

Influence of Substrate Temperature on Structural Properties of CdS Thin Films Prepared by Chemical Spray pyrolysis

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Abstract:

In the present work, CdS thin films have been prepared by chemical spray pyrolysis method on glass substrate with different temperature from cadmium nitrate with constant thickness (440 ± 10 nm), to study the effect of the substrate temperature on structure properties of prepared films.

The results of structural measurements showed through a Scanning Electron Microscope (SEM) for the homogeneity of the prepared films, and from the results of an Atomic Force Microscope (AFM) the nanoparticles are the composition and the square root value of the average roughness (RMS) of the thin films is equal (0.699nm). And from X-ray diffraction pattern the results showed that all the films are polycrystalline, hexagonal structure, grain size within the range of nano scale, and substrate temperature does not affect on the crystal structure of the films, and prepared film has a preferred orientation along (002) (i.e., the axis C perpendicular to the substrate).

Keywords: CdS, CSP, Synthetic properties.

Introduction

The study of thin films of materials is of interest to researchers as they are the key elements for the continued technological advances in the fields of electronic, optical, optical and magnetic devices[1].

The term thin films are used on materials consisting of one or several layers of matter whose thickness ranges from tens of nanometers to a few micrometers[2]. Due to the thin thickness of the thin film, it is easy to crack and therefore requires deposition on various other materials used as substrates. The base type depends on the nature of use and study such as glass, quartz, silicon and aluminum[3].

Several techniques were used for the preparation of CdS films, including the sublimation evaporation method [4], thermal evaporation [5],

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electron Beam deposition [6], chemical Bath deposition [7] Thermal Vacuum Evaporation [8] and thermal chemical deposition [9].

(CdS) is a semi-conductive component of the second group (VI-II). The crystalline structure of this material is the zinc blended and hexagonal. The hexagonal phase is more stable than the cubic phase at room temperature. The bond between sulfur and cadmium ions is a covalent beam due to two electrons between the sulfur and cadmium atoms. It also has a direct power gap and high optical conductivity and a power gap of 2.4eV, ie at wavelength (0.52 μ m) In the short area of the visible spectrum. CdS is highly absorbent at short wavelengths while transparent for long wavelengths, so CdS absorbs blue and green while yellow and red are applied, so the thin films appears yellowish red (n-type) and (p-type) depending on the preparation process and the type of defect. One of the most important applications used for this compound, it is used in solar cells and photovoltaic as an alternative to silicon cells because it is cheap The cost as well as ease of preparation in thin films of good quality at room temperature and availability of a chemical solution [10].

The current research aims to study the effect of alkaline temperature on the structure properties of cadmium sulfide films (CdS) prepared by thermal chemical decomposition technology, which are economical methods suitable for scientific studies and technological applications to obtain high quality thin films and discuss the results we have reached.

The temperature of the base plays an important role in determining the crystalline structure of the prepared membranes, especially the nanoparticles. A number of thin films have been prepared at different temperatures (250, 300, 350, 400 and 450) °C. We found that at low temperatures below 250°C, we did not have a well defined and good adhesion thin films. The temperature is the critical temperature for the CdS formation in the CSP system and the adhesion thin films had been proven to be really good at temperatures greater than 250°C. A number of temperatures had been selected in accordance with the other parts of the system (250, 300, 350, 400 and 450) °C, and thickness (440 $\pm$ 10 nm) with both sedimentation time and The pressure of the air to study the effect of the degree of the base temperature on the properties of synthetic thin films.

Practical side :

1. Preparation of Solution:

Cadmium supplied membranes were introduced in a chemical degradation manner:

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1. The water solution of the cadmium hydrothermal nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) was a quick soluble white substance in water of molecular weight (308.47g / mol) and purity (99.999%) which was a source of cadmium ions (Cd^{+2}) 0.1M) by dissolving a certain weight of cadmium nitrate using a magnetic mixer in a certain volume of distilled water according to the following relationship [11]:

$$M = \frac{W_t}{M_{wt}} \times \frac{1000}{V} \dots\dots\dots (1)$$

whereas :

M : Molecular concentration **W_t :** The weight required to melt.

V : Volume of distilled water **M_{wt} :** Molecular weight of matter

2. In the same way, the thiourea solution ($\text{CH}_4\text{N}_2\text{S}$), a white soluble powder (76.11g / mol) with purity (99%) and 0.1 mg, is a source of sulfur ions (S^{-2}).

2. Configure Rules:

The thin films deposited on thin glass substrate and are German-made. The process of cleaning the glass substrate is carried out in several stages to ensure good cleaning.

3. Thin film deposition:

CdS thin films were placed on the heated glass substrate, at different temperatures (250, 300, 350, 400, 450) with a spray of the solution of the cadmium nitrate and the thiourea solution by spray on the hot glass substrate, limiting the reaction by the heat. Cadmium supplied is deposited on the surface of the substrate according to the chemical reaction that follows:



4. Factors Influencing Thin Films Properties:

1. Substrate Temperature:

I attended samples of (CdS) with a temperature range of (250- 450) °C. They formed highly corrosive thin films with good homogeneity, free from aggregations and defects.

2. Solution Type:

The solution has an important role in the homogeneity and adhesion thin films and degree of crystallization where the solution of cadmium nitrate was used to prepare CdS membranes.

3. Substrate Position:

Place the substrata on the center of the electric heater plate to obtain homogeneity in the films and the spray device is vertical on the substrata.

4. Vertical Distance:

We obtained the best result at a height of (29 ± 1) cm. Increasing this distance leads to the volatilization of the solution spray away from the substrata surface. Reducing this distance leads to the concentration of the solution spray in one spot and thus the substrata is not homogeneous.

5. Spray Rate:

The spray rate is calculated by the flow of the solution from the solution per minute. The best spraying rate in this experiment is 5 ml / s.

6. Average Spray Time:

In this study, the solution was sprayed (7s) followed by a 2 min stop (2min) and repeated several times until the required thickness were reached.

7. Air Pressure:

Air pressure was installed in the glass chamber of the spray device when all thin films were prepared up to 10^5 N / m² for homogeneous membranes.

5. Study of prepared Thin films:

After thin films deposition, the best samples prepared for the study of structural properties were chosen, and from Results of (X-Ray Diffractions, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM)) We noted that they are distinguished by the following :

1. Be homogeneous and do not contain dark and light areas.
2. Has high adhesion strength with glass base and cannot be wiped by hand.
3. With smooth surfaces free of stains, cracks and discrete roots (membrane-free spaces).

5. Thin Film Thickness Measurement:

The thickness of the membrane is an important factor, because it involves in determining the physical properties of the membrane. These two methods were used to measure the thickness:

a) Optical Interference Method:

The thickness of the thin films was measured by the method of optical interference cores by the following relationship [12]:

$$t = (\lambda / 2) \times \Delta X / X \dots\dots\dots (2)$$

whereas :

t : thickness.

λ : The wavelength of light falling (cm).

ΔX : View the dark cedar.

X : The distance between the two consecutive blades ie the cilia display is

b) Weighting Method:

$$\mathbf{t} = (\Delta \mathbf{w} / \rho \cdot \mathbf{s}') \dots\dots\dots (3)$$

t : thickness **ρ** : Density of membrane material (g/cm^3) .

Results and Discussion:

Because of the importance of these tests in providing information on the crystalline structure of the material as well as the identification of the substance and its structural properties through the use of XRD, SEM and AFM, as follows:

By examining the XRD diffraction of membranes prepared in Fig (1) , we found that all the membranes were CdS crystallized and hexagonal, by comparing the results with the ASTM card numbered (41-1049) with slight difference (d_{hkl}) as in Table (1). This difference results from the mechanical stresses resulting from some defects formed during deposition of the membranes, and the absence of additional peaks. This means that there is no change in the hexagonal phase. The previous refers to the formation of the cubic phase at low temperatures and then turns into the hexagonal phase with the increase of the temperature of the gypsum (CdS) prepared from cadmium chloride solution [14,15,16] The hexagonal phase is the most stable phase of the cubic phase with temperature [17]. We also note from Figure (1) that the prevailing level is (002) for all membranes with some weak peaks indicating that the axis (c) is perpendicular to the base and this corresponds to the previous research [18,19,20,21,22,23,24]. As shown in Fig (2). change the value of (d_{002}) with the base temperature, where we note that the value of (d_{002}) increases with increasing the temperature of the substrate and that the temperature (350°C) was the optimum rate for obtaining the best thin film.

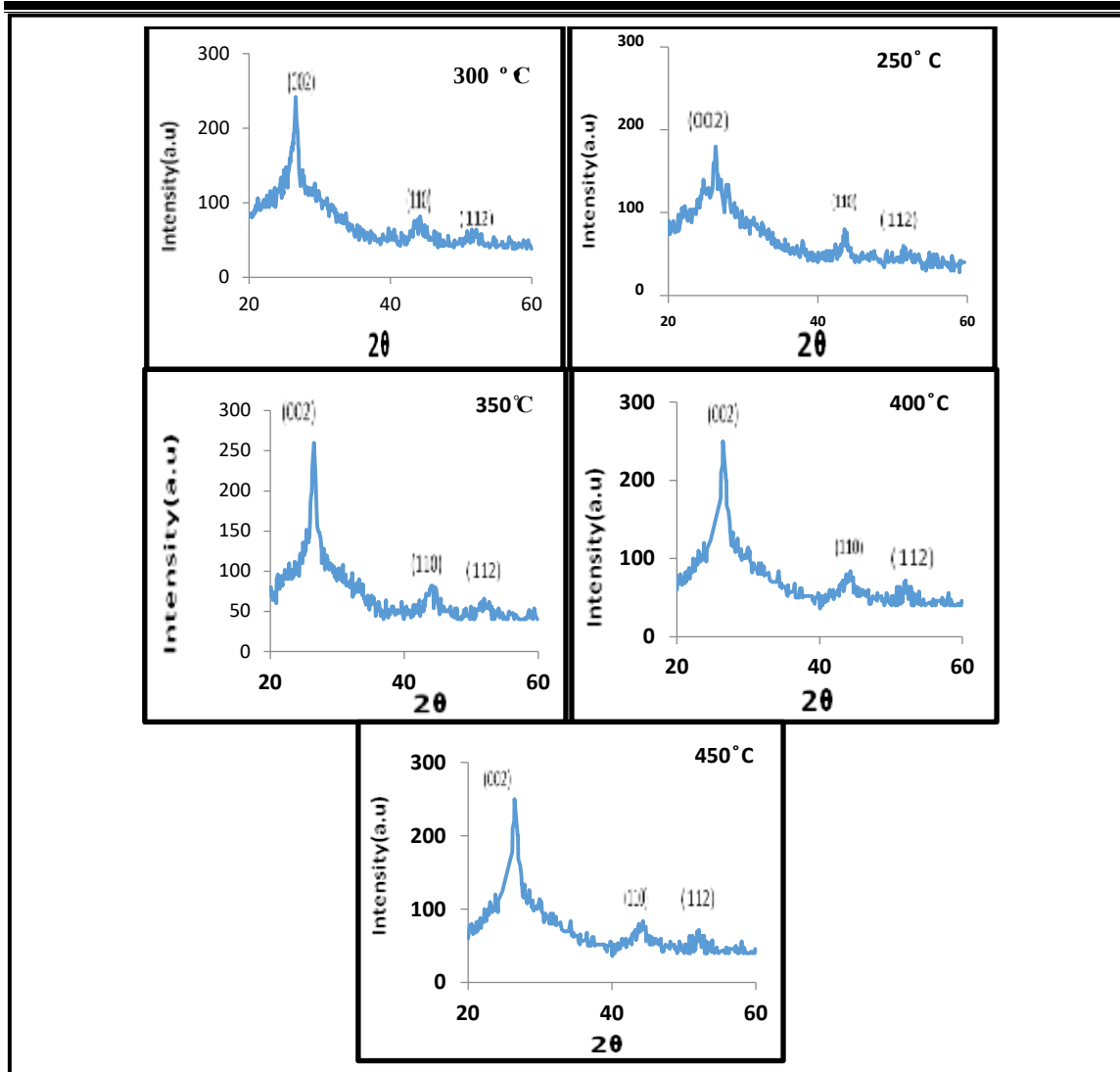


Figure (1) X-ray diffraction spectra of CdS thin films prepared at different substrate temperatures.

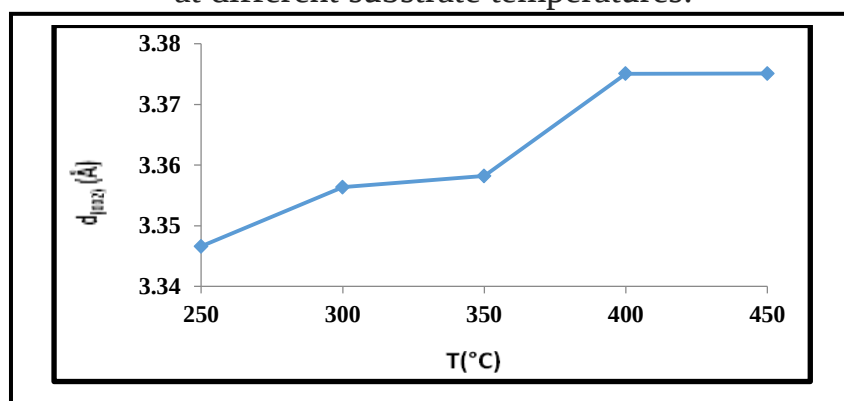


Figure (2) Interval as a function of substrate temperatures.

1. Lattice Constants

The values of the six-phase hexagonal constants (a_o , c_o) were calculated for all membranes prepared at different temperatures using the following equation [24]:

$$\frac{1}{d^2} = \frac{4}{3} \left[\frac{h^2 + hk + k^2}{a_o^2} \right] + \frac{l^2}{c_o^2} \dots\dots\dots (4)$$

whereas :

a_o, c_o : Hexagonal constants in hexagonal structure.

d_{hkl} : Interval of levels (hkl).

hkl : Miller coefficients.

Note that all these values are close to (ASTM) as shown in Table 1 and that these values change as the base temperature increases. As in Fig (3) and Figure (4), the mechanical stress may be due to temperature.

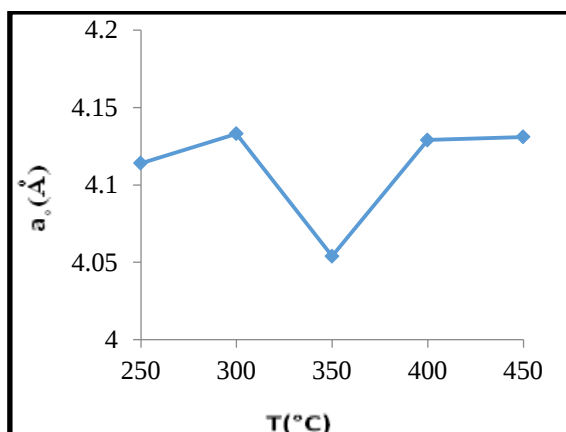


Figure (3) Fixed relationship of the lattice (a) with the substrate temperatures.

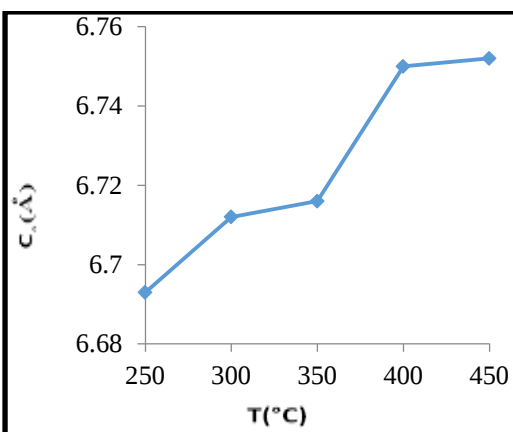


Figure (4) Fixed relationship splicing (c) with the substrate temperatures.

2. Crystallite Size:

The particle size (G) of the level (002) was calculated using the Scherrer equation represented by: [25]

$$G = \frac{b\lambda}{\beta \cos \theta} \dots\dots\dots (5)$$

whereas :

β : The curved width at the top of the FWHM peak, measured by the diagonal angle

λ : The wavelength of rays used.

θ : Brack angle degrees.

b: A numerical constant called Scherre's constant $[2(\ln 2/\pi)^{1/2}=0.94]$.

The density of the membranes within the nanoscale size ranges between (6.5 - 9.04) nm. The granular size increases with the increase of the base temperature as shown in Fig (5) and Table (1). This is due to the increased membrane crystallization with increasing temperature because the increase in temperature increases the kinetic energy of the atoms, making it easier to occupy the correct positions in the crystalline lattice and then increases the size of the grains and this corresponds to previous research [16, 19, 23, 26, 27, 28].

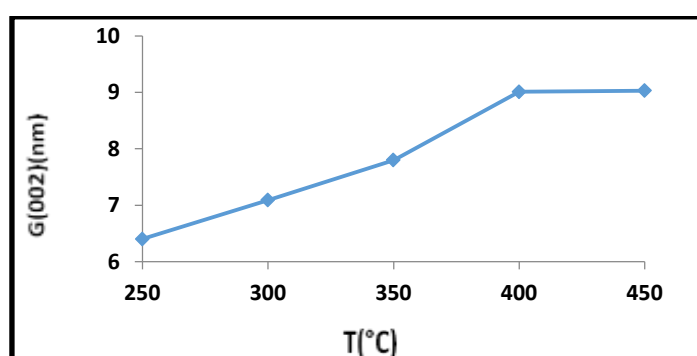


Figure (5) relationship of the Crystallite Size with the substrate temperatures.

3. Coefficient Texture:

The modulation factor (Tc) was calculated from the following equation: [29]

$$Tc(hkl) = \frac{I(hkl)/I_0(hkl)}{N^{-1} \sum_N I(hkl)/I_0(hkl)} \dots\dots\dots (6)$$

whereas :

N : The number of peaks in ray diffraction (XRD).

I (hkl) : The relative intensity measured for the level (hkl).

I₀ (hkl) : Standard intensity (hkl) from ASTM.

The table shows that the values of (Tc) and all membranes are more than (one) of the level (002) and as shown in Table (1). This means that the standard level of all membranes is (002) [18,19, 20,21,22,23,24].

4. Stress and Strain

Stress values are calculated using the following formula [29]:

$$Stress = -232.75 \frac{C_o - C_{ASTM}}{C_{ASTM}} \dots\dots\dots (7)$$

whereas :

C_o: X-ray diffraction constant measured.

C_{ASTM} : Standard slip of card (ASTM).

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We observe from Figure (6) and Table (1) that the crystalline stress was pressure stress up to temperature (350°C) and then shifted to tensile stress while continuing to increase the temperature of the base causing a significant change in the value of (2θ) and (d)) as previously noted.

As for compliance, they were calculated using the following equation [29]:

$$S = \left| \frac{C_o - C_{ASTM}}{C_{ASTM}} \right| \times 100\% \quad \dots\dots\dots (8)$$

It is caused by the crystal's exposure to stress. As shown in Fig (7) and Table (1), the degree (350°C) is the lowest degree of less stress and less strain. I also found that crystal is subjected to higher stress and resistance at (450°C).

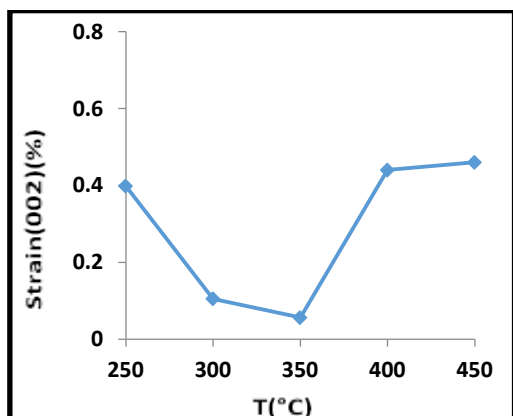


Figure (6) relationship of the stress with the substrate temperatures.

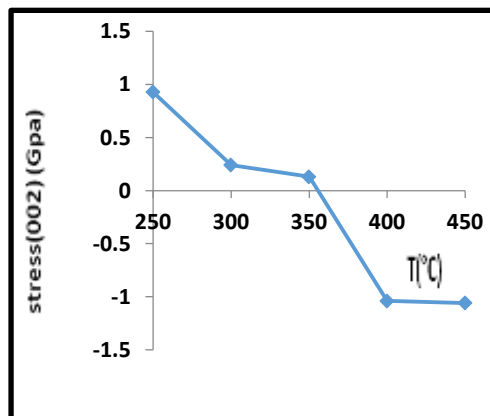


Figure (7) relationship of the strain with the substrate temperatures.

5. Dislocation Density and Number of Crystal

The density of dislocation (δ) of the level (002) was calculated using the following relationship, respectively [30]:

$$\delta = \frac{1}{G^2} \quad \dots\dots\dots (9)$$

The number of crystals (N₀) for the area unit of level (002) is calculated according to the following relationship: [31]

$$N_o = t \setminus G^3 \quad \dots\dots\dots (10)$$

whereas :

t : Thin film thickness

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Figure (8) and Figur (9) and Table (1) show that both the density of the dislocation and the number of crystals decrease with the increase in the temperature of the base. This is an expected result due to increasing the particle size by increasing the temperature of the base and that the values of (δ) and (N_o) grain size.

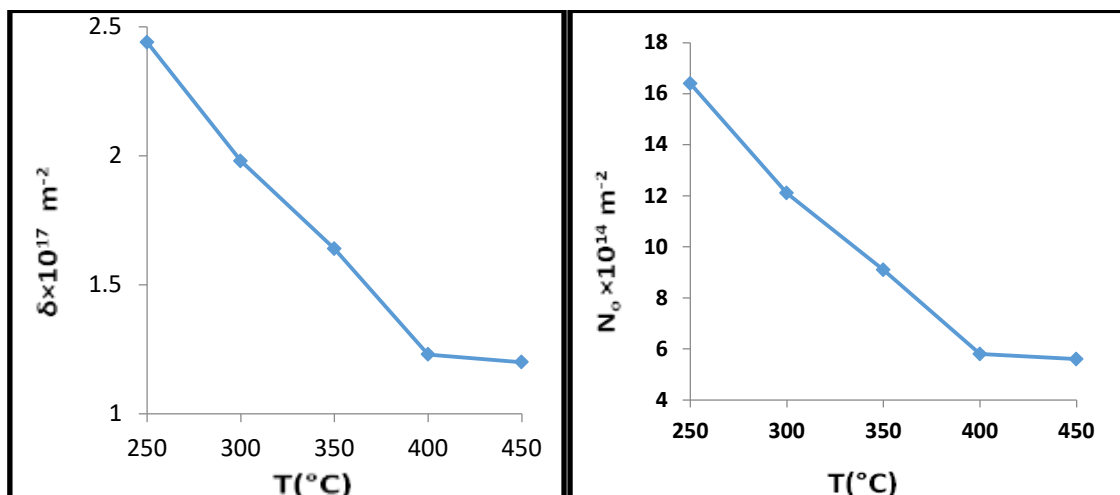


Figure (8) Relationship of the density of the dissociation with the substrate temperatures.

Figure (9) The relationship of the number of crystals with the substrate temperatures.

Table (1) Results obtained from X-ray diffraction of CdS thin films with changing with the substrate temperatures.

Sample		ASTM	250 $^{\circ}\text{C}$	300 $^{\circ}\text{C}$	350 $^{\circ}\text{C}$	400 $^{\circ}\text{C}$	450 $^{\circ}\text{C}$
$d_{(002)} (\text{\AA})$		3.3599	3.3466	3.3564	3.3582	3.3751	3.3751
Lattice Constants	$a_o(\text{\AA})$	4.140	4.114	4.133	4.054	4.129	4.131
	$c_o(\text{\AA})$	6.7198	6.693	6.712	6.716	6.750	6.752
(G) nm	(002)	-	6.40	7.09	7.80	9.01	9.05
Tc(hkl)	(002)	-	1.88	1.94	1.69	1.04	1.06
Stress (GPa)		-	0.928	0.240	0.130	-1.040	-1.060
Strain(%)		-	0.398	0.105	0.056	0.440	0.460
$\delta \times 10^{17} \text{ m}^{-2}$	(002)	-	2.44	1.98	1.64	1.23	1.20
$N_o \times 10^{14} \text{ m}^{-2}$	(002)	-	16.4	12.1	9.1	5.8	5.6

Results of Scanning Electron Microscopy (SEM)

SEM (Surface Morphology) and particle size (CdS) were used on a glass base at 350 ° C, and SEM results showed that the deposition thin films was a nanoscale and showed the homogeneity of the surface granules. grain size by means of the knowledge of the scale of the drawing (which is in the center of the bottom of the magnified membrane image by (20,000 times)) of the average diameter of several granules, Using mathematical calculations we found that the particle size of the membrane within the nanoparticles was (71.3 nm). We also note a slight difference between the grain size values obtained from the Scherrer equation as in Table (1) and Figure (10) , Through the same form notes the presence of a large number of particles on the surface of the membrane and a regular distribution on the base and often spherical shape.

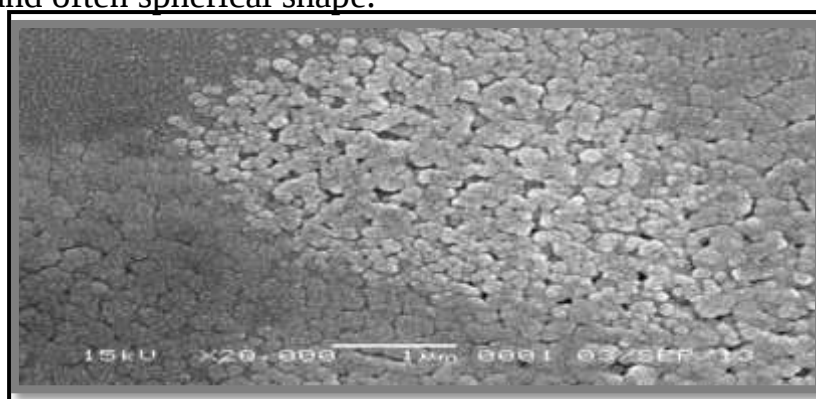


Figure (10) shows the results of SEM for CdS thin films and temperature (350°C).

Results of Atomic Force Microscopy (AFM)

The Atomic Force Microscope (AFM), which has the ability to analyze these surfaces, has been used to give very precise values for particle distribution and Roughness values based on the square root of the RMS [32].

Figure (11) shows the AFM image of the CdS membrane at the base temperature (350° C). As shown in the following figure of two and three dimensions, the granules are the nanoparticles and the RMS value of the membrane is 0.699nm.

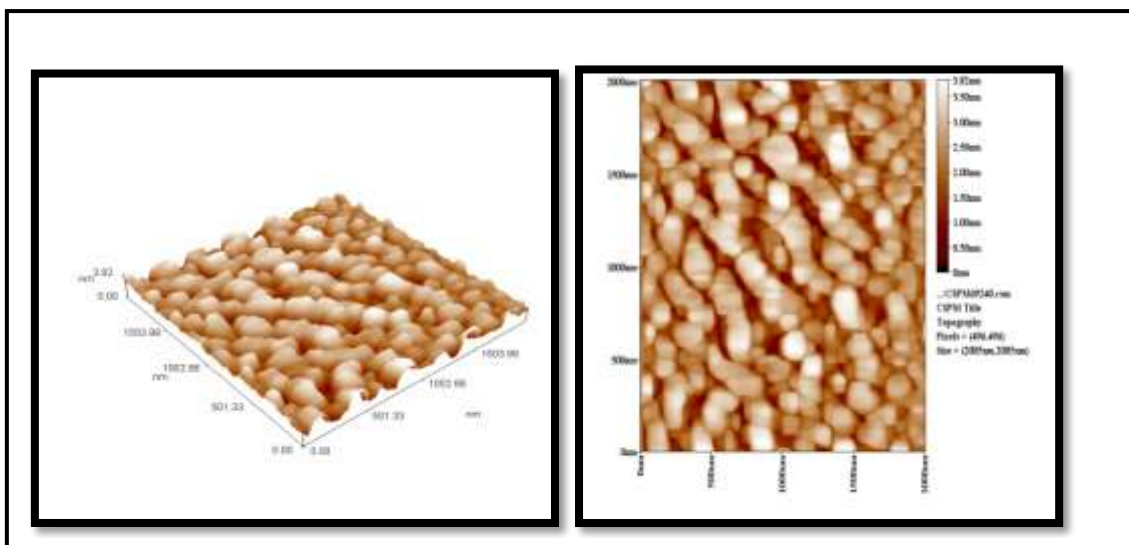


Figure (11) shows the AFM image of the CdS thin films at 30°C.

Conclusions :

1. All CdS thin films prepared by thermal chemical degradation and at different base temperatures are crystallized in a hexagonal and poly crystalline phase.
2. The standard level is (002) for all CdS membranes prepared by thermal chemical degradation at different base temperatures.
3. Change the value of (d_{002}) with the temperature of the base, where we note that the value of (d_{002}) increases with increasing the temperature of the base, and that the temperature (350°C) was the optimum degree to get the best membrane.
4. The particle size of the membrane was found within the nanoparticles and was (71.3 nm) and increased with the increase of the base temperature. And thus the possibility of obtaining CdS membranes in a thermal chemical decomposition method.
5. Both the density of the masses and the number of crystals decreases with the increase in the temperature of the base. This is an expected result due to increasing the particle size by increasing the temperature of the base and that the values of, and N_0 are inversely proportional to the particle size.

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