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Spray pyrolytic deposition of $CuBiS_2$ thin films

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Abstract. Thin films of $CuBiS_2$ have been deposited on glass substrates using spray pyrolysis technique. The effect of substrate temperature on the growth of $CuBiS_2$ thin films is studied in the range of 150 to 400°C. The best quality films are grown at substrate temperature 250°C with 0·1 M composition. Other preparative parameters like spray rate, pressure, height of the solution, etc are optimized with respect to substrate temperature. Some optical and electrical properties of $CuBiS_2$ films are also studied and reported.

Keywords. Spray pyrolysis technique; ternary chalcogenide films; spray rate.

1. Introduction

Ternary systems of the compound semiconductors are particularly interesting because of their technological applications in thin film devices and photovoltaic energy converters. Among the ternary semiconducting materials sulphur-containing compounds occupies an important place. These compounds can be prepared by employing various deposition methods, namely vacuum evaporation, chemical bath deposition, spray pyrolysis etc (Austin *et al* 1956; Rajebhosale and Pawar 1978; Pawar and Uplane 1983).

Spray pyrolysis technique has been successfully used in the deposition of a number of chalcogenide semiconductors (Feigelson *et al* 1977). However, no information is available on the preparation of $CuBiS_2$ thin films of the type I-III-VI_2 by spray pyrolysis technique. In the present study $CuBiS_2$ thin films were deposited on glass substrates to study the conditions for obtaining pure, uniform and adherent films of $CuBiS_2$. The effect of preparative parameters on optical and electrical properties of grown $CuBiS_2$ films has also been studied.

2. Experimental

Thin films of $CuBiS_2$ were deposited on ultrasonically cleaned glass substrates, employing spray pyrolysis technique (Chamberlin and Skarman 1966; Pawar *et al* 1985). The basic ingredients used were cuprous chloride (CuCl), bismuth trichloride ($BiCl_3$) and thiourea $[(NH_2)_2CS]$.

The starting solution was prepared by adding 100 c.c. of 0·1 M CuCl solution into 100 cc of 0·1 M $BiCl_3$ solution to maintain a Cu : Bi ratio of 1:1. Then 200 cc of 0·1 M thiourea solution was added to the solution to obtain a CuBi : S ratio of 1:2. This starting solution was sprayed through a specially designed glass nozzle. Air was used to atomize the spray. The substrate temperature was varied from 150°C to 400°C with an interval of 50°C. Fast cooling was used at the termination of spray, as slow cooling produces film with higher resistivity, possibly because of the reaction with oxygen in air over a longer time used in cooling (Feigelson *et al* 1977). The films were taken out and preserved for further study.

Films prepared at different substrate temperatures are described as S_{150}, S_{200}, S_{250}, S_{300}, S_{350} and S_{400}, the subscripts denoting the substrate temperature. The bandgap of the deposited material was determined by taking optical absorption using a monochromator (Carl Zeiss Jena). The resistivity was measured employing routine techniques. Thermovoltage of the films was recorded by using d.c. microvoltameter (P.P.9004) in the temperature range between 300 K and 450 K.

3. Results and discussion

The $CuBiS_2$ thin films were prepared by spray-pyrolysis technique. The aqueous complex solution was fed via an atomizer to hot substrates, where they decompose forming a heat-resistant compound of the copper, bismuth and sulphur. The reaction is as follows:

$$CuCl + BiCl_3 + 2\,S = C\begin{matrix} \diagup NH_2 \\ \diagdown NH_2 \end{matrix}\ (aqu) \xrightarrow{\Delta} CuBiS_2 + 4NH_3\uparrow + 2Co_2\uparrow + 2Cl_2\uparrow.$$

The decomposition of the complex compound depends on substrate temperature, spray rate, height of solution etc. It is observed that at lower temperature the films are powdery and porous in nature indicating that the decomposition of the complex compound is not complete. As substrate temperature increases, the decomposition rate increases. At higher substrate temperatures thin reflecting films are obtained which is ascribed to the evaporation rate of initial ingredients reducing the volumetric proportion of Cu, Bi and S in the film. The same effect is observed when the spray rate is high (10 cc/min) and the substrate temperature suddenly drops reducing the decomposition rate of the solution. When the spray rate is low the evaporation is high reducing the thickness of the thin film.

The $CuBiS_2$ thin films prepared by spray pyrolysis technique at different substrate temperatures are found to be uniform and adhere tightly to the substrate. However, the thickness of the films decreases with increase in the substrate temperature (Ugai *et al* 1978) which is attributed to the increase in evaporation rate of the initial products. The crystallinity of the films increases with substrate temperature. In order to optimize the substrate temperature of the films their optical and electrical properties were studied.

3.1 *Optical and electrical properties*

The optical absorption of the films was recorded in the wavelength range between 400 nm and 800 nm. The absorption coefficient α attained a minimum value at higher wavelength region and increases with decrease in wavelength (λ). This is attributed to the absorption edge of the semiconductor and homogeneity of the film. α lies in the order of $10^{-4}\ cm^{-1}$ indicating that the material is of direct energy gap in accordance with the pure Bi_2S_3 and Cu_2S compounds. Figure 1 shows the variation of $(\alpha h\nu)^2$ versus energy for the typical sample S_{250}. The linear extrapolation of this curve to the energy axis gives the value of optical gap of the film. In the present study the value of bandgap (E_g) obtained is 1·65 eV, which is somewhat larger than the bandgap of Bi_2S_3 (1·4 eV)

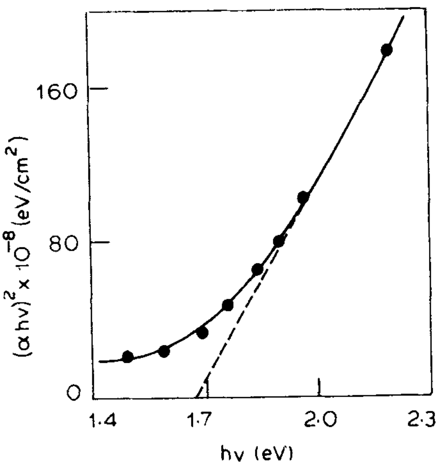

Figure 1. Plot of $(\alpha h\nu)^2$ versus energy ($h\nu$) for a typical sample S_{250}.

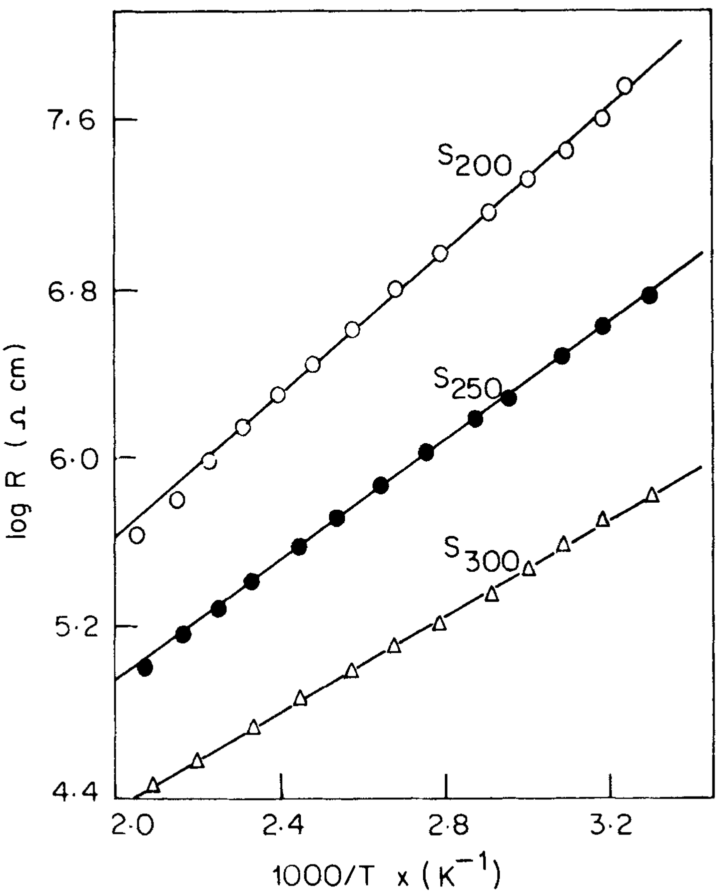

Figure 2. Variation of log R versus $1/T$ for the samples S_{200}, S_{250}, S_{300}.

(Pawar *et al* 1983) and Cu_2S (1·2 eV) (Mytton 1974). At higher substrate temperature excessive evaporation from the film takes place giving a nearly ionic ratio of 1 : 1 : 2. Beyond 450°C of substrate temperature, the evaporation rate of sulphur increases thereby forming the oxides of copper and bismuth. Better quality films were obtained between the substrate temperatures of 250°C and 300°C.

The dark resistivity measurements were carried out in the range between 300°k and 600°k. Figure 2 shows the variation of log R with the reciprocal of temperature for typical samples S_{200}, S_{250} and S_{300}. Films prepared at lower substrate temperature show greater resistance than films prepared at higher substrate temperature. Resistance decreases with increase in temperature confirming that $CuBiS_2$ is a semiconducting material. The activation energies for the samples S_{200}, S_{250} and S_{300} are 0·64 eV, 0·52 eV and 0·40 eV respectively. In the present investigation the resistivity of the films lies in the range of 10^4 to 10^7 ohm-cm.

Thermovoltage of the films was recorded to understand the conductivity and the as- grown $CuBiS_2$ thin films showed *n*-type conduction.

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