



Effect of Thickness on Structural and Optical Properties of CdO Thin Films Prepared by Chemical Spray Pyrolysis Method

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Abstract

Cadmium oxide thin films have been deposited on glass substrates at 400°C by using chemical spray pyrolysis technique show spray time dependence growth when the substrate temperature is constant. Thin films have different thickness of about (200,225,250) nm measured by gravimetric method. The XRD results presented that the nature of the films are polycrystalline with a cubic structure and the preferred orientation is (111). The crystallite size, texture coefficient, number of grains, dislocation density and micro strain were calculated. Field Emission Scanning Electron Microscopy results showed Multiple shapes nano structures as semispherical, plates and rods. The optical properties was studied in (300-900) nm wavelength range. The energy band gap E_g is in the range of (2.3–2.6)eV, the absorption coefficient value is high ($\alpha > 10^4 \text{ cm}^{-1}$) and its Suitable for solar cell uses.

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Key Words: n-type Semiconductor, Gravimetric Method, CdO Thin Film.

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Introduction

Cadmium Oxide considered an important transparent conducting oxide semiconductors (TCOs) which is have a high conductivity and transparency in the visible region of the electromagnetic spectrum, These distinctive features suitable for optical and thermal devices as a Transparent Thermal Material, Selectivity Absorbent Compound and Gases Sensor [1,2]. Cadmium oxide have a high carrier mobility and high potential which makes it suitable for many optoelectronic devices and it has been used as heat mirrors [1,3,4]. Due to the high conductivity of the CdO films has used to produce high-efficiency solar cells. Cadmium oxide is found in nature with two type structures: crystalline and amorphous, Its crystalline structure is of a brown or red color, while its amorphous structure is colorless [5]. The

crystalline structure is characterized by a crystalline (cubic) (Fcc) is similar to the synthesis of sodium chloride (NaCl). This means that the unit cell consists of four lattice points, each of which has a two-ion basis, one of which is the positive (Cd^{+2}) and the other negative oxygen ion (O^{2-}) Thus, the normal unit cell contains four positive ions of cadmium and four negative oxygen ions, ie, four cadmium oxide molecules. Positive cation ions occupy the eight cubic cell heads and their six focal points, while the negative oxygen ions occupy the center of the cubic cell and its twelve ribbons. Each ion is surrounded by six ions and is the first neighbor of the ion [6], n -type due to Oxygen Vacancies resulting from the non-stoichiometric compound[7]. spray pyrolysis an efficient method to deposit metal oxide films.

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Material and Methods

(CdO) thin films were grown onto soda-lime glass substrates, the used technique to deposited the films is chemical spray pyrolysis as a vacuum-free, inexpensive and fast. The slides are high-quality glass and their transparency is high, substrate dimensions are (25×25×1) mm, the substrate temperature was constant at 400°C along the spraying process to get high homogeneity and consistency in films.

The CdO thin films prepared from using cadmium chloride (CdCl₂) which is Molecular weight (201.33g/mol). 0.1M, (1.00665 g) of the cadmium chloride was dissolved in (50 ml)of distiller water. The spray solution was transferred to the hot substrate by using filtered air as carrier gas at a flow rate approximately to 5 mL/min. The spraying time period was 10 sec and the interval time was 3 minutes between any two successive sprayings. Other deposition conditions are kept constant: the carrier gas pressure (1.5 bar), vertical distance between nozzle and substrate (30 cm). the thickness of the deposited films was (200,225,250) nm measured by gravimetric method, In this method the difference of the mass of the glass

substrate is found after and before deposition using a sensitive electronic balance (Mettler, AE -160) with an extremely sensitive (10⁻⁴g), the difference between the two masses represent the amount of deposited CdO(Δm).the thickness (t) of the prepared film is calculated according to the relationship shown below [8]:

$$t = \frac{\Delta m}{\rho A} \dots (1)$$

Where ρ: density of the thin film material (g/cm³). (A):the surface area of the deposited film. The structural properties were determined by X-ray diffraction (XRD; Shimadzu 6000) with CuKα radiation as a source and Field Emission Scanning Electron Microscopy (FESEM) (MIRA3, TE-SCAN).The optical absorption and transmission spectra of the prepared films measured by (Shimadzu, UV- 1800) in the wavelength range of (300 – 900)nm.

Results and Discussion

XRD patterns shown a sharp peaks which refer to good crystallization of CdO thin films as in Figure (1).

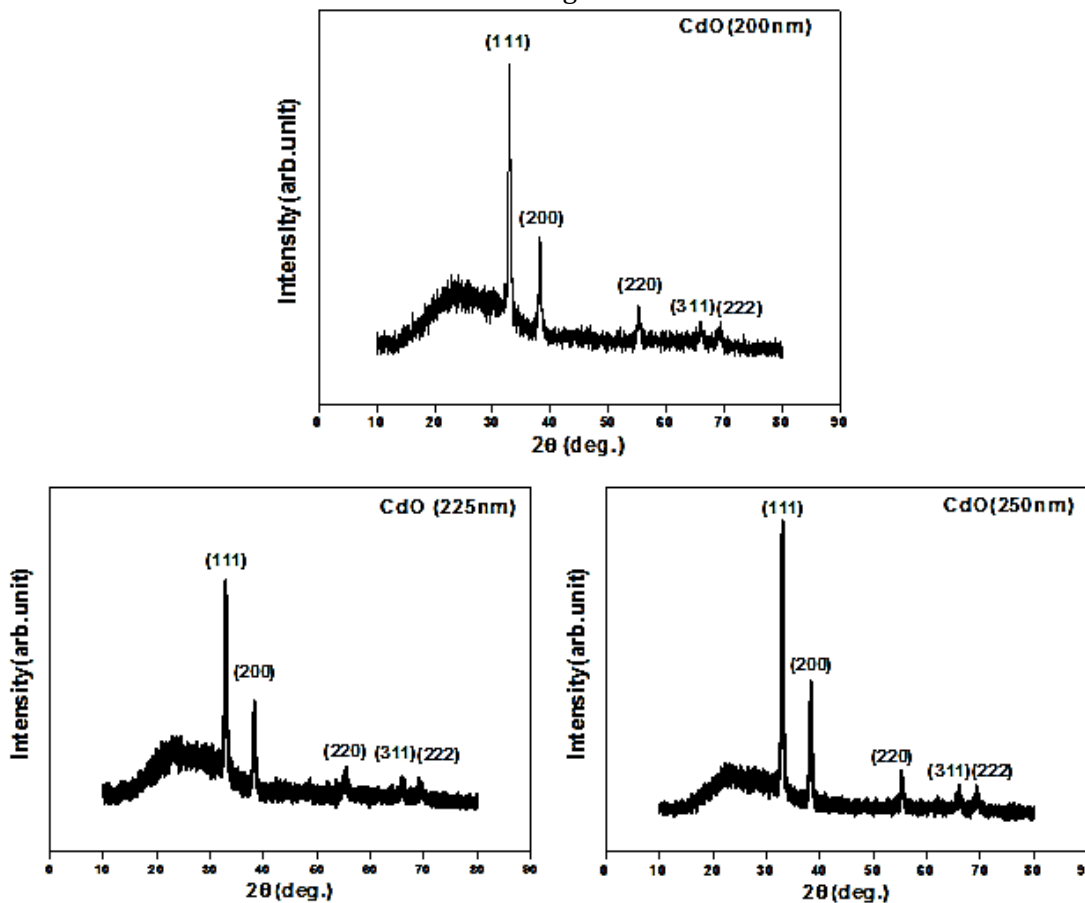


Figure 1. XRD patterns of the CdO thin films of different thickness



The figure shows a distinctive peak located at (2θ~33°,38.2°,55.2°, 65.9° and 69.2°) Attributed to (111), (200), (220), (311) and (222) plans respectively which is in agreement with (ICDD) card number 05-0640, all prepared films are preferentially orientated along(111) crystallographic directions. a number of diffraction peaks in XRD patterns indicates that the nature of the films are polycrystalline with a cubic structure which is in agreement with other reports [9-14].

The mean crystallites size(D) was calculated by using Debye Scherrer's equation[15, 16]:

$$D=0.9\lambda/\beta\cos\theta \dots(2)$$

Where θ is the Bragg angle. According to Table (1), the crystallites size Increases by increasing the thickness of the film.

Number of grains (N_o) and dislocation density(δ) of the prepared films It has been determined, its results Installed in table (1)show that(N_o) and(δ) are decreases with increase thickness of the films Because they are inversely proportional with crystalline size.

The texture coefficient Tc(hkl) is calculated for crystal plane (111) and its equation is given by [17, 18]:

14].From table (1), It can be noticed that the values of the diffraction angles do not change as the thickness changes.

The lattice vector (a) in cubic ideal (CdO) structure is4.695Å, in the this work the lattice vector is4.697Åand it is a matching to the ideal value, the various values of full width at half maximum (FWHM) (β) means that the crystallite size of CdO films is affected by changing the thickness of the films.

$$TC(hkl) = \frac{I(hkl)/I_o(hkl)}{N^{-1} \sum_N I(hkl)/I_o(hkl)} \dots\dots (3)$$

Where I(hkl) is the measured intensity, I_o(hkl) taken from the ICDD data and (N) is the number of peaks in the experimental pattern. The values of (Tc) are larger than 1express of that the profusion of grains in a given (hkl) direction.

Figure (2)show the crystallite size of the prepared films calculated by using W-H equation for the total peak broadening(lattice strain and crystallite size)which is given by [19, 20]:

$$\beta\cos\theta_{hkl} = 0.9\lambda/D + 4\epsilon\sin\theta_{hkl} \dots(4)$$

Whereβ_s: The strain induced broadening and its equal to 4εtanθ_{hkl}, ε:is the microstrain.

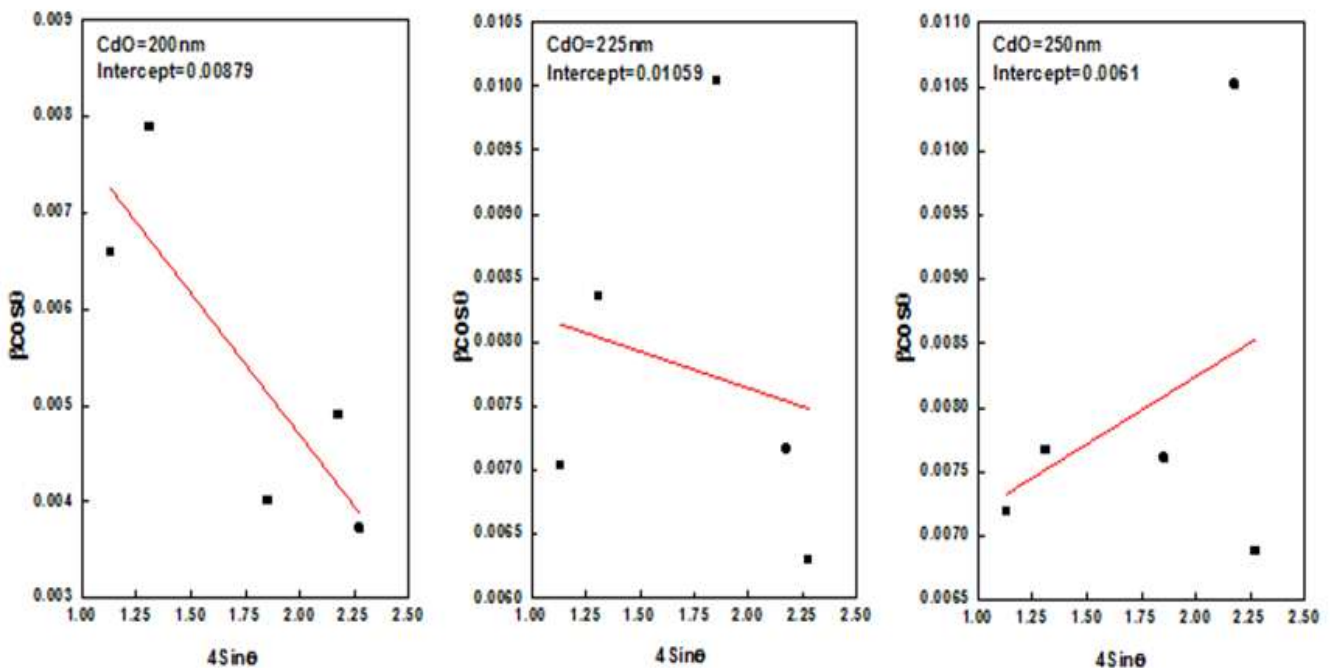


Figure 2. The W-H Analysis of CdO Thin Films

Table (1) depicted the results of average crystallite size, this results indicate that the crystallite size estimated by using Scherrer's and Williamson–Hall equations increases with increasing deposition time, the crystallite size calculated by Scherrer's

method are greater than that measured by Williamson–Hall.

The growth of the film sgenerated the micro strains, the negative values of micro strains indicate compression in the lattice as in CdO films prepared with thickness of about 200 and 225 nm, while the



positive values of microstrains Indicate an occurrence stretching in lattice as CdO film prepared with thickness of about 250nm.

Table 1. The structural parameters of the CdO thin film

CdO (nm)	2θ(deg.)	FWHM	D Scherrer (nm)	D W-H (nm)	Tc	Microstrain (S)	$\delta \cdot 10^{11}$ (cm ⁻²)	$N_o \cdot 10^{12}$ (cm ⁻²)
200	33	0.43	19.25	13.09	1.9	-0.0029	2.6	2.8
225	33	0.42	19.68	15.77	2.1	-0.0005	2.5	2.9
250	33	0.39	20.98	22.58	2.0	0.0010	2.2	2.7

Figure (3) shows surface topography using (FESEM). The images show that the CdO film with 200nm grew in the form Nano rods and nano plates with a particle size in the range of (15-20nm). while the

images of the (CdO=225,250)nm films show the formation of semi spherical nanostructures with an average particle size of (15-32nm),(17-26) nm respectively.

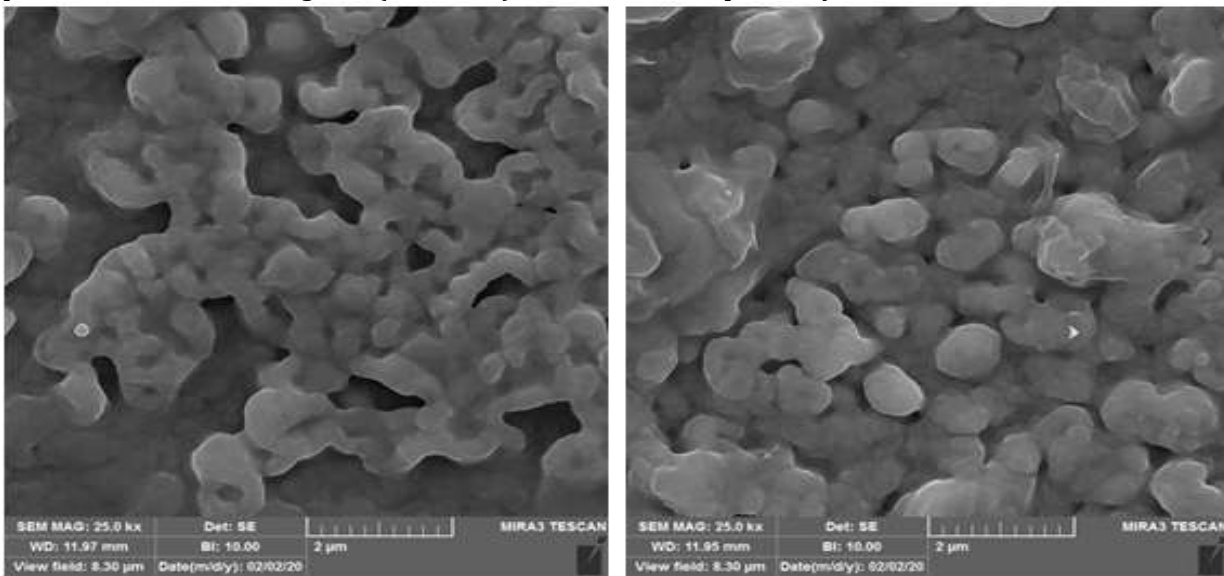


Figure 3. The FESEM images for CdO thin films

Optical transmittance spectra of Cadmium Oxide was studied in the region of (300-900)nm. The interaction of light with materials produces three processes that occur individually or double, The incident light beam may Absorbed, Reflected or Transmitted. Figure (4) shows that the absorbance (the thin films ability to absorb the light) increases as thickness increasing at the same wavelength. The highest absorbance value is at wavelengths (300-500) nm and it decreases at the high wavelengths for all prepared films. Figure (5) shows that the Least thickness films are more transmittance and the transmittance of the films increases at high wavelengths for all prepared samples.

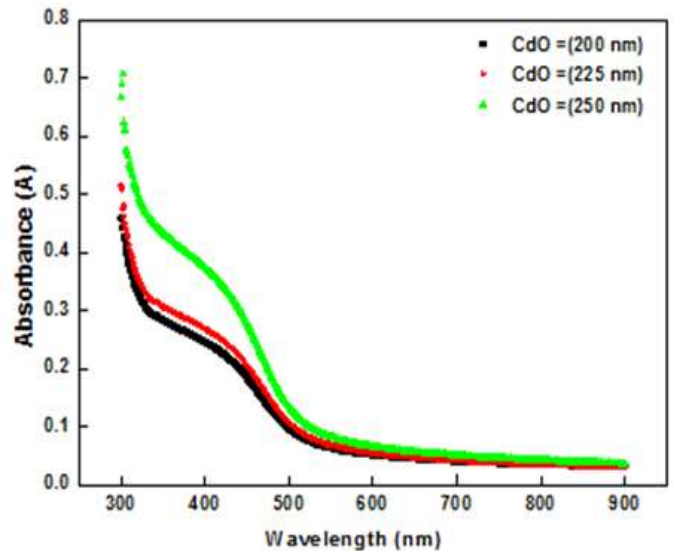


Figure 4. The Absorbance of CdO Thin Films



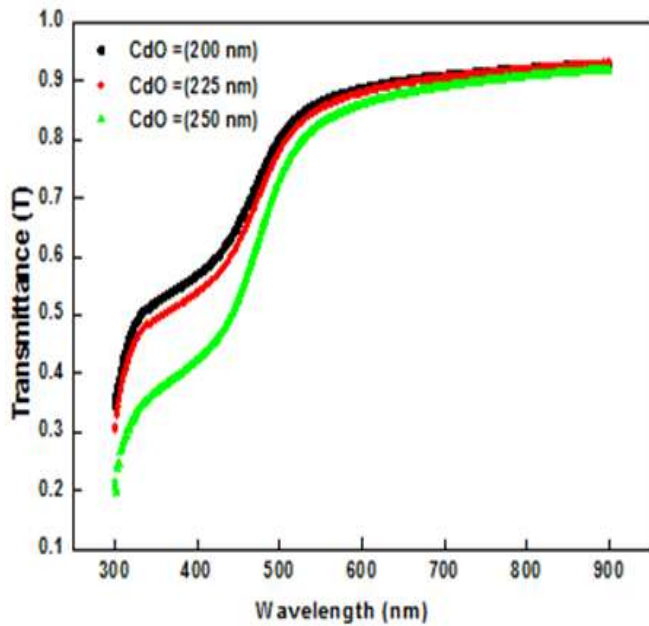


Figure 5. The Transmittance of CdO Thin Films

Figure (6) show the relation between CdO optical absorption coefficient and the photonenergy, The figure illustrates an increase in the absorption coefficient values as the energy of the incident photons increases, and its values ($\alpha > 10^4 \text{ cm}^{-1}$), this high value refers to increase the direct electronic transitions.

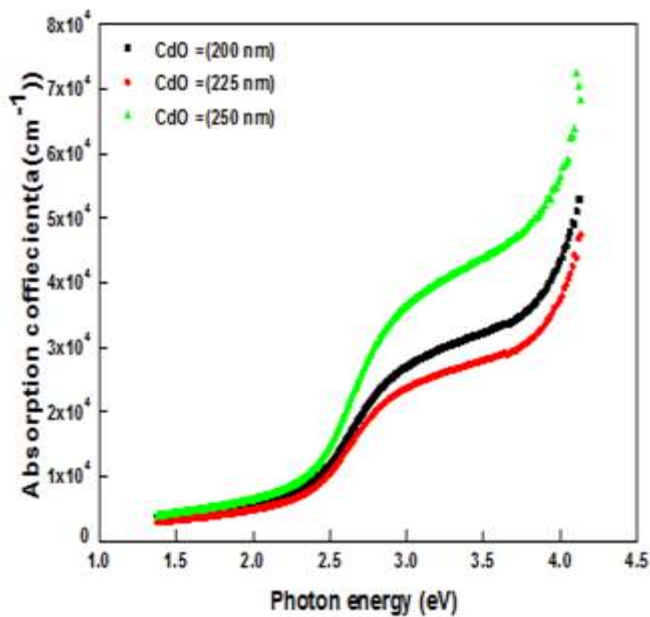


Figure 6. The Absorption Coefficient of CdO Thin Films

The refractive index (n) is a substantial factor in optical communication and in designing devices. The (n) values of the CdO films plotted versus the wavelength in Figure (7). It is clear that the refractive index values increasing as wavelength increases from (300-450)nm then the (n) values decrease gradually as wavelength increases.

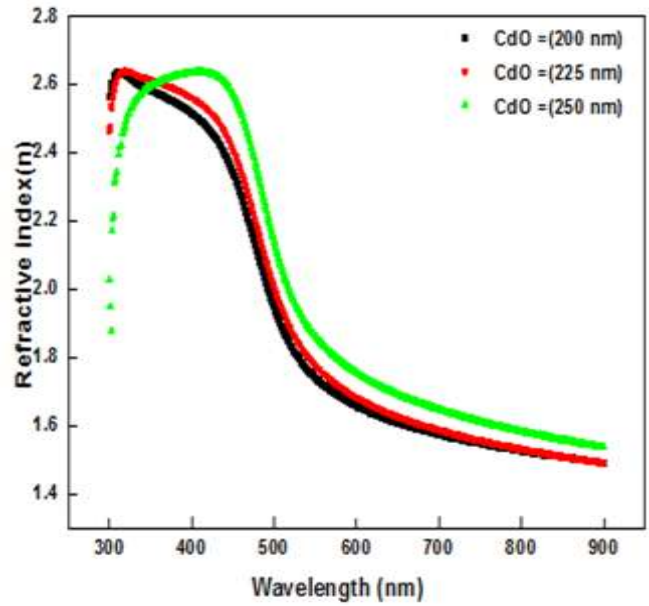


Figure 7. The Refractive Index of CdO Thin Films

CdO optical energy gap values calculated based on the absorption coefficient values. The energy gap values obtained by relation between $(\alpha hv)^2$ versus (hv) , As shown in Figure (8), Tauc equation was used to estimate The energy gap (E_g) [21, 22]:

$$\alpha hv = A(hv - E_g)^{1/2} \dots (4)$$

Where hv : is the photon energy, A : is a constant, E_g : is the energy gap. The energy gap values are influenced by the arrangement of the atoms in the crystal structure, the E_g values are (2.3, 2.5, and 2.6) eV for CdO thin films deposited at (200,225,250)nm respectively, This results refer to slightly increases of E_g values with the increasing thickness.



Conclusions

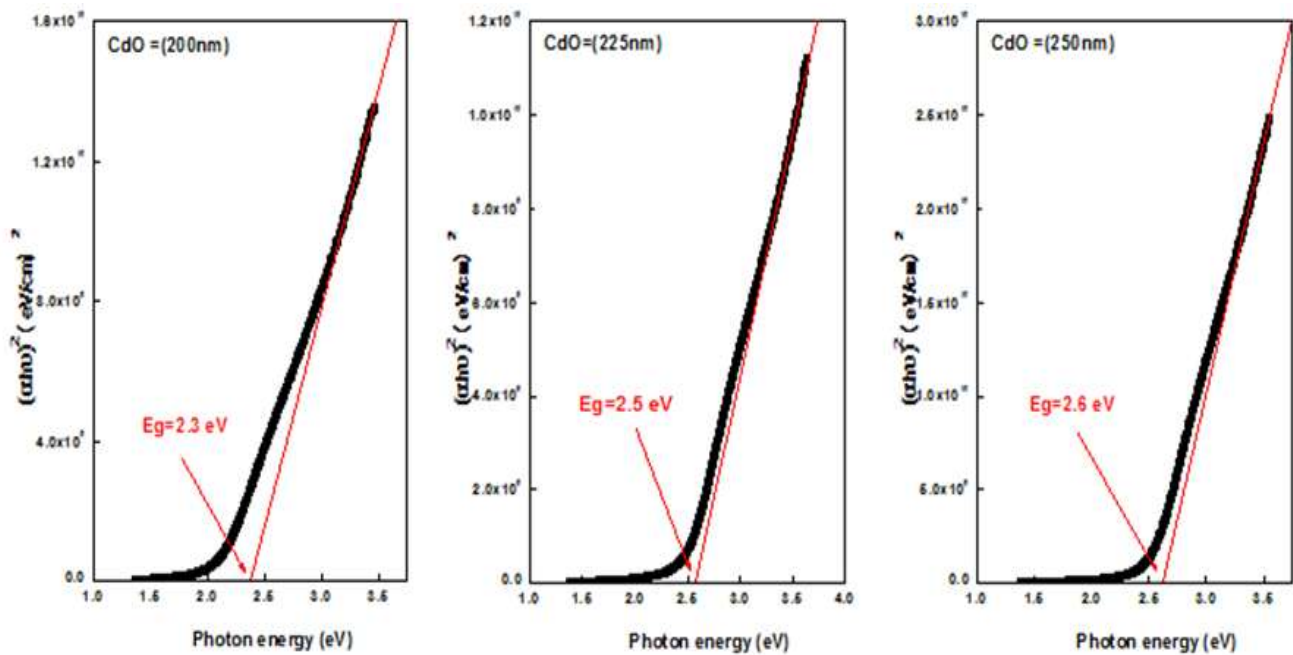


Figure 8. The $(\alpha h\nu)^2$ versus $(h\nu)$ of CdO Thin Films

Cadmium oxide thin films deposited on glass substrates at 400°C by using chemical spray pyrolysis technique. The films prepared with a thickness of about (200,225,250) nm. The structural properties refer to that crystallite size increases as thickness increases while number of grains and dislocation density are decreases as the film thickness increases. FESEM results showed the formation semi spherical nanostructures and nano rods. The energy gap values within (2.3 –2.6)eV. The prepared films have a good structural and optical properties suitable for many modern electronic applications such as Selectivity Absorbent Compound and Gases Sensor.

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