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Temperature Depedence of the Activation Energy of Thin Films of Zinc Sulphide, Copper Phthalocyanine and Multi-layer Zinc Sulphide-Copper Phthalocyanine

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Zinc sulphide (ZnS) thin films are prepared onto glass substrates by chemical bath deposition (CBD) technique. Thin films of copper phthalocyanine (CuPc) are also sublimed onto glass substrates in high vacuum at room temperature. Multi-layer ZnS-CuPc thin films are obtained from ZnS films grown on glass substrates by CBD technique and subsequently vacuum subliming CuPc onto them. These films are annealed in air at different temperatures. Electrical conductivity studies are made separately on ZnS, CuPc and multi-layer ZnS-CuPc thin films. Thermal activation energy of the as deposited and annealed samples are determined from the Arrhenius plot. It is found that the activation energy decreases with annealing temperature. This may be due to the reduction in trap sites during annealing.

Key Words: Temperature, Dependence, Activation energy, Thin-films, Zinc sulphide, Copper phthalocyanine.

INTRODUCTION

In the search for low-cost solar energy materials, organic-inorganic photovoltaic junctions in thin-film configuration deserves great attention. The first observations in this field have been made on inorganic semiconducting crystals by Horowitz and Garnier[1] who have investigated the GaAs-PT (PT = polythiophene) n-p hetero junction, followed by Frank *et al.*[2], who studied the CdS-PMeT (PMeT = poly-(3-methylthiophene)) Schottky junction. In both the cases the polymer was electrochemically grown on single crystals of the inorganic semi-conductors. Later, investigations were done on thin films CdS-PMeT solid state junctions[3–7]. Chartier *et al.*, studied the hybrid organic-inorganic photovoltaic junction of CdSe-poly (3-methylthiophene) thin films. ZnS 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 ZnS films is found to be *p*-type.[9]

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Phthalocyanines are one of the most widely investigated group of materials due to their potential applications as organic dyes, organic photoconductors and gas sensors[10–12]. These organic semiconductors exhibit high chemical and thermal stability. Semiconducting behaviour of all phthalocyanine films is found to be *p*-type at all temperatures[13].

Chemical bath deposition (CBD) is a convenient and low cost technique for producing large area thin film semiconducting materials[14–21]. In this paper we report the feasibility of multilayer ZnS-CuPc junctions based on ZnS films grown on glass substrates which is used as the substrate for depositing CuPc by thermal evaporation. The electrical conductivity, thermal activation energy and the effect of annealing on ZnS, CuPc and multi-layer ZnS-CuPc thin films are studied.

EXPERIMENTAL

Preparation of ZnS thin films

Chemical bath deposition is a technique for controlling the homogeneous precipitation of water-insoluble compounds and their solid solution[22, 23]. In this paper we describe the chemical deposition of ZnS thin films on pyrex glass substrates by the decomposition of thioacetamide in an alkaline solution containing a zinc salt[24, 25]. The chemical process consists of the slow release of Zn^{2+} and S^{2-} ions in solution which subsequently condenses on an ion-ion basis onto the glass substrate.[26]

Stock solutions of 1 M zinc sulfate and 1 M thioacetamide are prepared in tridistilled water[27, 28]. A 100 mL deposition bath is prepared by the sequential addition of the following. 15 mL of 1 M zinc sulfate, 4.4 mL of NH_3/NH_4Cl (Ph 10), 5.4 mL of 50% triethanolamine, 15 mL of 1 M thioacetamide and the rest deionized water to make up to 100 mL by volume. 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. Cleaned glass slides are kept vertically on the walls of the container with the deposition mixture. Depositions are done at room temperature for 24 h. The films are dried in air.

Preparation of CuPc and multi-layer ZnS-CuPc thin films

The copper phthalocyanine (CuPc) powder used in this study is obtained from Aldrich Chemical Company Inc., USA (97.99% pure). Thin films of CuPc are deposited at room temperature onto glass substrates and ZnS coated glass substrates at a base pressure of 10^{-5} torr using a Hind Hivac vacuum coating unit. The evaporation is carried out by resistive heating of the CuPc powder from a molybdenum boat and the rate of sublimation is kept constant.[29].

Thickness of the films is accurately determined by Tolanskys multiple beam interference technique[30]. Electrical conductivity is measured using the standard two probe method with a programmable Keithley electrometer (Model No. 617) and a constant current source. Ohmic contacts are made by thin copper strands which are fixed by silver paste. The film is loaded on the hollow copper block of the conductivity cell. Conductivity measurements are performed in the temperature range 320–505 K under a vacuum of 10^{-3} torr to avoid any type of

contamination. Temperature is monitored using a Chromel-Alumel thermocouple attached to the substrate.

RESULTS AND DISCUSSION

Electrical studies are done to determine the thermal activation energy and the effect of annealing on activation energy. The studies are carried out in the temperature range 320–505 K in a vacuum of 10^{-3} torr to avoid contamination of the film. The resistance R is noted at regular intervals of 5 K.

The temperature dependence on resistance is expressed as

$$R = R_0 \exp(-E_a/KT)$$

where E_a is the thermal activation energy and K is the Boltzmann constant.

The activation energy is obtained using the relation $\sigma = \sigma_0 \exp(-\Delta E_a/KT)$ where σ is the carrier conductivity, ΔE_a is the activation energy, K is the Boltzmann constant and T is the temperature in absolute scale. The electrical conductivity as a function of inverse of temperature of as deposited and annealed ZnS films are given in Fig. 1. Fig. 2 represents similar plots of as deposited and

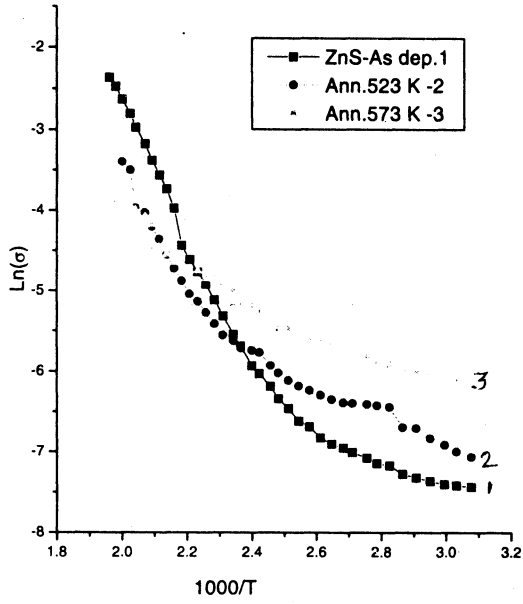

Fig. 1. Graph of electrical conductivity *vs.* inverse of temperature of as deposited and annealed ZnS thin films

annealed samples of CuPc films. Fig. 3 gives plots of as deposited and annealed samples of multi-layer ZnS-CuPc. From the slopes of these graphs, activation energies are determined. The activation energy of the samples varies with annealing temperature. Each graph has three linear regions which give E_1, E_2 and E_3. The activation energies in the intrinsic region (E_1) and impurity scattering regions (E_2 and E_3) are calculated. Tables 1–3 represent variation of activation

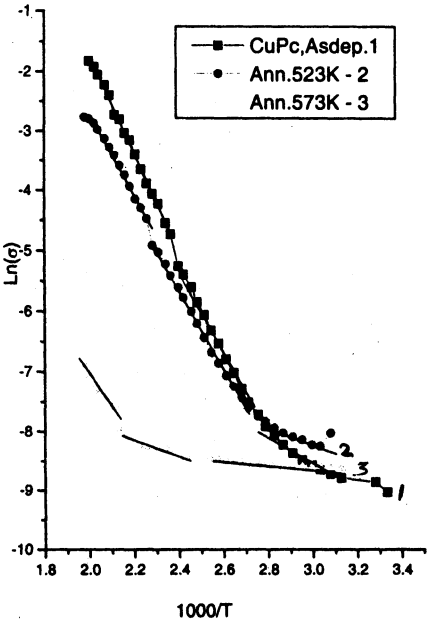

Fig. 2. Graph of electrical conductivity *vs.* inverse of temperature of as deposited and annealed CuPc thin films

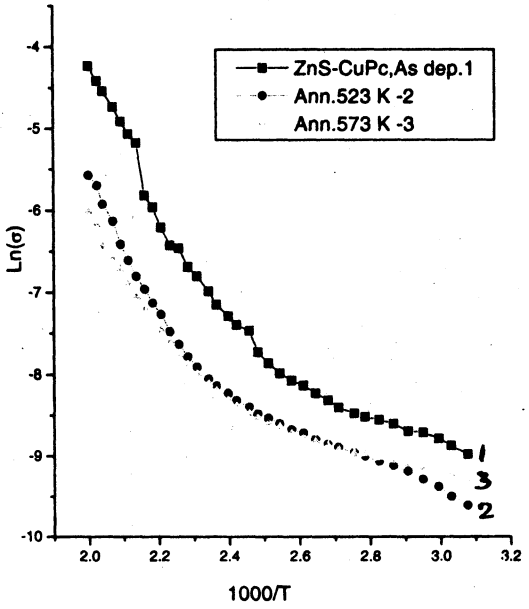

Fig. 3. Graph of electrical conductivity *vs.* inverse of temperature of as deposited and annealed multi-layer ZnS-CuPc thin films.

energies with annealing temperatures for ZnS, CuPc and multilayer ZnS-CuPc films respectively. The change in carrier activation energy is indicated by the change in the slope of the plot. Multiple donor and acceptor levels exist within

the forbidden energy gap and as temperature is lowered the deeper levels become progressively frozen out. The activation energy 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 thermal activation energy[31]. Sussman has reported that the distribution of trapping sites is altered by annealing[32,33].

TABLE-1
VARIATION OF ACTIVATION ENERGY WITH ANNEALING TEMPERATURE FOR ZnS FILMS OF THICKNESS 3215 Å

Samples	Activation energy (ev)		
	E_1	E_2	E_3
1. As deposited	0.6982	0.5612	0.1833
2. Annealed 523 K	0.5448	0.2137	0.1793
3. Annealed 573 K	0.2205	0.1921	0.1101

TABLE-2
VARIATION OF ACTIVATION ENERGY WITH ANNEALING TEMPERATURE FOR CuPc FILMS OF THICKNESS 2180 Å

Samples	Activation energy (ev)		
	E_1	E_2	E_3
1. As deposited	0.7065	0.6091	0.1851
2. Annealed 523 K	0.5859	0.5803	0.1725
3. Annealed 573 K	0.5003	0.2710	0.0551

TABLE-3
VARIATION OF ACTIVATION ENERGY WITH ANNEALING TEMPERATURE FOR MULTI LAYER ZnS-CuPc FILMS OF THICKNESS 6320 Å

Samples	Activation energy (ev)		
	E_1	E_2	E_3
1. As deposited	0.6299	0.5159	0.1872
2. Annealed 523 K	0.6254	0.1868	0.1799
3. Annealed 573 K	0.5778	0.1725	0.1027

Conclusion

Zinc Sulphide thin films are prepared on glass substrates by chemical bath deposition method. Thin films of copper phthalocyanine are sublimed onto glass substrates in high vacuum at room temperature. Multi-layer ZnS-CuPc thin films are obtained from ZnS films grown on glass substrates by CBD technique and subsequently vacuum subliming CuPc onto them. Electrical conductivity and thermal activation energy of the as deposited and annealed ZnS, CuPc and multi-layer ZnS-CuPc thin films have been studied. Electrical conductivity by thermal activation process is found to involve different conduction mechanisms. For CuPc in the high temperature range, intrinsic conductivity by holes is found to contribute to the conduction process whereas in the low temperature range

impurities are found to play an active role. Annealing causes a reduction in activation energy for all the films. This may be due to the reduction in trap sites because of annealing.

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