Chalcogenide Letters Vol. 8, No. 2,February 2011, p. 77 – 82

ACETYLACETONE AS COMPLEXING AGENT FOR CdS THIN FILMS GROW CHEMICAL BATH DEPOSITION

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The CdS thin films using Acetylacetone as complexing agent were prepared using the chemical bath deposition method, with bath temperature of 70^0C with differences times of reaction. The thin films were characterized by X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM), optical absorption spectroscopy and Atomic Force Microscopy (AFM). The XRD measurements showed that the films have hexagonal polycrystalline structure and the crystallites are oriented preferentially with the (002) and (110) planes. The optical absorption measurements shows the presence of direct transition with energy band gap of 2.37 eV and after increased to 2.40 eV.

(Received January 17, 2011; accepted February, 5, 2011)

Keywords. Acetylacetone, Semiconductor Thin Films, Cadmium Sulfide Thin Films.

1. Introduction

CdS thin films have attracted the attention of researchers for their potential optoelectronic applications. In the field of solar energy they have been used in the manufacture of solar cells because they have an energy band gap in the 2.42 to 2.45 eV interval [1]. Due to the above studies have been conducted on the influence of pH [2], temperature [3], cadmium sources [4], complexing agents [5-9], and others, on CdS thin films growth.

Several techniques have been used to deposit these thin films, among which is Chemical bath deposition (CBD). The CBD is a simple, low temperature, large area compatible and low cost process for the synthesis of several types of semiconductor thin films. It has been used for the deposition of CdS semiconductor thin films since the 60's decade [10,11].

The present work presents the preparations of CdS thin films employed the acetylacetone (Acac) as ligand and their characterization X-ray diffraction, UV-Visible spectrometer, SEM and AFM.

2. Experimental.

The CdS thin films were deposited on glass slides substrates by means of the chemical bath technique. The reactive substances in the solution were: 2 ml of Cadmium Nitrate Tetrahydrated (0.1 M), 2 drops of 99% acetylacetone, 6 drops of buffer pH 11 (NH_4OH/NH_4Cl), 2

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*Corresponding autor: apolinar@ciencias.uson.mx ml of Thiourea (1M) and two amounts of 10 ml of water, after the acetylacetone and before the thiourea.

The processes that occur in the CBD solution consist in general of the following steps:

CBD for chalcogenide films from a metal cation Cd^{2+} complexed by the ligand $(Acac)^{1-}$ these steps can be depicted as follows [12]:

1) Complexant-water equilibrium: $\left(\mathrm{Acac}\right)^{1-} + \mathrm{H_2O} \longleftrightarrow \left(\mathrm{Acac}\right)^{1-}\mathrm{H}^{1+} + \mathrm{OH}^{1-}$

2) Dissociation of water: $\mathrm{H_2O} \longleftrightarrow \mathrm{OH}^{1-} + \mathrm{H}^{1+}$

3) Displacement of ligands: $\mathrm{Cd}\left(\mathrm{NO_3}\right)_2 + \left(\mathrm{Acac}\right)^{1-} \rightarrow \left[\mathrm{Cd}^{2+}(\mathrm{Acac})^{1-}\right] + 2\mathrm{NO_3}$

4) Hydrolysis of Thiourea: $(\mathrm{NH_2})\mathrm{CS} + \mathrm{OH}^{1-} \leftrightarrow \mathrm{SH}^{1-} + \mathrm{H_2O} + \mathrm{H_2CN_2}$

$$\mathrm{SH}^{1-} + \mathrm{OH}^{1-} \leftrightarrow \mathrm{S}^{2-} + \mathrm{H_2O}$$

5) Total Reaction: $\left[\mathrm{Cd}^{2+}(\mathrm{Acac})^{1-}\right] + \mathrm{S}^{2-} \rightarrow \mathrm{CdS\,(s)} + \left(\mathrm{Acac}\right)^{1-}$,

i.e., (1) Time zero to equilibrium between the complexing agent and water; (2) Dissociation of water; (3) Formation and/or dissociation of ionic metal–ligand complexes $\left[\mathrm{Cd}^{2+}(\mathrm{Acac})^{1-}\right]$, where $(Acac)^{1-}$ denotes one of more ligands; (4) Hydrolysis of Thiourea, and (5) Formation of the solid. The films were deposited in the substrate into the solution between 65^0C to 75°C, they were kept in the solution for 1 h. The obtained CdS films were flat homogeneous, green-yellowish, transparent and with very good adherence to the substrate. The gap energy of the films were 2.37 and 2.40 eV, for 10 and 20 minutes, respectively. Their thickness was approximately 100 nm, and they had a hexagonal crystalline structure.

The X-ray diffraction measurements were performed using a Rigaku Ultima III-XRD. Optical absorption spectra of the bilayers were recorded by an Ocean Optics USB4000-UV-VIS spectrometer. Atomic Force Microscopy AFM measurements were done in a DM09 Veeco Atomic Force Microscope.

3. Results and discussion

The acetylacetone was used as a ligand in the CBD in order to obtain CdS thin films, the nature of this agent is bidentate ligand and is convenient for the coupling with Cd ions [13]. The reaction conditions were determined experimentally.

A hexagonal polycrystalline structure was showed by the X-ray analysis results in figure 1, the two peaks corresponding to the CdS structure [14]. In figure 2 the optical absorption spectra of the CdS thin films were showed, the gray line presents the behavior for 10 minutes of reaction time and the black line for 20 minutes of reaction time of acetyalacetone complexing agent. As can be observed both samples present their absorption low level between 550 and 750 nm.

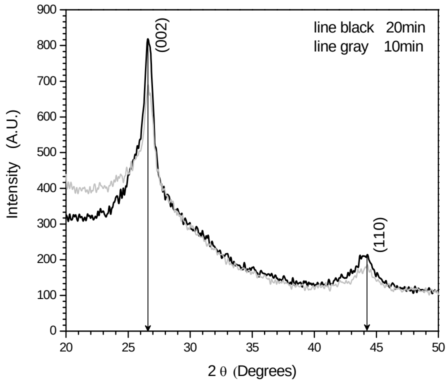


Fig. 1. X-Ray diffraction patterns of the CdS thin films for ten and twenty reaction times using acetylacetone as complexing agent. The gray line corresponds to 10 minutes of reaction and the dots for 20 minutes of reaction.

In addition, using linear adjustment of the square of the absorption coefficient yields a value of the direct energy gap of 2.37 and 2.42 eV for ten and twenty minutes of reaction time respectively, and at shows in figure 3. The difference on the energy gap for the two samples is negligible.

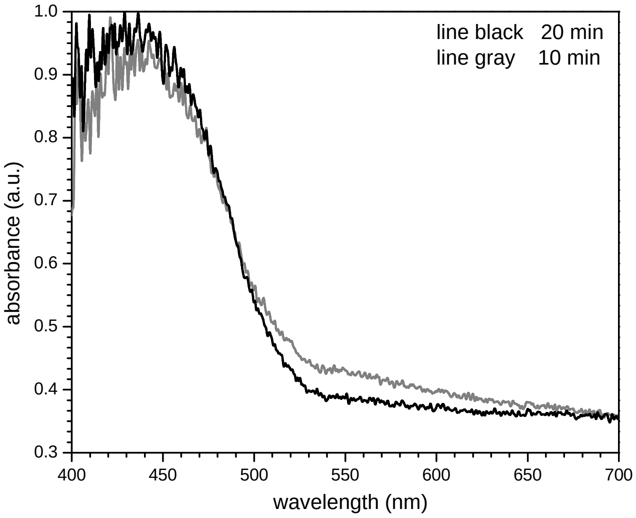


Fig. 2. Optical absorption spectra of the CdS thin films with acetylacetone as complexing agent. The gray line shows the behavior for 10 minutes of reaction time and the dots for 20 minutes of reaction time.

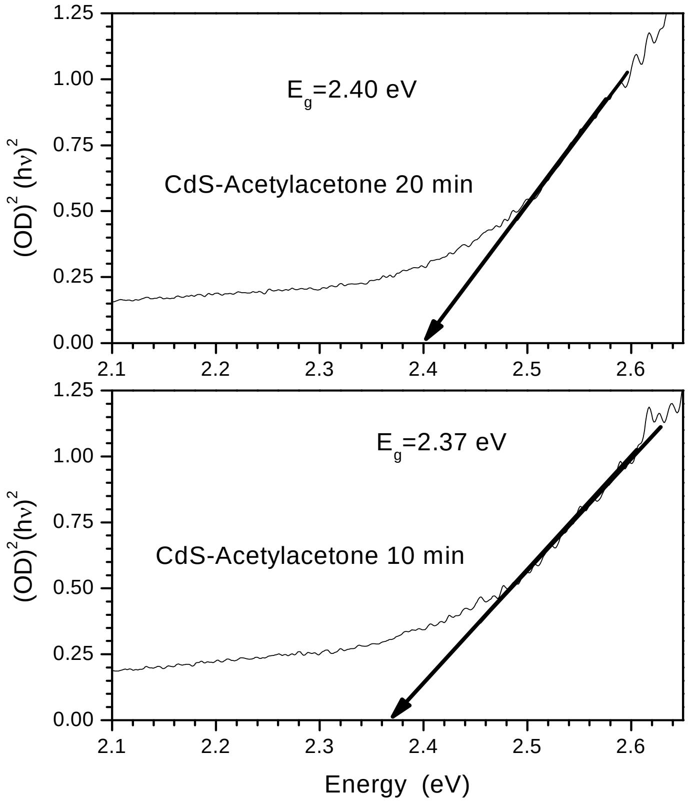
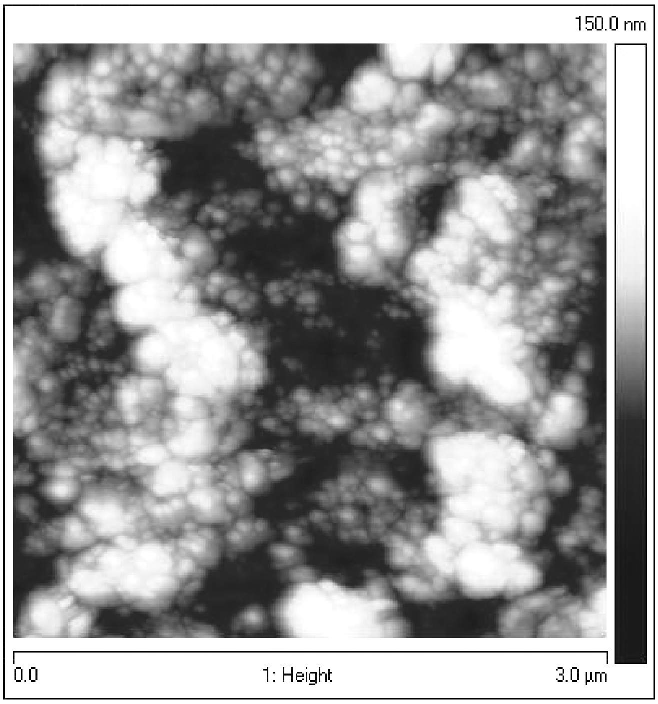
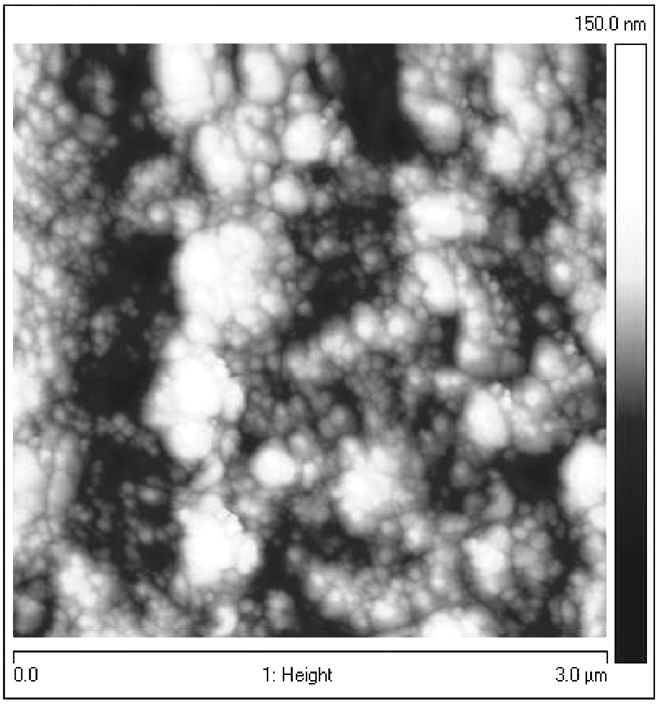


Fig.3. Plot of Square Optical Absorption multiplied by Square Energy, versus Energy for the samples of 10 and 20 minutes of reaction time of CdS thin films growth with acetylacetone as complexing agent.

The figure 4 shows a regular surface morphology which is representative across the overall sample extension, this images was obtained with AFM system.



a) 10 min.



b) 20 min.

Fig. 4. AFM images of CdS thin films growth with acetylacetone as complexing agent, (a) 10 minutes, and (b) 20 minutes of reaction time.

By another hand, the chemical elements that conforms the thin films were analyzed by the Scanning Electron Microscopy (SEM) and were illustrated in figure 5. Whereas the captured images by SEM can be interpreted at a change in the flatness of the surfaces due at the growing and the cluster of nanocrystals.

From this research we developed a process to synthesize CdS thin films of good quality, comparable to the obtained with another technique.

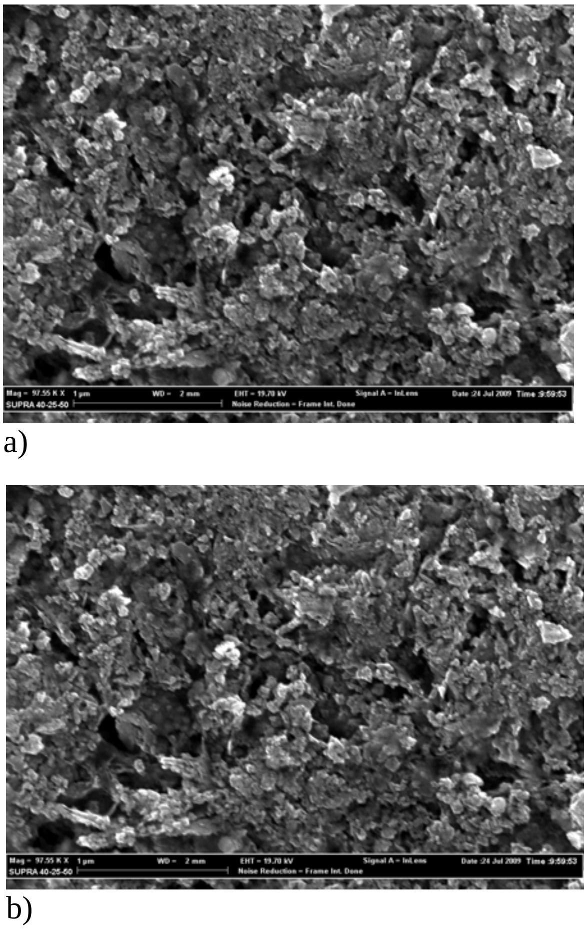


Fig. 5. SEM images of CdS thin films growth with acetylacetone as complexing agent with different reaction times: (a) 10 minutes and (b) 20 minutes.

4. Conclusions

The goal of this work was to change the complexing agent for the Cd ions in a process of Chemical Bath Deposition for CdS trying to improve the formation control of thin films. Where obtained homogeneous CdS thin films. As consequence, a complete set of condition reaction were determined and presented in the experimental part.

Our hexagonal CdS material presents a direct energy bandgap is around 2.40 eV according to those reported on literature [5, 15].

Acknowledgements

This work was supported Project CONACYT No. 90452. Thanks are due to Julius Horvath for his technical help.

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