



# Effect of Heat Treatment on Cds Thin Films by Chemical Bath Deposition

**Ricardo Gonzalez Valenzuela\*, Hilda Esparza Ponce, David Trejo and Cesar Gonzalez Valenzuela**

*Centro de Investigación en Materiales Avanzados, Chihuahua, México*

## Abstract

In recent years, the research on solar cells is focused on increasing its efficiency. The involved factors are numerous like irradiance, cell area, morphology, grain size, crystallographic phases, orientation (texture), band gap, thermal or surface treatment of the layers, etc. Through the development of the second generation of solar cells with thin films of chalcogenides, various investigations have been developed. Specifically in relation to enhancement the cell of CdS/CdTe in this work, CdS thin films for photovoltaic cells applications has been grown by chemical bath deposition over Glass [1] and Glass/ITO substrate [2]. After the deposition, thermal treatment has been applied by cadmium chloride solution 0.3 M. At the range of temperature from 400 C to 450 C under time periods of 10, 20 and 30 minutes in order to improve phase crystallization and grain size increasing. The thin films have been characterized by X-Ray Diffraction (XRD) before and after the thermal treatment. The optical transmittance was measured to the set of samples that were thermally treated over different conditions. It was found the recommended temperature and time in order to obtain good results. Also, it was observed a physical degradation in temperatures over 450 C and times longer than 20 min, when submitted to thermal treatment. This has also been noticed in the treatment with CdTe cells.

## Introduction

The Sulphur Cadmium (CdS) thin films have been used in photovoltaic cells applications and reported by many authors [1-11]. The CdS has been used in thin films development as window layer while Tellurium Cadmium (CdTe) works as the absorbent layer.

An important and typical study of CdS thin films is its efficiency. The efficiency of this kind of cells is influenced by its capacity for electric charge transportation. Then, it has been reported transmittance spectra efficiency of 87% in about 550 nm. The photovoltaic efficiency is about 12% when CdS were thermally annealed in muffle at atmospheric ambient [3], while other authors reported 20% [12]. In order to improve this electric behavior, the thin films must be free of imperfections, increasing crystals size and reducing inter-grain cavities.

The production of these kinds of materials requires easier and low cost methods. For this reason, the Chemical Bath Deposition (CBD) technique is widely recommended. CBD is the analog in liquid phase of the well-known chemical vapor deposition technique in the vapor phase. In CBD, the deposition of thin films takes place from aqueous solutions at low temperatures (near room temperature) by a chemical reaction between dissolved precursors. The CBD technique is simple, works at low temperature and it has an inexpensive large area deposition. CBD is presently attracting considerable attention as it does not require sophisticated instrumentation like vacuum system and other expensive equipment [5] like other growing techniques [10,13,14].

Also, one advantage on CBD's use is that the low temperature avoids oxidation and corrosion of metallic sub-

**\*Corresponding author:** Ricardo Gonzalez Valenzuela, Centro de Investigación en Materiales Avanzados, Chihuahua, México, E-mail: Ricardo.Gonzalez3@Honeywell.com

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strates. The operation parameters are easily controllable, too [15].

The CdS thin films present special characteristics reported in literature; once nucleation of CdS has begun on the substrate, it becomes easier for the film to grow. The crystals will continue to grow until the homogenous reaction dominates over the heterogeneous reaction [15].

The present work studies the impact of thermal treatment that is applied to the recent developed CdS thin films that are grown over simple glass and over glass/ITO substrates. These results are supported by microstructural characterization done by X-Ray analysis, AMF Morphological study and Optical performance evaluation [1,6-9,16].

Another important reason of doing the present work is because it is well known that among the group II-VI semiconductors, chemical bath deposition of CdS is the most extensively investigated [15,17-22].

Other authors have been studying the effect of ultrasonication instead of CBD and they found improved characteristics over CdS films [23]; however, it is out of this study.

The increase in grain size and a homogeneous surface in the semiconductor type n, allows an interaction between the interface of the p-type semiconductor and n, leading an efficient generation of electron-hole pairs.

## Experimental Procedure

The glass substrates were previously washed with mild soap and rinsed with water, followed by an ultrasonic bath in acetone. After that, they were washed in isopropyl alcohol, similar to other authors [1].

The CBD is a technique in which thin films are deposited on substrates immersed in dilute alkaline solution containing metal ions and the chalcogenide source. The method of deposition usually uses a complexing agent to control the slow release of metal ions ( $\text{Cd}^{2+}$ ) and Sulphur ions ( $\text{S}^{2-}$ ) in order to produce the controlled homogeneous precipitation of the film on the solid substrate [6].

Precursor solutions of  $\text{CdCl}_2$  0.05 M,  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$  0.5 M.,  $\text{KOH}$  0.5 M. and  $\text{SC}(\text{NH}_2)_2$  0.5 M. and distilled water were poured in a baker [6]. The thin films were deposited over Glass and Glass/ITO substrates using CBD technique by 20 minutes at 70 C in order to obtain approximately 60 nm thickness films. A second deposition (under the same conditions) was realized in order to obtain a final thickness approximately of 120 nm thickness.

During the reaction, due to alkaline medium, pH must be under control in order to avoid the formation of  $\text{Cd}(\text{OH})_2$  from ammonium dissociation [7].

The following reaction shows ions of  $\text{Cd}^{+2}$  and thiourea hydrolysis  $\text{SC}(\text{NH}_2)_2$  with the formation of sulfide ions giving the final product of CdS, as shown:

- 1)  $\text{CdCl}_2 + 2\text{KOH} \rightarrow \text{Cd}(\text{OH})_2 + 2\text{K}^+ + 2\text{Cl}^-$
- 2)  $\text{Cd}(\text{OH})_2 + \text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + \text{H}_2\text{O} \rightarrow [\text{Cd}(\text{C}_6\text{H}_5\text{O}_7)]^- + 3\text{Na}^+ + 2\text{OH}^-$
- 3)  $\text{Cd}(\text{C}_6\text{H}_5\text{O}_7)^- \rightarrow \text{Cd}^{+2} + (\text{C}_6\text{H}_5\text{O}_7)^-$
- 4)  $\text{Cd}(\text{C}_6\text{H}_5\text{O}_7)^- + \text{SC}(\text{NH}_2)_2 + \text{OH}^- \rightarrow \text{CdS}$  or other compounds like  $\text{CdCO}_3 + \text{CdS}$ ,  $\text{CdCO}_3$

Four samples were prepared and identified as CDS-6VA1, CDS6VA2, CDS6VB1, CDS6VB2, corresponding to the samples grown over Glass and CDS6IA1, CDS6IA2, CDS6IB1, CDS6IB2, corresponding to the samples grown over Glass/ITO.

Once the thin films were grown, their structural characteristics were studied by X-Ray Diffraction Analysis (XRD), using an Panalytical Xperpro equipment from 20° to 80° angles in steps of 0.05 and scanning times of 2.5 sec. [1,7,9].

The optical transmittance evaluation was done by UV-VIS Scan, using UV-Vis Perkin Elmer Lambda 10 equipment in a wavelength interval of 300 to 1000 nm.

The morphological study was performed by Atomic Force Microscopy (AFM) with a Multimode, Veeco Instrument. All the samples were evaluated under these 3 methods just after they were grown.

Once they were analyzed, a thermal treatment was performed into an air atmosphere in a range of temperature from 400 C to 450 C under time periods of 10, 20 and 30 min. This thermal procedure was compared to others reported in bibliography [6].

The XRD, optical transmittance and morphology analysis were done again.

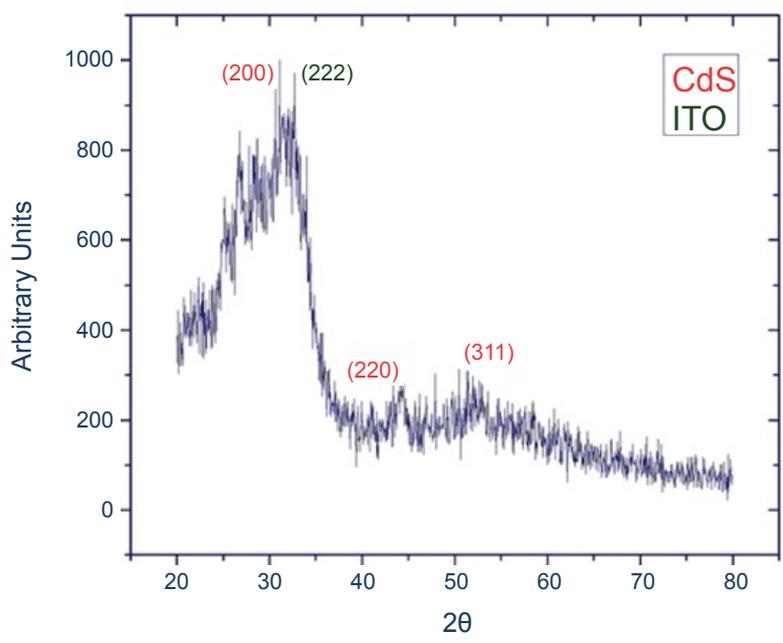
## Results and Discussion

The XRD studies revealed that all the deposited films were polycrystalline with hexagonal structure and exhibited (002) preferential orientation [6].

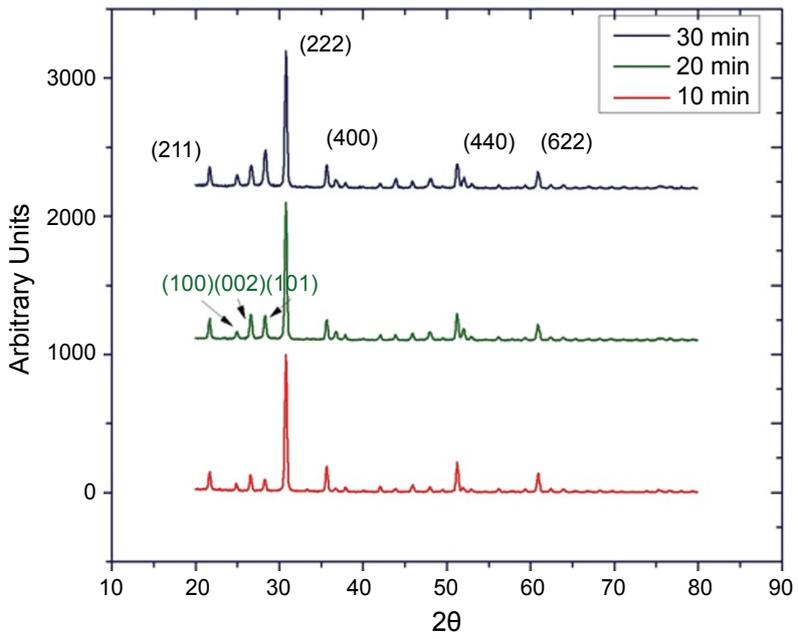
The XRD analysis that was done just after the samples were grown shows a very noisy signal. The planes (222) are related to the presence of ITO, while the planes (200), (220) and (311) belong to the CdS in cubic phase [3,5,9,12].

This behavior is according to expected due to the very small grain and crystal size of the sample (Figure 1). However, once the thermal treatment was performed, the XRD study is able to recognize its structural features because of the increased grain and crystal size.

The increase in crystal size after the thermal treatment



**Figure 1:** XRD pattern of CdS on ITO as was deposited by chemical bath deposition.



**Figure 2:** XRD pattern of CdS on ITO after thermal treatment to a 400 C for 10, 20 and 30 minutes.

**Table 1:** Standard ASTM card for CdS [10].

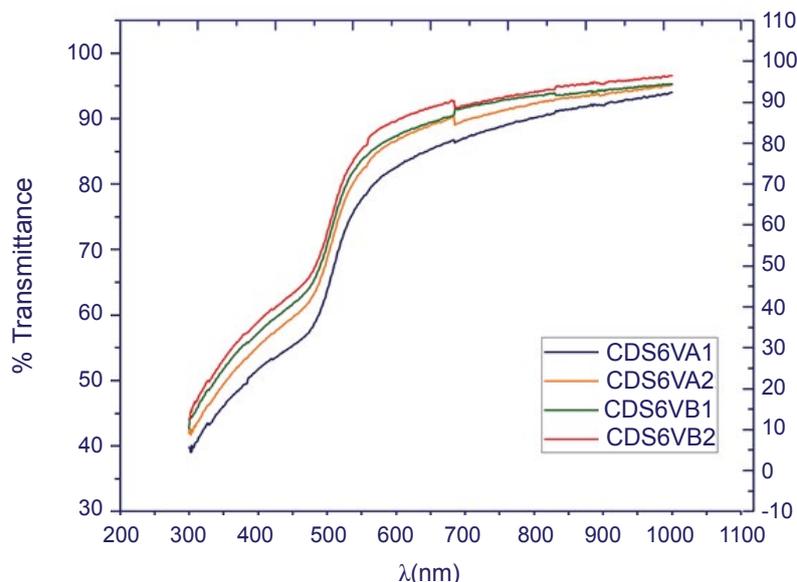
2θ	D(A°)	Hkl
24.828	3.580	100
26.449	3.360	002 α - CdS
28.216	3.159	101
36.648	-	102
43.735	2.067	110 α - CdS
51.875	1.761	112 β - CdS

reveals the presence of the main crystallographic planes ITO(211), (222) and (400) at 21.6°, 30.3° and 35.6°, respectively. While the CdS is identified by the presence of

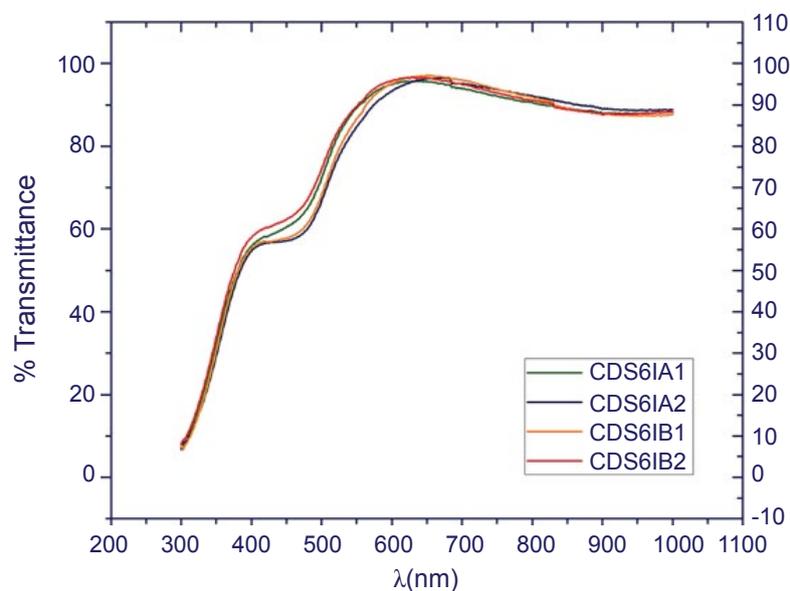
the planes (100), (002) and (101) at 24.9°, 26.6° and 28.3°, respectively, according to the proper information found in bibliography (Figure 2).

The angles and planes are supported on information reported in literature [11] (Table 1).

Later, the optical transmittance showed a regular behavior where the transmittance is proportional inversely to the incident energy, according to expected for a semiconductor. “Where the film thickness is maximum, the optical band gap is minimum” [15]. It is also reported



**Figure 3:** Plots % transmittance for thin films of CdS deposited on glass.



**Figure 4:** Plots % transmittance for thin films of CdS deposited on glass/ITO.

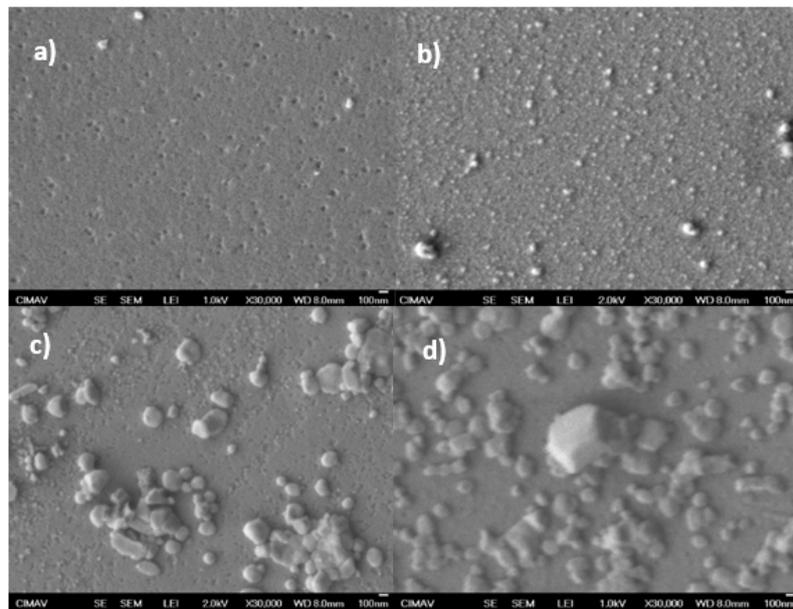
an inverse relationship between energy gap and grain size [15]; in which, the CdS deposited over Glass shows a notorious slope change between a specific energy range. This slope change obeys to an energy absorption variation when the energy value is very close to the valence and conductive band. When this happens, the energy is able to promote an electron from valence band to conductive band, “jumping” the energy gap known as the forbidden energy band (Figure 3). This transmittance or absorbance observation allows the present study to identify the material as a semiconductor.

Besides this analysis, the sample that was deposited over the Glass/ITO substrate shows 2 different slope changes. This result is also according to expected, due to

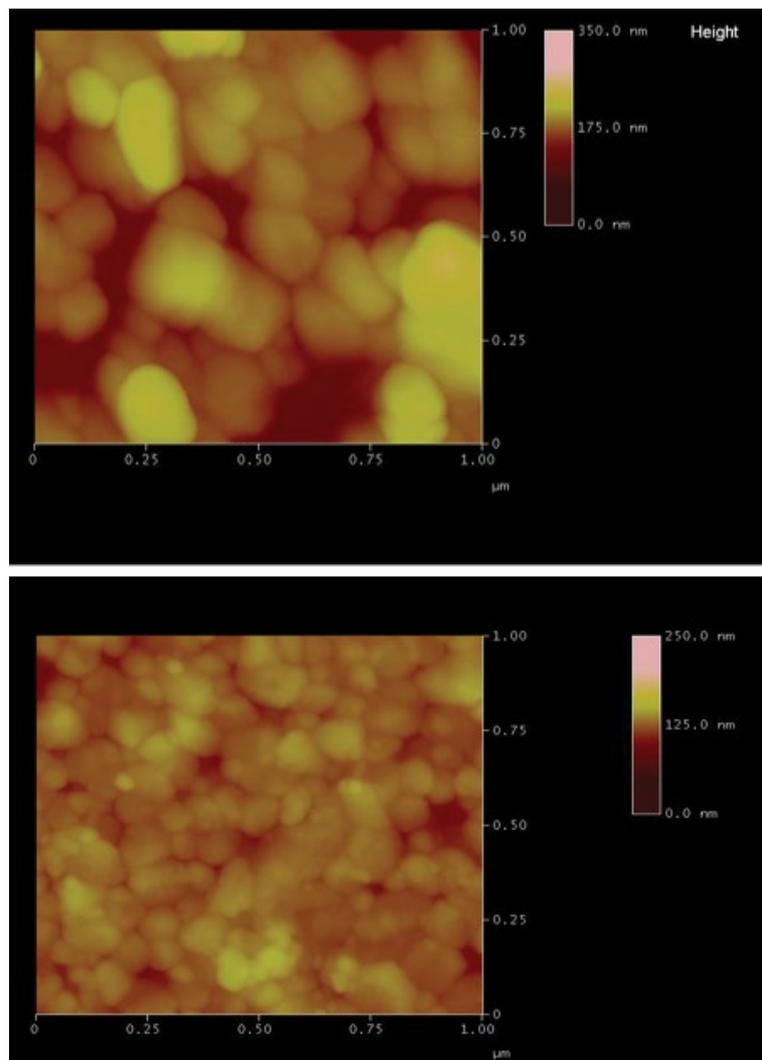
the 2 different components (ITO and CdS) present in the thin film (Figure 4).

The transmissivity spectra data is reported in literature, too [1,6,15].

As discussed before, the improved properties of the thin films is because of the crystal size increasing. This morphological change is visually observed in Figure 5, where the crystal size is bigger after several treatments as follows: The first picture shows the morphological state before any thermal treatment. The thermal treatment was done at 400 C at different time intervals. The following pictures show its new morphological situation after 10, 20 and 30 minutes, respectively. It is clear seen how the



**Figure 5:** SEM images a) Before thermal treatment and after thermal treatment at 400 C for; b) 10 minutes; c) 20 minutes and; d) 30 minutes.



**Figure 6:** Morphology by AFM between CdC deposited on a) Glass and; b) Glass/ITO.

grain size is increased considerably for about 10 times, achieving particle sizes of about 100 nm width. Similar pictures are reported for other authors [3].

As mentioned before, the goal of this work is the evaluation of the effect of the thermal treatment applied to thin films of CdS deposited on ITO. The optical transmittance showed an improved behavior before 30 minutes of treatment. However, over this time, it was observed that the optical transmittance has changed considerably, evidencing a material degradation. This material degradation has been proved based on the morphological analysis, too (Figure 6).

## Conclusions

This article demonstrates that CdS films were developed by CBD technique over glass and glass/ITO substrates, successfully. All samples showed good optical properties because its measured transmittance was more than 80% from 400 nm to beyond 1000 nm. The thermal treatment applied to conditions of 400 C and 10 minutes was the optimal formulation in order to get the best results. The structural and morphological study reveals that the thermal treatment offers a good alternative to photovoltaic cells of CdS because of the increased grain size. A very important finding was how long the temperature was applied; it was found that 30 min was the optimum. But also, although the material is big enough to improve its main behavior, the grain now is overly big to keep united to the substrate, causing an undesirable physical condition.

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