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Determination of the Energy Band Gap and Absorption Coefficient of Thin Films of Chemically Deposited Lead Sulphide, Copper Sulphide and Multilayer Lead Sulphide-Copper Sulphide Thin Films

MERCY IYPE*, SHAJI VARGHESE† E.J. MATHEW†† and C.S.MENON†
Department of Chemistry, Marthoma College, Tiruvalla–689 103, India
e-mail: mercyiype@rediffmail.com and shajiv2001in@yahoo.com

Lead sulphide (PbS) and copper sulphide (CuS) thin films are deposited on glass substrates by chemical bath deposition technique(CBD). Multilayer PbS-CuS thin films are also obtained by chemical bath deposition technique (CBD) by using CuS films as substrates for the deposition of PbS films. These films are annealed in air at different temperatures. Optical studies are separately done on PbS, CuS, and multi layer PbS-CuS films. Optical properties are studied (between 300 nm–900 nm) in a UV-Vis spectrophotometer and the absorbance recorded as a function of photon energy. The optical band gap and maximum absorption coefficient of the deposited and annealed samples are determined. Optical band gap and absorption coefficient decreases with annealing.

Key Words: Determination, Energy band gap, Absorption coefficient, Films, Lead sulphide, Copper sulphide, Multilayer.

INTRODUCTION

Chemical bath deposition is a technique in which thin semiconductor films are deposited on substrates immersed in dilute solutions containing metal ions and a source of hydroxide, sulphide or selenide ions.[1–8] The earliest reported work dates back to 1910 and dealt with the deposition of PbS thin films[9]. The number of possible materials to be produced through this technique is bound to multiply in subsequent years. This is due to the feasibility of producing multilayer films by this technique- the annealing of which promotes interfacial diffusion of metal ions and the production of new materials with improved thermal stabilities.[10,11]

Copper sulphide and lead sulphide are materials being tested in thin film devices and photovoltaic cells. CuS has a direct band gap and can be used as window material in photovoltaic solar cells. Direct energy gap materials result in large optical absorption which in turn permits the use of thin layers of active material. The semiconducting nature of CuS and PbS films are found to be

†School of Pure and Applied Physics, M.G. University, Kottayam, Kerala, India.
††Dept. of Chemistry, S.B. College, Changanacherry, Kerala, India.

p-type.[12] The interfacial diffusions in chemically deposited PbS-CuS coatings result in materials such as $Pb_X Cu_Y S_Z$ with p-type conductivities and are stable upto a temperature of 573K[13]. In this paper we report the feasibility of PbS-CuS junction based on CuS films grown on glass substrates by CBD technique which is used as the substrate for depositing PbS over it by CBD technique. The optical band gap, absorption coefficient and the effect of annealing on PbS, CuS and multilayer PbS-CuS thin films are studied.

EXPERIMENTAL

Preparation of CuS thin films: Chemical bath deposition is a technique for controlling the homogeneous precipitation of water insoluble compounds and their solid solution[14,15]. In this paper we describe the chemical deposition of CuS thin films on pyrex glass substrates by the decomposition of thiourea in an alkaline solution containing a copper salt[16,17]. The chemical process consists of the slow release of Cu^{2+} and S^{2-} ions in solution which subsequently condenses on an ion-ion basis on to the glass substrate. In the, triethanolamine complex method,[18] the film formation is based on the reaction,

$$[Cu(TEA)]^{2+} + SC(NH_2)_2 + 2OH^- \rightarrow CuS + TEA + OC(NH_2)_2 + H_2O$$

The deposition of CuS occurs when the ionic product of $[Cu^{2+}]$ and $[S^{2-}]$ exceeds the solubility product of CuS.

Stock solutions of 0.5 M $CuCl_2 \cdot 3H_2O$ and 0.5 M thiourea are prepared in tridistilled water [19.20]. Different bath constitutions can be employed by varying the volumes of cupric chloride solution and thiourea solution. Here 100 mL volume of deposition mixture is prepared by the sequential addition of the following; 15 mL of 0.5 M cupric chloride solution; 5 mL of triethanolamine; about 10 mL of 30% ammonium hydroxide solution; 10 mL of 1 M NaOH; 15 mL of thiourea solution; and the rest deionised water to make the volume 100 mL. Pyrex glass slides (4 cm × 1 cm) are used as substrates. The glass slides are washed with detergent solution, then with chromic acid and finally rinsed with deionised water prior to the deposition of the films. The cleaned glass slides are kept vertically on the walls of the container with the deposition mixture. The CuS films are chemically deposited at room temperature for 12 h. After the deposition, the films are dried in air.

Preparation of PbS thin films by CBD technique: A 100 mL deposition bath is prepared by the sequential addition of the following. 5 mL of 1 M Pb $(CH_3COO)_2 \cdot 3H_2O$; 20 mL of 1 M NaOH, 5 mL of 1M thiourea, 5 mL of 1 M triethanolamine and the rest deionised water. Cleaned glass slides are kept vertically on the walls of the container with the deposition mixture. Depositions are done at room temperature for 12 h. The films are dried in air.

Preparation of multilayer PbS-CuS thin films: CuS films are deposited onto glass subtrates by CBD technique. These films are used as substrates for the deposition of multi layer PbS-CuS films. CuS films are kept vertically on the walls of the container with the deposition mixture for PbS. Depositions are done at room temperature for 12 h. The multilayer PbS-CuS films are dried in air.

Measurements

The films are annealed in air for different temperatures. Thickness of the films are accurately determined by Tolanskys multiple beam interference technique[21]. UV-Visible absorption spectra are obtained from a Schimadzu 240 UV-Vis spectrophotometer. The absorption edge is analysed to obtain the optical band gap of PbS, CuS and multi layer PbS-CuS thin films.

RESULTS AND DISCUSSION

Optical studies are done to determine the band gap, maximum absorption coefficient and the effect of annealing on band gap. The optical absorption spectrum in the range 300–900 nm is recorded using the Shimadzu UV-Visible spectrophotometer. Figs. 1–3 represents absorption spectra of as deposited and annealed (523 K and 573 K) samples of PbS, CuS and multi layer PbS-CuS thin films respectively. To obtain information about the absorption, the fundamental absorption edge is analysed within the one electron theory of Bardeen.22

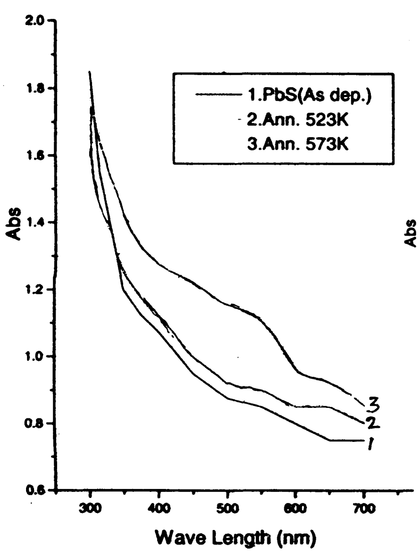

Fig. 1. Absorption spectra of as deposited and annealed PbS thin films.

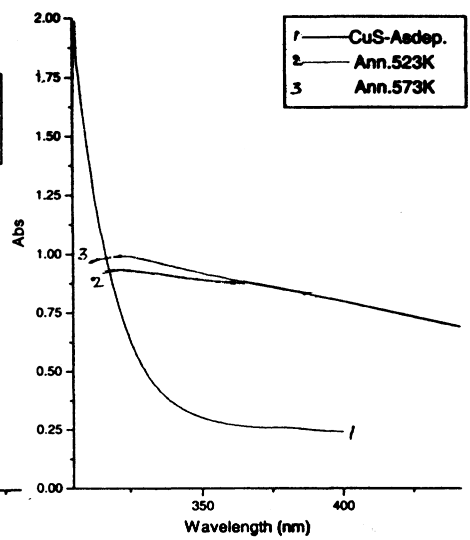

Fig. 2. Absorption spectra of as deposited and annealed CuS thin films.

The absorption coefficient α^2 is calculated and it is related to the band gap Eg and photon energy hv according to the relation, $\alpha = \alpha_0 (hv-Eg)^n$ where n = 1/2, for direct allowed transition. Graph of α_2 *vs* hv is plotted and is shown in Figs. 4–6 for as deposited and annealed PbS, CuS and multi layer PbS-CuS films respectively. The absorption coefficient α is calculated using the relation, $\alpha = 2.303$ A/t , A is the absorbance of the film, t is its thickness. Extrapolation of this plot to $\alpha^2 = 0$ gives the optical band gap. The optical band gap and maximum

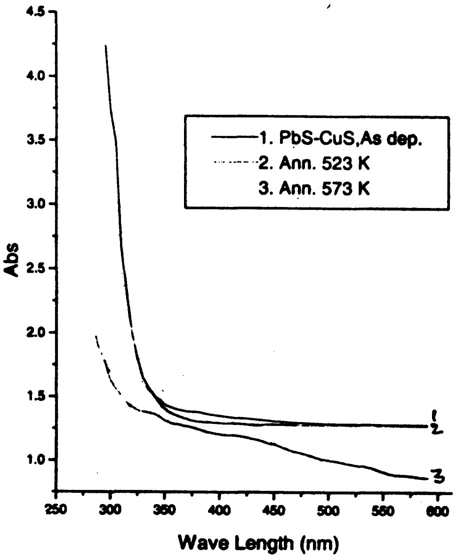

Fig. 3. Absorption spectra of as deposited and annealed multi layer PbS–CuS thin films.

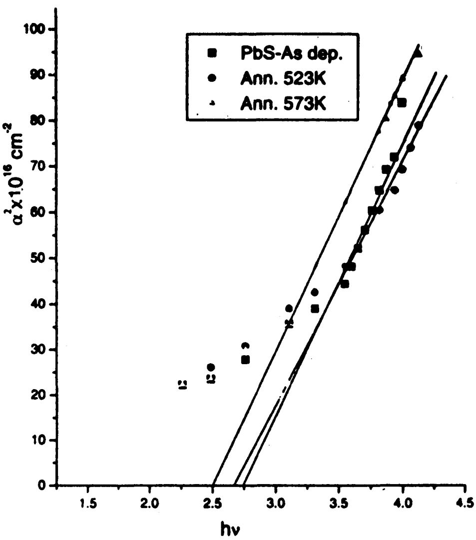

Fig. 4. Graph of α^2 *vs.* hν for as deposited and annealed PbS thin films.

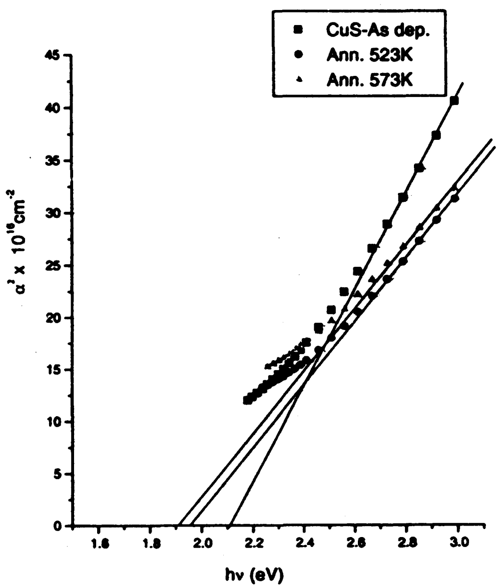

Fig. 5 Graph of α^2 *vs.* hν for as deposited and annealed CuS thin films.

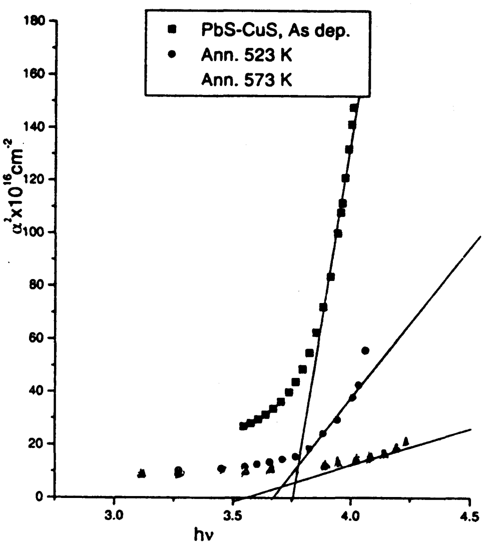

Fig. 6 Graph of α^2 *vs.* hν for as deposited and annealed multi layer PbS–CuS thin films.

absorption coefficient of as deposited and annealed PbS, CuS and multilayer PbS-CuS thin films are given in Tables 1–3 respectively.

TABLE-1
OPTICAL BAND GAP ENERGY AND ABSORPTION COEFFICIENT OF As DEPOSITED AND ANNEALED (A T 523 K AND 573 K) PbS THIN FILMS OF THICKNESS 4150 Å.

Sample	Optical band gap (ev)	Absorption coefficient × 10^8 cm^{-1}
1. PbS (As deposited)	2.75	1.10266
2. PbS (Annealed 523 K)	2.65	0.09980
3. PbS (Annealed 573K)	2.50	0.09711

TABLE-2
OPTICAL BAND GAP ENERGY AND ABSORPTION COEFFICIENT OF As DEPOSITED AND ANNEALED AT (523 K AND 573 K) CuS THIN FILMS OF THICKNESS 3120 Å.

Sample	Optical band gap (eV)	Absorption coefficient × 10^8 cm^{-1}
1. CuS (As deposited)	2.10	27.3070
2. CuS (Annealed 523K)	1.95	7.3385
3. CuS (Annealed 573K)	1.90	6.9252

TABLE-3
OPTICAL BAND GAP ENERGY AND ABSORPTION COEFFICIENT OF AS DEPOSITED AND ANNEALED (AT 523 K AND 573 K) MULTILAYER PbS–CuS THIN FILMS OF THICKNESS 9350 Å.

Sample	Optical band gap (eV)	Absorption coefficient $\times 10^8$ cm^{-1}
1. Multilayer PbS–CuS (As deposited	3.750	0.10453
2. Multilayer PbS–CuS (Annealed 523K)	3.625	0.07467
3. Multilayer PbS–CuS (Annealed 573K)	3.500	0.04002

The band gap energy is found to decrease with annealing. The estimated accuracy in the measurement of the energy gap is + or –0.02ev. Even though the material is considered to be pure, some trace elements like Cu, N, H, Ag in the form of impurities may be present in the film. These impurities can form traps in the forbidden energy gap. The energy band gap measurements provide a measure of the trapping levels. It has been reported that the removal of oxygen causes a redistribution of traps and hence a drop in band gap energy[23]. Sussman[24] has reported that the distribution of trapping sites is altered by annealing. In 1996 Shirai *et al.*[25] reported that the as deposited films usually have poor crystallinity and thermal annealing is needed to improve the quality. Therefore the annealing process is of critical importance in the solar cell fabrication.[26]

Conclusion

Lead sulphide (PbS) and copper sulphide (CuS) thin films are deposited on glass substrates by chemical bath deposition technique (CBD). Multi layer PbS-CuS thin films are also obtained by chemical bath deposition technique (CBD) by using CuS films as subtrates for the deposition of PbS films..These films are annealed in air at different temperatures. Optical studies are separately done on PbS, CuS and multilayer PbS-CuS films. Optical properties are studied (between 300–900 nm) in a UV-VIS-spectrophotometer and the absorbance recorded as a function of photon energy. The optical band gap and maximum absorption coefficient of the as deposited and annealed samples are determined. Optical band gap and absorption coefficient decreases with annealing. This may be due to the reduction in trap sites. The difference in band gap due to annealing could be due to the removal of the trapping levels in the forbidden band region during annealing. The major advantages of multilayer films are their potential low cost, easiness of fabrication, adaptability to flexible substrates and feasibility of large areas.

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