calculating stacking fault probability of material of the film and is found to be very small. Stacking fault probability of material of the film is found to be very small.

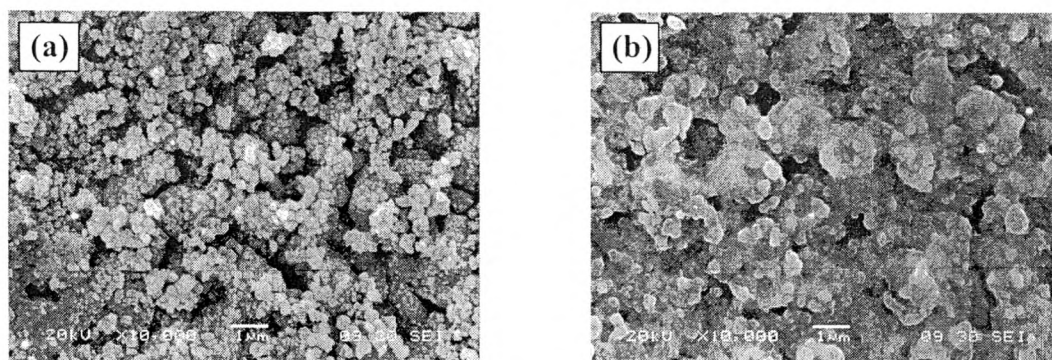
The stacking fault probability is determined using equation [37],

$$S_f = \frac{2\pi^2\beta}{45(3 \tan \theta_{200})^{1/2}} \quad (3.4)$$

The stacking fault probability for (200) plane of CdO thin films lies between 0.0028 and 0.0042. These values are very small as compared to the values reported for CdO by a modified reactive vacuum evaporation process [38]. The crystallite size is estimated by broadening of diffraction line using Scherer's formula along (200) and (111) planes. The average crystallite size is about 28 nm for (111) and 18 nm for (200) planes, which confirms that the films are nanocrystalline.

3.4.3.3 Scanning electron microscopy (SEM)

Fig.3.17 (a, b, c) shows scanning electron micrographs of spray deposited CdO thin films for different water to methanol solvent ratio.



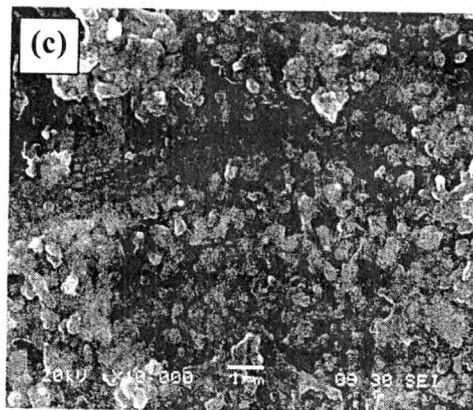


Fig.3.17 SEM micrographs of as deposited CdO thin films, (a) SEM image of CdO thin film for 50:00 water to methanol solvent ratio, (b) SEM image of CdO thin film for 25:25 water to methanol solvent ratio and (c) SEM image of CdO thin film for 00:50 water to methanol solvent ratio.

From SEM images it is seen that, (a) with water as major solvent (50:00), CdO film shows porous morphology with nanocrystalline spherical grains of size ~ 50 - 100 nm (b) with equal volume proportion (25:25) of water and methanol, grain size increases up to ~ 200 - 250 nm. The grains seem to be coagulated with each other forming amorphous spongy clusters with decreased porosity and (c) with methanol as only component (00:50) in the solvent, grain growth is observed with decreased porosity. The variation in grain size with water to methanol ratio in the solvent may be attributed to the difference in temperature during the grain growth. This results in decrease of porosity (Fig. 3.17 C)

3.4.3.4 Optical absorption and transmission studies

The optical absorption and transmission of the films is studied in wavelength range of 350-850 nm. Fig.3.18 gives the dependence of transmittance on wavelength with average transmittance of 60 %. The graph shows increasing trend of transmittance with the

increase of methanol quantity in the solvent. The transmittance of films is found to affect strongly by increased methanol quantity in the solvent.

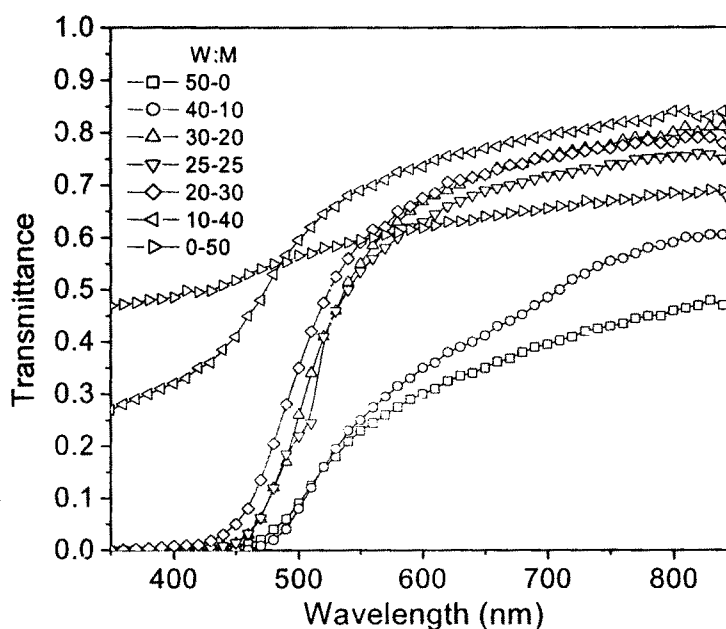


Fig.3.18 Transmittance spectra of spray deposited CdO thin films for different water to methanol solvent ratios

Fig.3.19 shows the plot of $(\alpha h\nu)^2$ versus $(h\nu)$ indicating the presence of direct band transition in CdO thin films. The band gap energy is found to vary significantly with the variation of water to methanol solvent ratio and it varies from 2.1 eV to 2.6 eV. The maximum band gap energy of 2.6 eV is found for 25:25 volumetric proportions of water to methanol in the spraying solution. This increase in band gap energy with increase of methanol quantity in the solution may be attributed to the low carrier concentration at 25:25 volumetric proportions of water to methanol in the spraying solution [39].

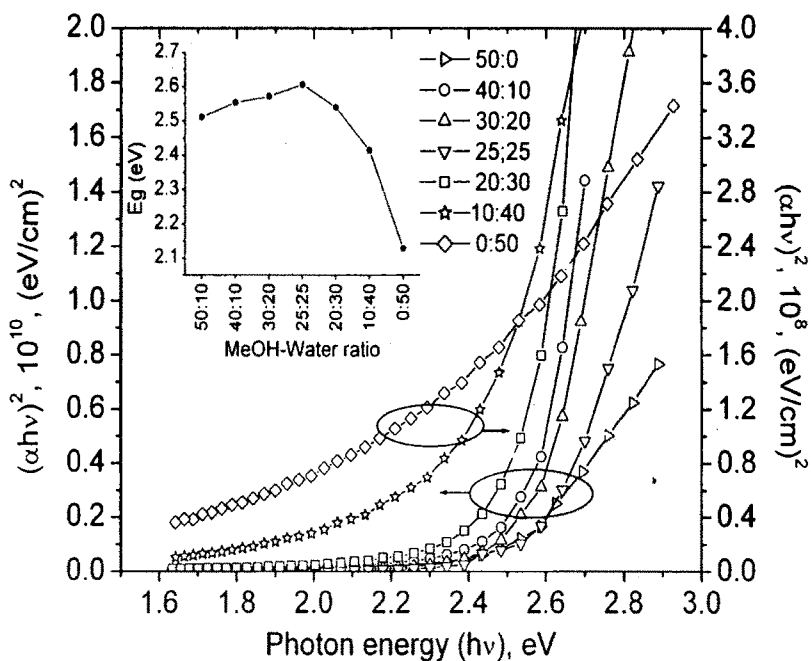


Fig.3.19 Variation of $(\alpha h\nu)^2$ versus $h\nu$ for spray deposited CdO thin films for different water to methanol solvent ratios.

3.4.3.5 Electrical resistivity

The van der Pauw technique was used for the measurement of the sheet resistance of the films. The sheet resistance shows increasing trend with increase in the methanol quantity in water to methanol solvent ratio. The variation of thickness of the films deposited by varying the water to methanol solvent ratio in the spraying solution is not uniform. Hence the resistivity of the films first increases from 1.86×10^{-3} to $6.45 \times 10^{-3} \Omega$ cm and then decreases. Maximum resistivity was found for the water to methanol solvent ratio of 25:25 as seen in Fig.3.20

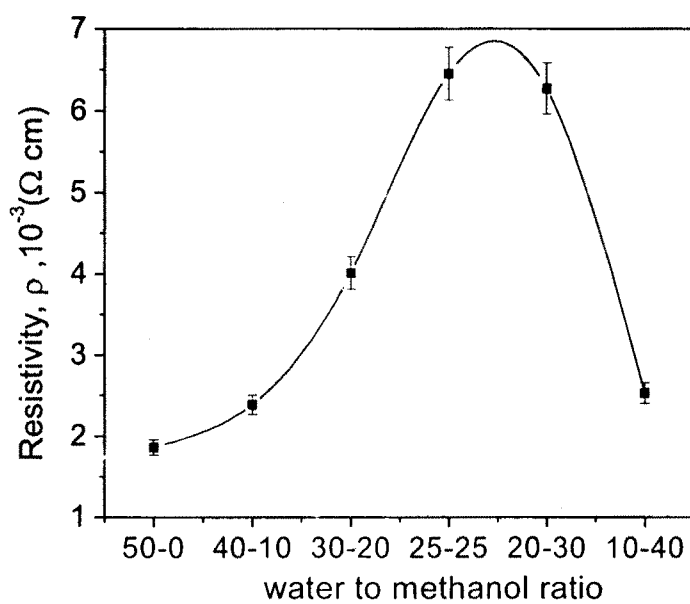


Fig.3.20 Variation of electrical resistivity of spray deposited CdO thin films obtained at substrate temperature of 275°C and concentration 0.05M with variation of water to methanol solvent ratios.

Fig.3.21 shows the plot of carrier concentration versus water to methanol solvent ratio. Initially, the carrier concentration of the film decreases with increasing quantity of methanol in the solvent, and becomes minimum at 25:25 volumetric proportions of water and methanol in the solvent and then increases.

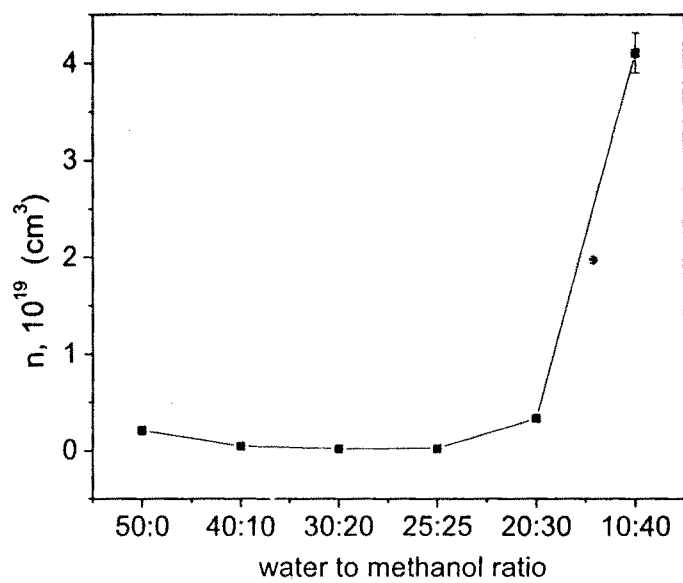


Fig.3.21 Variation of carrier concentration in spray deposited CdO thin films with different water to methanol solvent ratios in the spraying solution.

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