



RESEARCH ARTICLE

OPTICAL PROPERTIES AND ATOMIC FORCE MICROSCOPY OF CDS THIN FILMS PREPARED BY CHEMICAL BATH DEPOSITION AND CHEMICAL SPRAY PYROLYSIS METHODS

*Asaad A. Kamil

Department of Physics, College of Science, University of Diyala, Diyala, Iraq

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ABSTRACT

Nanocrystalline CdS thin films have been prepared on glass substrates by chemical bath deposition (CBD) and Chemical Spray Pyrolysis (CSP) methods. The optical properties of the films were studied by measuring their optical transmittance and reflectance spectra in the wavelength range of 300-900 nm. The optical absorption studies reveal that the electronic transition is direct with band gap value of 2.42 (eV) and 2.55 (eV) for the films deposited by (CBD) and (CSP) respectively. Other important optical constants, such as extinction coefficient and refractive index were calculated and analyzed. The morphology of the prepared films was investigated by Atomic Force Microscopy (AFM) for different regions of the samples using sampling areas of 5 μm x 5 μm and 10 μm x 10 μm . The AFM analysis showed that the samples present well defined nanosized grains in the range of 100-286 nm. It is found that the thin film deposited by (CBD) method is more homogeneous than the film deposited by (CSP) method.

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INTRODUCTION

The thin film cadmium sulphide solar cell has for several years been considered to be a promising alternative to the more widely used silicon devices (Zhu 1998). Thin CdS films deserve attention because of their expected gap emission lies very close to the highest sensitivity of the human eye. Thus, one might assume that thin CdS thin films are an appealing host for photonic devices (Bull 2005). Particular properties achieved in films depend on the deposition method and the conditions of preparation. CdS thin film can be prepared by chemical, physical and electrochemical methods such as molecular beam epitaxy, Successive Ionic Layer Adsorption and Reaction (SILAR), Chemical Bath Deposition (CBD), electro deposition, radio frequency planar magnetron sputtering and Chemical Spray Pyrolysis (CSP) (Ullrich *et al.*, 1999; Oliva *et al.*, 2003; Ates *et al.*, 2007; Sanap and Pawa 2009; Anuar *et al.*, 2005; Hernandez-Contreras 2002). Among them, (CBD) and (CSP) methods are best suited for thin film deposition because of simplicity, convenience, least expenses to produce uniform, adherent and reproducible large area thin films for solar related applications (Ashour 2003). In this work, we present the study of optical properties and atomic force microscopy of CdS thin films prepared by chemical bath deposition and chemical spray pyrolysis techniques.

MATERIALS AND METHODS

Chemical Bath Deposition (CBD) technique

The deposition process of CdS thin films was carried out on commercial glass slides with 1mm thickness and 2.5 * 2.5 cm² size. Before the deposition the substrates were cleaned by detergent solution then washed by distilled water and finally were cleaned by using ethanol solution. Every two samples should be put with their back sides facing each other so as to insure that the growth of the film well be done on one side of each glass substrates. The deposition arrangement consisted of a water bath on a hot plate. We used a 250 ml borosilicate glass flat bottom beaker for the process. The aqueous solutions of the reaction were 0.1 M cadmium chloride (CdCl₂), 1 M thiourea (CS(NH₂)₂), 0.7 M ammonium chloride (NH₄Cl), and 2 M ammonium hydroxide (NH₄OH). 50 ml of NH₄Cl and 50 ml of NH₄OH were dispensed into the beaker and 50 ml of CdCl₂ was added in drops to prevent Cd(OH)₂ formation in the solution. The substrates were placed vertically into the beaker and heated in the water bath to 85 °C. 50 ml of CS(NH₂)₂ solution was slowly dropped into the preheated solution in the beaker. The deposition process time was 100 minute and the thickness of the resultant films was about 200 nm measured by gravimetric method.

Chemical Spray Pyrolysis (CSP) technique

CdS thin films were prepared by chemical spray pyrolysis technique on glass substrates using a homemade spray system.

*Corresponding author: Asaad A. Kamil
Department of Physics, College of Science, University of Diyala, Diyala, Iraq

CdS thin films were prepared by spraying an aqueous solution of cadmium chloride (CdCl_2) and thiourea, (NH_2CSNH_2) on a glass substrates kept at 400°C . The chemical solution was atomized into a spray of fine droplets using air as a gas carrier. The spray rate was 10 ml/min through the nozzle ensures a uniform thickness which was measured by gravimetric method. The produced films have a thickness of 200 nm. Transmittance and reflectance spectra of the prepared samples were measured by normal incidence of light using a double beams UV/VIS Shimadzu spectrophotometer in the wavelength range of (300-1100) nm. The morphology of the prepared films was investigated by Atomic Force Microscopy (AFM) (model SPM AA 3000 Angstrom Co.USA). AFM micrographs were recorded for different regions of the samples using sampling areas of $5\ \mu\text{m} \times 5\ \mu\text{m}$ and $10\ \mu\text{m} \times 10\ \mu\text{m}$. The force applied by the tip was carefully adjusted to avoid any noticeable tip induced damage during scanning. The AFM topography data were used to calculate the average roughness and grain size of the samples.

RESULTS AND DISCUSSION

Figure (1) shows the optical transmittance of CdS thin films deposited by the two methods. The optical transmittance for the films prepared by Chemical Bath Deposition (CBD) are highly transparent in the visible region, and the optical transmittance of CdS films prepared by (CBD) became higher than the optical transmittance of CdS films prepared by (CSP).

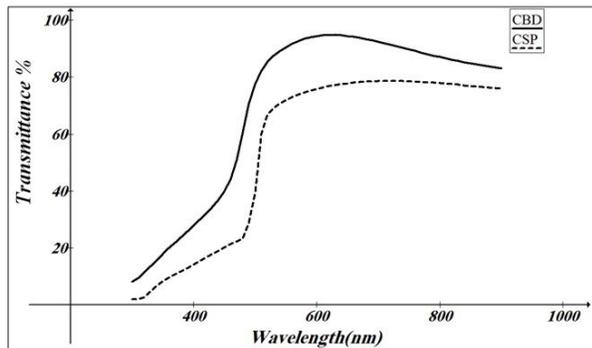


Fig. 1. Transmittance spectrum of CdS thin films deposited by the two methods

Figure (2) shows the reflectance spectrum of CdS thin films deposited by the two methods.

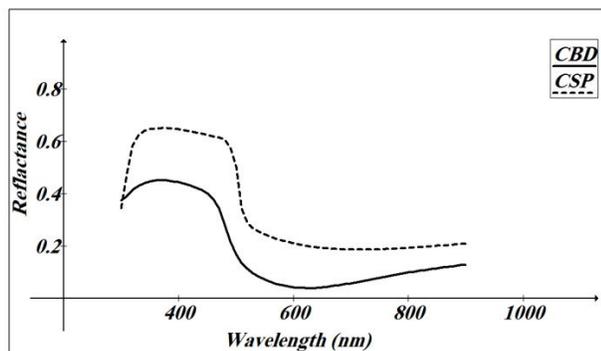


Fig. 2. Reflectance spectrum of CdS thin films deposited by the two methods

Figure (3) shows the absorption coefficient (α) of CdS films versus photon energy. From this figure α (CdS for (CBD) method) $>$ α (CdS for (CSP) method), this might be attributed to the increase of defect states which leads to increase absorption coefficient (Afaf Abdel-Aali *et al.*, 2005).

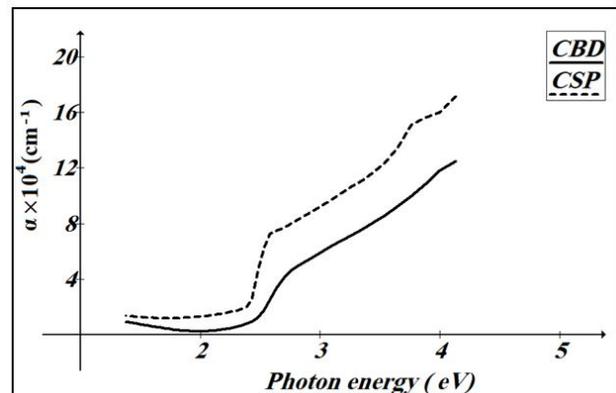


Fig. 3. Absorption coefficient for CdS thin films versus Photon energy

The optical band gap of the as deposited thin films was estimated by extrapolation of the linear portion of $(\alpha h\nu)^2$ versus $(h\nu)$ plots using the relation (Oral *et al.*, 2007):

$$(\alpha h\nu)^2 = A(h\nu - E_g)^{n/2} \dots\dots\dots(1)$$

Where α represents the absorption coefficient, $(h\nu)$ the photon energy, (A) is constant and (E_g) is the optical band gap. The direct ($n=2$) band gap value of CdS films by (CBD) method and CdS films by (CSP) method are found to be 2.42 eV and 2.55 eV respectively as shown in Figure (4).

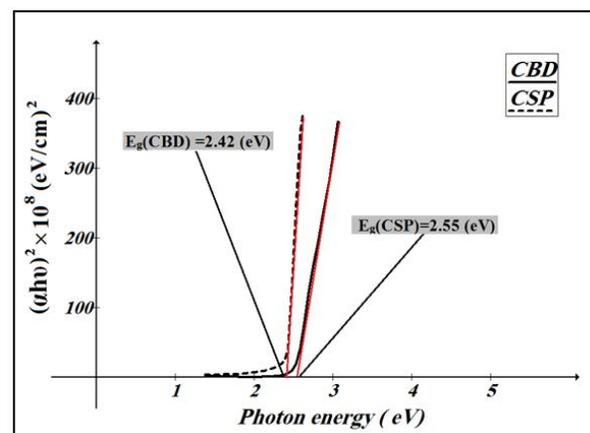


Fig. 4. Optical band gap for CdS thin films versus Photon energy

Refractive index is one of the fundamental properties for an optical material because it is closely related to the electronic polarizability of ions and the local field inside materials. The refractive index (n) is related to the optical reflectance (R) by the following relation (Balitska and Shpotyuk 1998):

$$n = \left(\left[\frac{4R}{(R-1)^2} - K \right]^{1/2} - \frac{R+1}{R-1} \right) \dots\dots\dots (2)$$

Figure (5) shows the variation of refractive index with respect to photon energy for the prepared films. It can be noticed that the refractive index of the films deposited by (CSP) method is greater than that of films deposited by (CBD) method. This is an expected behavior because the refractive index is closely related to the reflectance of the prepared films (see Fig. 2).

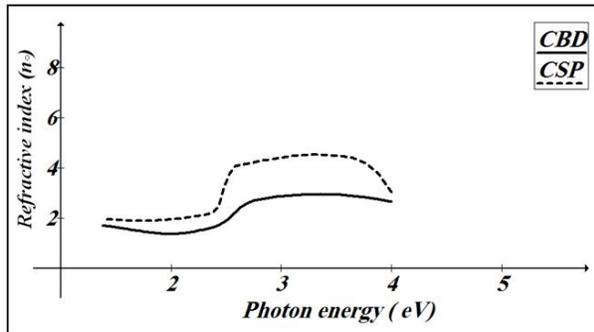


Fig. 5. Refractive index for CdS thin films versus Photon energy

It is known that the extinction and absorption coefficient can be related by (Sumangala *et al.*, 2005):

$$k_o = \frac{\alpha \lambda}{4 \pi} \dots\dots\dots (3)$$

Figure (6) shows the extinction coefficient of the deposited films as a function of photon energy. Again, it can be noticed that the extinction coefficient of the films deposited by (CSP) method is greater than that of films deposited by (CBD) method.

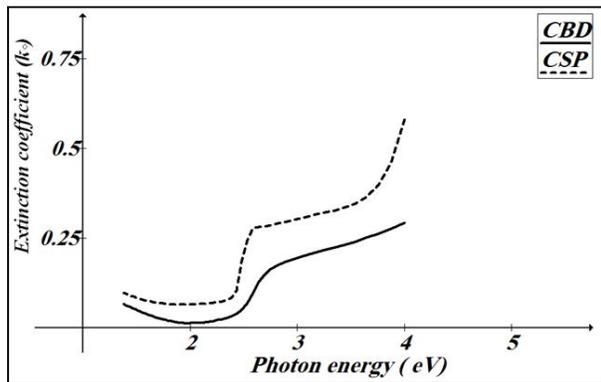
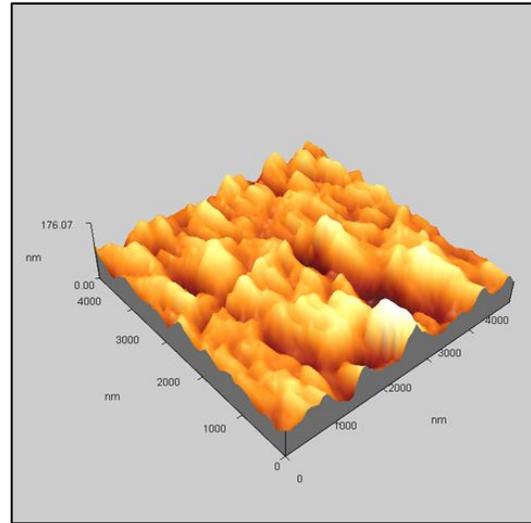


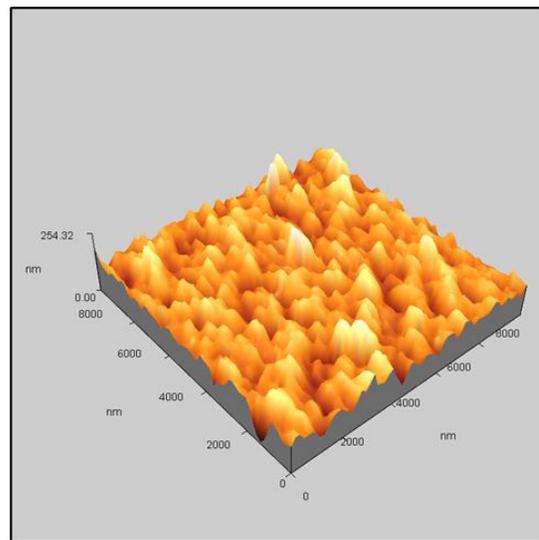
Fig. 6. Extinction coefficient for CdS thin films versus Photon energy

The morphological features of CdS thin films were examine using AFM microscope. Figures (7a) and (7b) represent the AFM images for the CdS sample prepared by (CBD) method

using sampling areas of 5 μm x 5 μm and 10 μm x 10 μm respectively.



(a)

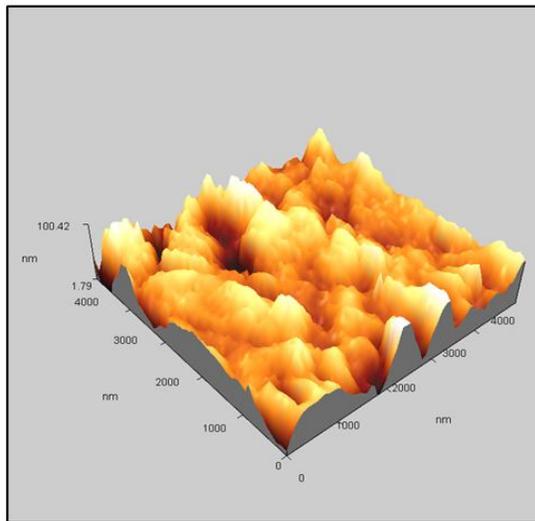


(b)

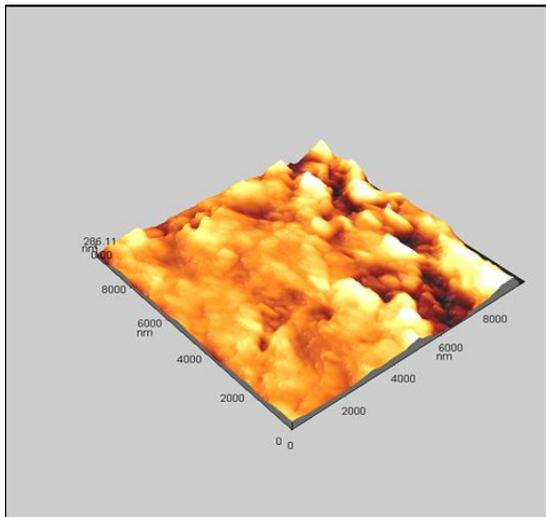
Fig. 7. The AFM images using sampling areas of 5 μm x 5 μm (a) and 10 μm x 10 μm (b) for the CdS samples prepared by (CBD) method

The AFM images showed that the sample presents well defined nanosized grains, having a roughness (RMS) value of ~23 nm and ~27 nm corresponding to the 5 μm x 5 μm and 10 μm x 10 μm sampling area respectively. The average grain size of this sample was ~ 176 nm and ~ 254 nm corresponding to the 5 μm x 5 μm and 10 μm x 10 μm sampling area respectively. Figures (8a) and (8b) represent the AFM images for the CdS sample prepared by (CSP) method using sampling areas of 5 μm x 5 μm and 10 μm x 10 μm respectively. The AFM images showed that the sample presents well defined nanosized grains, having a roughness (RMS) value of ~15 nm and ~48 nm corresponding to the 5 μm x 5 μm and 10 μm x 10 μm sampling area respectively. The average grain size of this sample was ~ 100 nm and ~ 286 nm corresponding to the 5 μm x 5 μm and 10 μm x 10 μm sampling area respectively. It is

clear that the thin film deposited by (CBD) method is more homogeneous than the film deposited by (CSP) method.

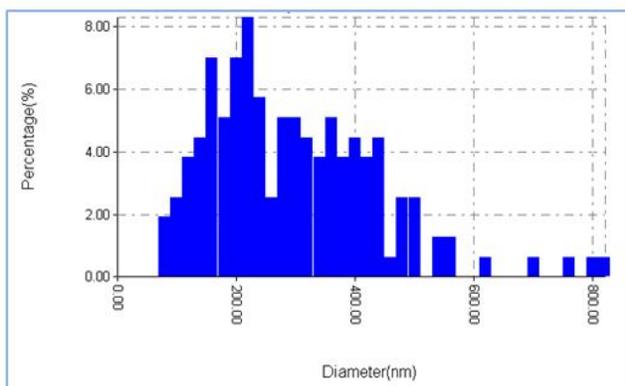


(a)

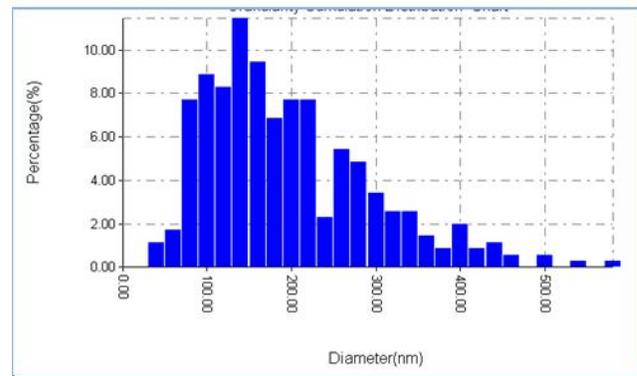


(b)

Fig.8. The AFM images using sampling areas of $5 \mu\text{m} \times 5 \mu\text{m}$ (a) and $10 \mu\text{m} \times 10 \mu\text{m}$ (b) for the CdS samples prepared by (CSP) method



(a)



(b)

Fig. 9. The granularity cumulative distribution charts for the films deposited by (CBD) and (CSP) methods respectively using $5 \mu\text{m} \times 5 \mu\text{m}$ sampling area

Figures (9a) and (9b) show the granularity cumulative distribution charts for the films deposited by (CBD) and (CSP) methods respectively using $5 \mu\text{m} \times 5 \mu\text{m}$ sampling area.

Conclusion

CdS thin films have been successfully deposited on glass substrates by chemical bath deposition (CBD) and chemical spray pyrolysis (CSP) methods. The UV-Visible spectroscopy analysis reveals that the transmittance of the films deposited by (CBD) method is higher than that of the film deposited by (CSP) method. The direct band gap value of CdS films prepared by (CBD) and (CSP) methods are found to be 2.42 eV and 2.55 eV respectively. The AFM analysis of the CdS film deposited by (CBD) method shows that the sample present well defined nanosized grains, having a roughness (RMS) value of ~ 23 nm and ~ 27 nm corresponding to the $5 \mu\text{m} \times 5 \mu\text{m}$ and $10 \mu\text{m} \times 10 \mu\text{m}$ sampling area respectively. The average grain size of this sample was ~ 176 nm and ~ 254 nm corresponding to the $5 \mu\text{m} \times 5 \mu\text{m}$ and $10 \mu\text{m} \times 10 \mu\text{m}$ sampling area respectively. While the AFM images for the CdS sample prepared by (CSP) method show that the sample has a roughness (RMS) value of ~ 15 nm and ~ 48 nm corresponding to the $5 \mu\text{m} \times 5 \mu\text{m}$ and $10 \mu\text{m} \times 10 \mu\text{m}$ sampling area respectively. The average grain size of this sample was ~ 100 nm and ~ 286 nm corresponding to the $5 \mu\text{m} \times 5 \mu\text{m}$ and $10 \mu\text{m} \times 10 \mu\text{m}$ sampling area respectively. It is found that the thin film deposited by (CBD) method is more homogeneous than the film deposited by (CSP) method.

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