PREPARATION AND CHARACTERIZATION OF MERCURY CADMIUM SULPHIDE THIN FILMS

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The precursor bis-(morpholinodithioato-s,s')-Cd-Hg was prepared and the thin films of mercury cadmium sulphide were deposited on sodalime glass substrate by Metallorganic Chemical Vapour Deposition (MOCVD) technique. The surface morphology was obtained using Stereoscan 430i LEICA Scanning Electron Microscope. The elemental analysis was carried out using Energy Disperse X-ray (EDX). The ratio of the elements in the prepared films obtained from the EDX was found to be Hg:Cd:S = 17.55:38.12:44.32, giving a stoichiometry of $Hg_xCd_{(1-x)}S_{(1-\delta)}$, $\delta = 0.20$. . A direct band gap of 2.36 eV was obtained from the analysis of the absorption spectrum. Electrical characterization was carried out both in the dark and normal room illumination. The dark and room illumination conductivities were found to be of the same order (10^{-6} $\Omega^{-1}cm^{-1}$) and the activation energy for both conditions are 0.12 eV and 0.19 eV respectively. The conductivity type was found to be p-type using the hot probe method.

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1. Introduction

CdS and various II-VI semiconductor compounds have been studied in various forms including thin films. The interest in this class of materials is because of their emission which covers the technologically attractive blue and green spectra regions [1]. In particular, more attention is focused on CdS thin films because their expected gap emission lies close to the highest sensitivity of the human eye. CdS thin films are versatile materials which are useful in electronic devices like field effect transistor, optical windows for solar cells [2], photovoltaic technology and optoelectronic devices such as thin film optical integrated circuits [3]. The use of CdS thin film as heterojunction window layer in the fabrication of semiconductor solar cells has also been reported [4]. Lately, the thin film of CdS solar cell has been considered to be promising alternative to more widely used silicon devices [5]. While CdS thin film is versatile, the appearance of pin holes in the structure, the degeneration of the material and the lattice mismatch are its major disadvantages [6].

HgS thin films have not been widely studied in the past because of the difficulties involved in their preparation [7]. However, the compound is now gaining more attention. Patil et al. [8], in their work deposited HgS thin films that exhibited cubic phase with optical band gap of 2.0 eV with n-type conductivity. β-HgS thin films have been found to be photoactive with p-type electrical conductivity [9] and show a blue shift in the band gap with a band gap of 0.54 eV [10].

A search for alternate window materials is in two folds, one is the search for a completely new material and the other is the addition of different elements to already known materials such as CdS, CdTe, ZnS, etc. This addition leads to the formation of miscible system such as $Zn_xCd_{1-x}S$,

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ZnCdInS, $Pb_{1-x}Cd_xS$ and $Cd_{1-x}M_xS$ (M = Sr, Ca, Mg, Pb, Sn) which have been reported by various authors [11-13]. One way of remedying the pinhole defect in CdS thin films is to use a thicker layer of comparable material [6]. This approach has made the tenary II-VI compounds potential materials for practical applications. The miscible systems, apart from reducing the degradation and improving other properties of CdS thin films also obey the Vegard's rule [14]. This process allows the band gap tailoring between the two end materials such as CdS and ZnS in $Zn_{1-x}Cd_xS$, CdS, ZnS and InS in ZnCdInS.

The properties of thin film materials depend on the method of preparation among other parameters such as the substrate, impurity level and post-deposition processing [15, 16]. Thin films of miscible systems have been prepared using techniques such as vacuum co-evaporation, electrodeposition, and Metal Organic Chemical Vapour Deposition (MOCVD) technique. Most of these techniques have their different deficiencies ranging from non-uniformity of films to lack of reproducibility in composition of films. This is due to the fact that two or more precursor sources of different aerosol properties are used. The use of a single solid source precursor was found to be more efficient in the preparation of clean and uniform films. The number of parameters determining the stoichiometric ratio of the elements in the film will also be reduced.

The Metallorganic Chemical Vapour Deposition (MOCVD) technique earlier reported by Ajayi [17] was used for the deposition of the mercury cadmium sulphide thin films. The films were obtained from the pyrolysis of a single solid source precursor, bis-(morpholinodithioato-s,s')-Cd-Hg. Morphological studies and elemental analysis of the thin films were performed using Scanning Electron Microscope (SEM) with spatial resolution and Energy Dispersive X-ray (EDX) facility attached to it. Optical and electrical properties of the mercury cadmium sulphide thin films were also investigated.

2. Experimental

2.1 Precursor Preparation

The single solid source precursor, bis-(morpholinodithioato-s,s')-Cd-Hg was prepared by the method which has been reported elsewhere [18]. The intermediate complex, ammonium morpholino-dithiocarbamate was prepared according to the method reported by Ajayi, et al. [18]

Ammonium morpholino-dithiocarbamate (4 g, 0.022 mol) was dissolved in 80:20 (v/v) of acetone-water solvent. Cadmium acetate (1.33 g, 0.0055 mol) was dissolved in 80:20 (v/v) of acetone-water solvent. The suspension of cadmium acetate in acetone-water solvent was gradually added to the suspension of ammonium morpholinodithiocarbamate and vigorously stirred. A suspension of mercury chloride (0.0055 mol) in the same solvent was then gradually added to the complex formed between cadmium acetate and ammonium morpholinodithiocabamate while still stirring vigorously. The product was vacuum-filtered and washed with acetone-water solvent and then vacuum dried.

2.2 Thin Film Deposition

The thin films of mercury cadmium sulphide were prepared by pyrolysing the precursor on sodalime glass substrate using a technique which has been reported earlier [17]. The set up for the deposition is shown in Fig. 1.

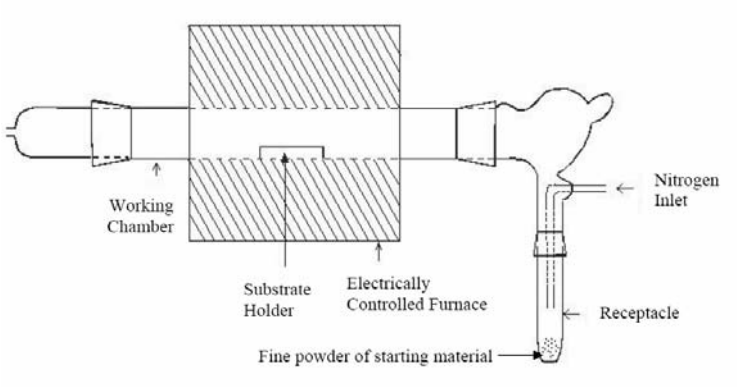

Fig. 1. Apparatus for pyrolysis of the precursor.

The fine powder of the precursor bis-(morpholinodithioato-s,s')-Cd-Hg was poured in an unheated receptacle and nitrogen gas, passed through calcium chloride pellets (drying agent) was blown at the rate of 2.5 dm^3/min. The nitrogen borne precursor was transported into the hot chamber maintained at 420 ^oC by an electrically heated furnace. Inside the working chamber, the substrates were supported on stainless steel blocks for good and uniform thermal contact. The deposition was carried out in a fume hood, thus minimizing some of the handling problems associated with mercury and sulphur.

2.3 Surface Morphology and Chemical Characterization.

The surface morphology and elemental analysis was carried out using Stereoscan 430i LEICA Scanning Electron Microscope with Energy Disperse X-ray (EDX) facility attached to it. The Scanning Electron Microscope (Stereoscan 430i LEICA) with Energy Disperse X-ray (EDX) facility attached to it has the following operating properties; Cathode voltage 25 kV, 15 kV and beam aperture 25 mm, 18 mm. The sample was coated with gold for both SEM and EDX analysis to avoid charging effect and enhance the SEM imaging.

2.4 Optical Characterization

Optical measurements constitute the most direct and perhaps the simplest approach for probing the band structure of the deposited films. Absorbance spectra of the thin films were measured as a function of incident photon wavelength at normal incidence and at room temperature using a double beam Pye Unicam SP8-400 Spectrophotometer. A blank substrate was used as the reference beam for all measurements.

2.5 Electrical Characterization

Conductivity measurements in the dark and under normal room illumination as a function of temperature (300-427 K) were carried out on the mercury cadmium sulphide thin films using the van der Pauw four point probe technique [19]. The thin film samples used for the conductivity measurements were of dimension 20 mm x 15 mm x 50 nm (estimated from a colour chart [20]). Four ohmic contacts of silver paint were made on each sample. Two of the terminals carried the current while the voltage was applied to the ends of the other two. A switching device was used to take the measurement of current and voltage in two modes. For the dark conductivity measurements, the sample was covered for three days with a metal shield and black polyethene material to eliminate all background photocurrents. For the normal room illumination conductivity measurements, the sample was uncovered and measurements were taken as in the case of the dark condition. The conductivity type was determined using the hot probe method.

3. Results and Discussion

3.1 Quality of Thin Films

There was no deposition of the film at 200 ^{o}C. At 300 ^{o}C, very thin layers were obtained but these showed poor adherence property. The adherence property of the films prepared at 350 ^{o}C was better but still very thin. However, films of good uniformity and adherence were obtained at the deposition temperature of 420 ^{o}C, which is in agreement with our earlier observation which have been reported elsewhere [18]. This shows that good quality films of mercury cadmium sulphide cannot be deposited at temperature lower than 420 ^{o}C using our facility. The films showed good adhesive ability when subjected to scotch tape test.

3.2 Surface Morphology and Chemical Characterization.

The micrographs of the film are shown in Figure 2 (a) and (b). The film appears to be dense, homogeneous and of compact structure with closely packed grains which covered the substrate well. The dimension of the grain is less than 1μm and this confirms the nanocrystalline nature of the film indicating the effectiveness of this technique on particle size distribution. Upon closer inspection at high magnification, the presence of micro crack was revealed. This is probably due to the growth of internal stress during the deposition process as was reported by Giouroudi et al. [21].

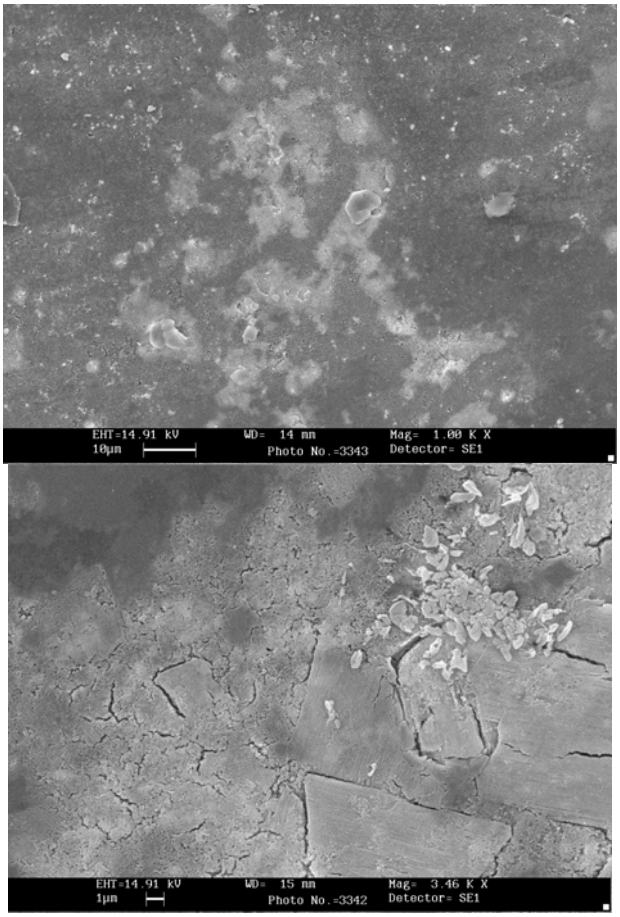

Fig. 2. Scanning Electron Micrograph of the thin film a)Magnification at 1 K X; b) Magnification at 3.46 K X

The elemental analysis of the thin film was done by EDX. Fig. 3 shows the EDX spectrum. The spectrum shows the signals of Hg, Cd, S, Na, C, O and Si. Na, Si and O are elements in the glass substrate. The ratio of the elements in the prepared films obtained from the EDX was found to be Hg:Cd:S = 17.55:38.12:44.32, giving a stoichiometry of $Hg_xCd_{(1-x)}S_{(1-\delta)}$, δ = 0.20.

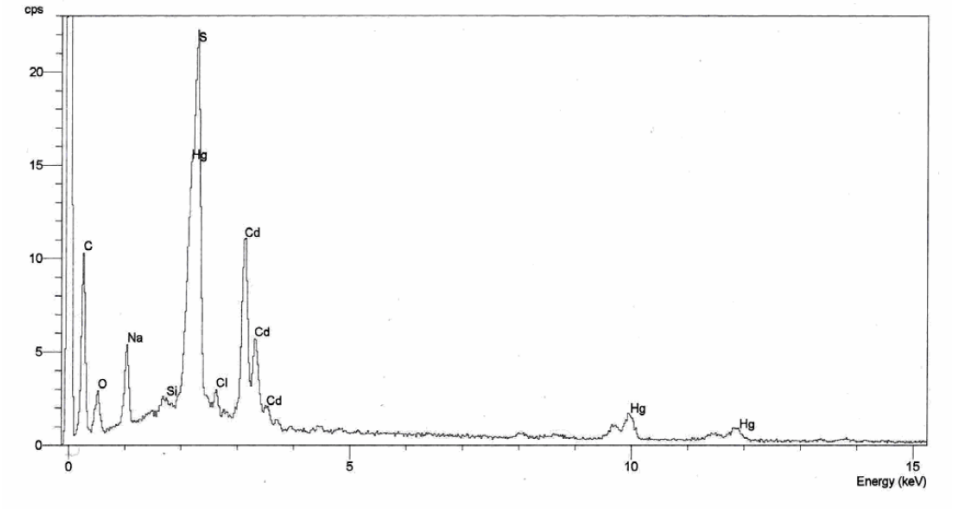

Fig. 3. EDX spectrum of the thin film

3.3 Optical Characterization

Figure 4 shows the absorbance-wavelength spectrum of the mercury cadmium sulphide films. From the absorbance and the thickness of the film, the absorption coefficient, α was calculated as a function of wavelength (and energy) using the relation

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

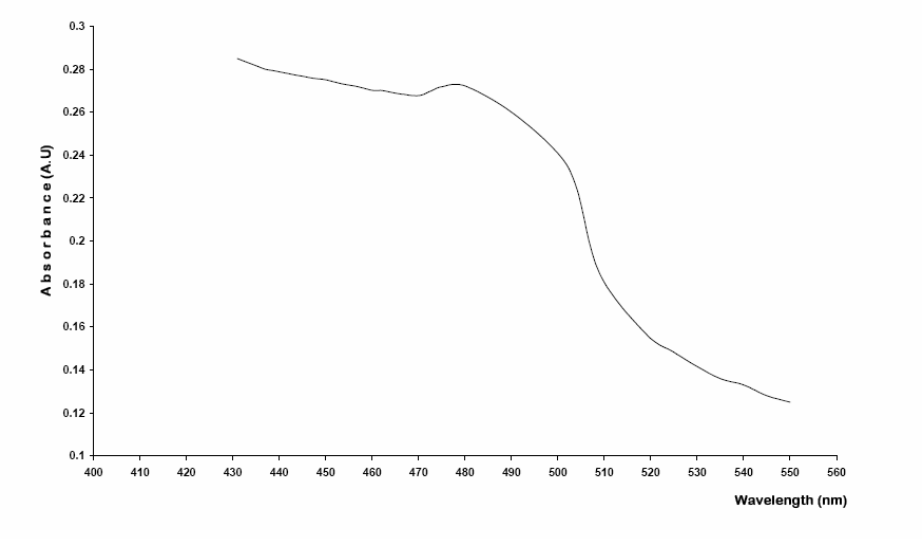

Fig. 4. Absorbance (arbitrary units) versus wavelength (nm) for the thin film

A plot of the square of the absorption coefficient, α^2 against energy (Fig. 5) for the direct allowed transition shows a linear portion around the edge of the material. An extrapolation of the

linear portion to the energy axis gave a band gap of 2.36 eV for the mercury cadmium sulphide thin films. An analogous system, mercury cadmium selenide was reported to have a band gap of 1.34 eV, which also falls between those of CdSe and HgSe [22].

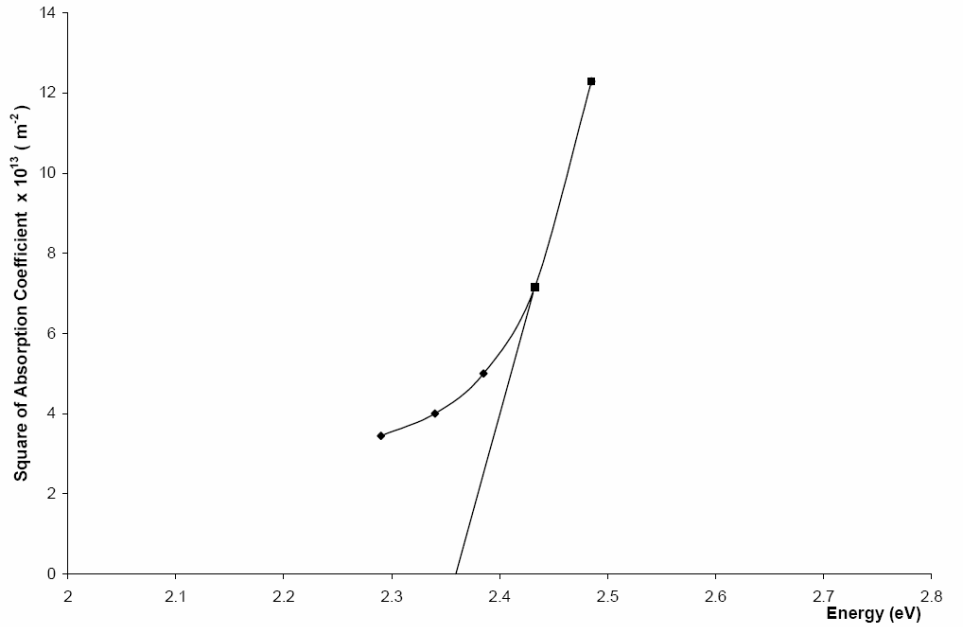

Fig. 5. Square of Absorption Coefficient versus energy for the thin film

The band gap of 2.36 eV obtained for the mercury cadmium sulphide falls between that of CdS thin film (2.4 eV) earlier reported by our group [18], and the band gap of α-Hg (2.1 eV) reported by Leyris et al. [7]. Although there is no data on the band gap variation with composition for mercury cadmium sulphide system the value obtained shows that it obeys the Vegard's rule of mixtures. This work is in agreement with our earlier scheme of alloying two or more II-VI compounds to prepare materials of particular band gap value for specific applications.

3.4 Electrical Characterization

The electrical characterization of the mercury cadmium sulphide thin films using hot probe method shows that the films are p-type semiconducting materials. The plots (Figures 6 and 7) illustrate the variation of the dark conductivity and the normal illumination conductivity as a function of reciprocal of temperature. The dark conductivity and the normal room illumination conductivity of mercury cadmium sulphide films are of the same order of magnitude (10^{-6} $\Omega^{-1}cm^{-1}$) and is higher than that of the pure α-HgS (10^{-10} $\Omega^{-1}cm^{-1}$) [7]. The values obtained in this work are lower than those reported by Bhuse and Hankare [22] for CdHgSe (10^{-2} $(\Omega m)^{-1}$), HgSe (10^{3} $(\Omega m)^{-1}$) and CdSe (10^{-6} $(\Omega m)^{-1}$) at room temperature. The activation energy in each case, was calculated from the expression

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{KT}\right) \tag{2}$$

where E_a is the activation energy. The values of 0.21 eV and 0.19 eV were obtained for the dark condition and the normal illumination respectively.

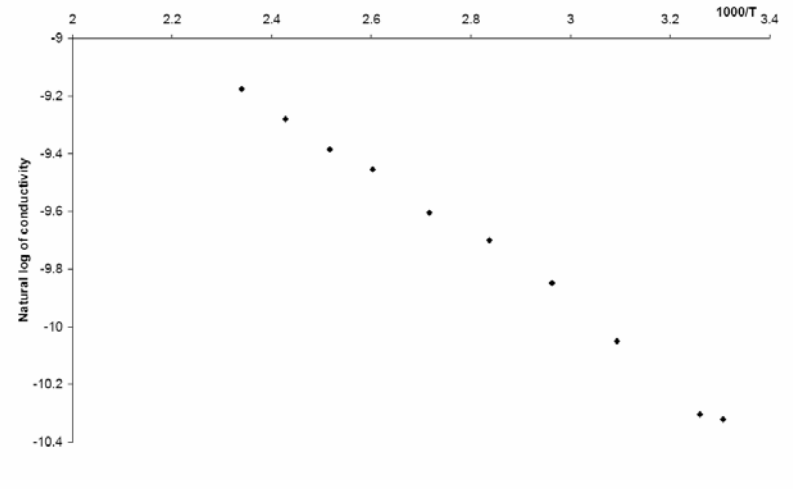

Fig. 6. Natural log of conductivity Inσ against $10^3/T$ (K^{-1}) for the thin film under normal room illumination condition

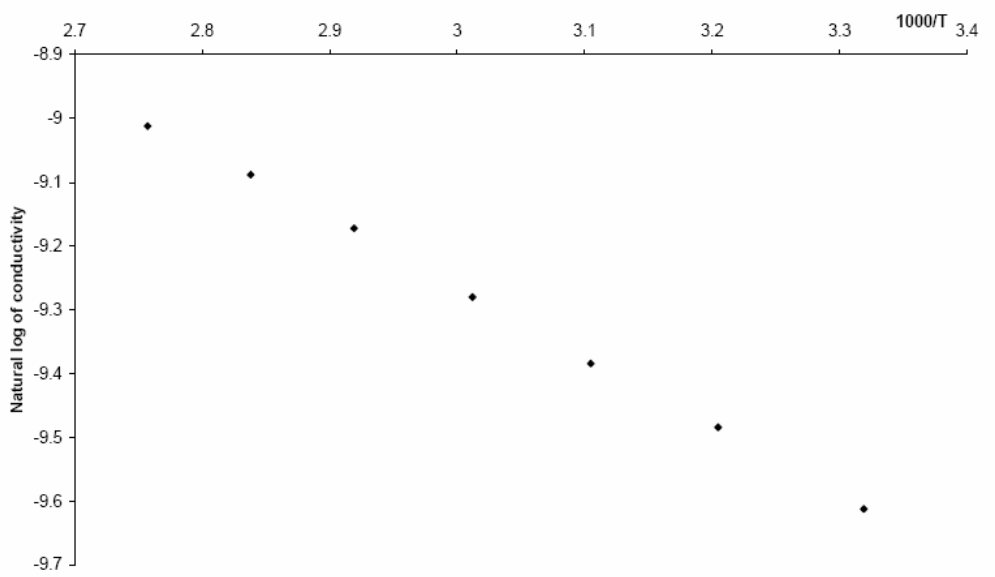

Fig. 7. Natural log of conductivity Inσ against $10^3/T$ (K^{-1}) for the thin film under dark condition

4. Conclusion

We have been able to prepare thin films of mercury cadmium sulphide through the pyrolysis of a single solid source precursor, bis-(morpholinodithioato-s,s')-Cd-Hg. The ratio of the elements in the prepared films obtained from the EDX was found to be Hg:Cd:S = 17.55:38.12:44.32, giving a stoichiometry of $Hg_xCd_{(1-x)}S_{(1-\delta)}$, $\delta = 0.20$. The optical band gap of the films was found to be 2.36 eV from the absorption spectrum. The dark and normal room illumination conductivities were found to be of the same order of magnitude (10^{-6} $\Omega^{-1}cm^{-1}$) and the activation energy for both conditions are 0.21 eV and 0.19 eV respectively.

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