

The Optical Properties of Cadmium Sulfide Thin Film prepared by Electrochemical Deposition Technique

Saeed J. Abbas

Dept. of Physics, Collage of science, Univ. of Basrah

Abstract

Cadmium Sulfide (CdS) thin films were prepared by electrodeposition technique using a simple cell, on stainless steel and ITO glass as electrodes. The films were investigated by XRD. The XRD pattern indicated that CdS films possessing a polycrystalline hexagonal structure with lattice constants ($a=4.223$, $c=6.684$ Å). The optical energy gap of these films were calculated from the absorbance measurements ($E_g = 2.45$ eV).

:

. ITO

($a=4.223$,

. $c=6.684$ Å)

($E_g=2.45$ eV)

1-Introduction:

In some applications, it is required to prepare a materials with a large surface area and with a lowest costs, as in solar cell panels. Therefore the simple and inexpensive methods are preferred from technical and economical viewpoints, because it is easy to commercialize the large area at reasonable cost.

In the last two decades, the methods, such as electrodeless(dipping),chemical bath deposition [1,2] and electrodeposition(E.D) [3-9] are very attractive. The E.D method had been used in preparation of large number of binary and ternary semiconductor compounds ,such as ,CdS, CdSe, PbS, PbTe,Cu(In,Ga)Se₂,and CdSexTe_{1-x} etc[3-9],and very recently, it was used to prepare microwire and nanowire of CdS and AgxO respectively [10,11]. The advantages of this method are low cost technology, ease of coating of large area, and can be prepared at low temperature compared with the conventional methods used to deposit the thin films of semiconductors, such as chemical vapor deposition(CVD) ,vacuum evaporation(VE), molecular beam epitaxial (MBE)[12] . Different results had been obtained by different workers who prepared CdS films by E.D method [3,6,8]. It has been found that the CdS properties are very sensitive to preparation conditions, such as, electrolytes, current density, temperature of electrolyte solution,etc. So that further investigation of these films prepared by this method is needed to understand and optimize these materials to qualified for the use in industry grade.

In the present work, we have prepared CdS by E.D method. Structural and optical properties were determined and compared with other works.

2-Experiments:***A-Sample preparation:***

The E.D method was used in CdS preparation .The electrochemical cell consists a beaker, provided with two electrodes from stainless steel, one act as anode and the other as a cathode for X-ray diffraction measurements. For

optical measurements, the cathode is replaced by commercial ITO glass. The electrodes were cleaned carefully by washing several times with distilled water, then immersing in dilute acid, and finally washed again with distilled water. The solvent of electrolyte solution was made up in a mixture containing one part water and nine parts DEG (Diethylene Glycol), and supporting electrolyte solution were (.055 M) CdCl₂ and (0.19 M) S, and (1 M) NH₄Cl, the choice of these concentrations depends on other work [3, 8]. The deposition was carried out at a constant current density of about (0.5-1) mA/cm² and at a constant temperature of the electrolyte solution of about 120° C. The films after prepared were left in free air at room temperature to dry. The heat treatment was achieved under vacuum at 200°C for three hours.

B-Measurement Devices:

X-ray diffraction (XRD) patterns are recorded by the X-ray diffractometer type Philips(PW4025) with wavelength of 1.54 Å from the CuKα line. The optical transmittance and absorbance spectra were measured by Heliosa(102024,v4.6) spectrophotometer (thermospectronics Co.) At the range of (300-900)nm. The other devices used in this work were: constant current source, coil heater, thermometer, power supply and digital millimeter.

C-Thickness Measurement:

The films thickness (d) calculated by Farady laws by the following equation [6]:

$$d = \frac{jM}{nF\rho}t \quad \dots(1)$$

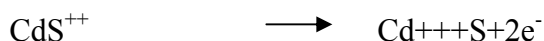
Where j is the current density,
 t is the time of deposition,

M is the molecular weight of CdS,

F is the Faraday (=96485 Coul./mole of electrons),

ρ Is the density of CdS(=4.82 g/cm³),

n is the number of electrons transferred(here n=2) computed from the chemical equation of CdS formation [6]:



The films thickness used for XRD and optical measurements were about 1.55 μm and 0.795 μm respectively.

3- Results and Discussion:

We observed that, the prepared films were homogenous, free from pinholes, no cracks, and it is in a good adhesion with a substrate even after heat treatment.

The XRD patterns for CdS films ,one as-grown and the second annealed at 200oC for three hours are shown in Figs.(1)and (2) respectively .It is obvious that the effect of annealing process leads to the presence of most peaks in Fig.2. On the other hand ,comparing the pattern in fig.2 with a standard pattern of CdS powder[13],indicates that Our CdS films possessing a polycrystalline hexagonal structure ,and peak heights of the pattern indicates strong c-axis preferred orientation [plane (002)]

The annealing process mainly leads to two effects, the grain growth and the recrystallization. When recrystllization occurs, the lines become sharp, while in grain growth the number of lines increasing. Therefore, the investigation of Figs. (1) And (2) leads to the conclusion that the peaks appearance may be attributed to the grain growth instand of the recrystallization [14]. The lattice constants were calculated (see Table 1) by the following equations [14] :

$$d_{hkl} \sin\theta = n\lambda \quad \dots(2)$$

and

$$\frac{1}{d^2_{hkl}} = \frac{4}{3} \left[\frac{h^2 + hk + k^2}{a^2} \right] + \frac{\lambda^2 l^2}{4c^2} \quad \dots(3)$$

$$\sin^2 \theta = \frac{\lambda^2}{3} \left[\frac{h^2 + hk + k^2}{a^2} \right] + \frac{\lambda^2 l^2}{4c^2} \quad \dots(4)$$

Where d_{hkl} is the interplanar spacing

2θ is the diffraction angle

hkl is the miller indices

n is the diffraction order ($n=1$)

λ is the x-ray wavelength

a and c are the lattice constants.

The grain size of the crystalline structure of the films were calculated from the XRD patterns for the preferred orientation (the largest peak in the pattern(Fig.(2)), the (002) peak) by Debye-Sherrers formula [7,14]:

$$D = \frac{0.94\lambda}{\beta \cos \theta} \quad \dots\dots\dots(5)$$

Where β is the full-width at half maximum of peaks expressed in radians.

In Eq. (5), the line broadening (width of spectral line), and the strain broadening are neglected. The strain broadening results from mismatching between the films and the substrates or from films shrinkage.

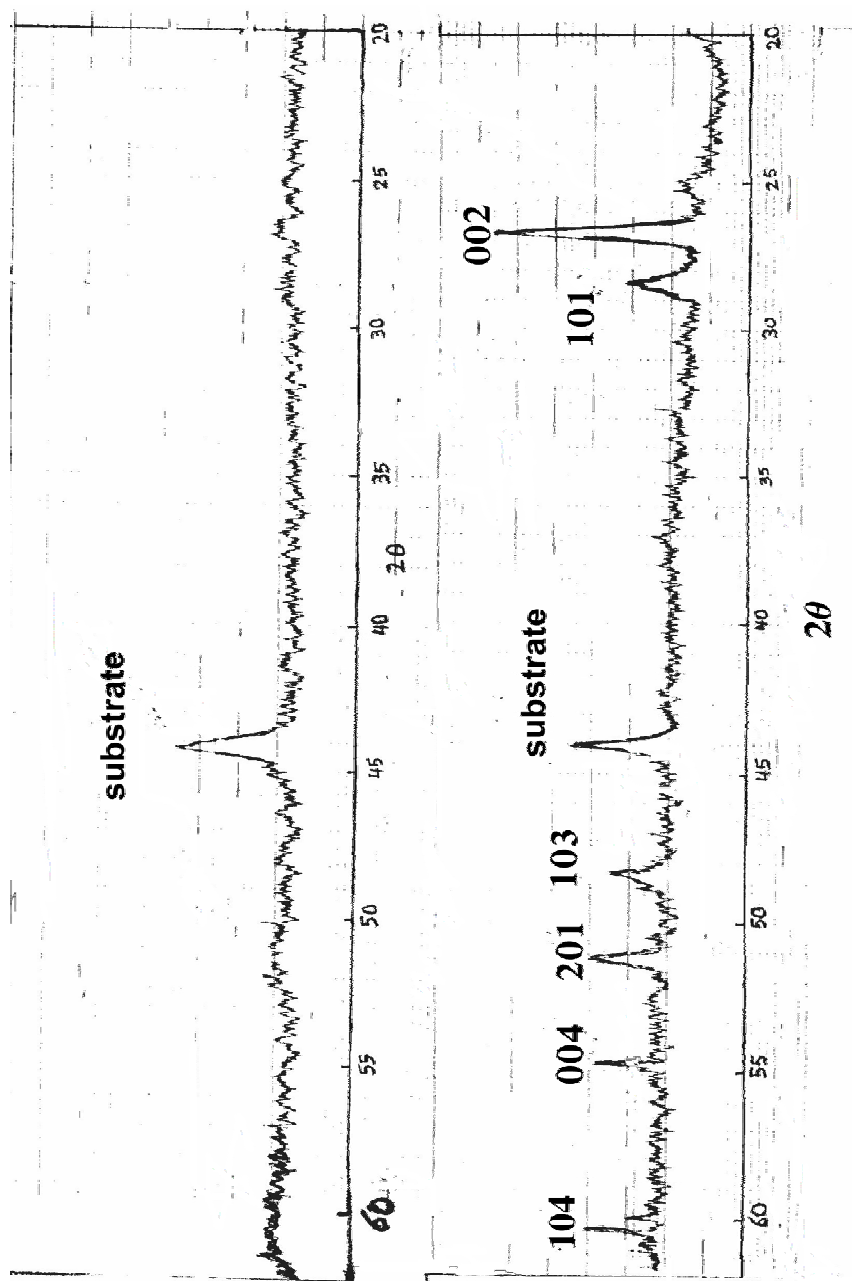


Fig. (1):(above) XRD pattern for CdS as grown
Fig. (2):(below) XRD pattern for CdS film annealing at 200° C

Table (1): Comparison between the present work and others.

Parameter	Present work	Others work	References	Remarks
Lattice constants (Å)	a= 4.233 c=6.684	a= 4.14 c=6.716	13 16	using different methods for preparation
Grain size D(nm)	28.26	10 56	16 ⁽¹⁾ 17 ⁽²⁾	=
Energy Gap (eV))	2.45	2.39-2.43	17 , 18	=

(1) Prepared at a substrate temperature = 200° C

(2) Without annealing, but drying at 20° C for 1.5 h.

The optical transmittance and absorptance as a function of wavelength in the range 300 – 900 nm is shown in Fig.3. The CdS films have high transmission in transparent region, and similar to these prepared by using other methods. This can be attributed to a good morphology, perfection and stoichiometry of film [12] .

The energy gap E_g was determined by analyzing the optical absorptance at fundamental edge ,using the relation [12] .

$$\alpha(h\nu) \approx (h\nu - E_g)^{1/2} / h\nu \quad \dots(6)$$

For allowed direct transition

Where $h\nu$ is the photon energy; α is the absorption coefficient.

The absorption coefficients were calculated according to the following relation [19] :

$$\alpha = \frac{2.303}{d} (A - A') \quad \dots(7)$$

where d is film thickness; A is the absorptance and A' is the correction factor used to cancel the affects of reflection losses ,its value represents of absorptance at the long wavelength tail of the absorption spectrum, where the absorptance approach constant value [19]. To verifying the direct transition the absorption coefficient plotted as a function of photon energy in Fig.(4),[the α values access 104],and as shown in Fig.(5),the plot of $(\alpha h\nu)^2$ versus $(h\nu)$ using eq.(6). Extrapolation of linear portion of the plot

to the zero absorption axis gives the direct energy gap value (2.45 eV), which is in agreement with the reported values by others [17,18]

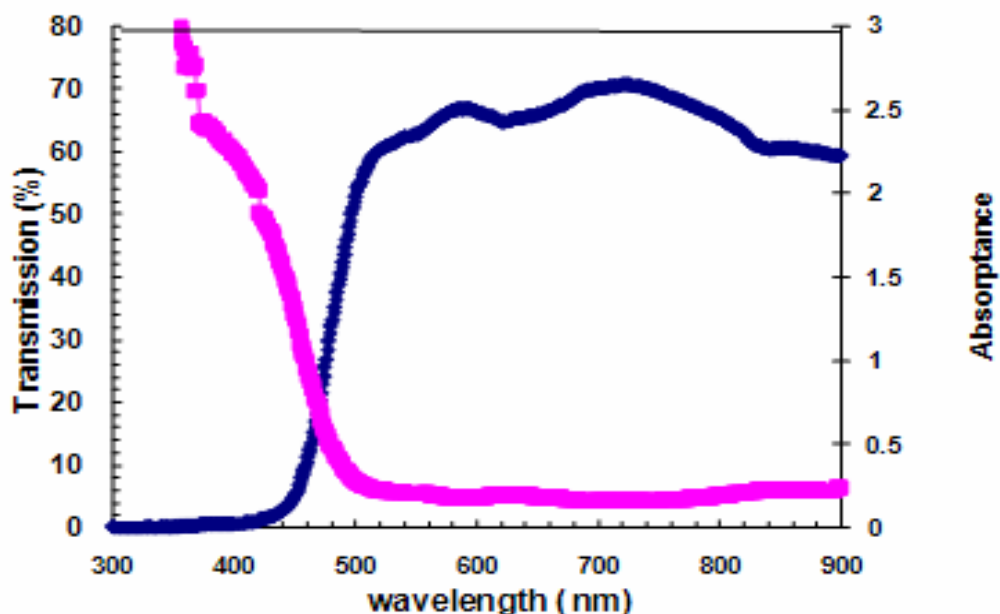


Fig.(3): Transmission and Absorption Spectra of CdS film prepared by electrodeposition method on ITO glass

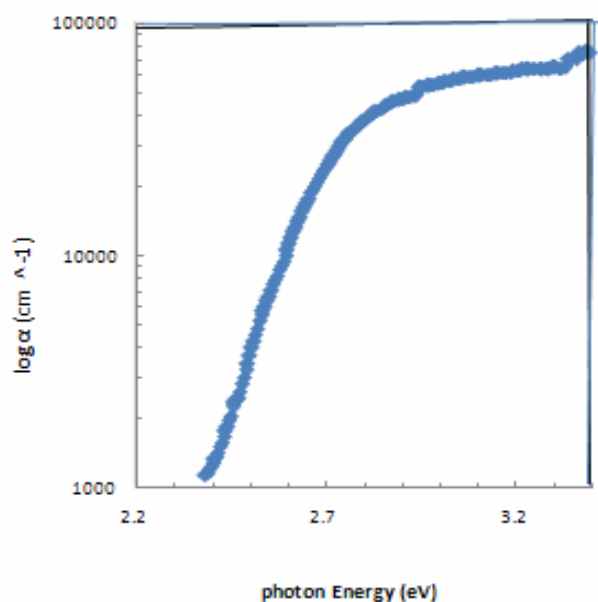


Fig.(4): The absorption coefficient versus photon energy

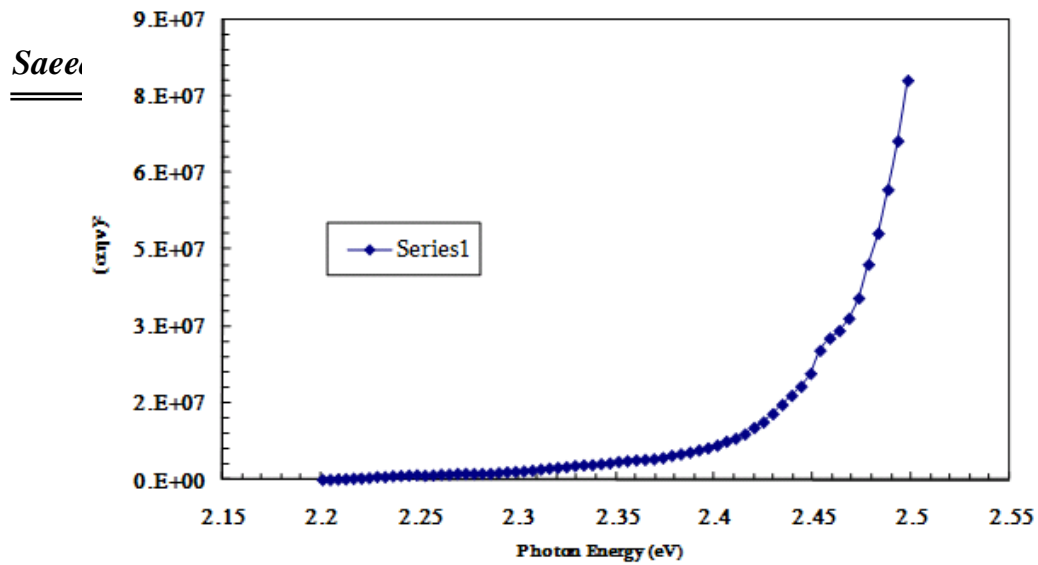


Fig. (5):($\alpha h\nu$)² versus photon energy .

4- Conclusions:

Cadmium sulfide thin films were cathodically electrodeposited from a mixture of CdCl₂, S, and NH₄Cl in a solution containing a nine parts of DEG and one part water. Its annealed film at 200°C is a polycrystalline and shows the hexagonal structure. The absorption data is interpreted due to an allowed direct transition of the energy gap of 2.45 eV .

Finally, We found, there are some differences between present work and others:

- a-There are (\pm) some shift in peaks situations between XRD pattern for CdS standard powder and present XRD pattern. And the highest peak in former is (101) while in present work is (002) ,as in(Ref.3).

- b-One of reported value of E_g of CdS electrodeposited on ITO glass is 3 eV[20] while E_g in present work is 2.45 eV .

- c-The CdS films electrodeposited on Pt is cubic [β -CdS] (Ref.6),while films on stainless steel are hexagonal(present work) .

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