Optical Properties of Annealed Cadmium Sulfide Thin Films Prepared by Chemical Bath Deposition

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CdS thin films were prepared by the chemical bath deposition technique. Annealing in air at different temperatures (300, 350, 400, 450, and 500)°C at constant time of 30min, also for different times (15, 30, 45, 60, and 90) min at constant temperature (300°C) is achieved. The CdS films showed, on average, 20% reflectance. The transmittance ranged between 80–92% for the films annealed at 60 and 45 min. On average, the refractive index of the CdS is 1.2 and the band gap is 2.4eV, the wide band gap semiconductor has a wide range of applications in areas including photocells and other photoconductive devices.

Keywords: CdS, Chemical bath deposition, Annealing conditions, Optical properties
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1. Introduction

There are many deposition techniques used to deposit thin film semiconductors, such as (evaporation, sputtering, spray pyrolysis, chemical bath deposition). The preparation of thin films by a chemical deposition process is advantageous because of its simplicity, ease and economic ability and the adjusting of the semiconductor properties by band-gap variation, doping, control over stiochiometry, etc., can be accomplished with greater accuracy [1].

Cadmium sulfide (CdS), an important [2] compound semiconductor, has a typical wide band gap of 2.4eV at room temperature [3]. The CdS compound semiconductors exhibit excellent electrical, chemical and optical properties which make them one of the promising candidates in the field of photovoltaic energy conversion. Direct band gap thin film cadmium sulfide has been the subject of intensive research because of its intermediate band gap, high absorption coefficient, reasonable conversion efficiency and stability [4]. Also it is used in light amplifiers, radiation detectors, thin film transistor and diodes [1], piezoelectric transducers, laser

Most CBD films reported are fairly transparent to very transparent, typically between 60 and 90% transparent in the subband gap region [7,8]. Annealing of the films increases [8] or decrease [9] the optical transmission, according to annealing condition and deposited film component. The absorption edge shifts towards lower energy region and decrease in the band gap [5,8,9], this is due to the interference effect in the compressed multilayered structure formation of CdS after annealing [8] while Grecu et al. attributed the decreasing of band gap for annealed films at (500°C) to a possible contamination with cadmium hydroxide as source of (CdO) [2]. George et al. related the decrease in the band gap in the heated films to the grain size growth and composition change taking place in the films [10].

The aim of this paper is study the optical properties of annealed CdS films prepared by CBD method. The effect of annealing at different temperature and time is reported.

2. 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 [11]. 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. Films were deposited on glass slides by, 30ml of 0.1M ($3CdSO_4.8H_2O$), 30ml 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°C). The solution was stirred with a magnetic stirrer type (MSH 300). Then, it was heated with continuous stirring to the required temperature of deposition, 30ml of 0.2M 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. All the samples were annealed in a furnace at different temperatures (300,350, 400, 450, and 500)°C for 30 min and different time (15, 30, 45, 60, 90) min at 300°C.

3. Measurements

A Cecile CE 7200 Spectrophotometer supplied by Aquarius Company was used to record the optical transmission and absorbance for CdS/glass thin films in the range (375–900nm). The data from transmission spectrum can be used in the calculation of the absorption coefficient (α) for CdS films, according to the following equation [13]:

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

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 (E_g) are related by [14]:

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

where h is Plank's constant and ν 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 [15]:

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

where n is the refractive index

In the range of frequencies in which the films are weakly absorbing $K^2 \ll (n-1)^2$, the following can be expressed [15]:

$$R = \frac{(n-1)^2}{(n+1)^2} \quad \text{or} \quad n = \frac{(1+R^{1/2})}{(1-R^{1/2})} \qquad (4)$$

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 (632nm) was used for this purpose and the thickness is determined using the formula:

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

where x is fringe width, Δx is the distance between two fringes and λ is the wavelength of laser light

4. Results and Discussions

The optical transmission spectra depend on the chemical and crystal structures of the films, and also on the film thickness and on films surface morphology. We have found that the films have high transmission at long wavelengths (70-80%), which decreases to (10%) at short wavelengths.

Annealing of the as-deposited films decreases the optical transmittance and the absorption edge shifts towards lower energy region and becomes much sharper as shown in Fig. (1).

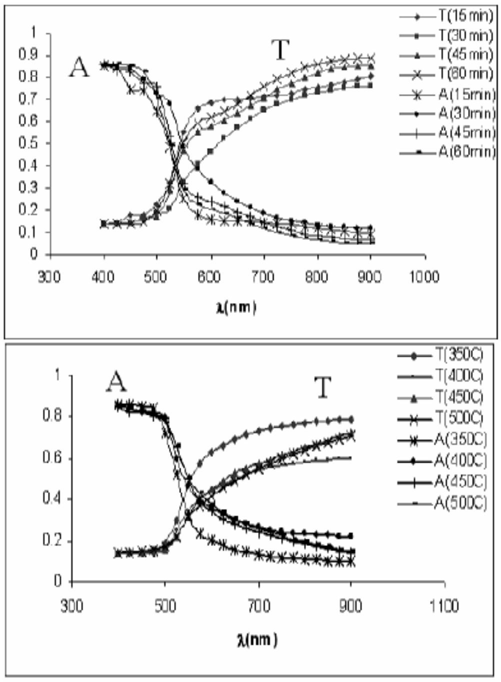

Fig. (1) Optical transmission spectra and absorption of CdS films at different annealing times (above) and different annealing temperatures (below)

The change of annealing conditions has a higher influence on the specular reflectance of CdS films, as shown in Fig. (2).

In general, the energy gap values depends 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 (E_g) value is calculated by extrapolation of the straight line of the plot of $(\alpha hv)^2$ versus photon energy for different annealing conditions as shown in Fig. (3). The linear dependence of $(\alpha hv)^2$ with hv indicates that the films have direct band gap. Figure (3) shows the effect of annealing conditions on band gap, where the band gap value is estimated by extrapolation of the straight line of the plot of $(\alpha hv)^2$ versus photon energy. The annealed samples show a relative decrease in band gap with both annealing temperature and time. These results are consistent with the previously published results [10] in which the decrease in the band gap of the annealed samples was attributed to the grain size growth and composition changes taking place in the samples by CdO. Conversely, Archbold [16] attributed his results to either the phase transition from the cubic-to-hexagonal, or a reduction in strain within the film structure.

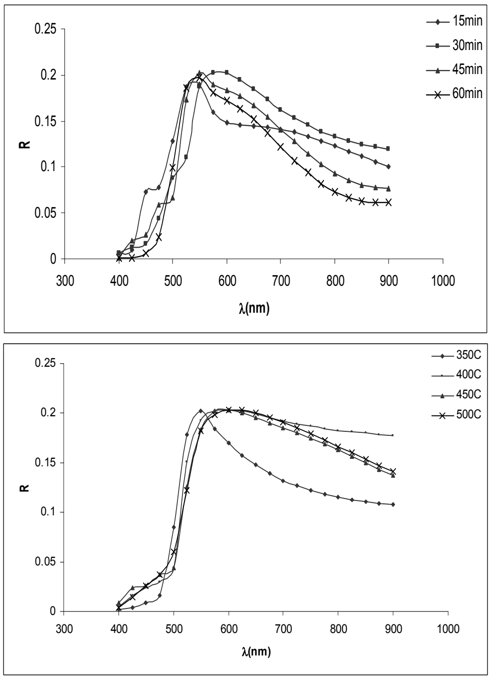

Fig. (2) Optical reflection spectra of CdS films at different annealing times (above) and different annealing temperatures (below)

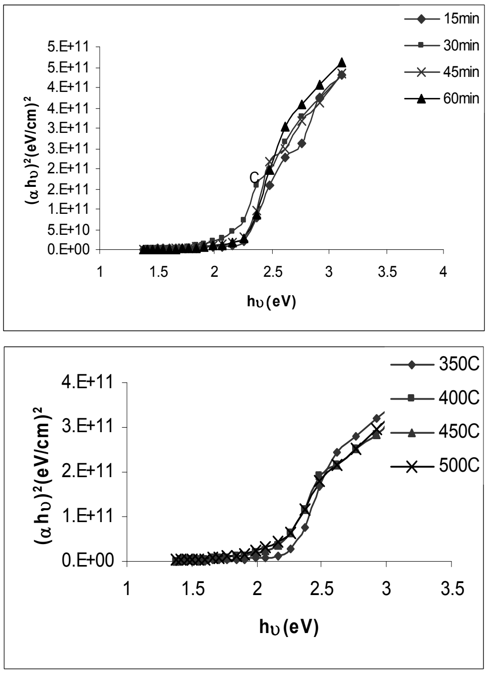

Fig. (3) Plot of (αhv)^2 versus (hv) at different annealing times (above) and different annealing temperatures (below)

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

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

where K is the extinction coefficient and α is the absorption coefficient

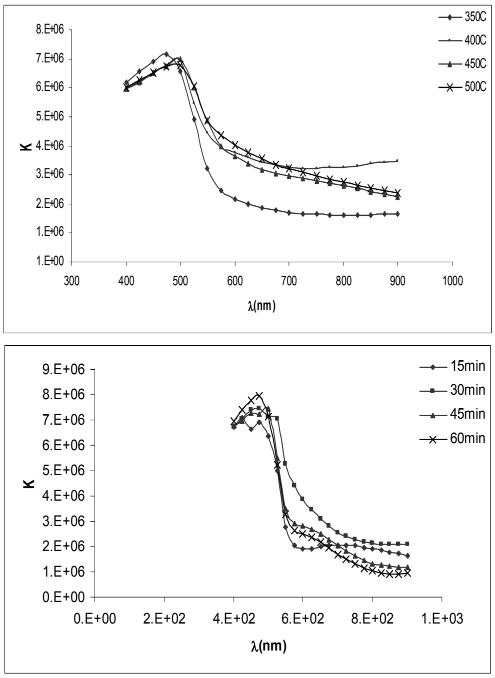

Fig. (5) Variation of extinction coefficient (*K*) with wavelength (λ) at different annealing times (above) and different annealing temperatures (below)

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. Refractive index of CdS is nearly equal to 1.2, which means that electromagnetic radiation is 1.2 times slower in the films than in the free space.

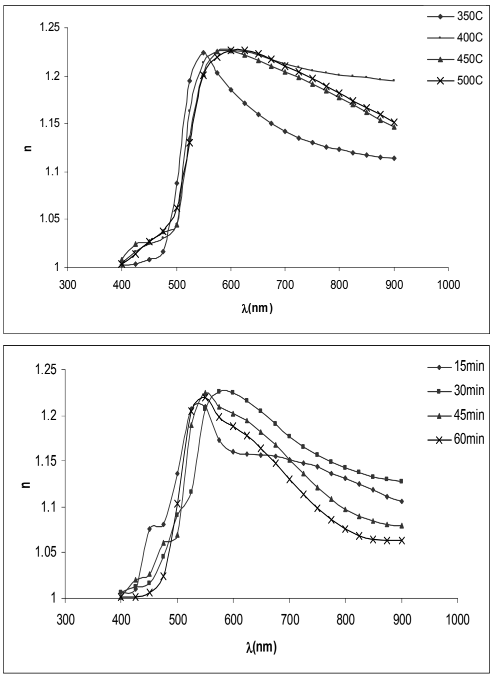

Fig. (6) Refractive index (*n*) as a function of wavelength (λ) at different annealing times (above) and different annealing temperatures (below)

The values of dielectric constant (ε_r) and optical conductivity (σ) have increased from the minus values in low energy regions to peak values at 2.4eV in the higher energy region and then decreased to low values in the same regions. The dielectric constant (ε_r) and optical conductivity (σ) are shown in Fig. (7) and (8).

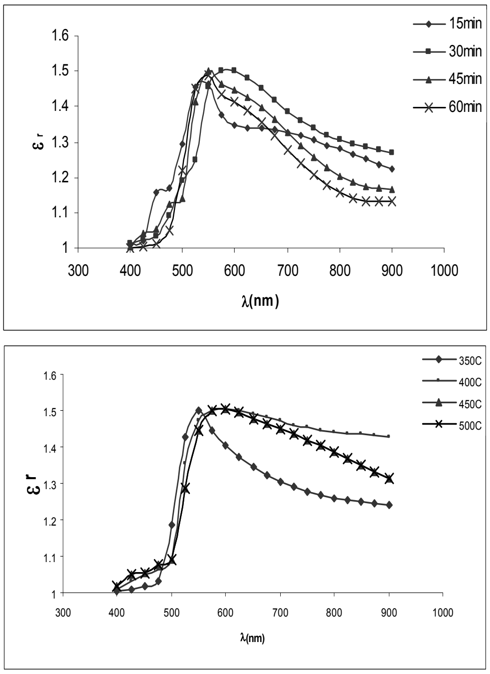

Fig. (7) dielectric constant (ε_r) as a function of wavelength (λ)at different annealing times (above) and different annealing temperatures (below)

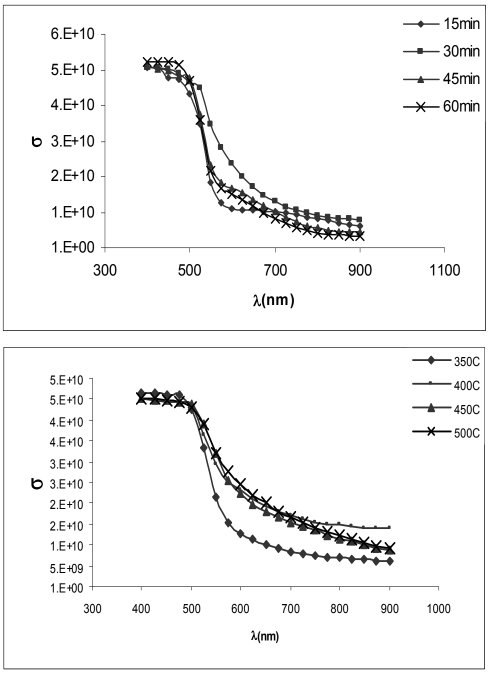

Fig. (8) Optical conductivity (σ) as a function of wavelength (λ) at different annealing times (above) and different annealing temperatures (below)

5. Conclusion

CdS thin films were successfully deposited in an alkaline medium using the chemical bath technique. The disparity between the properties of the films as grown and those annealed at higher temperature is a result of grain size growth and composition changes taking place in the samples by CdO. On average, CdS films show a reflectance in the range (5-20%) in the near infra-red region. They also have refractive index of 1.2 and band gap of 2.4eV.

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