Effect of Annealing Temperature on Structural and Optical Properties of CdS Thin Films Prepared by CBD and Thermal Evaporation Techniques

Mohammad M. Ali\(^a\)*, Saeed J. Abbas\(^a\) and Alaa S. Al-Kabbi\(^a\)

\(^a\)Department of Physics, College of Science, University of Basrah, Basrah, Iraq

*Corresponding author. Tel.: +9647802179823
E-mail: moh7077ali@gmail.com

Abstract

The CdS thin films were deposited on glass substrates by two different methods, chemical bath deposition (CBD) and thermal evaporation (T.E.). The effect of annealing temperature on the structural and optical properties of the CdS thin films were investigated. The structural properties of CdS thin film was studied by X-ray diffraction. It was observed that the films have a polycrystalline hexagonal (wurtzite) structure with preferred orientation along (002) plane. The crystallite size calculated from XRD increases as the annealing temperature is increased. We observed that the lattice constant, micro strain, dislocation densities and number of crystallites per unit area of the films are quite different in these processes from XRD analysis by considering high intense diffraction peaks of the as-deposited and annealed films. The energy band gap in nanocrystalline CdS thin films has been estimated from absorption measurements. The band gap values for CBD-CdS thin films decreased from 2.75 to 2.45 eV and for T.E.-CdS thin films decreased from 2.60 to 2.43 eV with increasing annealing temperature. Small nanocrystals display wide band gaps as a result of the quantum confinement experienced by nanocrystals of a certain size.

Keywords: CBD; thermal evaporation; CdS thin films; annealing temperature; structural and optical properties

1. Introduction

There is a close relationship between the particle size and the semiconductor band gap, where the band gap of semiconductor increases with decrease in the particle size which is known as the quantum size effect. Therefore there is much interest in physical properties of nanometer size semiconductor materials due to their novelties; their properties are different and often superior to those coarse grained polycrystalline materials and also amorphous alloys of same...
composition [1,2]. This arising from the confinement effects or quantum size effects which are of special attention in nanotechnology. There is a great interest in the effects of the quantum size of nanocrystalline semiconductors towards the metal-chalcogenide based system in solar cell. The thin films of nanocrystalline of CdX and PbX (X=S, Se, and Te) are important in harvesting photons in the visible and infrared region, are of great interest[3]. Among all of these materials, cadmium sulphide (CdS) is an important material which can be used as n-type materials for thin film heterojunction solar cells; low resistivity CdS films are needed in heterojunction solar cells to lower the cell series resistance. CdS has attracted technological interest because the energy gap can be tuned and the lattice parameters can be varied [4,5]. In recent years, researchers have moved to the preparation of CdS quantum dots which resulted in physical and electronic properties that differ significantly from those in bulk and thin film. This material has been used in the construct of a single electron transistor and UV light emitting diode [6-8]. In addition to increased strength, hardness, enhanced diffusivity, improved quality, roughness, reduced elastic modulus, higher thermal expansion coefficient, lower thermal conductivity and superior soft magnetic properties[9].

Different vacuum and non-vacuum deposition methods have been reported for the deposition of CdS thin films, including vacuum evaporation [10,11], chemical bath deposition (CBD) [12,13], closed space sublimation (CCS) [14], spray pyrolysis [15,16], successive ionic layer adsorption and reaction (SILAR) [17], pulsed laser deposition (PLD) [18–20] and sol-gel [21]. Each technique has its own parameters and produces films with different properties, which should be optimized for specific applications. Where the techniques are divided into non-vacuum deposition techniques and vacuum deposition techniques. Since non-vacuum techniques for thin film deposition are inherently more susceptible to oxidation and contamination, vacuum deposition techniques are more suitable for CdS film preparation [22]. These methods are convenient for preparing pinhole free, homogenous and smooth thin films with the required thicknesses. The various structural and physical properties of CdS thin films prepared by thermal evaporation in different deposition conditions have been discussed in research papers [23-26]. CBD is known to be a simple method, with low temperature and inexpensive large area deposition technique, it use an aqueous solution and then we can control the chemical parameters of solution like (temperature, molar concentration, PH, time of deposition, stirring rate, etc.)[27,28]. It is well known that the deposition conditions (bath compositions, reagents concentrations, temperature and pH, etc.) have a significant effect on the quality of the films which prepared by CBD. S. Rondiya et.al.[29] studied the effect of bath temperature on optical and morphology properties of CdS thin films and showed that the thickness and crystallite size of the films increased while the values of band gap decreased with increasing of bath temperature.

The effect of annealing temperature on the properties of CdS thin films prepared by different methods were studied by a number of reports. The aim of this post-deposition procedure is to improve the structural, morphological and chemical quality of the films. A. Djelloul et.al. [30] studied the effect of annealing temperature (300, 400 and 500°C) on the properties of CdS thin films prepared by CBD and showed that the recrystallization process densified the film and eliminated the defects in the material, where the spherical shaped nanoparticles with vacant spaces were observed, while on annealing the film consists of dense layer of small crystallites and the nanoparticles convert into bigger clusters due to the coalescence or diffusion of large number of CdS nanoparticles. A. Hasnat et.al. [31] and Dipalee J. Desale [32] studied the effect of annealing temperature on the properties of CdS thin films prepared by SILAR method. M. A. Islam et.al. [33] studied the comparison of structural and optical properties of CdS thin
films grown by three different processes; CSVT, CBD and sputtering techniques.

In this work we report and compare the structural and optical properties of CdS thin films deposited by CBD and thermal evaporation techniques. The effect of annealing temperature in vacuum (~10^{-2} torr) at 250, 350 and 450°C on these properties are discussed.

2. Experimental Details

2.1. Preparation of CdS thin films

Thin films of cadmium sulphide (CdS) have been grown by chemical bath deposition (CBD) and vacuum evaporation techniques. First method; CBD: using cadmium chloride (CdCl₂) as Cd²⁺ ion source, thiourea [CS(NH₂)₂] as S²⁻ ion source and ammonia (AR grade). Aqueous solution of 0.1 M cadmium chloride, 0.2 M thiourea with cadmium to sulphur (Cd:S) molar ratio 1:2, and complexing agent liquor ammonia (33% NH₃) was used. The typical procedure for the film growth is described as follows, 15 ml of cadmium chloride (CdCl₂) solution into 50 ml glass beaker was used. This solution was stirred well for 30 min, and then 3 ml drop by drop NH₃ solution is added until the initially formed white precipitate is completely dissolved and then the solution becomes homogeneous under continuous stirring. The clean glass slides were vertically immersed in the bath using Teflon holder, then 15 ml of thiourea [CS(NH₂)₂] is added in the bath solution and stirred for 20-30 min. The temperature is gradually increased to 70°C for all samples. As the reaction was started the solution color gradually changed from transparent to light yellow and after completion of the reaction this turns bright yellow. The films removed from the bath after 60 min were highly transparent and uniform with well adhesion to the glass substrate and therefore used for further characterization. After deposition, the CdS films were rinsed with double distilled water and alcohol to remove the loosely adhered CdS particles on the film and finally dried in air at room temperature. Thicknesses of the thin films of the samples were found to in the range 80 to 90 nm.

Second method; CdS nanocrystalline thin films were deposited on glass substrates by thermal evaporation technique in a vacuum of ~ 10^{-6} Torr with the help of vacuum coating unit ( DENTON VACUUM, INC. model no DV 502 evaporator) at room temperature for substrates. This value of vacuum (10^{-6} Torr) was attained in vacuum chamber by the combination of rotary and diffusion pump. A clean evaporation source molybdenum boat was fixed in the filament holder inside the chamber and glass substrates which were placed directly above the source at a distance of nearly about 12 cm. Stoichiometric CdS powder was purchased from Sigma-Aldrich Company with high purity around 99.999% was placed in a molybdenum boat. The heater was then connected to the evaporation source, which in turn slowly heated the CdS source to temperatures greater than melting point. This allowed the evaporation of CdS material, with a deposition rate, \( r_d = 20 \text{ Å/s} \). Thin films of CdS that have thickness around 300 nm. In both prepared methods the thickness of thin films were measured with commonly used weight difference method by using a sensitive microbalance.

After finishing the deposition of all the samples from CBD and thermal evaporation techniques, the CdS thin films were subjected to an annealed at 250°C, 350°C and 450°C, in vacuum (~ 10^{-2} torr) for one hour. Annealed which is performed by a tubular furnace, afterwards the sample was allowed to cool down naturally.
2.2. Characterizations

X-ray diffraction (XRD) is the oldest but still more powerful technique of characterization for obtaining information about the crystallographic aspects of a thin films [34]. The structural properties of the as-deposited and thermally annealed CdS nanocrystals films are investigated from the X-ray diffraction (XRD) data taken by (XRD, Panalytical X’Pert Pro) diffractometer with CuKα as the X-ray source (λ=1.5406 Å) in 2θ range from 20°-70°.

The optical properties such as transmission, absorption and optical energy band gap of the thin films are studied by using double beam spectrophotometer (HeλIOS α UV-Vis-NIR spectrometer) in the wavelength range 300-1000 nm.

3. Results and discussion

3.1. Structural studies

The crystallite size and crystal structure of the CdS thin films were determined from X-ray diffraction pattern. It has been reported that the preferred orientation of thin film on glass substrate is affected by the experimental parameters in different deposition techniques [35,36]. CdS is known to exist in either cubic or hexagonal structure or sometimes a mixture of both phases [37-39]. Figure 1 shows the XRD pattern of as-deposited and annealed CdS thin films. The XRD peaks indicate that the films are nanocrystalline in nature. Figure 1(a) shows the X-ray diffraction pattern of the as-deposited CdS thin films by CBD technique and annealed films at different temperatures. The film shows poor crystalline structure at deposited as compared to the other films annealed at 250, 350 and 450°C. Because of the little thickness of the films can show the broad lump in the range of scanning angle of 20° to 40° in figure 1(a1) is due to the amorphous glass substrate [30]. All the films have a hexagonal structure (Wurtzite type, which is the most thermodynamically stable [40]) with a preferred orientation of (002). As can be seen from XRD pattern, the crystallinity of thin films get improved with increasing of annealing temperature. This improvement may be attributed to recrystallization of the films structure, by enhancement of the rearrangement of Cd and S atoms in the film crystallites after annealing [30]. With the increasing of annealing temperature, intensity of hexagonal peak of thin films is also increased. But it remains much lower than the intensity of the peaks in X-ray diffraction pattern of the films resulting from thermal evaporation due to the little thickness of the films.

Figure 1(b) shows the X-ray diffraction pattern of the as-deposited CdS thin films by thermal evaporation technique and annealed films at different temperatures. These results indicate that all the films have a polycrystalline structure. We can observe from the diffraction patterns increase the peak intensity with the annealing temperature indicating a good improvement in the crystallization of the material. In the present diffraction pattern of XRD for the as-deposited and annealed CdS thin films at 250°C, 350°C and 450°C, seven strong diffraction peaks are assigned to the (100), (002), (101), (102), (110), (103), and (112) planes of CdS are seen with hexagonal structure, respectively. These planes are confirmed from JCPD card no. 01-070-2553. The relatively stronger peak along (002) plane in all the films indicates that the films are highly oriented along the c-axis, perpendicular to the substrate plane. The similar film structure has also been reported by other researches [41-43].

Elemental cadmium and /or CdO are not present in the diffractograms, suggesting that oxidation is prevented during thin film growth. However, peak height along (002) plane is observed quite higher for T.E.-CdS film indicating the better crystalline quality. Furthermore, raising the annealing temperature did not lead to the formation of other phases. It has been observed that the FWHM of XRD peak decreases with increase of temperature (figure 2). It is well known that the lattice parameters are temperature...
dependent, and an increase in temperature leads to expansion of the lattice [44,45].

The lattice parameters, a and c of the unit cell of the hexagonal CdS thin films were evaluated from [26]:

\[
\frac{1}{d^2} = \frac{4}{3} \frac{h^2+k^2+k^2}{a^2} + \frac{l^2}{c^2}
\]  (1)

Where \(d\) is the inter-planar spacing of the atomic planes, \((h,k,l)\) are Miller indices. Crystallite size of the prepared CdS films for different annealed conditions were determined from the stronger peak of (002) plane from each XRD patterns using Scherrer formula [46].

\[
D = \frac{k\lambda}{\beta_2 \cos \theta}
\]  (2)

Where \(k\) is a constant (shape factor) taken to be 0.9, \(\lambda\) is the wavelength of X-ray source (\(\lambda=1.5406\) Å), \(\beta_2\) is the full width at half maximum (FWHM) of (002) peak of XRD pattern and \(\theta\) is the Bragg’s diffraction angle in degree. It is observed that the crystallite size and lattice parameter of CdS increase with increasing temperature as mentioned in Table 1.

The dislocation is imperfection in the crystal which is created during growth of the thin film. The dislocation density \(\delta\) was calculated from the crystallite size of the deposited samples using Williamson and Smallman’s formula [47].

\[
\delta = \frac{1}{D^2}
\]  (3)

The strain \(\varepsilon\) in thin film is defined as the disarrangement of lattice created during their deposition and depends upon the deposition parameters. The micro strain \(\varepsilon\) is obtained by using the relation [48] given in Eq. (4).

\[
\varepsilon = \frac{\beta}{4\tan \theta}
\]  (4)

The number of crystallites per unit area \((N)\) of the films were determined with the use of the following formulae [49]:

\[
N = \frac{t}{D^3}
\]  (5)

Where \(t\) is the thickness of the film.

The increase in crystallite size is due to the aggregation or coalescence of small nanocrystalline particles. It was found that the average size of the crystallites increases and the average dislocation density decreases with increasing annealing temperature. The line broadening gets reduced because of annealing temperature, owing to increase in crystallite size and decrease in strain of the material [50,51].

Table 1 illustrates the structural parameters of as-deposited and annealed CdS thin films.
Figure 1. XRD patterns for as-grown (a): CBD-CdS and (b): thermal evaporation-CdS thin films, with annealed conditions.
Table 1. Structural parameters of as-deposited and annealed CdS thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ann. Temp.</th>
<th>Lattice constant (Å)</th>
<th>FWHM</th>
<th>Crystalline size (nm)</th>
<th>No. of Grains/Area</th>
<th>Dislocation density (10^12/cm^2)</th>
<th>Strain (10^-3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBD</td>
<td>As-deposited</td>
<td>......</td>
<td>......</td>
<td>......</td>
<td>......</td>
<td>......</td>
<td>......</td>
</tr>
<tr>
<td>CdS</td>
<td>250</td>
<td>4.1266</td>
<td>6.5506</td>
<td>0.0114</td>
<td>12.50</td>
<td>4.10</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>4.1744</td>
<td>6.6621</td>
<td>0.0087</td>
<td>16.24</td>
<td>7.00</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>4.1858</td>
<td>6.6750</td>
<td>0.0043</td>
<td>32.86</td>
<td>0.84</td>
<td>0.10</td>
</tr>
<tr>
<td>T.E</td>
<td>As-deposited</td>
<td>4.1265</td>
<td>6.5506</td>
<td>0.0164</td>
<td>8.66</td>
<td>46.19</td>
<td>1.33</td>
</tr>
<tr>
<td>CdS</td>
<td>250</td>
<td>4.1594</td>
<td>6.6063</td>
<td>0.0114</td>
<td>12.40</td>
<td>15.73</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>4.1744</td>
<td>6.6621</td>
<td>0.0087</td>
<td>16.24</td>
<td>7.00</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>4.1858</td>
<td>6.6750</td>
<td>0.0043</td>
<td>32.86</td>
<td>0.84</td>
<td>0.10</td>
</tr>
</tbody>
</table>

3.2. Optical studies

The optical properties of the films deposited on glass substrates were determined from the transmission and absorption measurements in the range 300-1000 nm. The wavelength dependence of the optical transmittance spectra of as deposited and annealed of CdS thin films prepared by CBD methods are shown in figure 3(a1) measured at room temperature. As seen, all CdS thin films have high transmittance in visible and NIR region of solar spectrum. The average optical transmittance of as-deposited CBD-CdS thin films is about 84%, while after annealing at
250°C, 350°C and 450°C, the transmittance is 86%, 90% and 92%, respectively. While, it is apparent that the absorption spectra in figure 3 (a2) of annealed CBD-CdS thin films get reduced compared to the film as-deposited at room temperature. These increases in optical transmittance and decreases in optical absorbance spectra with increase of annealing temperature, it may be due to the reduction in voids, lattice imperfections and in addition to increment in crystallite size which is in correlation with measured value of crystal size in Table 1. Figure 3 (b1) shows the transmittance of as-deposited and annealed of T.E.-CdS thin films. Relatively high transmittion of CdS films and sharp fall of transmission at band edge is an indication of low surface roughness and good homogeneity of the film [52]. The average optical transmittance of as-deposited T.E.-CdS thin films is about 92%, while after annealing the transmittance is 83%, 78% and 78%, respectively. The oscillations of transmittance are due to thin film interference effects. Interference maxima and minima due to multiple reflections on the film surfaces can be observed in the transmission spectra. The appearance of interference fringes in these spectra indicates the excellent surface quality and films are free from any inhomogeneity. Optical investigations of films reveal that there is a band to band direct transition. It is evident from figure 3 (a2 and b2) that all films exhibit absorbance edges which are blue shifted with respect to bulk CdS, indicating quantum confinement effect in nanocrystalline film.

Absorbance coefficient α associated with the strong absorption region of the films was calculated from absorbance (A) and the film thickness (t) using relation [53,54]:

\[
\alpha = \frac{2.3026 \ A}{t} \quad (6)
\]

The sharp decrease in the optical absorption at the longer wavelength resulted from the excitation of charge carriers across the optical band gap, \(E_g\), which may be estimated by using the following relation and Tauc plot [55]:

\[
\alpha \nu = A(h\nu - E_g)^n \quad (7)
\]

Where A is constant (is characteristic parameter independent of photon energy), \(\nu\) the incident photon energy and \(n\) is a constant which depends on the nature of the transition between the top of the valence band and the bottom of the conduction band. Now \(n\) in the equation (7) can have values 1/2, 2, 3/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. The variation of \((\alpha \nu)^2\) versus \(\nu\) (figure 3 (a3 and b3)) is linear at the absorption edge which confirms that CdS is a semiconductor with a direct band gap. The extrapolation of the straight line to \((\alpha \nu)^2 = 0\) axis gives the energy band gap of the film material and listed in Table 2, for as-deposited and annealed films. The \(E_g\) for as-deposited CBD-CdS and T.E.-CdS films was found to be 2.75 eV and 2.60 eV, respectively, which gradually decreased to 2.45 eV and 2.43 eV with increasing of annealing temperature. The decrement of the optical band gap, \(E_g\), may be attributed the enhancement of crystallite size, the improvement of the film microstructure and amorphous to crystalline transition occurs by increasing annealing temperature.

From the band gap values, the crystallite sizes were estimated using effective mass approximation (EMA) method and following equation [56].

\[
E_{th} - E_{gb} = \left[ \frac{\hbar^2 \pi^2}{2 R^2} \left( \frac{1}{m'} \right) \right] \quad (8)
\]
Where $E_{th}$ is the band gap of CdS thin films, $E_{gb}$ the band gap of bulk CdS (2.42 eV), $m^*$ is the reduced mass [$\frac{1}{m^*} = \left( \frac{1}{m_e} + \frac{1}{m_h^*} \right)$], $m_e^*$ is the effective mass of electron ($= 0.19 m_e$), $m_h^*$ is the effective mass of the hole ($= 0.8 m_e$) and $R$ is the radius of CdS crystallite size. From the calculation, it is found that the crystallite size increases with the increase of annealing temperature. The observations are shown in Table 2. Figure 4(a) shows the variation of crystallite size with annealing temperature. The annealed samples show a relative decrease in band gap with annealing temperature, figure 4(b).

![Figure 3](image1.png)

**Figure 3.** Transmittance, absorption spectra and band gap for as-grown (a): CBD-CdS and (b): T.E.-CdS thin films, with annealed conditions.
4. Conclusions

The semiconducting thin films of CdS were successfully deposited on glass substrates using two different methods: CBD and vacuum evaporation techniques. XRD results reveal that the CdS films exhibit a hexagonal structure with strong orientation along (002) direction, irrespective of annealing temperature, and no mixed phases...
were observed. As can be seen from the micro strain and dislocation densities values that the crystallinity of thin films prepared by T.E., showed good quality as compare to these prepared by CBD, as well as are highly adhesive and smooth surface (optical quality). Also the XRD measurements reveal that crystallite size increases as the annealing temperature increases. The optical transmittance and absorbance varied with the annealing temperature. Blue shifting of the absorption edge showed that the prepared films are composed of nanocrystals of CdS. Maximum band gap of 2.75 eV for CBD-CdS and 2.60 eV for thermal evaporation-CdS were calculated from the shift in absorption edge as a consequence of quantum confinement effect.

Acknowledgment
The authors are thankful to the Department of Physics, College of Science, University of Basrah for providing the opportunity to complete this work in the laboratories of the department and to providing data of UV-Vis spectrophotometer.

References
تأثیر درجه حرارة التلذین على الخواص الترکیبیة والضوئیة للغشیت الرقیقة لکبریتید الكادمیوم

الخلاصة:

رُسِبت الأغشیة الرقیقة لـ CdS على الگوان الزجاجیة بطریقین متفاوتین، ترسبіن الحمام المعنیCBD والتیک الحراری T.E. (T.E.). تم دراسة تأثیر درجه حرارة التلذین على الخواص الترکیبیة والضوئیة للغشیة الرقیقة لـ CdS ودیاً. تم دراسة الخواص الترکیبیة للغشیة الرقیقة T.E. (T.E.) باستخدام طیبیة جودة الأشعة السیبیة XRD. حسبت من هذه الأغشیة لـ تکریب (هیكل) ${\text{CdS}}$ مع اتجاه مفضّل للنمو على طول المستوی (002). زداد حجم البیلورات المستحیل من XRD مع زيادة درجة حرارة التلذین. لاحظنا أن تکریم الشیبیة، الاجهاد المایکرو (الصغیر)، وكثافات الاتخاذ (الخلع) بعد البیلورات في وحدة المساحة تكون ذات قیم متغیرة، جسمیة من بين هذه الصلابات والمحسوبة من درجات حرارة التلذینREGION. تحلیل XRD عن طریق قمدي الگوان العالیة للغشیة الرقیقة المرسیة والمدمنة. تم حساب (تقدير) قمدي نطاق الطاقة الضوئیة للغشیة الرقیقة لـ البیلورات النانویة من قیاسات الامتصاصیة. انخفضت قم فجوة نطاق الطاقة للغشیة الرقیقة T.E.-CdS من 2.45 eV إلى 2.75 eV من CBD-CdS الناتجة من طریقة عدد البیلورات النانویة F3 من T.E.-CdS من 1.60 کمی (کیفیتیة للتقید (الحبس) الرقیقة) من البیلورات النانویة بحجم معین.