# Investigation of optical properties of cadmium sulfide (CdS) thin films by chemical bath deposition.

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## Abstract:

Thin films of CdS were deposited on glass substrates using a chemical bath deposition technique from aqueous solutions of Cadmium sulfate (CdS) and thiouria. The films grown from the bath are uniform and adherent, have a high transmittance in the visible region. The CdS films properties studied include optical transmission, optical constant, dielectric constant, optical conductivity, and band gaps. The films in this study produced fairly high transmission (> 86% between 500 and 900). Band gaps of (2.4 eV) for direct transition were obtained. Such films could be used as photocells and other photoconductive devices, thin film transistors and diodes, piezoelectric ultrasonic transducers and amplifiers, piezoelectric acoustic resonators and electron beam-pumped lasers.

**Key words:** CdS thin film, CBD, optical properties.

## Introduction:

At present the importance of Cadmium Sulfide thin films as wide energy gap semiconductors has experienced a fast rising mainly due to its applications in piezoelectric transducers, laser materials and photovoltaic cells. The commonly used methods for depositing CdS thin films are vacuum evaporation, sputtering, spray pyrolisis, molecular beam epitaxy and electro deposition. The electron beam obtains in anew method recently developed. The chemical bath deposition (CBD) is an,, electroless,, technique is attractive as a simple and low cost method un fortunately, the deposition condition (Bath composition, reagent composition, temperature, PH, time, etc..) Strongly influence the film stoichiometry, microstructure and cristallinity. It is

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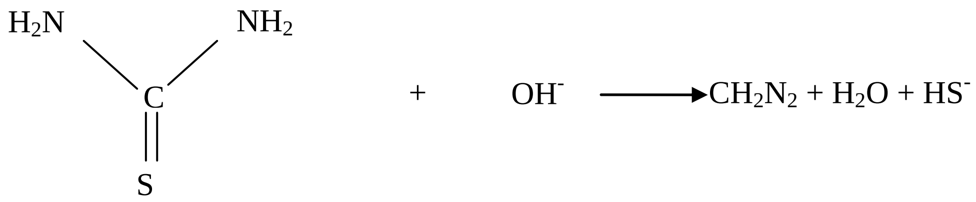
well known that these characteristics determine the optical and electrical properties of CdS films. Cadmium sulfide films were prepared from cadmium salt and thiourea by chemical bath deposition in alkaline solution[1].

A reaction mechanism for the formation of CdS is suggested below[2]:

1) Cadmium salt reacts with ammonia to from the complex compound.

$$CdSo_4 + 4(NH_3) \rightarrow (Cd(NH_3)4)So_4$$

2) Diffusion of the thiourea on CdS catalytic surface in an alkaline medium.




3) Formation of bivalent sulfide ions.

$$HS^- + oH^- \rightarrow S^{--} + H_2o$$

4) Formation of CdS.

$$Cd(NH_3)_4^{++} + S^{--} \rightarrow CdS + 2NH_3$$

The aim of this paper is study the optical properties of CdS films prepared by CBD method. The effect of bath concentration, PH value, temperature, and time on the optical properties and the band gap energy Eg of as-grown is reported [1].

## 1. Experimental work:

Substrate used for deposition CdS is borosilicate glass slides, which were first cleaned in distilled water in order to remove the impurities and residuals from their surfaces, followed by rinsing in chromic acid (for one day), to introduce functional groups called nucleation and / or epitaxial centers, which formed the basis for the thin films growth [3]. Then the samples were washed repeatedly in deionized water, and finally put in ultrasonic agitation with distilled water for 15 min then dried.

Cadmium sulfide films were prepared from cadmium sulfate and thiourea by chemical bath deposition in alkaline solution. The deposition of CdS films is achieved from dilute solutions. Sulfide ions are released in the bath by the hydrolysis of thiourea, in the presence of $OH^-$ ions. $Cd^{2+}$ ions are complexed with one or more of the complex agents like $NH_3$ [directly added as $NH_3$ (aq)], or $NH_4Cl$. This ensures slow release of $Cd^{2+}$ ions in the solution [1].

Films were deposited on glass slides by, 30 ml of 0.1M ($3CdSO_4.8H_2O$), 30 ml $NH_3$ solution and distilled water were mixed slowly at room temperature with continuous stirring. Substrates were then immersed in a beaker containing the reaction mixture. The beaker was placed in a water bath at temperature (80 ± 2 $^oC$). The solution was stirred with a magnetic stirrer type (MSH 300). Then, it was heated with continuous stirring to the required temperature of deposition, 30 ml of 0.2 M thiourea solution was then added with continuous stirring, and the pH measured with pH meter type (BIBBY). Substrates were then taken out after a suitable time, they were washed with distilled water and ultrasonic agitation to remove the porous cadmium sulfide over layer, then dried.

## 2. Measurements

A Cecile CE 7200 Spectrophotometer supplied by Aquarius company was used to record the optical transmission and absorbance for CdS/glass thin films for the range (375 – 900 nm). The data from transmission spectrum can be used in the calculation of the absorption coefficient (α) for CdS films, according to the following equation[4]:

$$\alpha = \frac{1}{d} \ln \frac{1}{T} \ \ldots\ldots.. \ (1)$$

Where d is the thickness of thin film, and T is the transmission.

In the direct band gap structure or direct transition semiconductors (present case), the absorption coefficient and optical band gap (Eg) are related by [5].

$$\alpha = (h\upsilon - Eg)^{1/2} \ \ldots\ldots\ldots \ (2)$$

Where h is Plank's constant and $\upsilon$ is the frequency of the incident photon.

The reflectance at normal incidence can be expressed in terms of the optical constants n and K as follows[6]:

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \ldots\ldots\ldots\ldots(3)$$

Where n is the refractive index. In the range of frequencies in which the films are weakly absorbing $K^2 << (n-1)^2$, the following can be expressed[6]:

$$R = \frac{(n-1)^2}{(n+1)^2} \text{.............} (4a)$$

*or*,

$$n = \frac{(1+R^{1/2})}{(1-R^{1/2})} \text{...........} (4b)$$

Film thickness is measured by optical interferometer method. The method is based on interference of the light beam reflection from thin film surface and substrate bottom.

He – Ne Laser (0.632 µm) is used and the thickness is determined using the formula:-

$$d = \frac{\Delta x}{x} . \frac{\lambda}{2} \text{..........} (5)$$

Where: x is fringe width, $\Delta$x is the distance between two fringes and $\lambda$ is the wave length of laser light.

## Results & Discussion

### 1. Transmission and Absorption

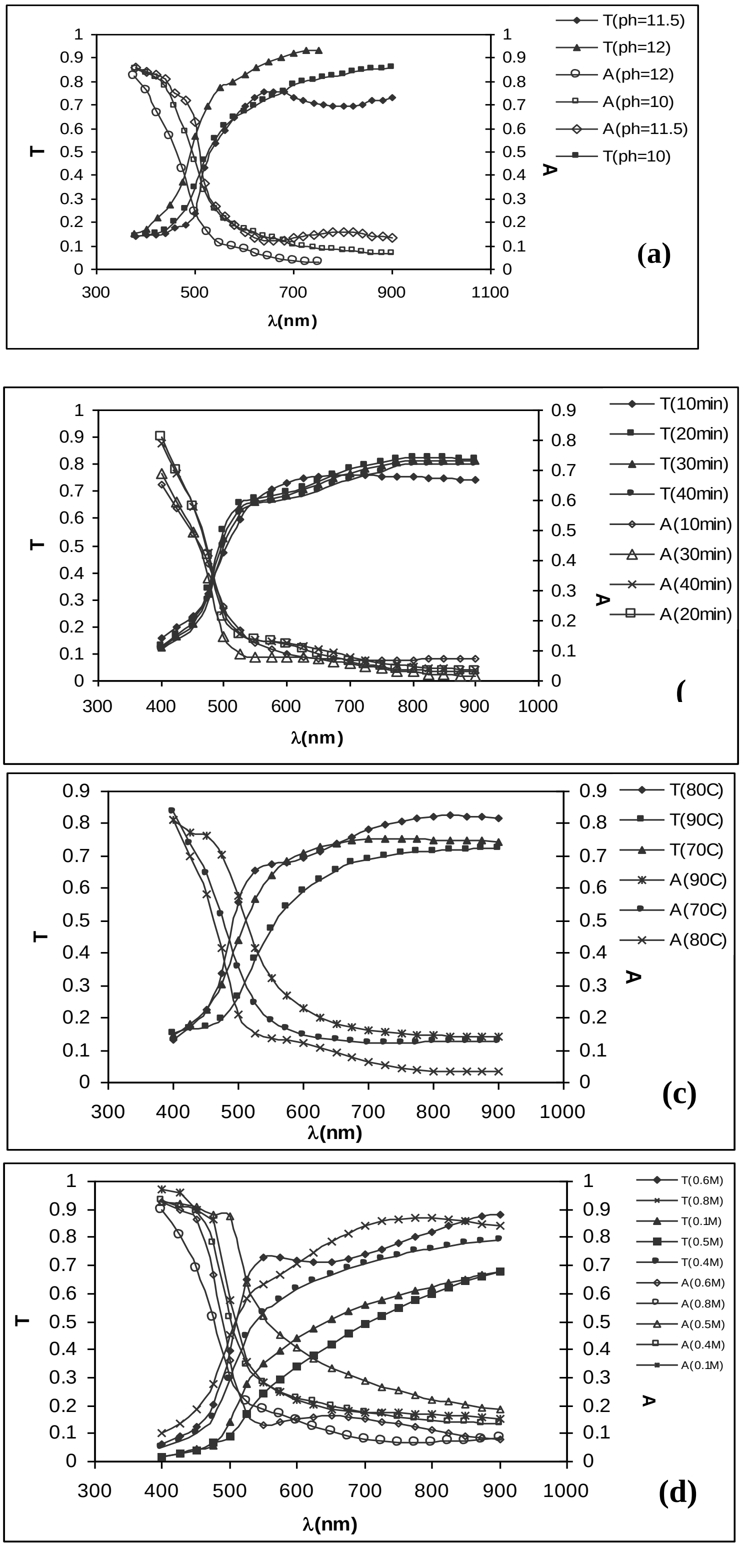
Many studies present optical absorption or transmission spectra of the resulting films. The purpose of these spectra is usually to show that the deposits are of high quality (in most cases, scattering is undesirable) and are indeed made of the material claimed (as seen from the band gap value, which can be estimated from these spectra) [7]. Scattering is usually caused by optically large nonhomogeneous aggregates; this often occurs by sedimentation of colloidal aggregates onto the substrate. There have been few studies on control of scattering in $(CBD)$ at lower deposition temperatures. However, another study, using a triethanolamine bath, reported more aggregates at higher deposition temperature, although not in a regular manner, resulting in generally lower transmission at higher deposition temperatures. Therefore, as is generally the case, such specific results should not automatically be applied to all $(CBD)(CdS)$ films [8].

Transmittance and absorbance as functions of wavelength are shown in figures (1) at different condition. We have found that the films have high transmission at long wave lengths approximately (70 – 80 %), and decreasing transmission to (10%) at short wave lengths.

Films transmission decreases with increasing deposition time and temperature at wave lengths higher than the absorption edge. On the other hand increasing thiourea ion concentration increases transmission.

These opposite effects could be attributed to the increased abundance and or size of the single crystallite overgrowth. The figure shows the effect of $[pH]$ on the optical transmission spectra of the as–deposited $(CdS)$ films . It was observed that the transmission of the film decreases with increasing in $[pH]$ up to (11.5) after which it starts increasing with further increase in $[pH]$. The increase and decrease in the transmittance percentage during the continuous increase in $[pH]$ is due to the transition of $(CdS)$ phase from mixed cubic and hexagonal to hexagonal structure, and also due to change in the films thickness with the $[pH]$ of the solution. With this result we thing that pH 11.5 is the optimum value to deposit CdS film for photovoltaic application.

The variation in the absorbance of the films was a result of the presence of water molecules in the films




**(a) A& T For different pH.**

**(b) A&T for different times.**

**(c)A&T For different thiourea ion concentrations**

**(d)A&T For different temperatures.**

**Fig. (1): Transmittance (T) and Absorbance (A) as a function of wavelength (λ) for CdS at different condition.**

### 2. Reflection

The change of bath condition has a higher influence on the speculer reflectance of CdS films. As shown in figure (2). The films prepared at different condition.

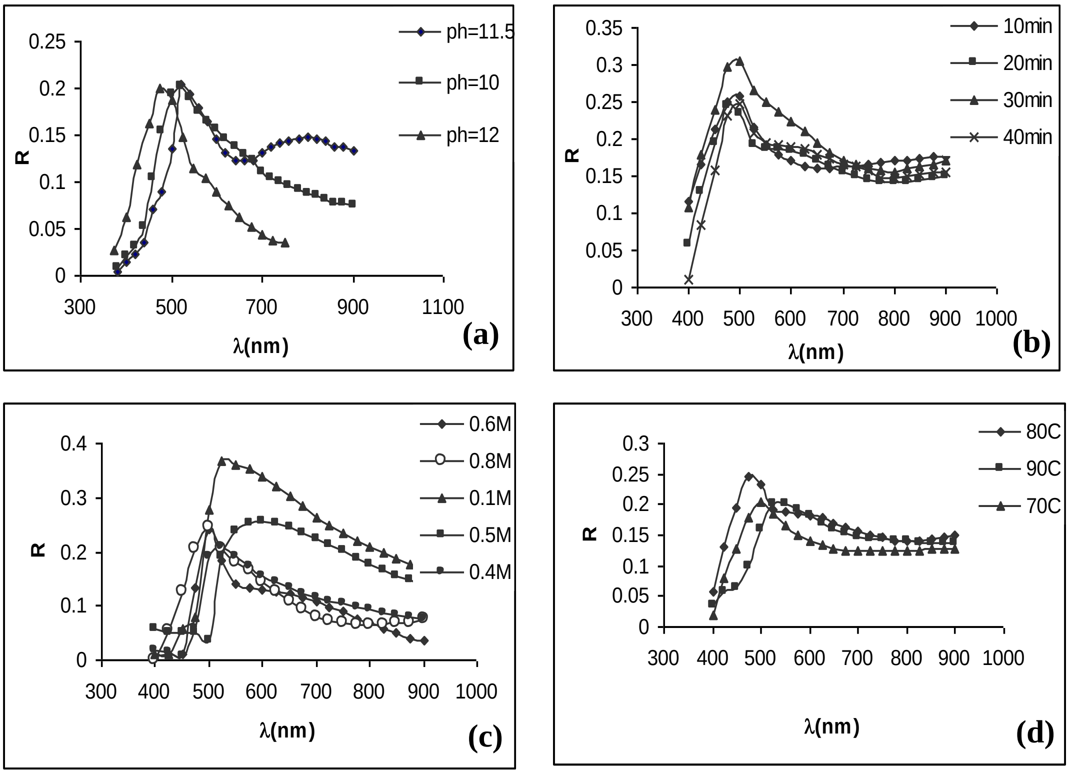



**Fig. (2): Reflectance (R) as a function of wavelength (λ) at different condition. (a) For different pH. (b) For different times. (c) For different thiourea ion concentrations. (d) For different temperatures.**

### 3. Absorption Coefficient

The data from transmission spectrum are used to calculate absorption coefficient by using equation (1). Figure (3) shows the optical absorption spectra recorded for the $(CdS)$ films for different deposition parameters. It is clear that the films have high absorption coefficient at short wave length range (375 – 500 nm), then decrease at different rates dependence on the films structure to reach constant values at long wave lengths which it above from the (520 nm), where the films become transparence at this wave lengths. The approximately same fundamental absorption edge is observed at about (520 nm) for all the samples with some difference. The figure shows results of the films prepared at high temperature, and low thiourea ion concentration have high optical absorption coefficient, where the value reaches more than ($1.8*10^5$ $cm^{-1}$) as a result of high crystallinity as is evident from the X – ray diffraction.

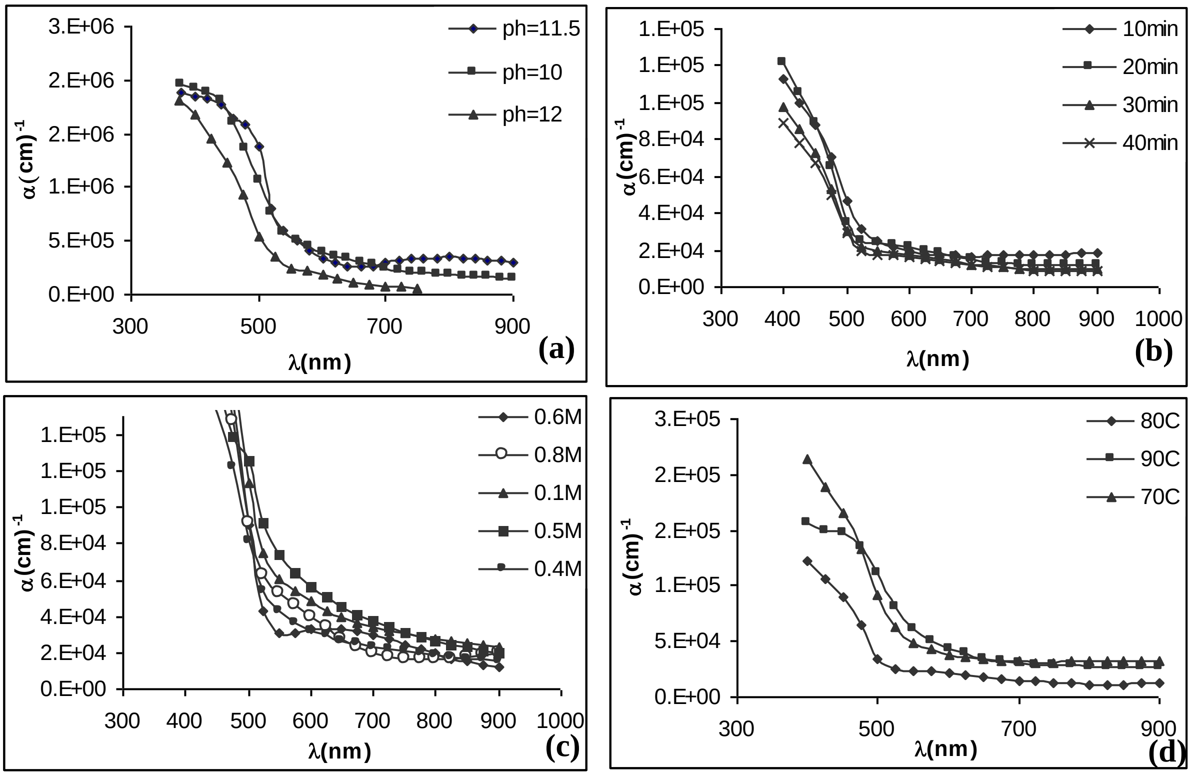



**Figure (3) The absorption coefficient ($\alpha$) as a function of wavelength ($\lambda$). (a) For different pH. (b) For different times. (c) For different thiourea ion concentrations. (d) For different temperatures.**

### 4. Optical Energy Gap

The energy gap values depends in general on the films crystal structure, the arrangement and distribution of atoms in the crystal lattice, also it is affected by crystal regularity. The energy gap (Eg) value is calculated by extrapolation of the straight line of the plot of $(\alpha h\upsilon)^2$ versus photon energy for different deposition parameters as shown in Figure (4). The linear dependence of $(\alpha h\upsilon)^2$ with $(h\upsilon)$ indicates direct band gap. The band gap increases with the increase in thiourea ion concentration. More probably this is related to the decrease in grain size with increasing deposition rate. The deposition rate influences the c – lattice constant, which is determined by the amount of strain at the substrate–larger interface [9]. The band gap changes with the $\left[ pH \right]$ of the solution at constant thiourea ion concentration. Here also we could attributed this to the decrease in grain size with increase in deposition rate.

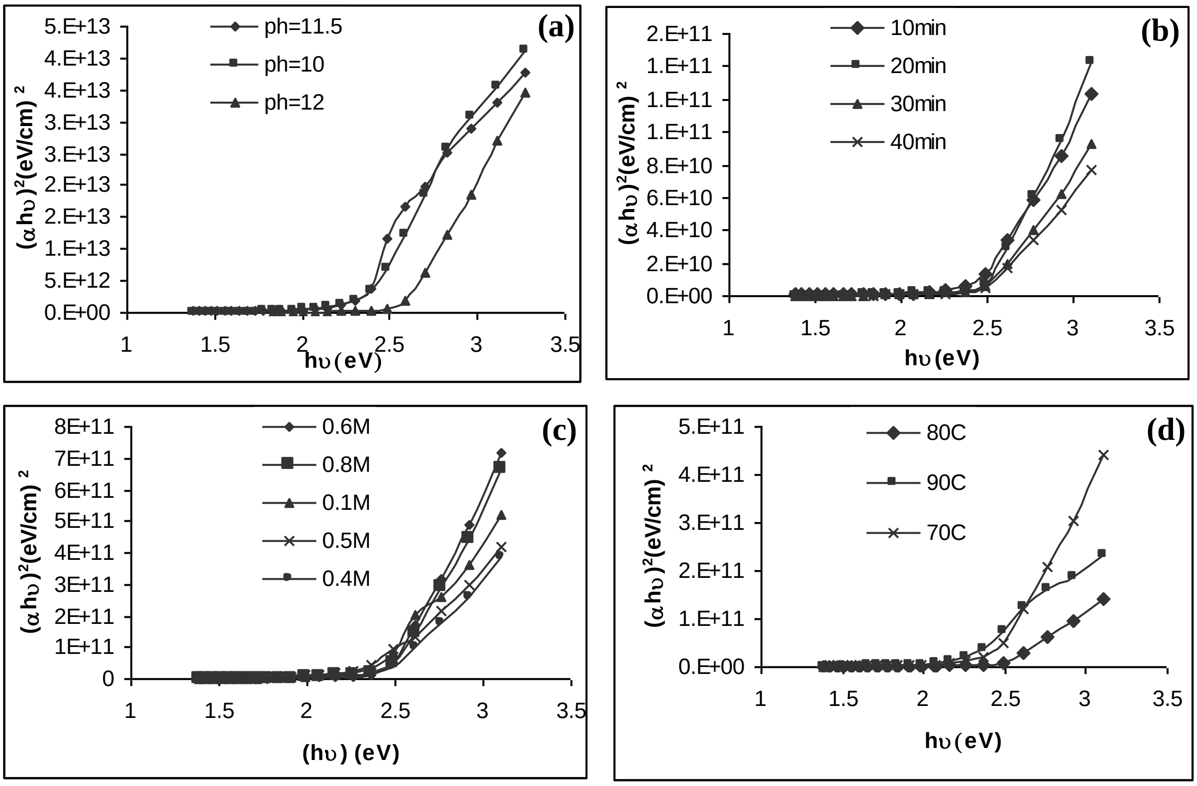



**Fig.(4): A plot of $(\alpha h\nu)^2$ as a function of energy (hν) for CdS. (a) For different times.**
**(b) For different temperatures. (c) For different thiourea ion concentrations. (d) For different pH.**

**5. The extinction coefficient**

Variation of the extinction coefficient with wavelength shown in figure (5). The linear relationship indication sharp increases in the absorption with increasing wavelength. This conforms to the relation:

$$K = \frac{\alpha\lambda}{4\pi} \text{............(6)}$$

Where (K) is the extinction coefficient, (□α)□ the absorption coefficient, and the wavelength (λ)□.

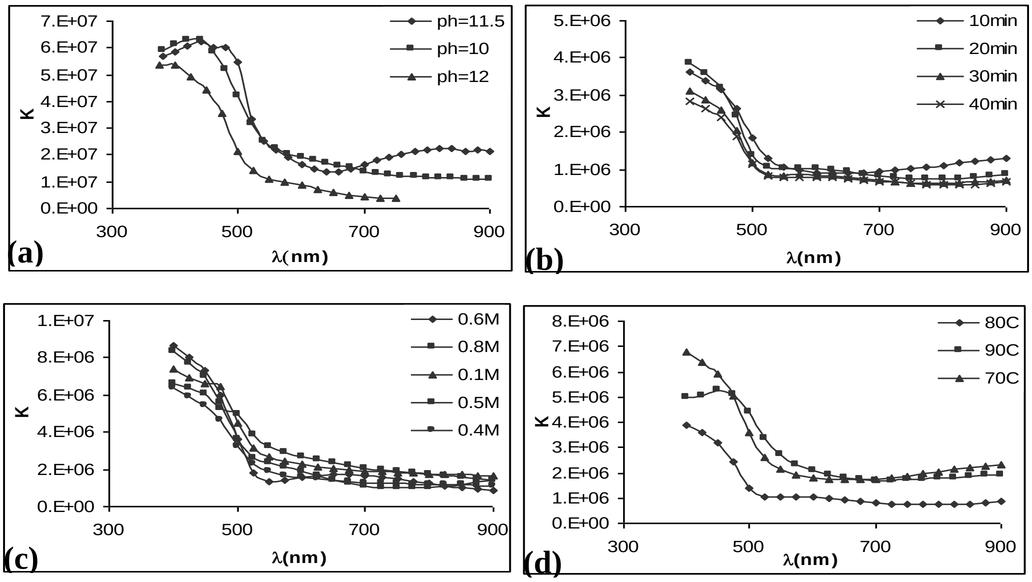



**Fig. ( 5 ) Variation of extinction coefficient (K) with wavelength (λ) for CdS at different condition. (a) For different times. (b) For different temperatures. (c) For different thiourea ion concentrations. (d) For different pH.**

## 6. The refractive index

The refractive index (n) is the range of frequencies in which films are weakly absorbing. Figure (6) shows the variation of refractive index of CdS with wavelength. That the refractive index of CdS ≈1.4 means that electromagnetic radiation is 1.4 times slower in the films than in the free space.

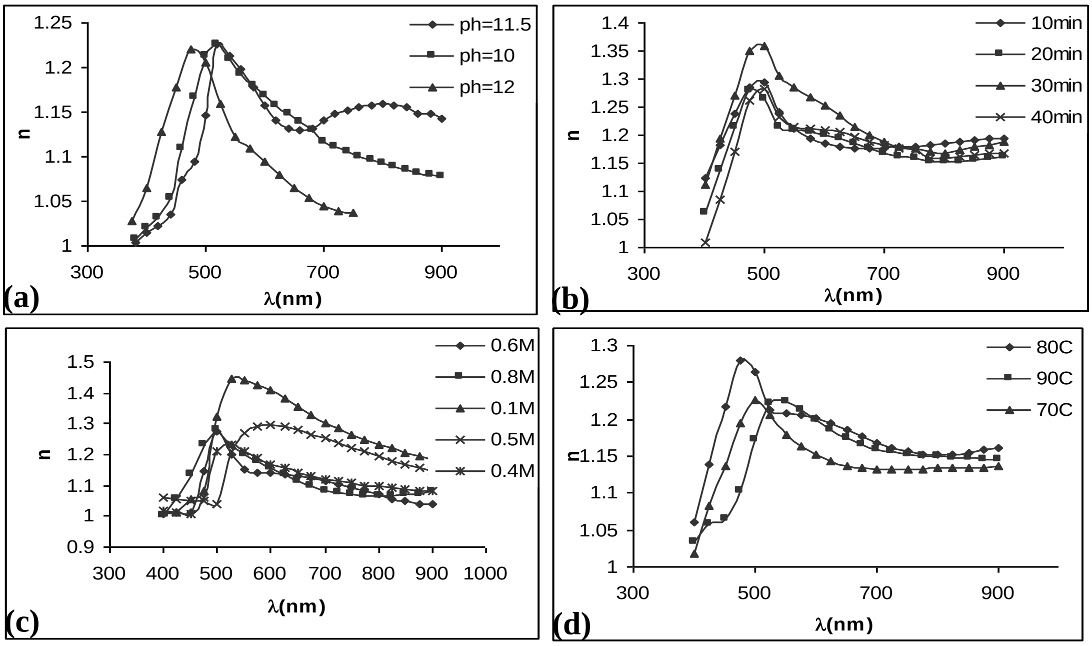



**Fig.(6) Refractive index (n) as a function of wavelength (λ)for CdS at different condition. (a) For different times. (b) For different temperatures. (c) For different thiourea ion concentrations. (d) For different pH.**

## 7. The dielectric constant and optical conductivity

The values for dielectric constant ($\varepsilon_r$) and optical conductivity ($\sigma$) increased from the minus values in low energy regions to peak values at 2.4 eV in the higher energy region and then decreased to low values in the same regions.

The dielectric constant ($\varepsilon_r$) and optical conductivity ($\sigma$) shown in figures (7, 8).

The relationship between ε and k is given by eq.7[10]:

$$\varepsilon = \varepsilon_r + \varepsilon_i = (n + ik)^2 \text{.............}(7)$$

Where $\varepsilon_r$ and $\varepsilon_i$ is are real and imaginary parts of $\varepsilon$ respectively.
Optical conductivity (σ) is given by eq.8[10]:

$$\sigma = \alpha nc / 4\pi \text{...........}(8)$$

Where c is the velocity of light.

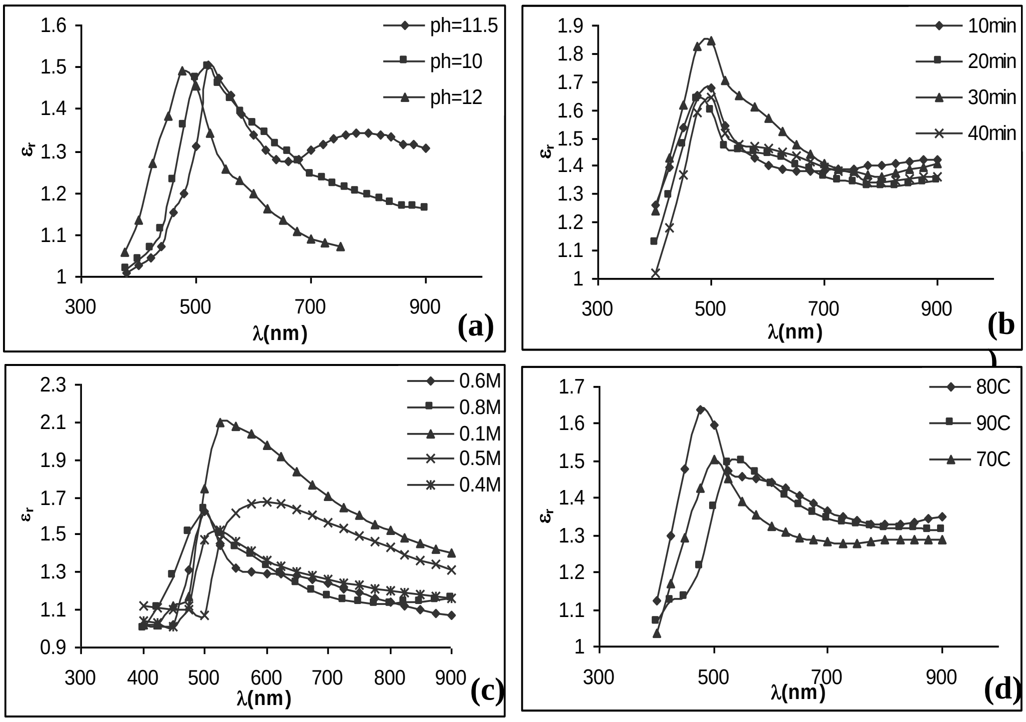



**Fig.(7) dielectric constant ($\varepsilon_r$) as a function of wavelength (λ)for CdS at different condition.**
**(a) For different times. (b) For different temperatures. (c) For different thiourea ion concentrations. (d) For different pH.**

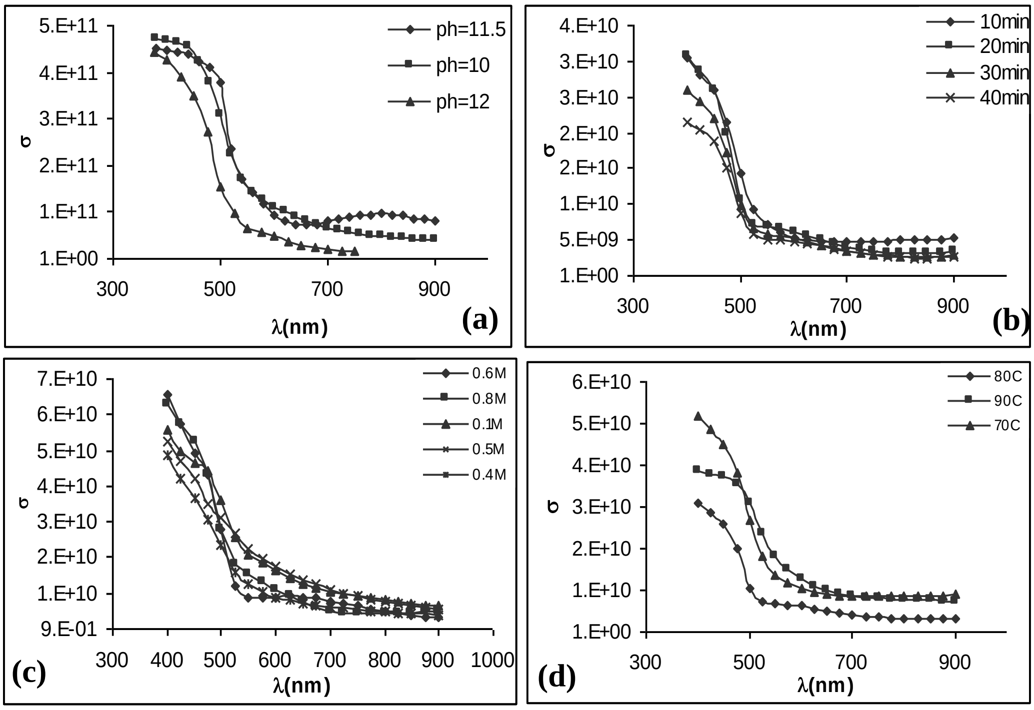



**Fig.(8) optical conductivity (σ) as a function of wavelength (λ)for CdS at different condition.**
**(a) For different times. (b) For different temperatures. (c) For different thiourea ion concentrations. (d) For different pH.**

### 8. Conclusions.

CdS thin films were successfully deposited in an alkaline medium using the chemical bath technique. The films produced in this study were found high transmittance in the range between (73% and 96%) in the visible region; hence, they have potential for use as both thermal control window coatings. The large band gap (2.4 eV) and high visible transmission (> 86%) also make the films suitable for use in the window layer of solar cells.

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# دراسة الخصائص البصرية لأغشية رقيقة لمركب كبريتيد الكادميوم بأستخدام طريقة الترسيب بالحمام الكيميائي

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**الخلاصة:**

في هذا البحث تم ترسيب الاغشية الرقيقة لكبريتيد الكادميوم على قواعد من الزجاج بأستعمال تقنية الترسيب بالحمام الكيميائي من محلول مائي لكبريتيد الكادميوم (CdS) والثايوريا. الاغشية المحضرة تمتاز بكونها منتظمة ،ذات التصاقية وتمتلك نفاذية عالية في المنطقة المرئية . الدراسة التي تمت لأغشية كبريتيد الكادميوم تتضمن النفاذية البصرية، الثابت البصري ،ثابت العزل الكهربائي ،التوصيلية الضوئية ،فجوة الطاقة . الاغشية التي تمت دراستها في هذا البحث لها نفاذية عالية تصل الى اكبر من 86% لأطوال موجية تتراوح بين (500نانومتر الى 900نانومتر) وفجوة الطاقة 2.4 الكترون فولت.