

# Temperature dependence growth of CdO thin film prepared by spray pyrolysis

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## Abstract

CdO thin films prepared by spray pyrolysis technique show temperature dependence growth when the spray time is constant. In contrast, the growth is film thickness dependent when the substrate temperature is constant. The films are polycrystalline in the covered spray time and substrate temperature ranges. The crystallite size and microstrain are calculated and analyzed. The Atomic Force Microscopy (AFM) micrographs prove that the grains are uniformly distributed within the scanning areas ( $5\ \mu\text{m} \times 5\ \mu\text{m}$ ) and ( $50\ \mu\text{m} \times 50\ \mu\text{m}$ ). The roughness shows a considerable decrease with substrate temperature. All samples show an abrupt change in transmission which indicates a direct transition and good crystallinity. The transmission of films is increased up to 80% with increasing substrate temperature in wavelength ranged from 450 nm to 1000 nm. Also, a broad absorption band is observed in the range 1500–2000 nm. This band could be attributed to the increase in free carrier concentration which confirmed by a reasonable decrease in the film sheet resistance. The band gap  $E_g$  is determined and found to be in the range 2.45–2.55 eV. The sheet resistance is reduced with increasing deposition temperature due to the increase in free carrier concentration and found to be  $66\ \Omega/\square$  at  $450\ ^\circ\text{C}$ . © 2014 Production and hosting by Elsevier B.V. on behalf of Electronics Research Institute (ERI).

**Keywords:** Cadmium oxide; Electrical; Optical and structural properties; Spray pyrolysis; Thin films

## 1. Introduction

Recently transparent conducting oxide (TCO) thin films such as tin oxide (Kim et al., 2008; Moholkar et al., 2008), indium tin oxide and cadmium oxide (Ma et al., 2003; Chandiramouli and Jeyaprakash, 2013) have attracted considerable attention because of their simultaneously high transparency in the visible spectrum and low resistivity. The majority of known TCO materials are n-type semiconductors where defects such as oxygen vacancies, impurity substitutions and interstitials donate electrons to the conduction band providing charge carriers for the flow of electric current. The increasing use of transparent conductors in various opto-electronic devices (Ortega et al., 2000; Gupta

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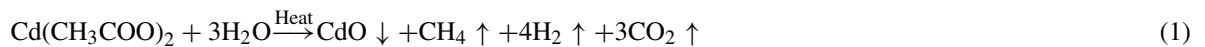
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et al., 2008), heterojunction solar cells (Santos-Cruz et al., 2006; Zaïen et al., 2012) and heat mirror prompted interest in electro-optical applications of thin films. CdO is a degenerate semiconductor with wide bandgap that varies from 2.2 to 2.9 eV with increasing carrier density. It shows high n-type conductivity due to the presence of interstitial Cd atoms and oxygen vacancies which both act as donors. It has been prepared using various techniques such as sputtering (Saha et al., 2008; Zhou et al., 2007), sol–gel (Aksoy et al., 2009), evaporation (Dakhel and Henari, 2003), pulsed laser deposition (Zhao et al., 2002; Gupta et al., 2009), chemical vapour deposition (Yahya and Adel, 2012) and spray pyrolysis (Bhosale et al., 2005; Jeyaprakash et al., 2011). CdO thin film has been prepared using spray pyrolysis technique. Spray pyrolysis method is an effective production leads to short production time, homogeneous particle composition, and one step production method. The main preparation conditions are the nature of the precursor and solvents which influence film properties profoundly. The present paper reports preparation, investigations and characterization of cadmium oxide thin films deposited by spray pyrolysis technique at various substrate (deposition) temperatures and spray time.

## 2. Experimental

Pure CdO thin films have been prepared by spraying a solution of 0.1 M composed of cadmium acetate dissolved in a mixture of methanol and bidistilled water (1:1). Methanol is used to complete oxidation and enhance the spray droplet mobilities. The spray set-up was described elsewhere (Afify et al., 2005). The spray parameters are varied alternatively until a film with apparent homogenous feature is obtained. The films are deposited on a cleaned glass (25 mm × 12.5 mm × 2 mm) substrate at different substrate temperature and different spray time. The substrate temperature is varied from 300 °C to 450 °C while the other spray parameters are kept at their optimum values. Substrate temperature was controlled by a chrome-nickel thermocouple fed to a temperature controller with an accuracy of ±2 °C. The carrier gas (air) flow rate is 20 L/min, the solution flow rate is 1.32 ml/min and the nozzle to substrate distance is 35 cm. When the droplets of sprayed solution reached the hot substrate, owing to the pyrolytic decomposition of solution, a well adherent, pinhole free, uniform yellowish colored films of cadmium oxide are formed on the substrate surface according to the following reaction (Seo, 2004; Uplane et al., 2000):



Thickness of the film is measured by stylus method. X-ray diffraction (XRD) is carried out using Philips (PW-1710) diffractometer using Cu K $\alpha$  radiation source by varying diffraction angle,  $2\theta$  from 30° to 80° by step width of 0.02°. Specular transmission and reflection are carried out using Hitachi double beam spectrophotometer (UV-Vis-NIR) model 330 in the wavelength range 250–2500 nm. The sheet resistance is measured by using two probes method. The film topography is elucidated by atomic force microscope (AFM). XRD line broadening analysis was conducted at a slow scan of 0.01° per second for the highly intense planes to calculate the crystallite size and strain. This work is focus on the substrate temperature dependent film structure and related physical properties such as particle size,  $E_g$ , sheet resistance and surface roughness.

## 3. Results and discussion

### 3.1. Structure properties

#### 3.1.1. Effect of film thickness

XRD patterns are used for structure analysis of the investigated CdO films. The XRD patterns of CdO films deposited at constant substrate temperature (425 °C) and different spray time are shown in Fig. 1. Five salient peaks are observed indicating a polycrystalline nature of the deposited films. Two peaks are corresponding to (111) and (200) high intensity while the other three corresponding to (220), (311), (222) have weak intensity and show slight change with spray time. The main growth plane (111) at short spray time is changed to be (200) at longer spray time which means that the film growth is thickness dependent. The inter plane spacing ( $d$ ) for these peaks is calculated and indexed to [JCPD; 05-0640] for standard bulk CdO. The obtained XRD patterns are matched well with bulk CdO has cubic structure and lattice parameter  $a = 4.690 \text{ \AA}$  which is in good agreement with the calculated values ranged from 4.646 and 4.690 Å for investigated samples (Gurumurugan et al., 1995).

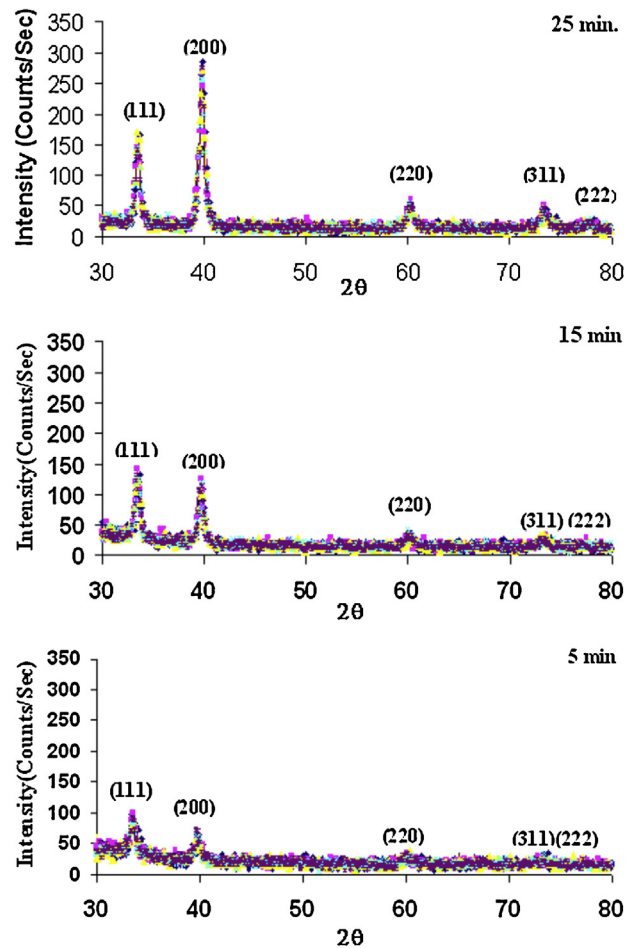


Fig. 1. X-ray diffraction pattern for CdO thin film prepared at substrate temperature 425 °C and different spray time; 5 min, 15 min, 25 min.

### 3.1.2. Effect of substrate temperature

**3.1.2.1. XRD study.** X-ray diffraction patterns for CdO thin films prepared at different substrate temperature and 25 min spray time are shown in Fig. 2. At constant spray time and variable substrate temperature it is expected that the change in film thickness will be unreasonable at low substrate temperature as compared with that at higher substrate temperature.

This may be due to the film growth is dominant at low substrate temperature while the formed film evaporation at higher substrate temperature is a considerable factor actuating the reduction in the film thickness. This explain the lower intensity of (111) and (200) at 450 °C. The XRD patterns do not show significant peak shift but show noticeable broadening. This indicates the presence of microstrain rather than macrostrain. The intensity of (200) increases as the substrate temperature increased. In spite of the (111) intensity is nearly constant. This means that the film growth via (200) is temperature dependent. However, with increase in substrate temperature, the intensity of peaks increased, indicating better crystallinity and grain size.

XRD peak profile for the high intense (111) and (200) peaks is carried out for the investigated samples, to determine well the broadening ( $\beta$ ) which is the main parameter to calculate the crystallite size. A representative one for CdO thin film deposited at substrate temperature 425 °C and spray time 25 min is shown in Fig. 3. The crystallite size and the microstrain are determined by using Williamson–Hall equation (Jeyaprkash et al., 2011):

$$\beta \cos \theta = \frac{k\lambda}{D} + \xi \sin \theta \quad (2)$$

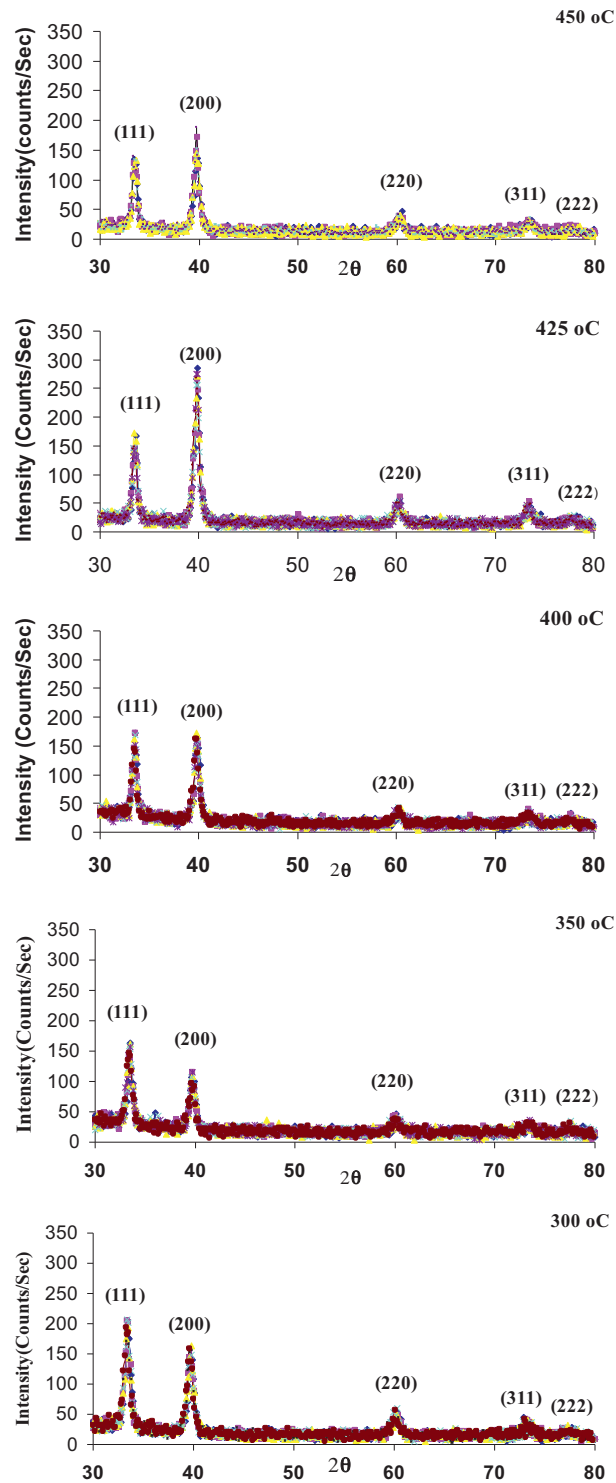


Fig. 2. X-ray diffraction pattern for CdO thin film prepared a different substrate temperature, 300 °C, 350 °C, 400 °C, 425 °C and 450 °C and spray time 25 min.

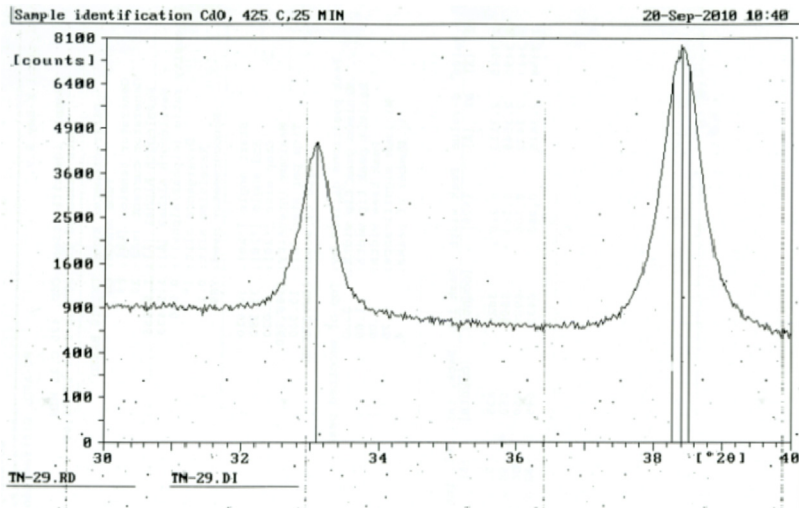


Fig. 3. X-ray broadening for CdO thin film deposited at substrate temperature 425°C and spray time 25 min

**Grain size of plane (111) and (200) for CdO thin film prepared at different substrate temperature and 25 min**

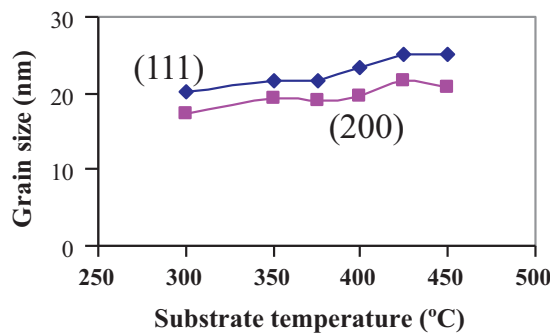


Fig. 4. Grain size of CdO thin films prepared at different substrate temperature.

where  $D$  is the crystallite size,  $K$  is a constant taken to be 0.94,  $\beta$  is the corrected full width at half maximum (FWHM) by subtracting the predetermined  $\beta$  for the instrument and  $\lambda$  is the wave length of the X-rays. Plotting  $\beta \cos \theta$  with a  $\sin \theta$  straight line is produced its slope is a measure for the strain ( $\xi$ ) while the intercept with  $Y$  axes gives the grain size. The variation of grain size with substrate temperature is shown in Fig. 4. It seems that the crystallite size calculated from (111) and (200) peaks nearly have the same behavior with substrate temperature. Also, the observed change is not reasonable. The variation of microstrain with substrate temperature is shown in Fig. 5.

It is clearly observed that microstrain changes is noticeable. The microstrain is higher for the film deposited at low temperature and attains lower values at high temperature.

**3.1.2.2. Surface morphology.** Fig. 6A and B shows the two and three-dimensional AFM images of the CdO thin films deposited at spray time 25 min and substrate temperatures of 300, 350, 375 and 400 °C. The surface morphology of the CdO thin films as observed from the AFM micrographs proves that the grains are uniformly distributed within the scanning areas (5  $\mu\text{m} \times 5 \mu\text{m}$ ) and (50  $\mu\text{m} \times 50 \mu\text{m}$ ) with individual columnar grains extending upwards. The image show closely packed uniform spherical shape grains. Also, as the substrate temperature increase, the grains increased in size. The roughness for samples deposited at 300, 350, 375 and 400 °C oxide is measured and found to be 66.84, 83.32, 70.90 and 66.23 nm respectively as shown in Fig. 7.

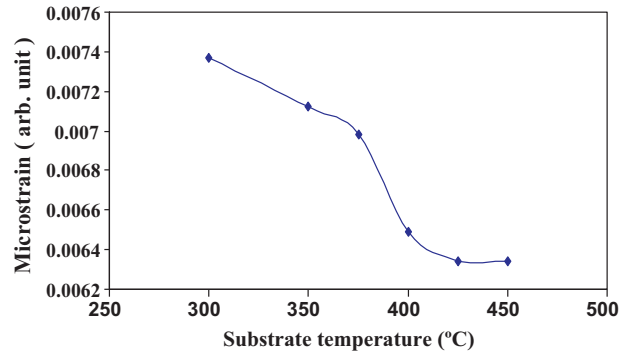


Fig. 5. Microstrain vs substrate temperature for CdO thin films deposited at 25 min spray time.

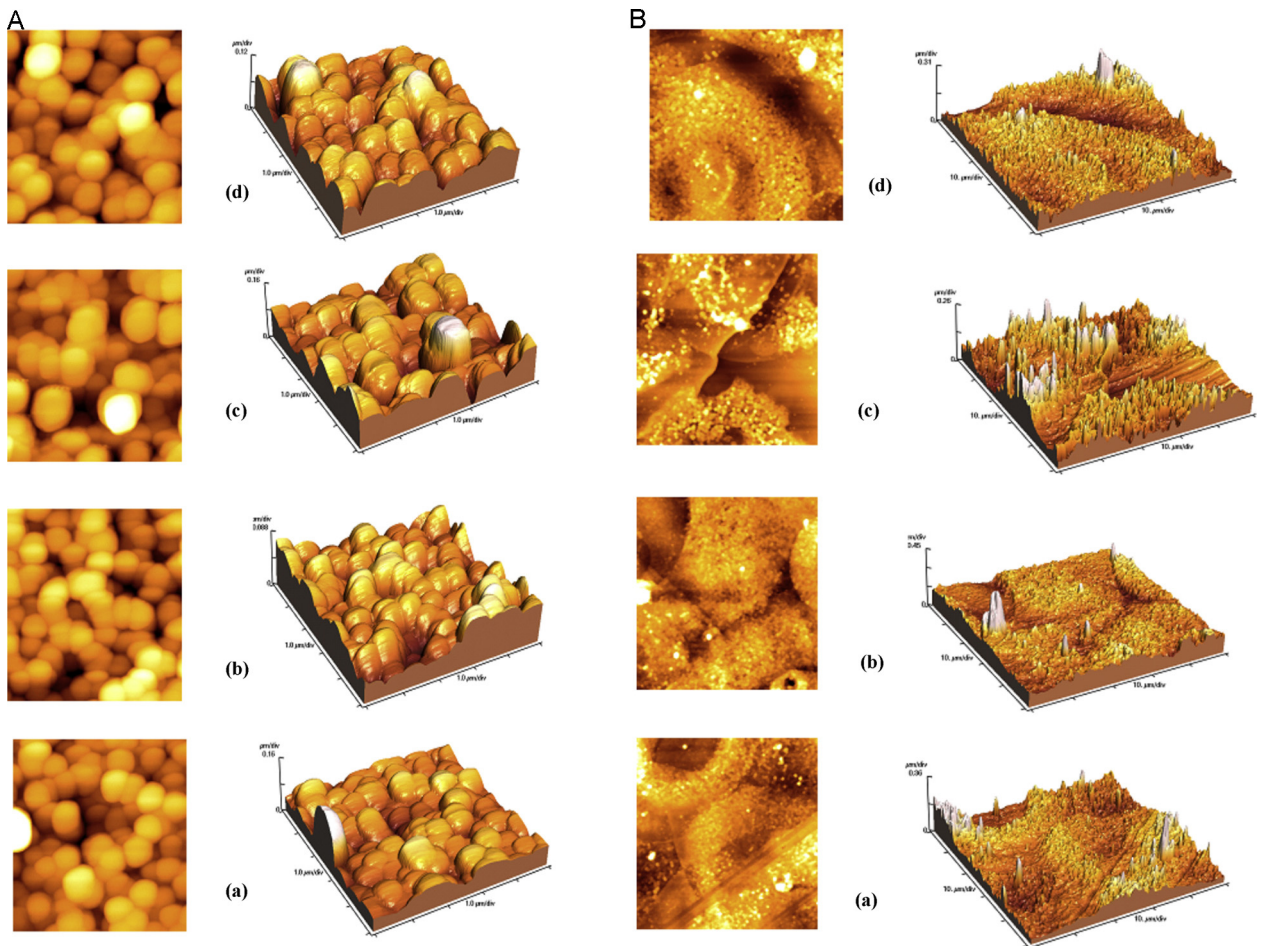


Fig. 6. (A) Two and three dimensions AFM images for scanning area ( $5\ \mu\text{m} \times 5\ \mu\text{m}$ ) of CdO thin films deposited at spray time 25 min and different substrate temperatures (a)  $300\ ^\circ\text{C}$ , (b)  $350\ ^\circ\text{C}$ , (c)  $375\ ^\circ\text{C}$ , (d)  $400\ ^\circ\text{C}$ . (B) Two and three dimensions AFM images for scanning area ( $50\ \mu\text{m} \times 50\ \mu\text{m}$ ) of CdO thin films deposited at spray time 25 min and different substrate temperatures (a)  $300\ ^\circ\text{C}$ , (b)  $350\ ^\circ\text{C}$ , (c)  $375\ ^\circ\text{C}$ , (d)  $400\ ^\circ\text{C}$ .

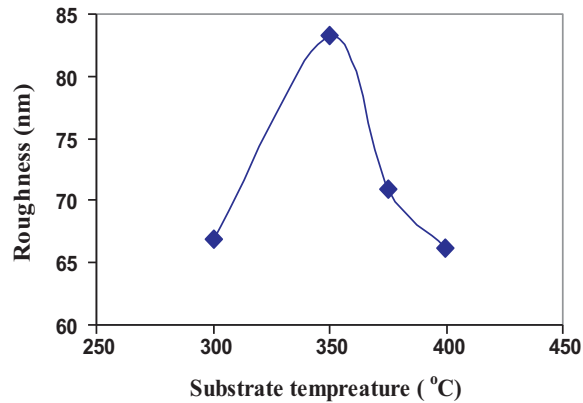


Fig. 7. Surface roughness of CdO thin films deposited at 300 °C, 350 °C, 375 °C and 400 °C and 25 min spray time.

### 3.2. Optical properties

#### 3.2.1. Effect of substrate temperature

The variation of transmission spectra of CdO thin films prepared at spray time 25 min and different substrate temperature is shown in Fig. 8. All samples show an abrupt change in transmission which indicates direct transition and good crystallinity. The transparency of films is increased up to 80% with increasing substrate temperature in wavelength ranged from 450 nm to 1000 nm. Also, a broad absorption is matched in the range 1500–2000 nm. This band could be attributed to the increase in free carrier concentration which confirmed by the reasonable decrease in the film sheet resistance (as shown in Fig. 11). The absorption coefficient ( $\alpha$ ) is determined from the transmittance data using this relation  $\exp(-\alpha d) = T$ , where  $d$  is the thickness of the film and  $T$  is the transmittance. The estimated  $\alpha$  values are ranging from  $1.87$  to  $4.33 \times 10^4 \text{ cm}^{-1}$  at wavelength 500 nm. For a direct transition, the absorption coefficient is related to the band gap by the following equation as (Seo, 2004; Murthy and Rao, 1999):

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \tag{3}$$

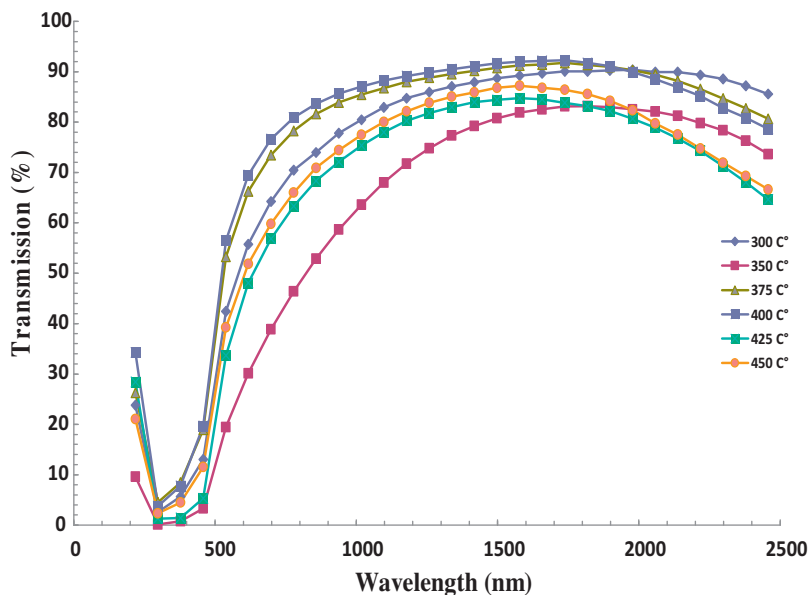


Fig. 8. Optical transmission of CdO thin films prepared at spray time 25 min and different substrate temperatures, 300 °C, 350 °C, 375 °C, 400 °C, 425 °C and 450 °C.

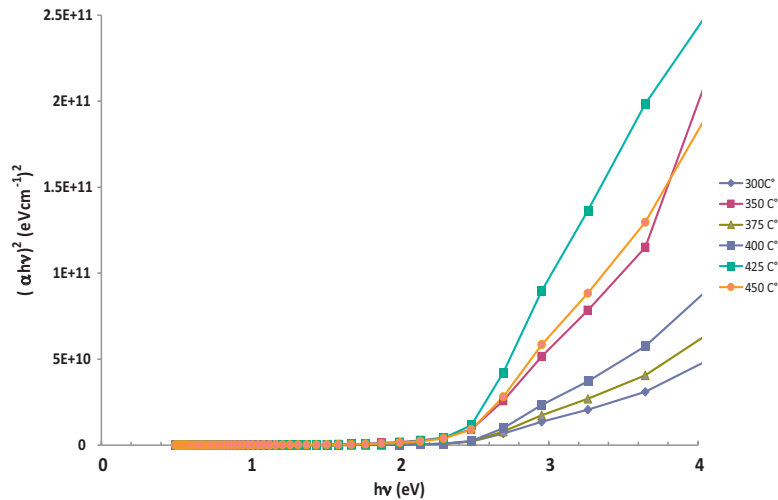


Fig. 9. Plots of  $(\alpha hv)^2$  vs photon energy ( $h\nu$ ) for CdO films deposited at spray time 25 min and different substrate temperature.

where  $A$  is constant,  $h\nu$  is the energy of the incident light and  $E_g$  is the CdO film energy gap. The plot of  $(\alpha hv)^2$  vs  $h\nu$  for CdO thin films prepared at spray time 25 min and different substrate temperature is shown in Fig. 9. The band gap  $E_g$  is determined by extrapolating the linear portion of  $(\alpha hv)^2$  vs.  $h\nu$  plot to  $h\nu$  axis. The obtained band gaps values are found to be ranged from 2.45 to 2.55 eV which are in good agreement with the reported data which ranged from 2.35 up to 2.5 eV (Lokhande and Uplane, 2001). This change in optical band gap may be attributed to change in crystallite size with temperature (Lokhande and Uplane, 2001).

### 3.2.2. Effect of spray time

The transmission spectra for CdO films prepared at 425 °C and different spray time (from 5 min to 30 min) is shown in Fig. 10. The observed distinct reduction of transmittance with increasing spray time can be attributed to the increase of film thickness. The transmission is ranged from 80% up to 60% with increasing the spray time from 5 min to 30 min. The obtained energy gap as calculated previously is found to be ranged from 2.4 to 2.45 eV which is nearly the same as that obtained for samples prepared at different substrate temperature. This means that the energy gap for the prepared CdO film samples is independent on substrate temperature and spray time.

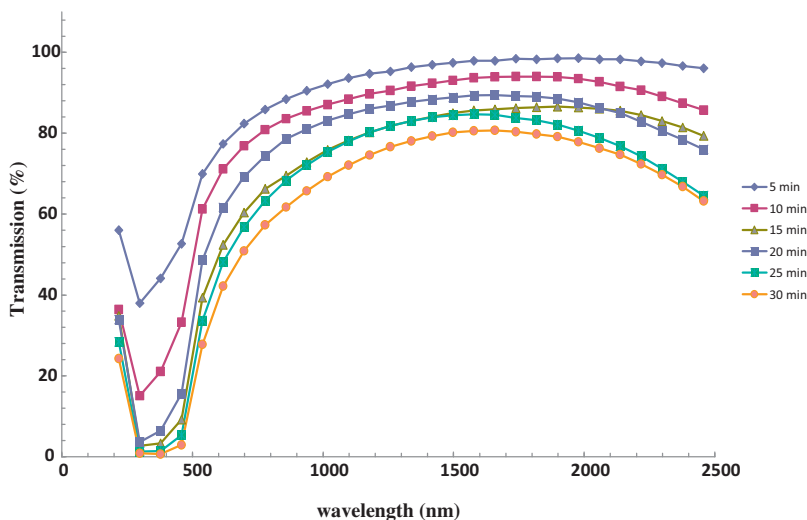


Fig. 10. Optical transmission of CdO thin films prepared at substrate temperatures, 425 °C and different spray time 5 min, 10 min, 15 min, 20 min, 25 min and 30 min.



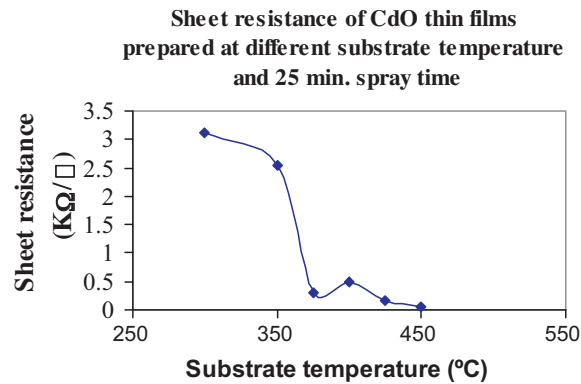


Fig. 11. Sheet resistance of CdO thin film deposited at different substrate temperatures and 25 min spray time.

### 3.3. Electrical properties

Sheet resistance of CdO thin films was measured as a function of substrate temperature in the range of 300 °C to 450 °C using two-probes method. Fig. 11 shows the variation of sheet resistance with substrate temperature, it is observed that, sheet resistance is reduced with increasing deposition temperature due to increase in free carrier concentration. The films deposited at a substrate temperature of 300 °C were found to be highly resistive. With the increase in substrate temperature, the sheet resistance of the films was found to decrease to a minimum value of 66 Ω/□ at 450 °C.

## 4. Conclusion

CdO thin films with good adherence, homogeneity and pin free were obtained using spray pyrolysis technique. XRD studies shows that films are polycrystalline with a cubic structure. Energy gap in the range 2.45–2.55 eV is obtained. It is found that film deposited at 425 °C substrate temperature and spray time 25 min exhibits a better structural, optical and electrical characteristic.

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