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Substrate Temperature Effects on the Nanostructural and Optical Parameters of CdO Thin Films

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ABSTRACT

CdO thin films were prepared by the chemical spray pyrolysis technique under different glass substrate temperature (300, 350, 400, 450 and 500 °C). XRD anaylsis confirms the cubic polycrystalline nature of the deposited thin films with a preferred orientation along (111) plane. The average crystallite size suggests the formation of nanostructure of the deposited films. The average particle size obtained by AFM assure the existence of nanostructure. The values of the energy gap obtained from the derivative of absorbance with respect to the incident photon energy were found to increase from 2.610 nm to 2.666 nm as the substrate temperature increase.the values of refractive index and extinction coefficient were decreased by the increasing substrate temperature.

Keywords: chemical spray pryrolysis, CdO thin films, structural parameters, optical parameters

1. INTRODUCTION

Metal oxide especially cadmium oxide has gained great importance by many researchers [1-6], due its unique properties like wide band gap, high transparencies in the visible and near infrared regions, good luminescence and low resistivity [7,8]. Owing to these properties, CdO was used in many applications like solar cells [9], phototransistors [10], photodetectors [11], Gas sensors [12], nanodevices [13], heat mirrors [14] photovoltaic cells [15], and nonlinear optics [16].

Different experimental methods have been adopted to prepare cadmium oxide such as vacuum evaporation [17], sol-gel spin coating technique [18], pulsed laser deposition [19,20], Successive Ionic Layer Adsorption and Reaction (SILAR) [21], metallo-organic chemical vapor deposition (MOCVD) [22], pulsed filtered cathodic arc deposition (PFCAD) [23], radio-frequency sputtering [24] and spray pyrolysis [25, 26]. The aim of this work is to prepare CdO at different substrate temperature and study some structural and optical properties during substrate temperature variations.

2. EXPERIMENTAL DETAIL

CdO thin films were prepared on glass substrates by well known and cheap chemical spray pyrolysis method. The substrate was subjected to clean process inception from rinse with re-distilled water, placed in an ultrasonic bath filled with ethanol absolute, dunk in acetone and finally rinse with re-distilled water, dried with hot air. An aqueous solution of 0.1 M $Cd(CH_3COO)_2 \cdot 2H_2O$ dissolve in 100 ml re-distilled water, were used as a source of cadmium.

The optimum preparing conditions were arrived at the following: the substrate temperature was varied from (300-500 °C), distance between nozzle and substrate was kept at 30 cm, spray rate was 5 ml/min, spray time was fixed at 9 s followed by 90 s waiting to avoid excessive cooling and to prevent glass cracking, during waiting the samples were rotated at the heater in order to obtain a homogeneous films and the nitrogen atmosphere into the chamber was operated at a flow rate of 6×10^3 cm^3/min.

The film thickness was obtained by gravimetric method and their values was around 250 ±25 nm. Optical measurments were carried out using a double beam spectrophotometer supplied by (Schimadzu UV probe 1650 Japan) in the wavelength range (300-900) nm. XRD measurements were performed using (Shimadzu XRD -6000) with a Cu K_α (λ = 1.541 Å) monochromatic source. Surface topography was carried out using atomic force microscopy AFM using digital instruments, Inc. nanoscope III and dimension 3100.

3. RESULTS AND DISCUSSION

The XRD analysis revealed that all the deposited thin films with different substrate temperature were polycrystlline,cubic These results was checked according to JCPDS 5-0640. Fig. 1 depicts XRD patterns for CdO with different substrate tempertures. The preferred orientation for all the samples were (111) planned, other peaks concerning (200), (220), (311) and (222) are also noticed.These results were in good agreement with the results obtained by Sahin *et al*. [27].

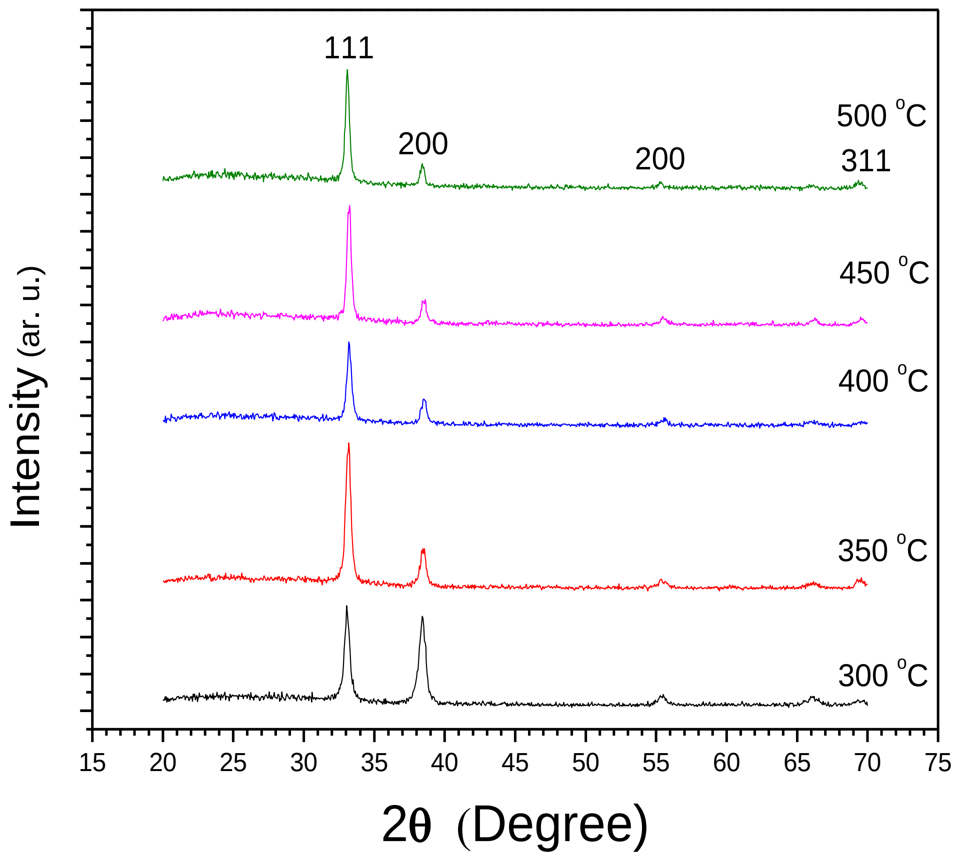


Fig. 1. XRD pattern of CdO thin films deposited at different substrate temperature.

The average crystallite size was checked utilizing a Scherrer formula [28]

$$D_{av} = \frac{0.9\,\lambda}{\beta\, cos\theta} \qquad .....(1)$$

where β is the full width at half maximum in radian, λ is the wavelength of the incident X-Rays, θ is Bragg's angle.

It can be seen from Table 1 that the average crystallite size increases with the increasing with substrate temperature and their values was in the range of (17.447-25.31 nm) indicate the formation of nanostructure. The increase of average crystallite size could be attributed to increases in crystal disorder by increasing the substrate temperature and a decrease in dislocation density (inverse square of average crystallite size) as can be seen from Table 1 these results are in good agreement with the results obtained by Santos *et al.* [29]. The micro strain (ε) that occurs in the thin films might be obtained from the following relation [30]

$$\epsilon = (\,\beta\, cot\theta)/4 \quad ....(2)$$

The values of microstrain were listed in Table 1. These values decreased with the increasing in substrate temperature ,which again confirm the increase in order of crystallinity by decreasing the value of microstrain.the no. of crystallites per unit area was calculated using the following formula [31]

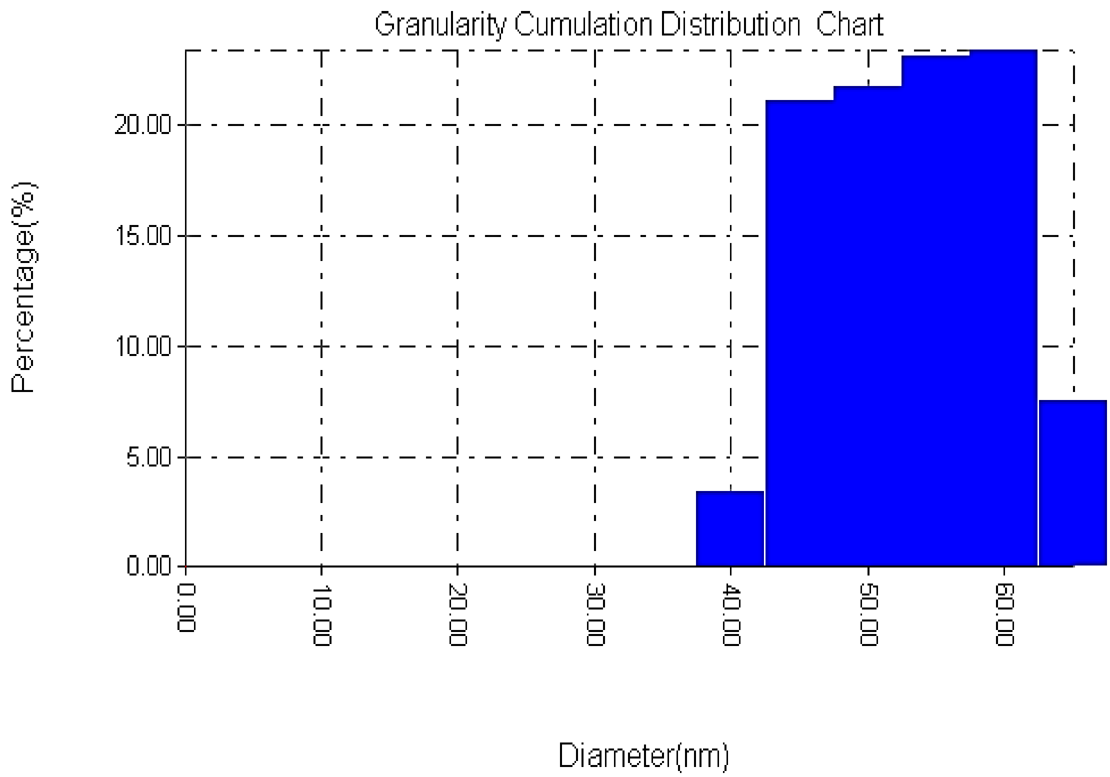
$$N_o = \frac{t}{D_{av}^3} \qquad \text{........(3)}$$

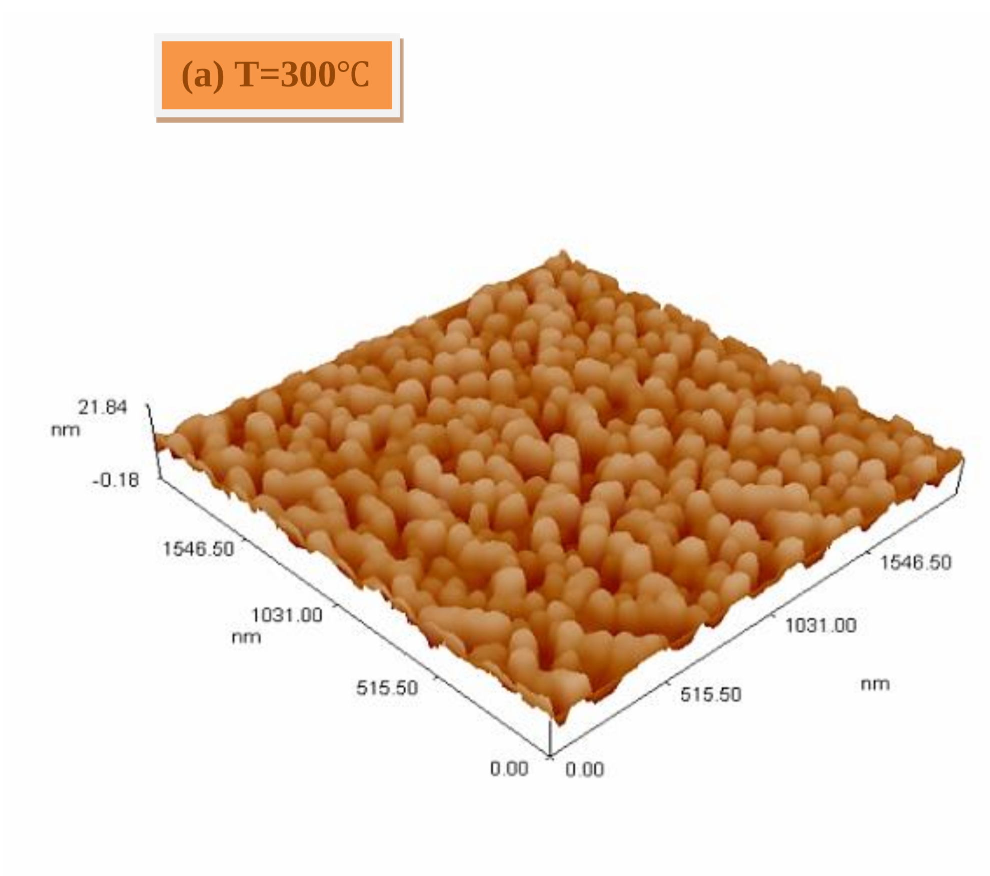
where t is the film thickness, their values are listed in Table 1 and shows a decrease in its value as the substrate temperature increase

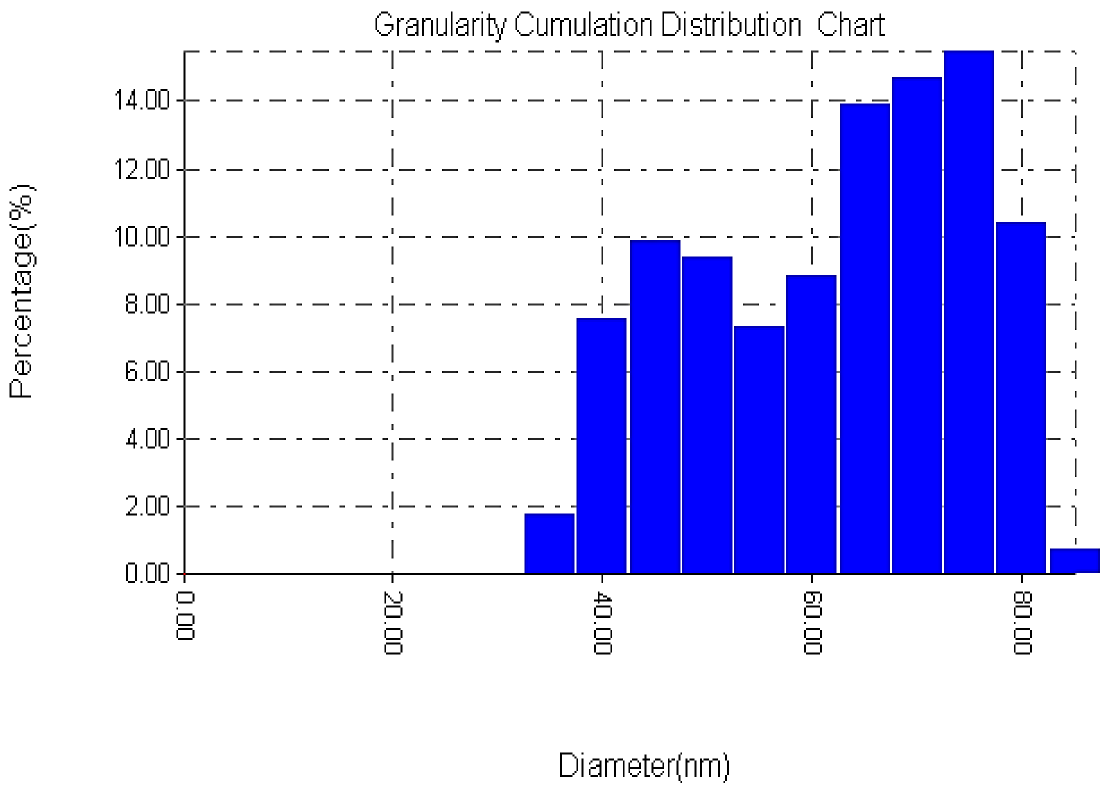
Table 1. The structural parameters of CdO thin films deposited at different substrate temperatures.

Sample	CdO at T = 300 °C	CdO at T = 350 °C	CdO at T = 400 °C	CdO at T = 450 °C	CdO at T = 500 °C
hkl	111	111	111	111	111
2θ(deg)	33.0877	33.1722	33.2396	33.2302	33.1158
d(Å)	2.70519	2.69849	2.69317	2.69391	2.70296
FWHM(deg)	0.46250	0.44980	0.37920	0.36110	0.31890
Lattice Constant($a_\circ$)(Å)	4.685	4.673	4.664	4.665	4.681
D_{av}(nm)	17.447	17.94	21.29	22.35	25.31
ε	0.00679	0.00658	0.00554	0.00527	0.00454
δ $(nm)^{-2}$	0.00328	0.00310	0.00220	0.00200	0.00156
$N_\circ$ $(nm)^{-2}$	0.04707	0.04329	0.02590	0.02239	0.01541

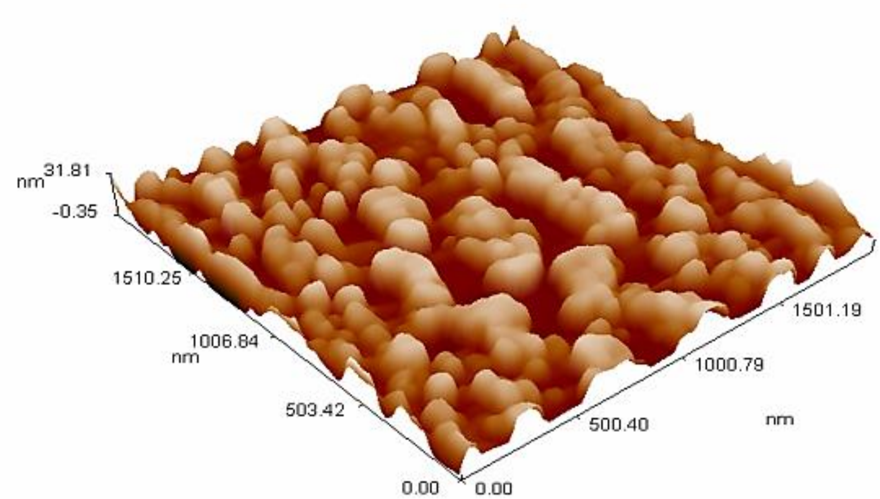
Fig. (2) depicts the AFM micrograph of CdO thin films grown on glass substrates with various substrate temperatures, the measurement was carried out on an area of $2\mu m - 2\mu m$ dimensions.

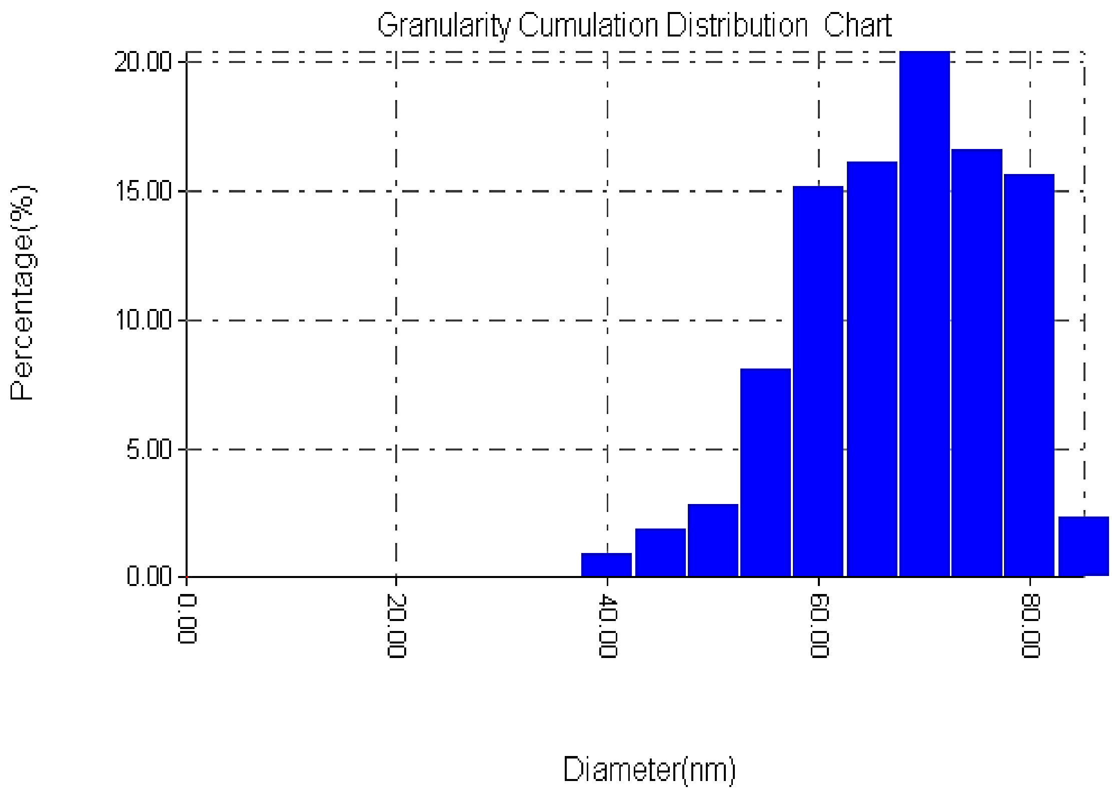

Granularity Cumulation Distribution Chart
Percentage(%)
20.00
15.00
10.00
5.00
0.00
0.00
10.00
20.00
30.00
40.00
50.00
60.00
Diameter(nm)


(a) T=300℃
21.84
nm
-0.18
1546.50
1031.00
nm
515.50
0.00
0.00
515.50
1031.00
1546.50
nm

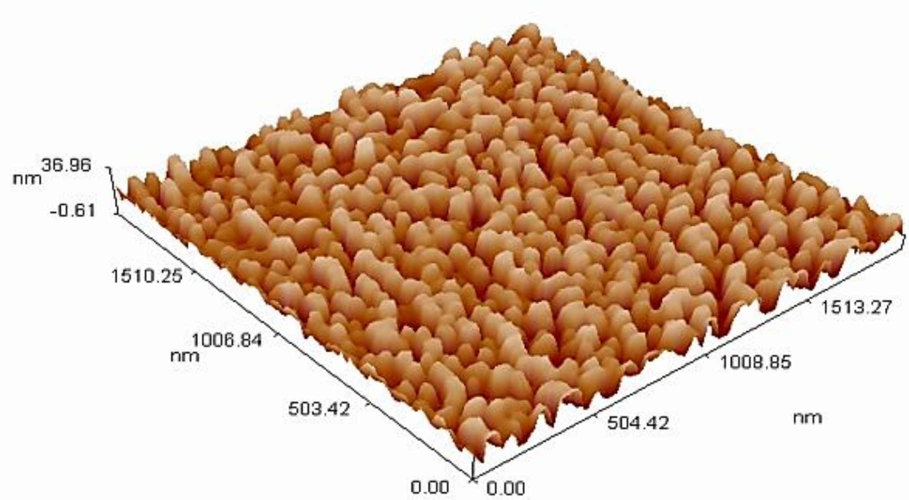

Granularity Cumulation Distribution Chart
Percentage(%)
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0.00
20.00
40.00
60.00
80.00
Diameter(nm)

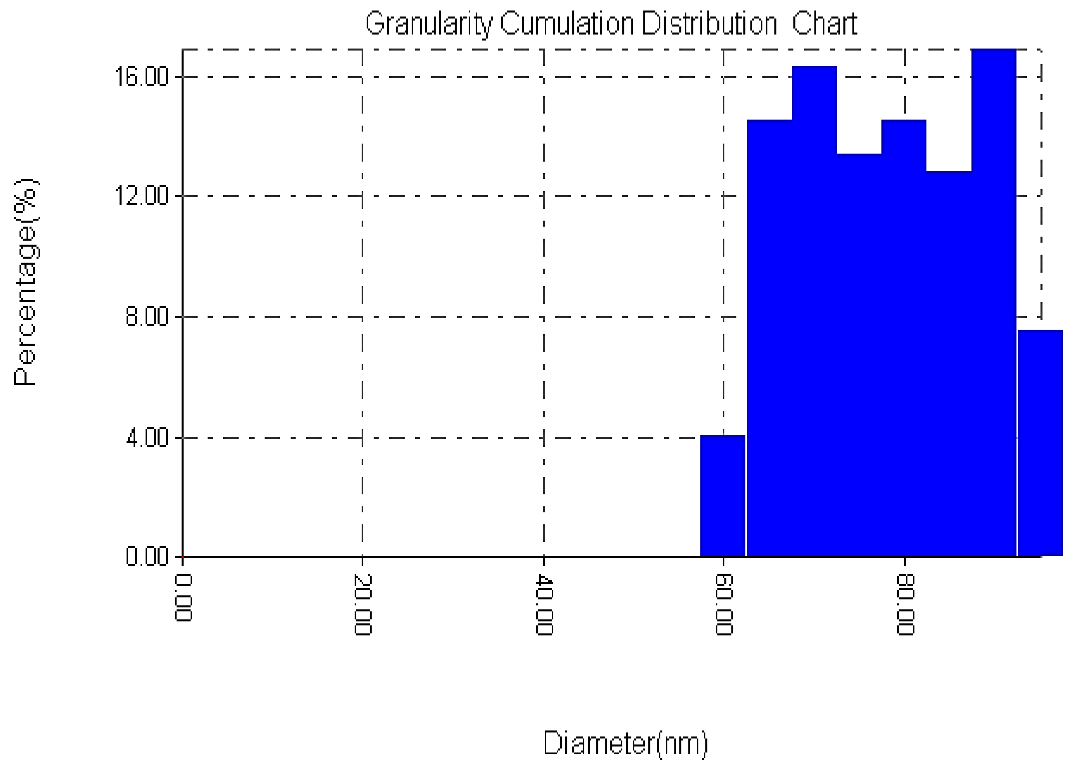
(b) T=350℃

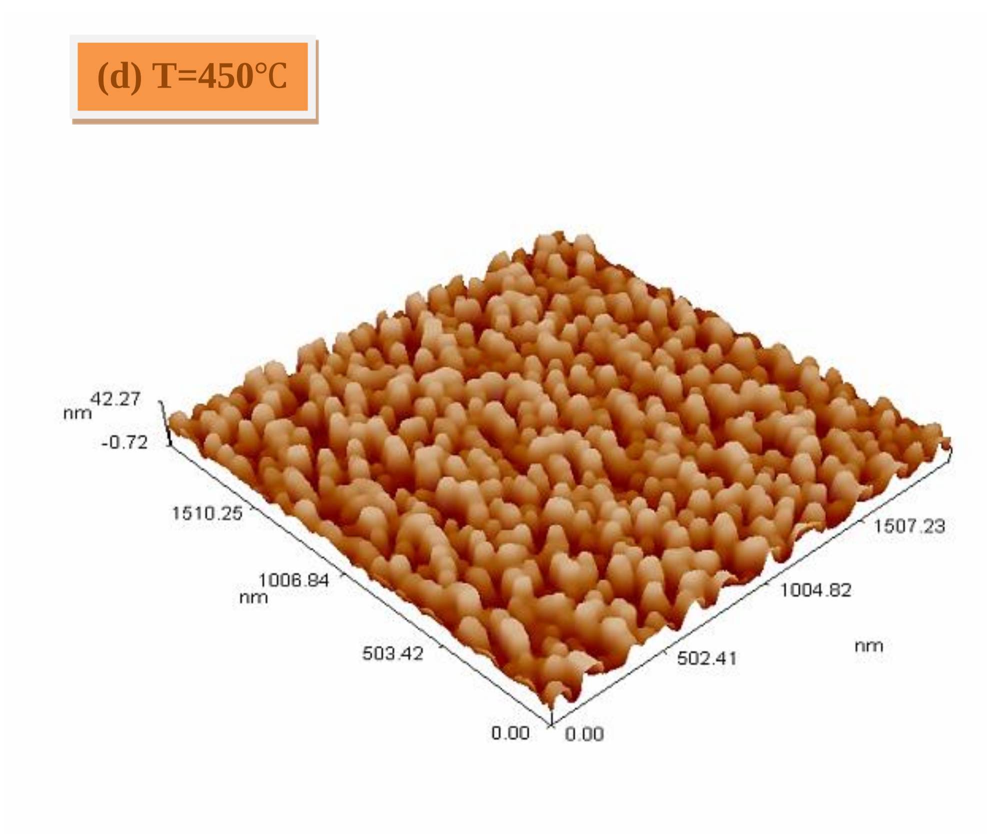

nm
31.81
-0.35
1510.25
1006.84
nm
503.42
0.00
0.00
500.40
1000.79
1501.19
nm

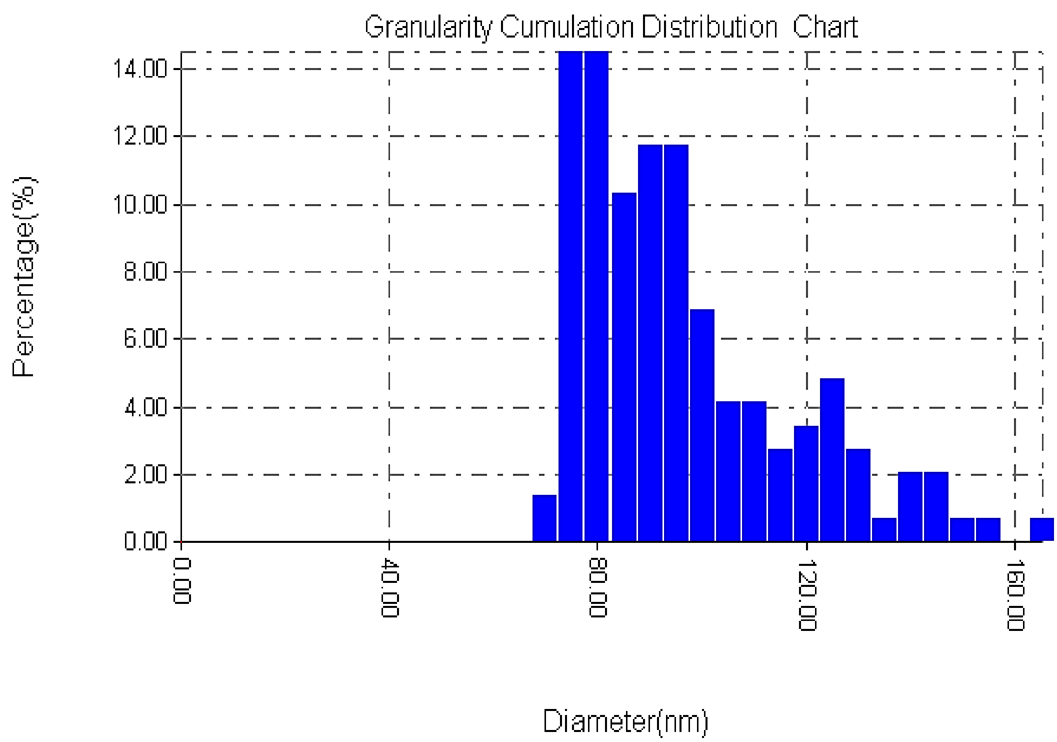

Granularity Cumulation Distribution Chart
Percentage(%)
20.00
15.00
10.00
5.00
0.00
0.00
20.00
40.00
60.00
80.00
Diameter(nm)

(c) T=400℃


nm
36.96
-0.61
1510.25
1006.84
nm
503.42
0.00
0.00
504.42
1008.85
1513.27
nm


Granularity Cumulation Distribution Chart
Percentage(%)
16.00
12.00
8.00
4.00
0.00
0.00
20.00
40.00
60.00
80.00
Diameter(nm)


(d) T=450℃
nm
42.27
-0.72
1510.25
1006.84
nm
503.42
0.00
0.00
502.41
1004.82
1507.23
nm



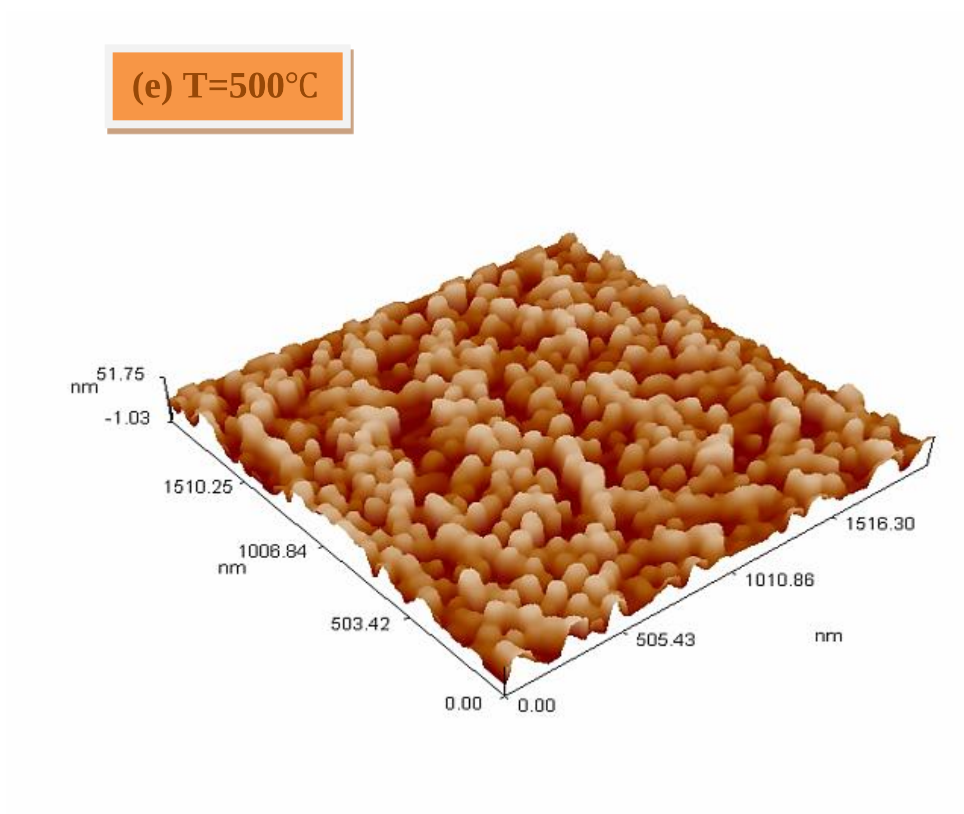


Fig. 2. AFM images of CdO thin films with different substrate temperatures.

The surface roughness and the root mean square value shows the same tendency that their values were increased as the substrate temperature increase as illustrated in Table 2. The particle size diameter obtained by AFM confirms the existence of nanostructures shown in Table 2, these values are much higher as compared with the values obtained from XRD. This comes from the fact that XRD gives the average crystallite size while AFM offer the agglomeration of the particle.

Table 2. AFM parameters of CdO thin films with different substrate temperatures.

Sample	surface roughness(nm)	RMS(nm)	D_{av}(nm)
CdO (300 °C)	2.43	2.85	60.00
CdO (350 °C)	5.4	6.21	75.00
CdO (400 °C)	5.54	6.45	80.00
CdO (450 °C)	6.8	7.93	90.00
CdO (500 °C)	8.22	9.48	80.00

Fig. 3 shows the absorbance versus wavelength,it can be clearly seen that the absorbance of the deposited thin films decreases with the increase in substrate temperature. The absorption edge was shifted toward lower wavelength (blue shift). This decrease in absorbance may be attributed to the particle size effect (quantum confinement). The derivative of the absorbance with respect to energy was displayed in in Fig. 4 which, shows an increase in the value of the optical energy gap with the increase in substrate temperature. This increment could be attributed to Burstein-Moos effect.

One of the most important parameters is the refractive index, which, gives us an information about local field ,electronic polarzability and for obtaining the color density inside the film. The refractive index was calculated by the following relationship [32]:

$$R = \frac{(n-1)^2 + k_o}{(n+1)^2 - k_0} \quad ....(4)$$

The extinction coefficient could be calculated using the following relation [33]:

$$k = \frac{\alpha \lambda}{4 \pi} \quad ....(5).$$

Fig. 6 shows the variation of extinction coefficient with substrate temperature, their values were decreasing as the substrate temperature increase, this behavior may be due to change in the crystallite size of these films [33].

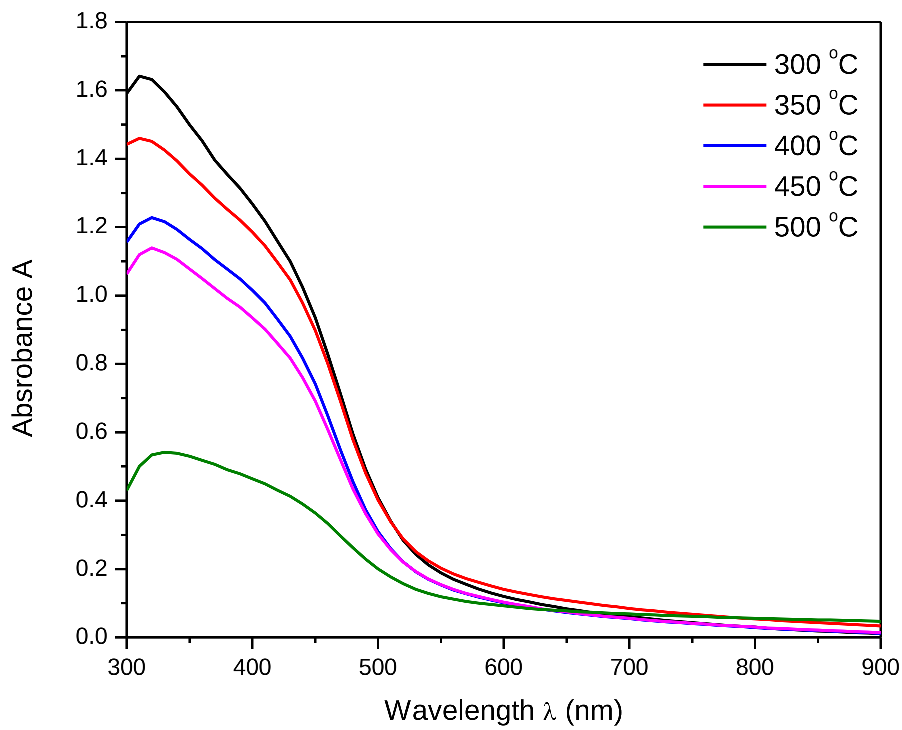
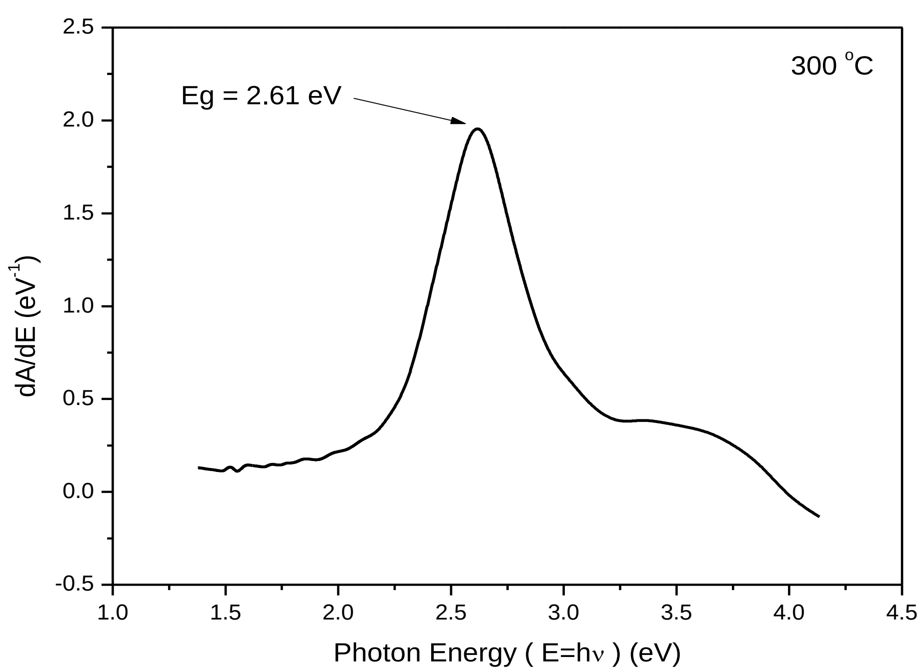
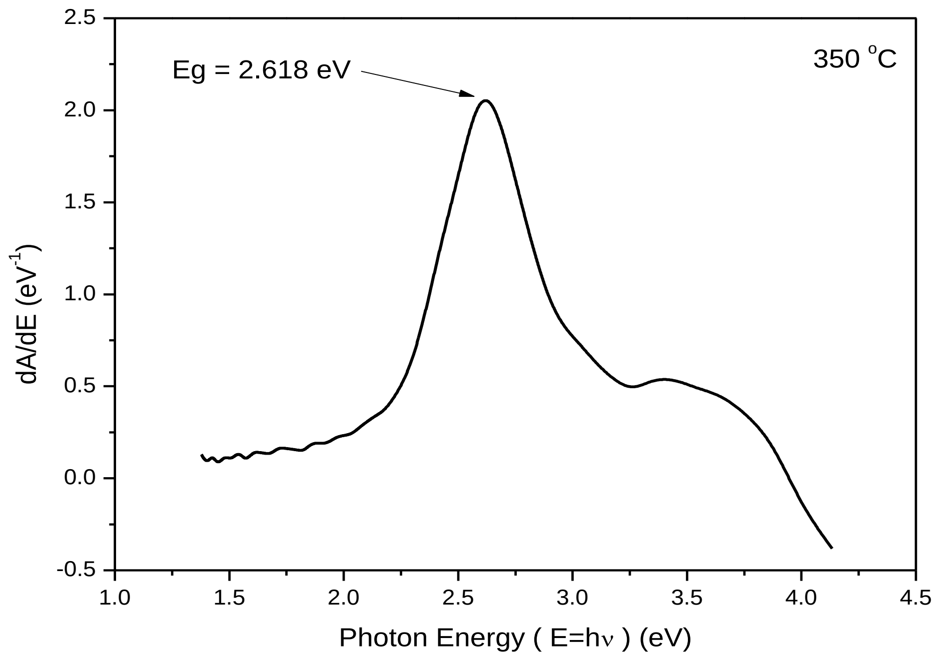
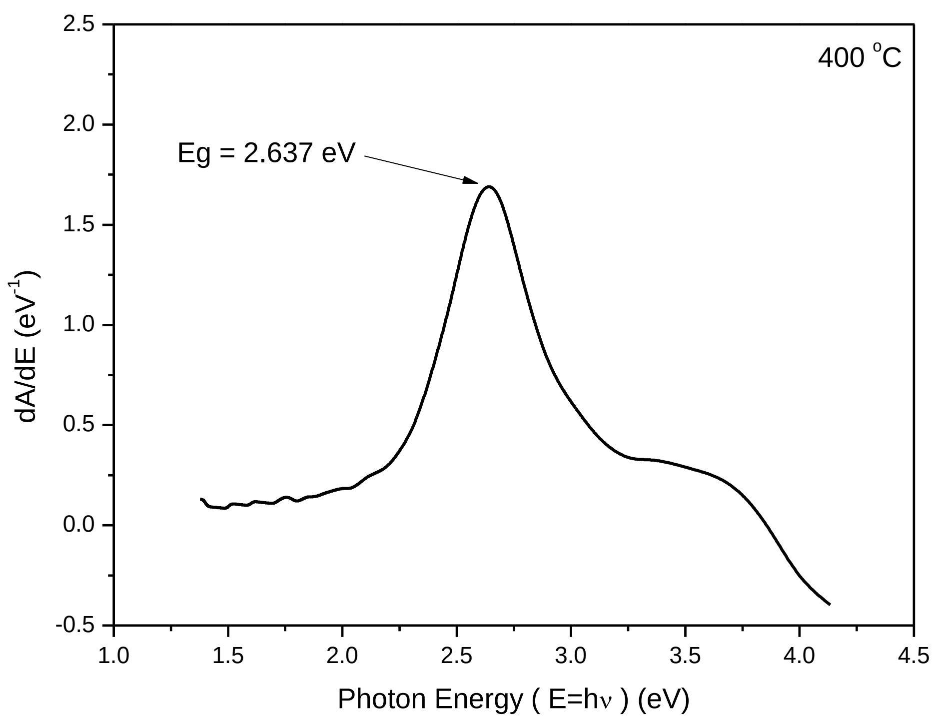
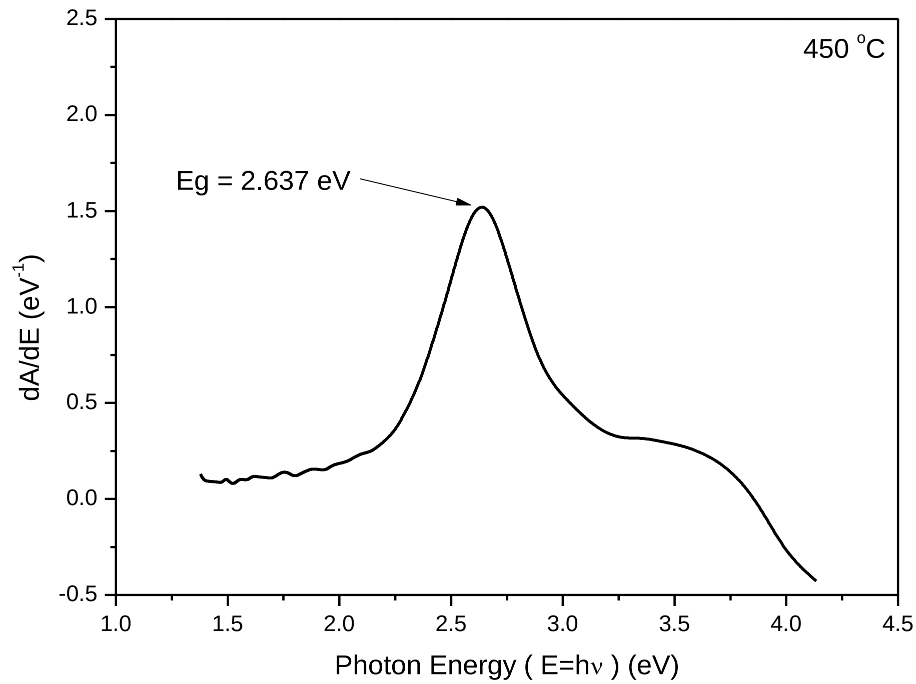


Fig. 3. Absorbance versus wavelength of CdO thin films deposited at different substrate temperatures.




350 °C
Eg = 2.618 eV
dA/dE (eV-1)
Photon Energy (E=hν) (eV)
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5


400 °C
Eg = 2.637 eV
dA/dE (eV-1)
Photon Energy (E=hν) (eV)
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5



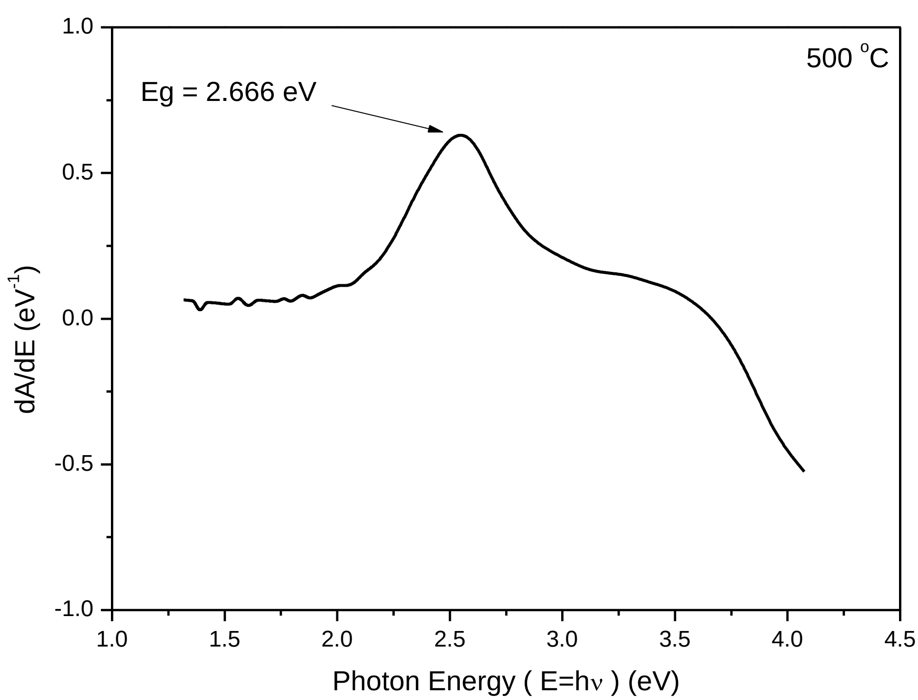


Fig. 4. dA/dE versus photon energy for CdO thin films deposited at different substrate temperatures.

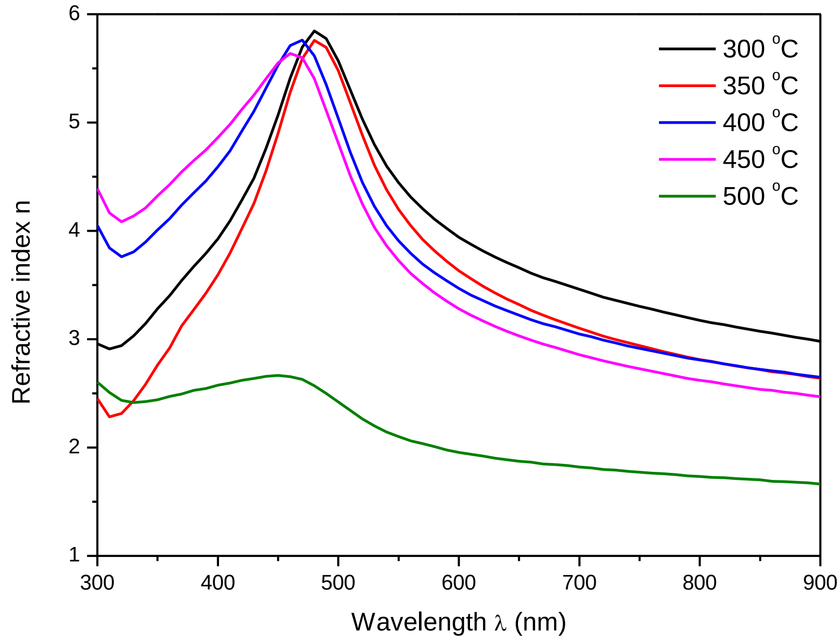


Fig. 5. Refractive index versus wavelength of CdO thin films deposited at different substrate temperatures.

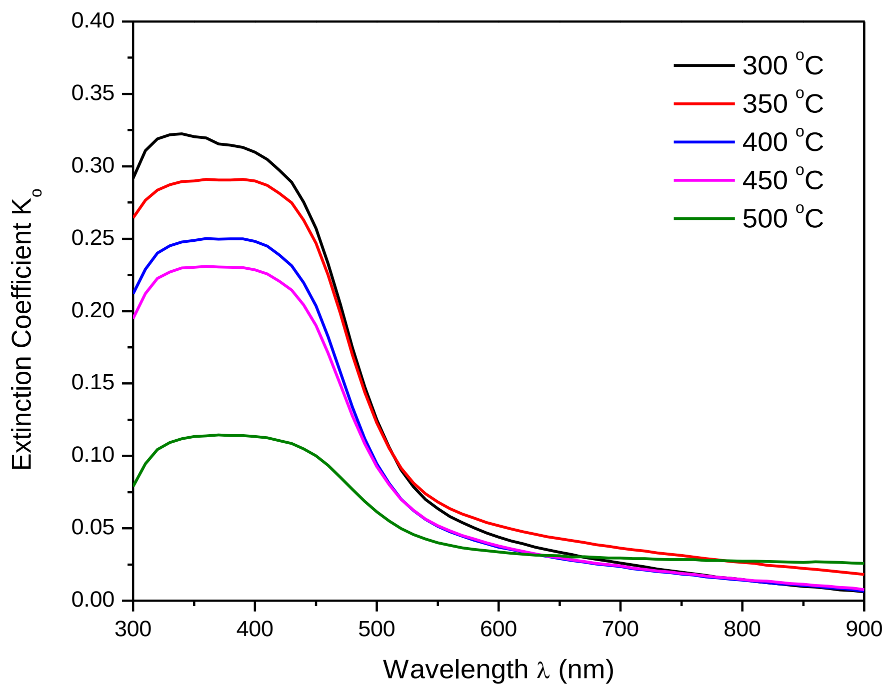


Fig. 6. Extinction coefficient versus wavelength of CdO thin films deposited at different substrate temperatures.

4. CONCLUSION

CdO thin films were fabricated successfully utilizing chemical spray pyrolysis method. XRD patterns reveal that all the deposited films were polycrystalline having a preferred orientation along (111). AFM micrographs confirms the presence of nanostructure thin films. The optical energy gap was increased with the increasing of substrate temperature while, refractive index and extinction coefficient show a decrease in their value with the increase of substrate temperature.

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