Structural and Optical Properties of Chemical Deposition CdS thin films

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Abstract

CdS thin films have been prepared by chemical bath deposition (CBD) method on glass substrates at solution temperature 80 $^{\circ}$C. Cadmium acetate was used as a source of Cd^{+2} and thiourea as a source S^{-2}. After three times of sequences deposition a 100 nm CdS thin films is obtained.

The Structure of these films studied by X-Ray diffraction were polycrystalline hexagonal phase .The films exhibited high optical transmittance T~50-100 % and low reflectance in the wavelength (500-900)nm which make them useful as a transparent window in solar cells. The optical constants (n,k) were also calculated in the same spectrum region. The optical transitions were due to direct allowed in quantum mechanical sense. The value of the optical energy gap for the as deposited and annealed films was in the range (2.35-2.43) eV. Vacuum annealing at (200,300)$^{\circ}$C improved the crystalline structure of the films.

1. Introduction

The use of thin film polycrystalline semiconductors have attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices . The technological interest in polycrystalline based devices are mainly caused by their low production cost[1].

Among the II-VI semiconductors,CdS polycrystalline thin films is a representative material with many applications such as large area electronic devices and solar cells, it has a wide direct band gap (2.42 eV) so has been used as a window material together with several semiconductors such as CdTe ,Cu_2S and $CuInSe_2$. Also the interest in CdS thin films stems from its piezoelectric properties and potential laser applications.[2,3,4]

Many techniques have been reported in deposition of CdS thin films. These include evaporation, sputtering, spray pyrolysis, molecular beam epitaxy (MBE) technique, photochemical deposition, successive ionic layer adsorption and reaction (SILAR) method [5-12].In all of these deposition methods there are some problems in each of them, for example , it

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is difficult to obtain a stiochiometric CdS films by evaporation technique and a high substrate temperature is required in spray deposition.[13]

The chemical bath deposition (CBD) method appears to be a relatively simple, in expansion method to prepare a homogenous films with controlled composition [14]. In particular CBD is widely used for a achieving good-quality CdS thin films [15] .The CBD method gives poor crystalline quality of CdS layers in comparison with other deposition techniques but films which deposited by this method gives best photoconductivity and morphological properties such as roughness and pinhole density as compared with films processed other techniques[16] .

In this paper , chemical bath deposition has been carried out to prepare CdS thin films by using cadmium acetate as a source of cadmium ions(Cd^{+2})and thiouriea as a source of sulfur ions (S^{-2}) as well as ammonium acetate acts as buffer solution .The structural and optical properties of CdS thin films were also studied.

2. Mechanism of CdS films formation

Formation of cadmium sulfide thin films using CBD method is based upon two main mechanisms[17]:
1. heterogeneous mechanism: growth occurs ion-by-ion on substrate surface ,which is responsible of formation well crystallized adherent films of CdS on glass substrate.
2. homogenous mechanism : growth of colloidal particles of CdS mainly on the bath solution and particularly upon the substrate leading to formation poorly adherent films .

Ammonium formation is given by:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$
(1)

The PH or OH concentration play main role in reaction and the PH calculated from the equation:

$$PH = PK_w - PK_b + \log\left(\frac{[salt]}{[base]}\right)$$
(2)

Where: [salt] the concentration of salt (ammonium acetate).
[base] the concentration of base (ammonia).
PK_w: dissociation constant of water
PK_b: : dissociation constant of base(9.2 at 25 ^{o}C)

The method of the preparation of cadmium sulfide (CdS) includes the reaction of cadmium(II) ion(Cd^{2+}) with sulfide ion(S^{-2}). Sulfide ions found in solution from thiourea as shown in the equations 3,4 below:

$$(NH_2)_2 CS + OH^- \leftrightarrow SH^- + CN_2H_2 + H_2O.........3$$
$$SH^- + OH^- \leftrightarrow S^{2-} + H_2O........4$$
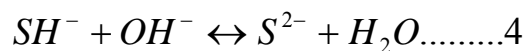
The reaction achieved in basic medium PH(9-10) using a buffer solution (ammonia and ammonium acetate) and the cadmium ion react with base as presented in equations 5,6

$$Cd^{2+} + 2OH^- \leftrightarrow Cd(OH)_2 \downarrow \qquad (5)$$

$$Cd(OH)_2 + 4NH_2OH \rightarrow \left[Cd(NH_3)_4\right]^{2+} \qquad (6)$$
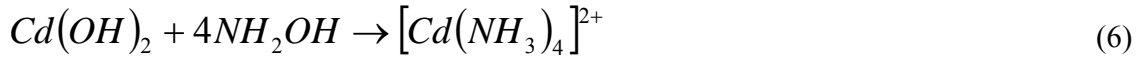
To form cadmium tetramine complex ions $\left(Cd(NH_3)_4^{2+}\right)$ the NH_3 concentration must be enough to ensure that the product of $\left[Cd^{2+}\right]$ and $\left[OH^-\right]$ is less than the solubility product of $Cd(OH)_2$ ($2x10^{-14}$) which form by the reaction.

Cadmium ions Cd^{2+} will react with sulfide ions to form CdS, equation 7 :

$$\left[Cd(NH_3)_4\right]^{2+} + S^{2-} \leftrightarrow CdS + 4NH_3 \qquad (7)$$
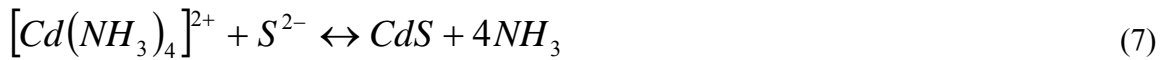
3. Experimental details
3(a) Film preparation

The CdS films were prepared using [11] aqueous solutions of cadmium acetate $(Cd(CH_3COO)_2)$, thiourea $((NH_2)_2CN)$, ammonium acetate $(NH_4(CH_3COO))$ and ammonia(NH_3). cadmium acetate of 0.03M and thiourea 0.06M were employed as a cadmium and sulfur ions sources. Ammonium acetate 1.0M was used as a buffer solution to controll the reaction rate .

In the reaction bath 5 ml of NH_3 solution was added into a 50 ml distilled water contained 2ml of 0.03M cadmium acetate .This mixture was stirred after 10 ml of 0.06M thiourea added slowly with continue stirred. DI water added to raise in volume to 125ml and PH kept at 9.5-10. Very cleaned glass substrates (25x75x2) mm was mounted vertically in solution with temperature kept at 80±2 ^{0}C for three times. The first deposition time was 2 hours, the second was 3 hours and the last was 2 hours. The deposition parameters are the same in all times. After the formations of the films are complete, the substrates were removed from the bath and rinsed in warm DI water.

Samples were annealed in closed quartz ampoule evacuated to 10^{-2} torr at temperatures 200 ^{0}C and 300 ^{0}C for 1 hour.

3(b) Measurements

Structural data for thin films were obtained using Philips PW 1253 X-ray diffractometer with CuKα radiation (wavelength = 1.541 A^0) .Room temperature optical measurements of all thin films were carried out using UV-VIS spectrophotometer (type Thermo spectronic) in the wavelength range 300-800nm**.**
The thickness of CdS thin films is found by using interference fringes method as illustrated below [18]:

At first remove part of thin films from substrate and placing it as viewed in figure (1) then light (sodium source) illuminated the slide .

Adjusted the lens and glass plate to get the parallel interference fringes formed in which air can be seen it by vernier reading microscope.

Film's thickness t is calculated from the equation:

$$t = \frac{\lambda L}{2w} \qquad (8)$$

Where λ :sodium light wavelength(589.3 nm)and w: the distance of a number of interference fringes .The actual thickness was 110 nm measured using Filmetrics F20 Film Measurement System(USA), Model No (205-0135). The disagreement measurement ratio with the above method was not more than 10%.
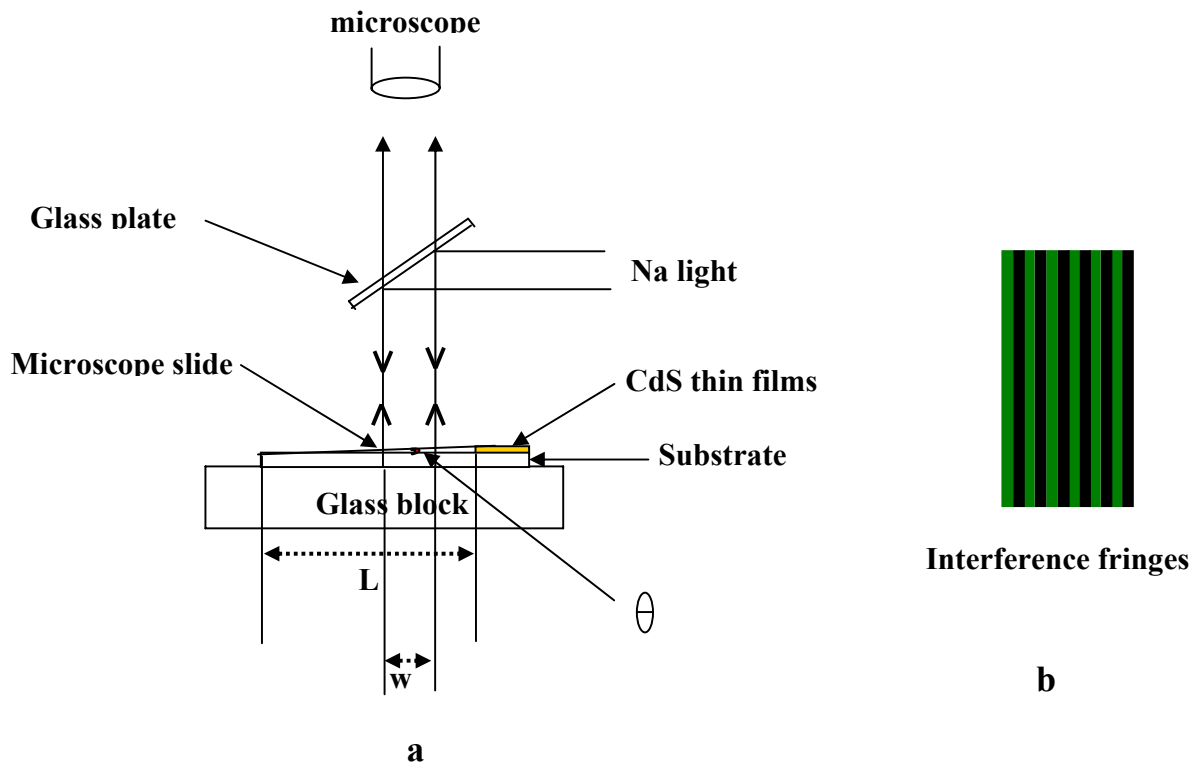

Fig.1: a: Schematic illustration of thin films thickness measurement
b: interference fringes

4. Results and discussion
4(a) Structural properties

The X-ray diffraction patterns of the CBD-CdS thin films (figure 1) that they are polycrystalline hexagonal (wurtzite) structure.

Films formation have a single peak represented (002) direction and it has a good agreement with standard X-ray diffraction data which reported in JCPD6-314 [3]. By using different preparation methods, CdS can exist in three crystal structure: hexagonal (wurtzite), cubic (zincblende) and both tetrahedrally coordinated and cubic (rock salt). Except the last phase, the other two phases have been reported in CdS thin films which formed by CBD method. The wurtzite phase is thermodynamically slightly more stable than zincblende and its can be gained by heating zinc blend phase to above 300-400 ^{o}C.[19]

Usually low temperature in CBD method led to zincblende CdS thin films phase. There are many variables affect the crystal structure, including the nature of the complex, the substrate and sometimes even stirring.

Lee [16] studied (used the same our materials) the substrates affect on the structure phase of CBD CdS thin films. The recourse of that different substrates led to hexagonal or cubic phase but a glass substrate gives hexagonal which agree with our results.

Some researchers noted that low ammonia concentration in solution lead to fabricate wurtzite phase of CdS because the Cd(OH)$_2$ will be clearly visible suspension (not completely dissolve).[20]

The films which annealed at 200°C and 300°C have another peak returned to (100) direction and the peaks becomes more sharp by increasing temperature of heat treatment which is indicated that the crystallinity of films were improving. Soubane et al [17] also studies the effect of heat treatment upon the CdS thin films which deposited by CBD method and concluding that the degree of crystallinity was improved.

The affect of annealing temperature on grain size (GS) of films also investigated. Grain size was determined from the (002) diffraction line using Sherrer formula [21]

$$GS = K\lambda / \beta \cos\theta \qquad (9)$$

Where β is the full width at half maximum (FWHM) of the peak corrected for instrumental broadening, λ is the wavelength of the X-ray and (K) is the Scherrer constant, which generally depends on the crystallite shape.

The grain size calculated of as deposited CdS thin films were 32 nm but after annealing at 200 0C and 300 0C for 1 hour the grain size becomes 38 nm and 47nm respectively.

Annealing thin films led to increasing in grain size because of decreases in the density of nucleation centers thus a smaller number of centers start to grow, resulting in large grains.
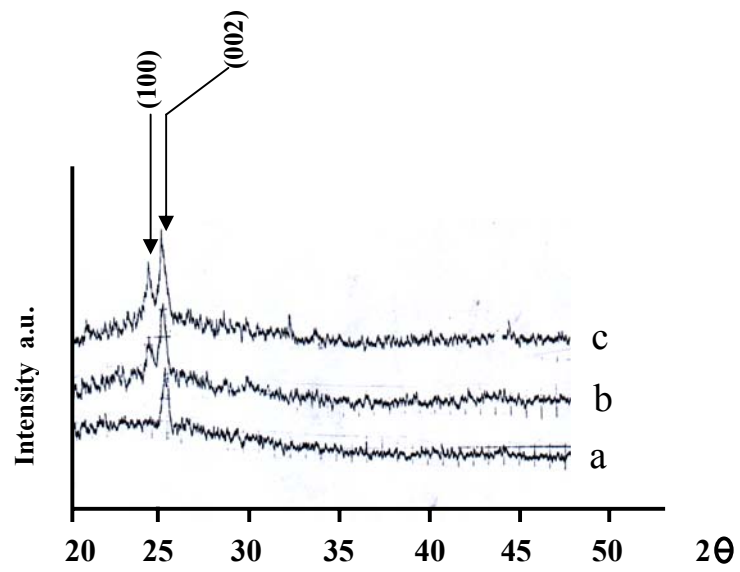
Fig.2: X-ray diffraction pattern a:as deposited b: annealed at 200 ^{o}C c: annealed at 300 ^{o}C

4(b) Optical analysis

Transmission spectra of as-grown and annealed films at 200 ^{o}C and 300 ^{o}C were taken from near ultraviolet (300nm) to near infrared (900nm) regions are shown in figure 3. The optical transmission edge is sharper when the films were annealed at 200°C and 300 ^{o}C indicating that annealing temperature can improve the crystallinity. Also we found that all films have high light transmission in the visible region so CdS thin films which deposited by CBD of the same conditions can actively used as the window material in solar cells.
Reflectance R of thin films was calculated from the equation:.[22]

$$R = 1 - \sqrt{\frac{T}{\exp(-\alpha t)}} \tag{10}$$

Where:
T: transmittance and (α) is the absorption coefficient.
The refractive index (n) was calculated from the equation:

$$n = \frac{1 + R^{1/2}}{1 - R^{1/2}} \tag{11}$$

Figures 4 and 5 show the plot of the reflectance and refractive index as a function of wavelength for as deposition films and annealed at 200°C and 300°C .The refractive index of a solid and in thin films gives information on the electronic polarizability, local field and for determining the density of colors inside the material[23].Both R and n decrease rapidly to approach constant values at long wavelengths.
From figures (2,3) it is found that the films exhibited high transmittance from 50-100% and low reflectance less than 20% .This property makes these films a good candidate as transparent window in solar cells.

The absorption coefficient α is given by:

$$\alpha = \frac{\ln(1/T)}{t} \tag{12}$$

The optical band gap was calculated using the Tauc relationship which is given by the formula [24]:

$$(\alpha h \upsilon) = A(h\upsilon - E_g)^n \tag{13}$$

Where (hυ) is photon energy, (E_g) is the optical band gap of the material, A is a constant and n = 1/2 for direct band gap material. . When $(\alpha h\upsilon)^2$ is plotted as a function of (hυ),the linear portion of the curve is extrapolated to $(\alpha h\upsilon)^2 = 0$,the band gap of the CBD CdS thin films as deposited and annealed found from figure 6.

We found that the value of E_g for the as deposited CdS thin film is (2.35) eV. After annealing at 200^oC and $300\ ^oC$ the films have an energy gap equal 2.43eV and 2.32eV respectively. Annealing lead to sharp absorption edge because the films becomes more crystalline and the grain size increase with increase annealing temperature.
The extinction coefficient (k) also calculated from the relation:[22]

$$k = \frac{\alpha \lambda}{4\pi}$$

(14)

Figure 7 show the variation of the extinction coefficient (k) versus the wave length of the as deposited and annealed CdS thin films.
Optical conductivity σ_{op} was calculated from the relation[22]:

$$\sigma_{op} = \frac{\alpha n c}{4\pi}$$

(15)

Where (c) is the velocity of light, figure 8 shows variation of optical conductivity with photon energy for CdS thin films as deposition and after annealing.
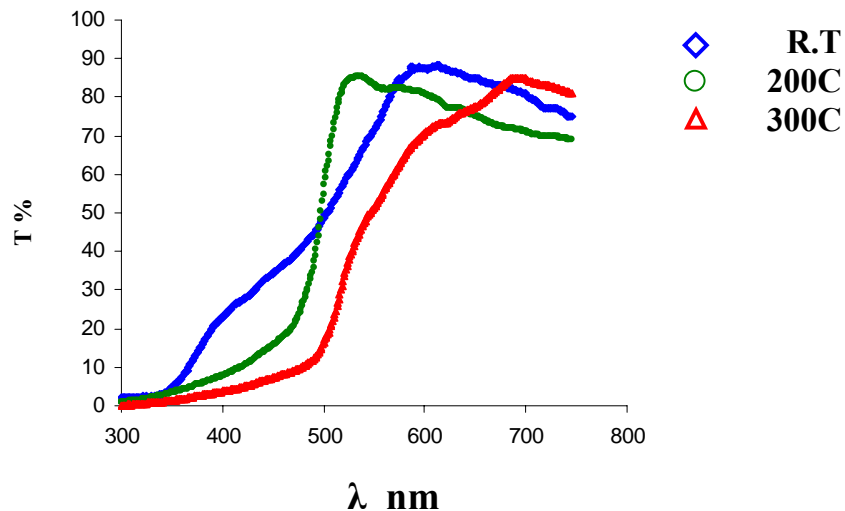

Fig.3:The transmittance as a function of the wavelength for CBD CdS thin films
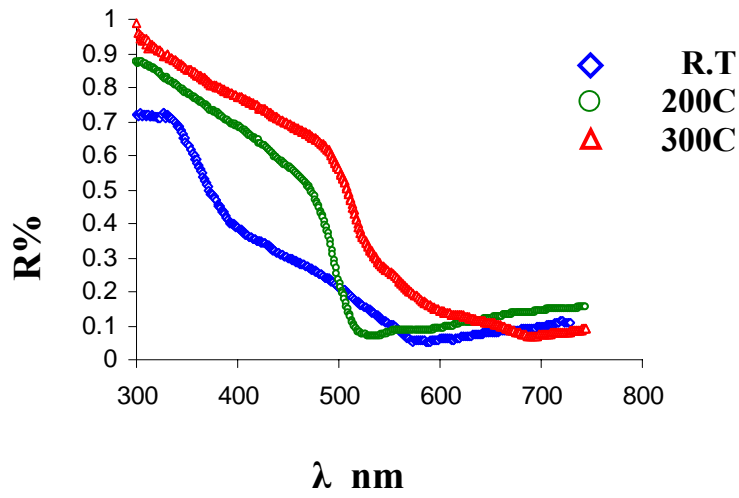
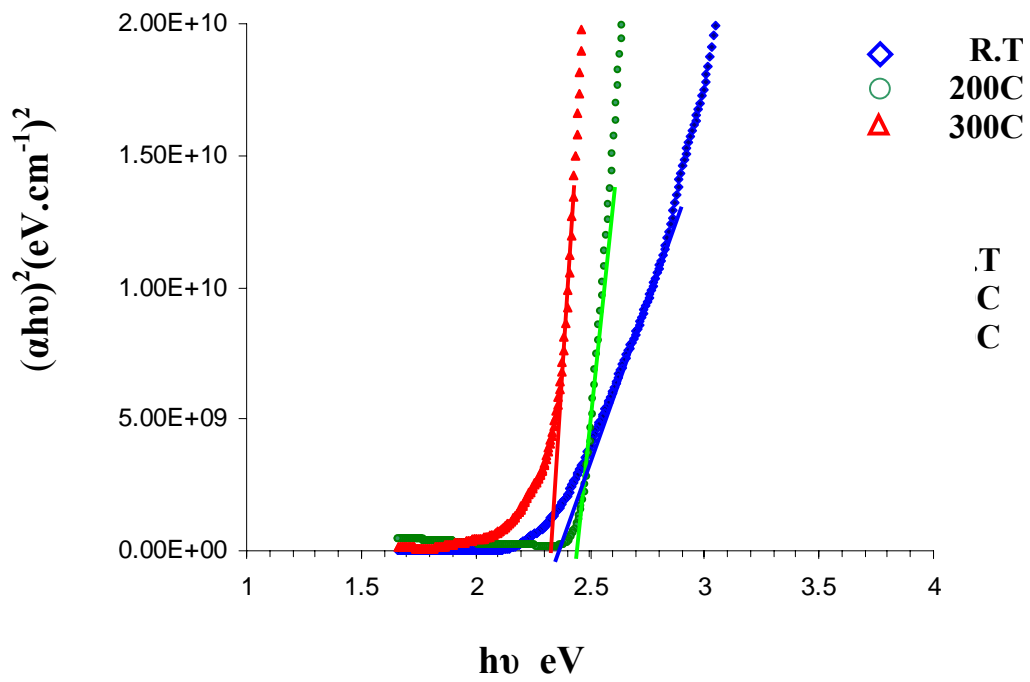Fig.4:The reflectance as a function of the wavelength for CBD   CdS thin films

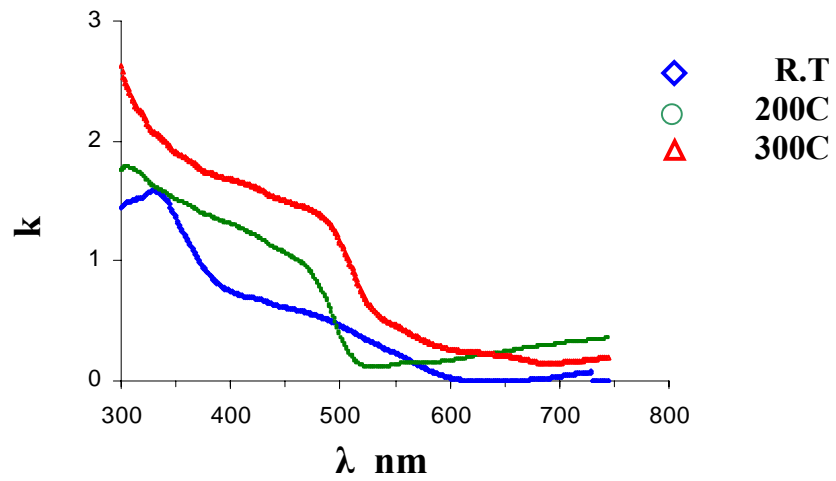Fig.6 :A plot of (αυ)² of as a function of photon energy for CBD CdS thin films

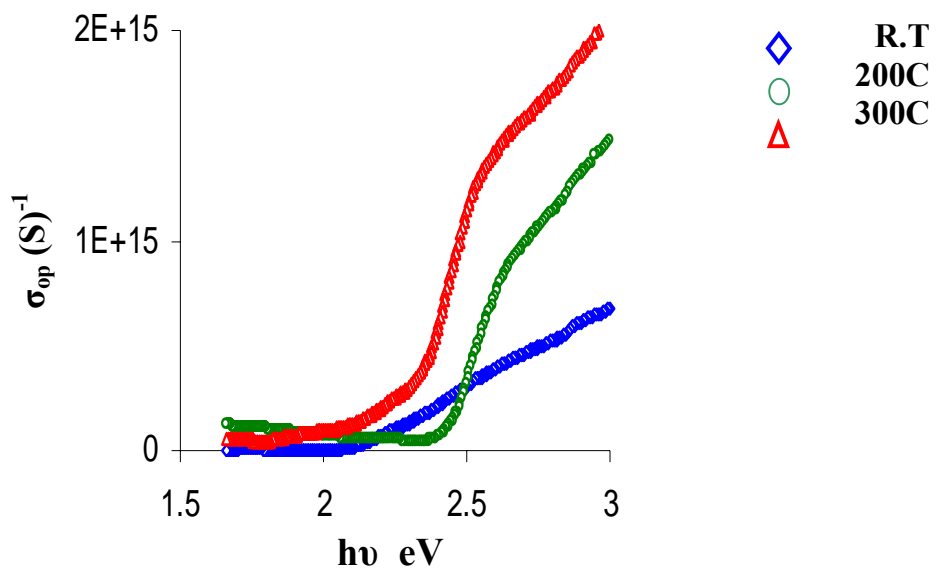Fig.7: The extinction coefficient vs. the wavelength for CBD CdS thin films

Fig.8: The optical conductivity vs. the photon energy for CBD CdS thin films

5. Conclusion

Chemical bath deposition (CBD) which is designed in the present work is an accurate method that can be used to prepare stiochiometric cadmium sulfide (CdS) thin films. The structural study of the as-deposited thin films shows that they have hexagonal single phase (wurtzite). Other reported papers which use CBD method to form CdS films obtained cubic structure or mixed phases, hexagonal and cubic but the hexagonal structure is more stable than the cubic in solar cells and other optoelectronic devices.

The present thin films show a high transparency in the visible region of the electromagnetic spectrum so it is possible to use them as a window layer in solar cells.

Annealing process made these films more crystalline and also changed the value of the energy gap. The preferred annealing temperature is 200 ^{o}C which gives thin film's energy gap= 2.43 eV.

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