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# Characterization of Cadmium Sulfide Films Deposited By Chemical Bath Method

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## Abstract

Thin film cadmium sulfide is a leading candidate in the fabrication of large area solar cells. The chemical bath deposition method is one of the least expensive sources for the fabrication of device quality cadmium sulfide thin films. In the present work, the deposition of CdS films on glass substrate from an aqueous solution containing cadmium acetate, ammonia, ammonium acetate, and thiourea are investigated. The structural properties of CdS films are characterized. Good quality thin films within 0.1 - 0.5 μm thickness were obtained in 30 minute deposition time, and at 70°-90°C. The films show preferential orientations. The optical transmittance of the films are in the range of 40-65% for wavelengths above the band gap absorption, making the films suitable as a window material in hetero-junction solar cells.

## Introduction

Cadmium sulfide (CdS) is a promising TCS (transparent conducting semiconductor) material to be used in a hetero-junction solar cell due to its large bandgap (2.42 eV) at room temperature and good photo-conductivity (Chu and Chu, 1993; Sahu and Chandra, 1987). It is commensurate with two of the leading photovoltaic absorber materials CdTe & $CuInGaSe_2$. The deposition of CdS films on substrates from an aqueous solution is a low cost scalable technique for the manufacture of thin film solar cells. In the solution growth process, a cadmium complex and an organic sulfiding agent provide very low concentration of $Cd^{2+}$ and $S^{2-}$ in solution. When the product of ion concentration exceeds the solubility product of CdS (1.4E-29 at 25°C), a chemical reaction takes place, precipitating CdS (Chu et al., 1992). $CdAc_2$, $CdSO_4$, $Cd(NO_3)_2$, $CdCI_2$ etc. can be used as cadmium salt in the chemical solution (Kaur, I., D.K. Pandya, and K.L. Chopra). The present paper describes the deposition of CdS on a glass substrate by using aqueous solution of different molar concentration of cadmium acetate ($CdAc_2$), thiourea [$(NH_2)_2CS$], ammonium acetate ($NH_4Ac$) and 30% ammonium hydroxide ($NH_4OH$). This paper also discusses the structural and electrical properties of these films that have been found after the characterization.

## Materials and Methods

Figure 1 shows a simple setup for chemical bath method for the deposition of CdS films. CdS thin films were deposited on chemically cleaned glass substrate using aqueous solution of cadmium acetate ($CdAc_2$), thiourea [$(NH_2)_2CS$], ammonium acetate ($NH_4Ac$) and 30% ammonium hydroxide ($NH_4OH$). Here $NH_3$ acts as a completing agent, thiourea furnishes $S^{2-}$, cadmium acetate furnishes $Cd^{2+}$, and $NH_4Ac/NH_3$ serves as a buffer.

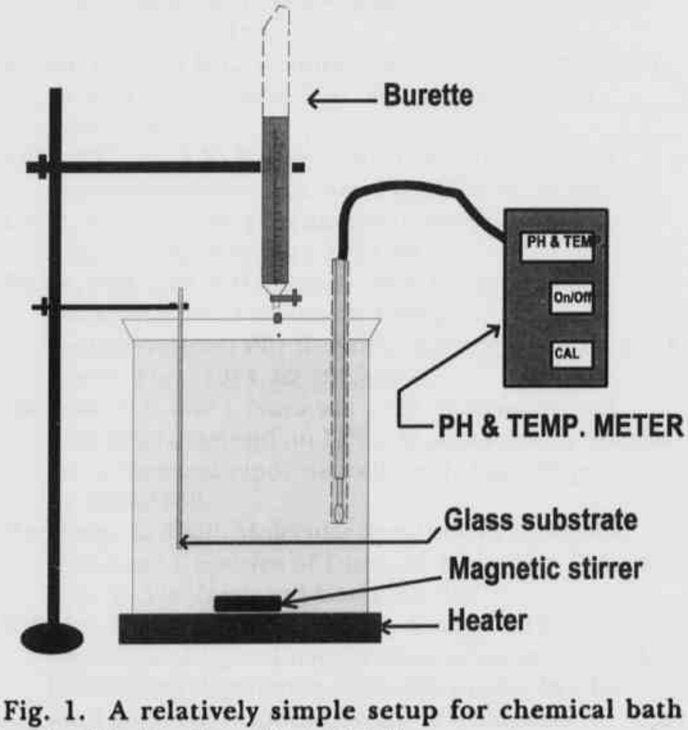

**Fig. 1.** A relatively simple setup for chemical bath method for the deposition of CdS.

CdS film can deposit heterogeneously on glass substrate, or homogeneously in the solution, producing CdS precipitate. Since we desire a thin film of CdS with a uniform thickness and which should be strongly adherent to glass substrate, the homogeneous process is undesirable. The homogenous process can be suppressed by using a relatively very low molar concentration of cadmium acetate and thiourea with respect to ammonium acetate and ammonia in the chemical solution.

The deposition of CdS films was studied by using different molar concentration of cadmium acetate (0.005M - 0.02M), ammonium acetate (0.1M - 0,4M), thiourea (0.005M - 0.02M) and with 30% ammonium hydroxide of known volume. The deposition conditions were identified by using a certain volume of cadmium acetate/thiourea, ammonium acetate and ammonium hydroxide and monitoring the volumetric addition of cadmium acetate/thiourea of known molar concentration. The chemical solutions were heated and stirred vigorously with the help of a magnetic stirrer, and the glass substrates were kept immersed vertically in the solution during the deposition processes. When the heterogeneous deposition begins on the glass substrate, it is identified by observing a slight yellow tint within the solution. Further deposition then completes within next 30 - 45 minutes depending on the deposition conditions. The pH of the solutions were varied in the range of 8 - 13.5. Best depositions were found at molar concentrations of 0.005 - 0.01 M and 0.008 - 0.015 M for cadmium acetate and thiourea respectively with concentration of ammonium acetate in the range of 0.1 - 0.2 M. The temperature and pH of the solution mainly controls the rate of deposition. Typical deposition rate was found to be 0.01 - 0.015 µm/minute.

***Techniques used for the characterization of CdS films.***-- The crystallographic properties of the films were studied using Phillips Analytical X,PERT X-ray diffractometer at the HIDEC facility of the University of Arkansas. The diffraction spectra were obtained by scanning 2θ in the range of 25-120°.

For thickness measurement of the films, first a uniform step was made by masking one portion of the film and then etching the unmasked portion by immersing and withdrawing the film quickly in 50% HC1 acid. Dektak 3030 thickness monitor at the Physics measurement laboratory of the University of Arkansas was used to measure the step height.

Digital Instrument's Nanoscope machine which uses Atomic Force Microscopy (AFM) technique was used to study the surface topography and roughness of the surface. SEM pictures were taken to view the surface morphology of the films.

A diode array visible UV photo-spectrometer was used to obtain the optical transmittance and absorption spectra for a wavelength range of 300 nm to 820 nm.

The dark-current and photo-current responses of the films were measured by using Keithley Source Measurement Unit (SMU) coupled with Oriel AM1.5 Solar Simulator. Two collinear ohmic contacts were made using colloidal silver paint and later on using indium shots. The voltage at these two contacts was swept from 0 to 50 V in a 0.5V steps, and the corresponding changes in current were measured in the dark and under illumination.

## Results and Discussion

Figure 2 shows the plot of the deposition rate of CdS with the variation of pH. A decrease in deposition rate was observed with the increase of pH of the solution. At a given temperature, the rate of formation of CdS is determined by the concentration of $Cd^{2+}$ provided by $Cd(NH_3)_4{}^{2+}$ and the concentration of $S^{2-}$ from the hydrolysis of $(NH_2)_2CS$. The rate of hydrolysis of $(NH_2)_2CS$ depends on the pH and temperature of the solution. The various reactions involved in the chemical bath are as follows (Chu et al., 1992):

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^- \qquad [1]$$

$$Cd^{2+} + 2\,OH^- \leftrightarrows Cd(OH)_2 \qquad [2]$$

$$Cd^{2+} + 4NH_3 \leftrightarrows Cd(NH_3)_4{}^{2+} \qquad [3]$$

$$(NH_2)_2CS + 2\,OH^- \leftrightarrows S^{2-} + 2H_2O + H_2CN_2 \qquad [4]$$

$$Cd^{2+} + S^{2-} \leftrightarrows CdS \qquad [5]$$

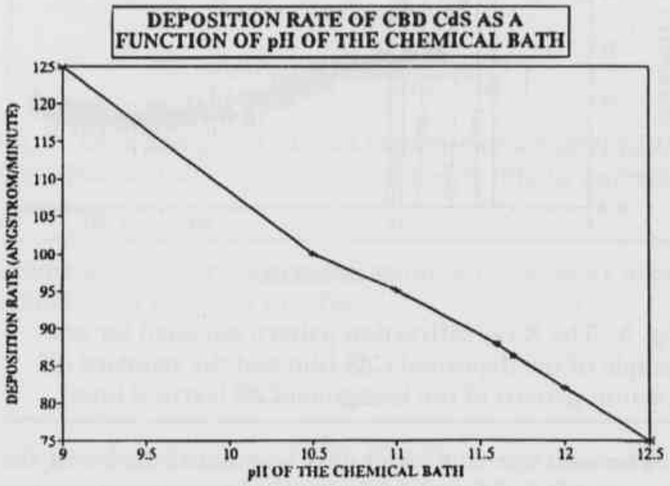

Fig. 2. The dependence of growth rate of CdS with pH of the solution in CBD method.

The presence of $NH_4^+$ salt in the solution shifts the equilibrium position of reaction 1, increasing the concentration of $Cd(NH_3)_4^{2+}$ and reducing the concentration of $Cd^{2+}$. Thus, the rate of formation of CdS can be controlled by varying the concentration of ammonia and $NH_4$ -salt in the solution, which leads to a change of pH of the solution. Further, the hydrolysis of $(NH_2)_2CS$ is greatly enhanced as the temperature is increased, increasing the concentration of $S^{2-}$ in the solution (Chu et al., 1992). Which also leads to the enhancement of the rate of formation of CdS.

The deposited films demonstrate good adherence to the glass substrate. The XRD analysis shows a strong diffraction peak at 2θ = 26.61° for CdS film of the deposited batches. Some minor peaks were obtained at 2θ = 44.105°, 111.125° etc. Polycrystalline hexagonal and cubic CdS of random orientation are known to show many strong X-ray diffraction peaks. Figure 3 shows a diffraction plot for a 2θ scan from 25° to 120° of a typical film superimposed with the standard diffraction peaks of hexagonal CdS of random orientation. The single strong peak at 26.61° indicates a preferred crystallographic orientation associated with the (002) reflection of hexagonal CdS. The preferred orientation of this type is due to the controlled nucleation process associated with the low deposition rate of CdS.

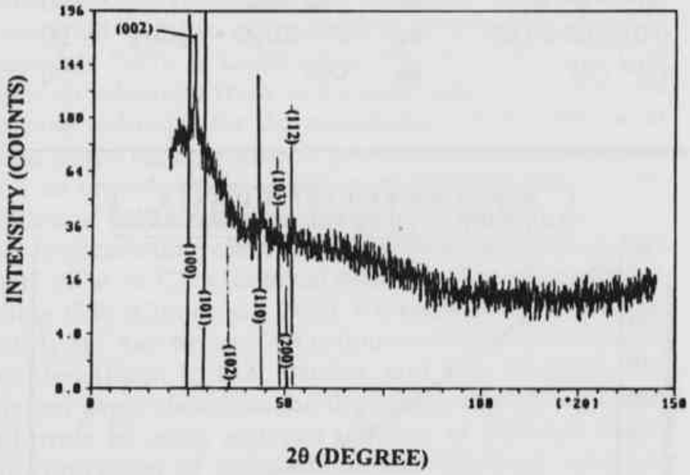

Fig. 3. The X-ray diffraction pattern obtained for one sample of the deposited CdS film and the standard diffraction pattern of the hexagonal CdS (vertical lines).

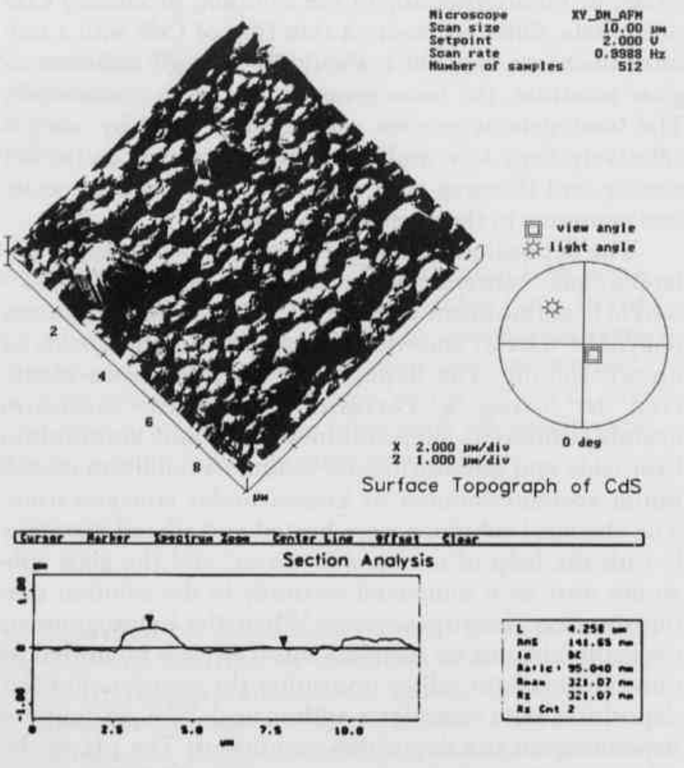

Fig. 4. AFM plot for surface topography and section analysis a. Surface topography; b. Section analysis

The average film thickness was found to be in the range of 0.1-0.5 µm from the Dektak measurements. Figure 4 shows the AFM plot of a typical CdS film depicting the surface topography. The maximum roughness was found in the range of 80-100 nm in the smoother region on the film surface from the AFM analysis. Since CdS will be used as window material in the hetero-junction solar cell fabrication, surface roughness of this range is desirable. In this case the surface roughness will help the base absorber semiconductor to absorb more incident light energy due to the scattering of light in the CdS window surface which ultimatly leads to an increase in short circuit current density, $I_{sc}$ in the solar cell improving it's efficiency. The average grain size is 0.1-0.5 µm, though some large grains of 1 µm dimension visible in the AFM plot. The large grains are undesirable in solar cell fabrication, and should be eliminated by a controlled nucleation process of the CdS films.

Figure 5 shows UV spectrometer plot for percent transmittance vs wavelength. Percent-transmittance is 64.9% above the bandgap energy for this CdS film, and the overall percent-transmittance was found in the range of 40-65%. The actual transmittance of the films is reduced somewhat due to the scattering of light on the rough crystallographic surface of CdS. An integrating sphere spectrometer might help to get the true transmittance of these chemically deposited CdS films.

The optical bandgap energy deduced from absorbance square vs. photon energy plot in the wavelength range of 300-820 nm is about 2.42 eV as shown in Fig. 6, which

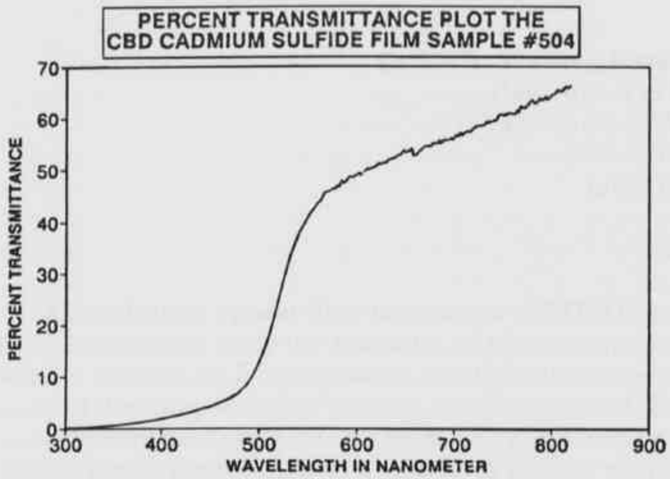

Fig. 5. Percent transmittance plot from the UV spectrometer data for CBD CdS film.

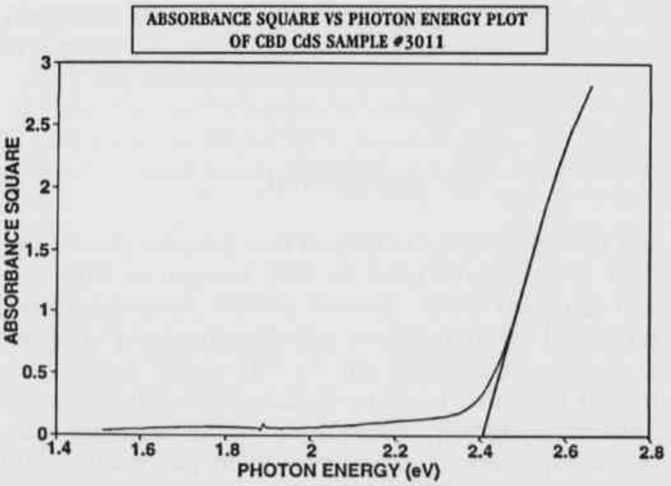

Fig. 6. Absorbance square versus photon energy plot for CBD CdS film.

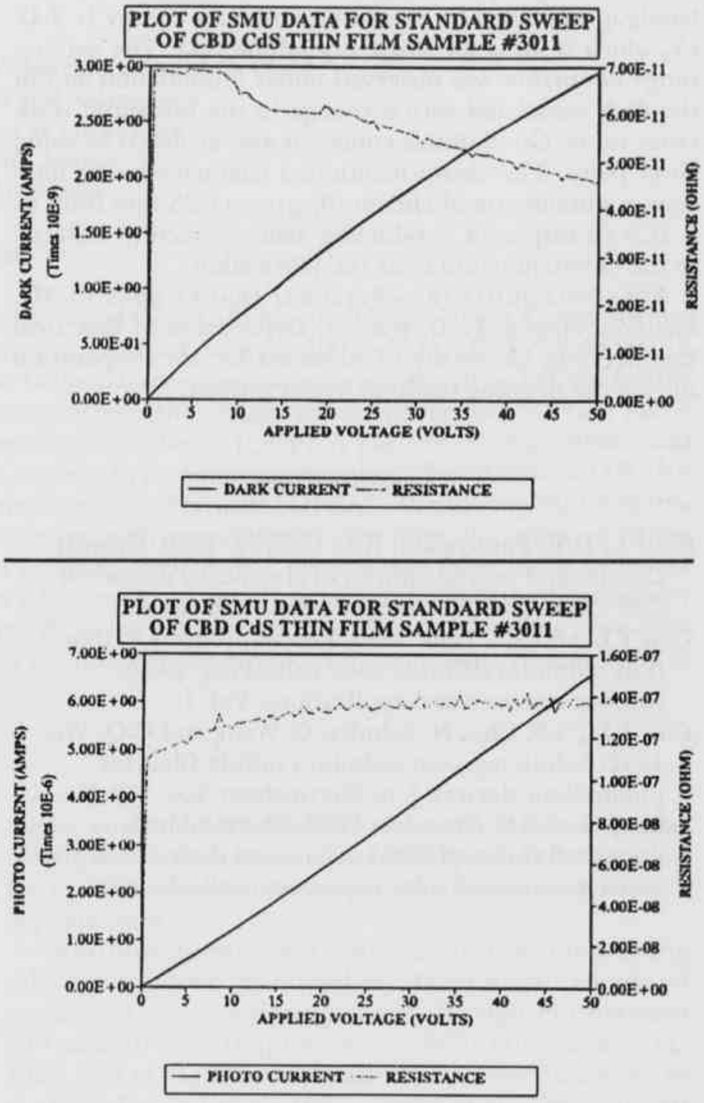

Fig. 7. Dark and photo current response of a typical CBD CdS film. a. Dark current response; b. Photo current response.

matches with the bandgap energy of single crystalline CdS which is also 2.42 eV.

Figure 7 shows voltage vs. current and a voltage vs. resistance plot in the dark and under AM 1.5 illumination. An increase of current was observed under illumination. The overall dark resistance observed for films of different thickness is of the order of $10^6$-$10^9$, and decrement of resistance was observed with films of higher thickness. The ratio of dark resistance to photo resistance varies in the range of 300-800. Typical dark resistivity of the films obtained was 2 x $10^4$ ohm-em and photo-resistivity was about 4 ohm-cm under AM 1.5 solar radiation.The observations shows silver paint makes good ohmic contact than indium shots with CdS thin films.

## Conclusions

The characterization of CdS thin films was done after the deposition by the chemical bath method. Preferred (002) hexagonal crystal orientation was observed from the X-ray diffraction analysis. The AFM plot provides an average grain size of 0.1 - 0.5 μm with a surface roughness analysis of 80-100 nm in a smoother region on the film. Observed optical transmittance is 40-65% above the bandgap energy. The measured bandgap energy is 2.42 eV, which is ideal for single crystalline CdS. The varying range of current was observed under illumination and in the dark associated with a change in the measured resistance value. Good ohmic contact is also achieved by using silver paint. The above mentioned characterization indicates a suitable use of chemically grown CdS thin films as a TCS (transparent conducting semiconductor) material in the hetero-junction solar cell fabrication.

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