

# Preparation and Characterization of Chemically Deposited Cadmium Sulphide Thin Films.

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## ABSTRACT

A thin film of Cadmium Sulphide on quartz substrate was deposited by Chemical Bath Method (CBD). The deposition was done at room temperature and annealed for 1hr at 160°C. A band gap of 2.41eV was recorded by optical absorption measurement. The dark conductivity of as prepared film E was 18mA and a photocurrent of 30mA under a 1kWm<sup>-2</sup> tungsten Halogen illumination.

When annealed, the dark current was increased to about 38mA and a photocurrent of about 60mA was obtained. This result shows that post deposition annealing will enhance the performance of CdS films in the area of optoelectronic application.

(Keywords: thin film, optoelectronic, photocurrent, annealing, transmittance, CBD)

## INTRODUCTION

The heterojunction of Cadmium Sulphide other than CdS/Cu<sub>x</sub>S which has been known as a useful photovoltaic cell has been explored by various researchers. For example, Matsumoto et al. (1984) have demonstrated an efficiency of 12.8% with a 78mm<sup>2</sup> cell of screen-printed CdS/CdTe and Rom et al. (1985) have made junctions of CuInSe or CuInS with Cadmium or Zinc Sulphide using a totally sprayed process. The efficiencies demonstrated by these authors as mentioned above did not exceed 3%, but they noted that the ternaries can be doped controllably as both p- and n-type, and homo-junction cells are expected to have very good efficiencies up to 30%.

Martinuzzi (1982) has reviewed the properties of CdS/Cu<sub>x</sub>S solar cells and methods of preparation including thermal evaporation, sputtering and spraying. He concluded that spraying will probably

be the most economical process. Ajayi et al. (1994) have demonstrated that thin films of CdS suitable for device application can be obtained by the pyrolysis of bis-(morpholinodithioato-ss) cadmium.

The process adapted is the various researchers as explained involve expensive equipments which are not usually readily available for further research works. This work however considers a very simple method: CBD method. Chemical bath deposition method of producing CdS films is about thirty years old and may be said to be at the infant stage as far as the technological applications are concerned (Miller and Heller 1976). The Chemical bath deposition of CdS films was initiated by such workers as Kitaev et al. (1960), Mokrushin and Thacher (1961) and later on pursued by many other researches.

The reason for much interest in CdS film research is the fact that it is one of the most sensitive photoconductors (Babe, 1960) and that polycrystalline CdS film have been used to produce thin film solar cells (Carlson et al., 1958). Other applications of CdS films include photoconductive devices (Nair et al., 1987), image intensifiers (Call et al., 1980), and electroluminescent devices (Chandra et al., 1980), as well as electro-beam pump caser (Chopra et al. 1982).

In this work, we have demonstrated a simplified and inexpensive chemical bath deposition method of obtaining CdS films of good adhesive and uniform thickness. The effect of post deposition annealing and photoconductivity characteristics of these films are also presented

## EXPERIMENTAL DETAILS

Basically, the deposition process involves the choice of a suitable complexing agent (Ligands L)

such as  $\text{NH}_3$ , Triethanolamine (TEA),  $\text{OH}^-$ ,  $\text{CN}^-$ , etc, that forms complex with the metal ion;  $\text{M} + n\text{L} \leftrightarrow \text{ML}_n$ , where  $n$  is the number of Ligands directly bounded to the metal ion  $\text{M}$ ; which on dissociation through the reverse reaction facilitates the controlled release of metal ion that combines with the sulphide ion available in the solution through the hydrolysis of thiourea or thioacetamide (Chopra et al., 1982).

## DEPOSITION

Three basic phases are involved in the deposition mechanism. The growth phase which is initiated by chemical reaction, the nucleation phase in which a hydroxide layer is deposited on the glass substrate and a terminal phase where the bath is depleted of constituent ions. The terminal phase is manifested in different ways. In the case of CdS thin films, it is dominated by the growth of tiny crystallites on the thin film on which the particles precipitating in the bath get absorbed. This gives the appearance of particulate deposition since the presence of the thin film underneath the surface is fully concealed (Nair et al 1988) and Nair et al (1987).

In this work, the films were deposited on clean glass slides (25mm × 75mm × 1mm) from aqueous amonical solutions containing  $\text{Cd}^{2+}$  and thiourea 1:1 and 1:2 molar ratios. Analytical reagents grade chemicals (Thiourea, Triethanolamine and Ammonia solution) were used for the preparation of the solutions. The reaction mixture was prepared following basically the same procedure as reported by Nair et al (1987). The clean glass slides were mounted vertically, supported on the walls of the beakers to which the reaction mixture was transferred.

The deposition was carried out at room temperature ( $27^\circ\text{C}$ ). The coated substrates were removed from the bath at the end of each deposition time chosen, washed in distilled water and dried. These samples are referred to as "as prepared" films. The samples were then annealed.

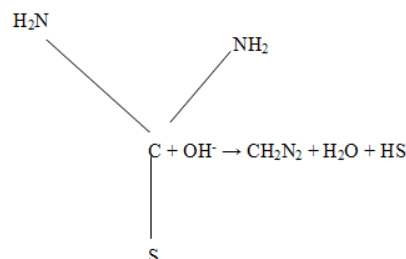
Measurement of Optical absorbance  $A$ , defined as  $A = -\log_{10} T$ , where  $T$  is the transmittance of the thin film, were made at room temperature from 0.35 to  $0.70\mu\text{m}$  by the use of a UV/Vis spectrophotometer. Standardization was done and within the wavelength of interest there was optical balance.

In order to record the photo-current response, the conducting silver paste was used to form copper electrodes 2cm apart on the films. The sample was then placed under a  $1\text{KWm}^{-2}$  halogen lamp. A bias voltage for the sample was supplied by an IC regulated power supply and the current flowing was measured with digital DC micro ammeter. The photo-current response curves for the samples were recorded during a 500 second period. 100s dark, 200s under illumination and 200s in darkness.

## RESULTS AND DISCUSSION

The reaction mechanism for the CdS film formation is given (Pavaska et al, 1977) as:

- i. Formation of a complex compound  
 $\text{CdSO}_4 + 4\text{NH}_3 \rightarrow \text{Cd}[(\text{NH}_3)_4]\text{SO}_4$
- ii. Diffusion of ions  $\text{Cd}[(\text{NH}_3)_4]^{2+}$   $\text{OH}^-$  and thiourea to the catalytic surface of CdS
- iii. Dissociation of thiourea is an alkaline medium



- iv. Formation of sulphide ion  
 $\text{HS} + \text{OH}^- \rightarrow \text{S}^{2-} + \text{H}_2\text{O}$
- v. Formation of CdS  
 $\text{Cd}(\text{NH}_3)_4^{2+} + \text{S}^{2-} \rightarrow \text{CdS} + 4\text{NH}_3$

## UV/ VISIBLE SPECTROPHOTOMETRY

The absorption coefficient  $\alpha$  was calculated from the relationship

$$\alpha = \frac{1}{x} \left( I_n \frac{1}{T} \right)$$

where  $x$  is the film thickness. For a direct band-gap material of which CdS is one, the absorption coefficient has the relationship (Bube, 1974).

$$\alpha = K(E - E_g)^{1/2}$$

where  $k$  is a constant of proportionality and  $E_g$  is the band-gap energy. From a plot of  $\alpha^2$  against  $E$  one obtains the energy of the band-gap.

Figure 1 shows the absorbance spectrum as obtained and the maximum slope of the curve occurred at the wavelength 492nm and 512nm

representing the band edge of undoped CdS (Ray et al., 1981). From both the absorbance spectrum and film thickness  $x$  obtained by gravimetry approximation, we calculate the square of the absorption coefficient  $\alpha^2$ .

Figure 2 shows the graph of  $\alpha^2$  against  $E_g$ . The intercept on the energy axis gives the value of 2.35eV which is the band-gap energy. This value of band edge is consistent with other values obtained for films prepared by other methods (Bube 1995, Mahdjoubi 1982, Okiti et al. 1982, and Ajayi et al. 1994).

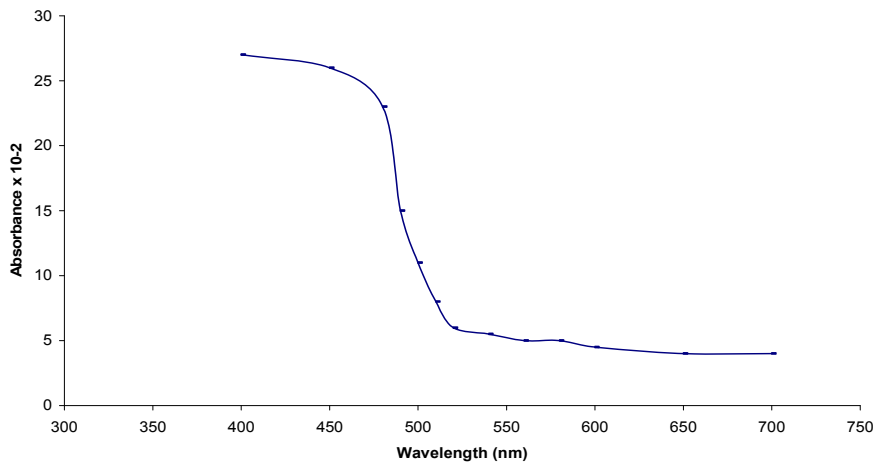


Figure 1: UV/Visible Spectrum of Absorbance (Optical Density) Obtained for CdS Thin Film.

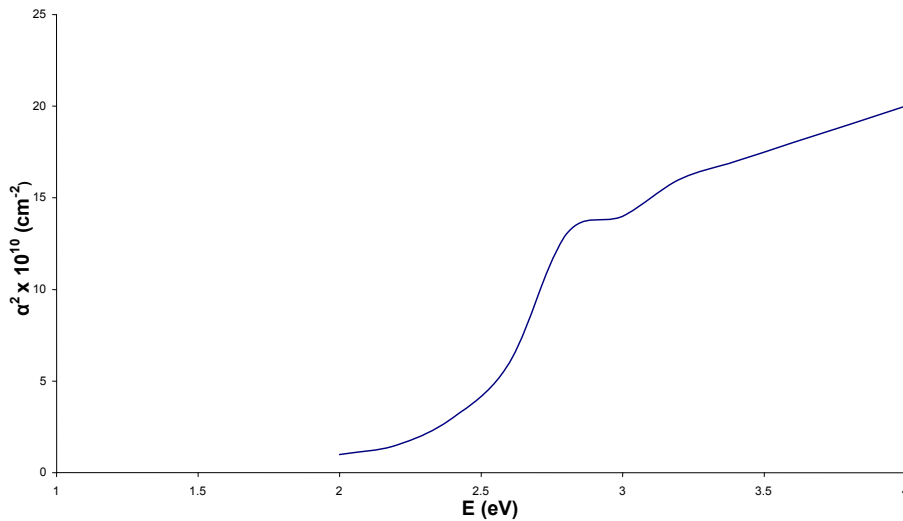


Figure 2:  $\alpha^2$  Vs Energy for the CdS Thin Film

## PHOTO-CURRENT RESPONSE

The photo current response i.e. the dark current  $I_d$  the photocurrent  $I_{ph}$  as well as the spectral response of the photocurrent in metal chalcogenide thin films such as PbS (Nair et al. 1987) are known to be drastically dependent on the deposition conditions and post deposition processing of the films. In the case of PbS thin films as prepared films are known to be only feebly photoconductive and air annealing is an essential step in the preparation of photosensitive PbS thin films, (Fajinmi et al., 2001).

Figure 3 shows the effect of air annealing on the photocurrent response of CdS films. The dark

current of the as prepared sample  $E_1$  is 18mA and it increased to 38mA after 1hr annealing at  $160^{\circ}\text{C}$ . The effect of air annealing is also shown in Figure 4 where the dark current for as prepared in bath ratio 1:2 is 20mA and increased to 40mA after annealing.

It is seen that the increase in dark to photo current in bath ratios of 1:2 (Figure 4) is greater than that for bath ratios of 1:1 (Figure 3). This observation may be attributed to the presence of excess sulfur atoms in 1:2 bath resulting in a thicker film. The enhancement of trapping mechanism during annealing is believed to be responsible for the lower photocurrent decay in the annealed samples.

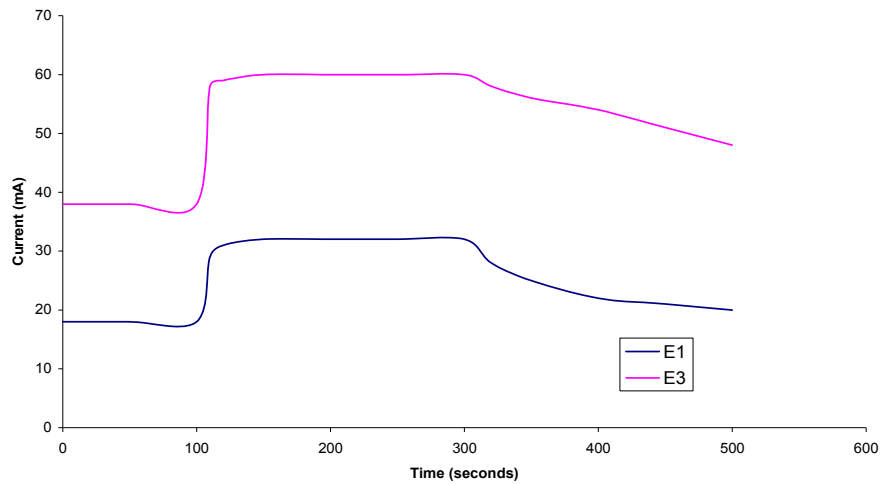


Figure 3: Photocurrent 1:1

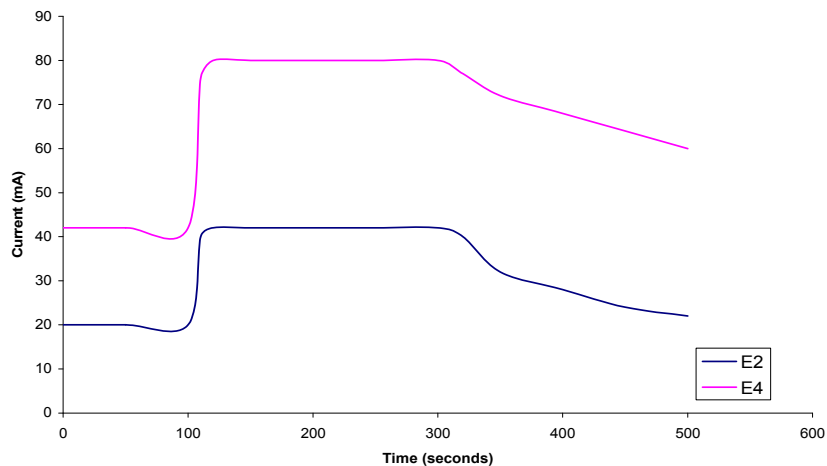


Figure 4: Photocurrent 1:2

The mechanism underlying the variation of photo and dark conductivities upon annealing may involve process like amorphous to crystallinity including modification of inter-grain boundaries. It is observed that the photo to dark current ratio is high compared to that of PbS (Fajinmi et al., 2001) and Bi<sub>2</sub>S<sub>3</sub> (Nair et al., 1990). This may be attributed to the presence of chemisorbed oxygen at the inter-grain boundaries which results in the increase in inter-grain barrier height and lowers the dark current but enables the films to exhibit up to a 100-fold increase in electron mobility under illumination due to inter-grain barrier lowering and hence a higher photosensitivity (Micheleti et al., 1967 and Orton et al., 1980).

## CONCLUSION

We have been able to demonstrate the ease and simplicity of depositing a good quality Cadmium Sulphide thin film from chemical baths. The films are found to be photoconductive. It was also shown that post deposition annealing can have a remarkable effect on the optoelectronic properties of these films.

For example air annealing, a film of bath ratio 1.2 at 160°C for 1hr changes the dark conductivity from 20mA to 43mA (Figure 4). There is the possibility of modifying the film properties by depositing at different bath ratios and annealing temperatures. We hope that this work may stimulate further work on these possibilities.

**Table 1:** Sample Specification to Study the Photocurrent Response.

Sample Label	Heat Process	Bath Ratio
E <sub>1</sub>	As prepared	1:1
E <sub>2</sub>	As prepared	1:2
E <sub>3</sub>	Annealed at 160°C for 1hr	1:1
E <sub>4</sub>	Annealed at 160°C for 1hr	1:2

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