Studying the Effect of Deposition Time on Optical Properties of CdS Thin Films

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Abstract. We have studied in this work the effect of deposition time on the absorption spectra and the optical energy gap of CdS thin film. That prepared by chemical bath deposition method (CBD) on glass substrate at temperature of (80 ± 5)°C. The structural features were examined by X-ray diffraction (XRD) is wurtzite structure for all samples. Transmittance spectra have been recorded in order to determine absorbance, reflectivity, absorption coefficient and the optical constants such as refractive index, extinction coefficient, real and imaginary part of dielectric constant. It was seen that all the parameters under investigation affected by deposition time (1, 2, 3, and 4) hours.

Key words: chemical bath technique, optical constants, Cadmium sulfide

1. Introduction

Direct band gap thin film cadmium sulfide (CdS) has been doing the subject of intensive research because of its intermediate band gap, high absorption coefficient, reasonable conversion efficiency and stability [1]. CdS thin films are being widely investigated for applications in photo electrochemical cells, photo catalysis, optical switching and single electron transistors, light emitting diodes, laser materials, optical waveguides, electrochemical cells, gas sensors, and metal-Schottky barrier cells [2]. There are various techniques have been explored to deposition of CdS film, such as thermal evaporation, sputtering, molecular beam epitaxy, spray pyrolysis, chemical bath deposition, and close space sublimation (CSS), etc [3-8].

The chemical bath deposition (CBD) is a simple and inexpensive deposition technique most widely employed to obtain homogeneous, hard, adherent, transparent and stoichiometric CdS thin films [9]. Most CBD films reported are fairly transparent to very transparent, typically between 60 and 90% transparent in the sub-band gap region [10-12]. The deposition time of the films increases [13] or decrease [10] the optical transmission, according to deposition time of film. The absorption edge shifts towards higher energy region and increase in the band gap [11,13, 14]. Ali et al related the grain size dependence on the band gap for the films [10].

The aim of this work is studying the effect of various deposition time (1,2,3,and 4) hours on optical properties of CdS thin films prepared by CBD method. In the optical studies of CdS thin films showed a
high absorbance in the area of visible region, this made the deposited film suitable in the designing of solar cells.

2. Experimental Work

CdS thin films were deposited on a cleaned glass substrate by the chemical bath deposition CBD method at various deposition times. First, placed 0.384gm of cadmium chloride (CdCl₂) as a source of cadmium in 240ml distilled water under vigorous stirring about 15 min, (NaOH) was added drop by drop in (CdCl₂) solution under stirring to maintain the pH value of the solution is (10.5) and a fuzzy solution was obtained, then placed 0.768gm of thiourea CS(NH₂)₂ as a source of sulfur in 240ml distilled water under vigorous stirring about 15 min.

The solution was mixed in 500 ml beaker with added distilled water to complete 500ml with continuous stirring by magnetic stirrer about 20 min, the solution temperature was kept constant at (80 ±5 °C), the solution color change from fuzzy to yellow. This equation illustrates the interaction[3]:

\[
\text{CdCl}_2 + \text{CS(NH}_2)_2 + 2\text{H}_2\text{O} \rightarrow \downarrow \text{CdS} + \uparrow 2\text{NH}_4\text{Cl} + \uparrow \text{CO}_2
\]

The glass substrate that used for deposition CdS was cleaned by methanol and acetone for 10 min by using an ultrasonic cleaner and then cleaned with de ionized water and dried. The clean glass slides were vertically immersed in the beaker contain the solution whose temperature were kept around (80 ±5 °C) during the growth. After the deposition time was change from (1,2,3and 4) hours, the samples were pulled out from the bath and washed in distilled water and finally dried in air. CdS films obtained were hard, and had very good adhesion to the glass substrate. Finally, all films of CdS annealing at (300°C) about 45 min. Figure 1 shows CdS thin film deposited on glass-substrate by CBD method with deposition time at 1hour. The measurements of CdS thin films were investigated using SP-3000NANO optima (UV-Vis spectrophotometer) in the wavelength region of (200 to 1100) nm to exam the optical transmission and absorbance, while XRD results of these films where measured by SHIMADZU-6000 (CuKα with wavelength 1.54056Å), the 2θ around (20 – 80°).

![Figure 1. CdS thin film deposited on glass-substrate by CBD method with deposition time at 1hour.](image)

3. Results and Discussion

3.1 Structural Properties by XRD

Figure 2 shows the crystalline structure that analyses by XRD of the CdS thin films are prepared by chemical bath deposition on the glass substrate with varying deposition times (1,2,3and 4) hours
respectively, all deposited films have polycrystalline with the hexagonal phase also all diffraction peaks of CdS samples at different deposition time correspond to ( JCPDS no. 77-2306) this agreement with [15], it indicates that the very intense (002) plane with a preferential orientation (001) for all sample of wurtize CdS also two lattice constants a = 4.1409Å, c= 6.7198Å. The average crystal size (D) of CdS thin films about (22.25 nm) was derived from FWHM of peak corresponding to 2θ= 24.93 for sample that calculates using Scherer’s equation [16]:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  

(1)

Where D is the average grain size, \( \lambda \) is of X-ray wavelength (0.15418 nm), \( \beta \) is the full-width at half maximum (FWHM) of the peak which has maximum intensity and \( \theta \) is the Bragg’s angle, this obvious that the films made up of nanocrystal particles this agreement with [17], the range of 2θ  20° to 80°. In fact, CdS has three forms of structure are cubic, hexagonal and rock salt, the structure more stable is the hexagonal phase due to the method of preparation cadmium sulfide in addition to be the structure more favorable for manufacturing of a solar cells [1].

![Figure 2: Thin films of CdS deposited on glass substrate by CBD at different time.](image)

3.2 The Transmission and Absorption

Optical transmittance and absorbance spectra as a function of wavelength for CdS thin films at different deposition times (1,2,3 and 4) hours, are shown in figure 3. A maximum value transmittance at (77%) in the near-infrared region for CdS film at deposition time (1 hour) while increased to (82, 83, 86)% for CdS film at deposition time (2,3,4) hours, respectively. The increase in transmittance in the near infra-red region shows decrease absorbance as the wavelength increases along the near infra-red region of the spectrum and height absorption in the visible light region for all samples of CdS this result is good agreement with research [13].
3.3 The Absorption Coefficient:

The absorption coefficient \( \alpha \) associated with the strong absorption region of the film was calculated from absorbance \( A \) and the thin film thickness \( t \) as equation [18]:

\[
\alpha = 2.303 \frac{A}{t} \quad \text{.... (2)}
\]

Where \( A = \log \frac{1}{T} \) is the absorbance and \( t \) is the thickness of the CdS film about 100 nm was measured by gravimetric method.

The behavior of absorption coefficient \( \alpha \) of CdS thin films for different deposition times (1, 2, 3 and 4) hours as a function of photon energy and wavelength is shown in figure 4. Absorption coefficient \( \alpha \) decrease in the law photon energy because the probability of the electrical transfer between valence band and the conduction band is very rare and it will gradual increase in the absorption coefficient toward the high energy \( (h \nu > 2eV) \) for all the samples [19], as the deposition time increase, there is a blue shift of the absorption edge (i.e. shift towards short wavelengths). This result is a good agreement with result of literature [20].
3.4 The Optical Band Gap

The absorption coefficient and optical band gap \((E_g)\) are related by Tauc equation [21]:

\[
\alpha = (\hbar \nu - E_g)^2 
\]

... (3)

Where \(\hbar\) is the incident photon energy, \(\hbar\) Planck constant, \(\nu\) the frequency of incident photon, \(E_g\) the optical band gap.

The \((\alpha \hbar \nu)^2\) versus \((\hbar \nu)\) plots for CdS films at different deposition times (1,2,3 and 4) hours are shown in figure 5. The optical band gap \((E_g)\) value is determined by extrapolating the linear part of the plot \((\alpha \hbar \nu)^2\) versus \((\hbar \nu)\) in the abscissa (x axis), which indicates a direct optical transition. The band gap value of the CdS film was found increases from (2.25, 2.4, 2.5 and 2.65) eV with increasing deposition times at (1,2,3 and 4) hours, respectively. This behavior is identical to the results of previous researches [10,11,13,14]. The increase in band gap value is due to crystal size decreases below a certain limiting size, associated with its exciton Bohr diameter. The spacing between levels in the bands becomes larger so that the energy structure changes from continuum band to discontinuous or discrete quantized levels and the band gap increases.
Figure 5. Variation of band gap for CdS thin films prepared by CBD at different deposition times.

3.5 The Extinction Coefficient

The extinction coefficient was evaluated using equation [22]:

\[ K = \frac{\alpha}{4\pi} \] ... (4)
Figure 6 shows variation of the extinction coefficient with wavelength for CdS films with different deposition time. The extinction coefficient decreases as the wavelength increases, and its decreases as the deposition time increases. This decrease in $K$ is due to the deposition time working on decrease the absorbance where $K$ depends on the absorption coefficient ($\alpha$) as which comes from decreasing the tails width of the localized states within the energy gap and then decreasing $K$ according to equation 4.

![Graph showing extinction coefficient as a function of wavelength for CdS films at different deposition times.]

**Figure 6.** Extinction coefficient as a function of wavelength $\lambda$ for CdS films at different deposition time.

3.6 The Refractive Index

The refraction index can be calculated from the relationship [23]:

$$n = \frac{1 + R^2}{1 - R^2} \cdots (5)$$

Where $R = 1 - T - A$ is the reflection of the films.

Figure 7 shows the variation of refractive index of CdS films with wavelength at different deposition time. The increase in the deposition time results in the overall decrease in the refractive index. This decrease in the refractive index indicates that the deposition time acts on the surface change of the film, leading to a change in the accurate structure of the film. Thus decreasing the packing density which increase the speed of light in thin film material, leads to decrease in the reflectance with the deposition time and decrease refractive index, according to equation 5.
Figure 7. Refractive index as a function of wavelength $\lambda$ for CdS films at different deposition time.

3.7 The Dielectric Constant

The real and imaginary parts of complex dielectric constant given by the following relations [24]:

$$\epsilon_1 = n^2 - K^2 \quad \text{... (6)}$$

$$\epsilon_2 = 2nK \quad \text{... (7)}$$

Figure 8 shows the variation of real and imaginary part of dielectric constant of the CdS thin films with wavelength at different deposition time (1, 2, 3 and 4) hours. The obtained results show that both values of real part $\epsilon_1$ and imaginary part $\epsilon_2$ of dielectric constant are decreased with increasing of wavelength for CdS thin films, and are decrease with increasing of deposition time. The behavior of $\epsilon_1$ with the wavelength and the deposition time is the same as the behavior of the refractive index $n$ to adopt $\epsilon_1$ on the refractive index according to equation 6, While the behavior of $\epsilon_2$ with the wavelength and the deposition time is the same as the extinction coefficient $K$, according to equation 7.
Figure 8. The Real and Imaginary Parts of Dielectric Constant as a function of wavelength $\lambda$ for CdS films at different deposition time.

3.8 The Optical Conductivity

To calculate the optical conductivity used the equation [25]

$$\sigma_{optical} = \frac{\alpha n c}{4 \pi} \quad \ldots (8)$$

Where $\sigma_{optical}$ is the optical conductance, $c$ is the velocity of the radiation in the space, $n$ is the refractive index and $\alpha$ is the absorption coefficient.

Figure 9. Shows the variation of optical conductivity as a function of photon energy for different deposition time of CdS thin films. From the figure, the optical conductivity of CdS thin films were increased with photon energy. This suggests that the increase in optical conductivity is due to electron exited by photon energy, and the optical conductivity of the films decreases with increasing deposition time.
Figure 9. The Optical Conductivity of CdS thin films with different deposition time.

4. Conclusions

The CdS thin films with different deposition time (1, 2, 3 and 4) hours were prepared by chemical bath deposition method on glass substrate. The structure of the four films is hexagonal structure (Wurtize) according to XRD measurements. The optical properties showed that the transmittance for all films increased with the increasing in the wavelength range, and increases with the increase in the deposition time. The band gap increases when the deposition time increases and the band gap changed from 2.25 eV (for dep. time 1 hour) to 2.65 eV (for dep. Time 4 hour), as a result of quantum confinement, which can be used in the application of thin film as window layer in solar cell fabrication.

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