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Studies on K-Sb-S films deposited at different substrate temperatures and their photoelectrochemical behaviour

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Abstract. The electrical and optical properties of thin films of K-Sb-S prepared by spraying a solution of antimony potassium tartrate and thiourea onto heated conducting and non-conducting glass substrates are described. The polycrystalline films produced at an optimum spray rate and at different substrate temperatures were characterized for semi-quantitative analysis. The films show variation in thickness with substrate temperature. Photoelectrochemical cells formed with the K-Sb-S film electrode, 0·5 M ferrocene in dimethylsulphoxide as the electrolyte and carbon as the counterelectrode were studied for their current voltage characteristics in dark and in light. Variation of short circuit current and open circuit voltage with light excitation intensity is also described.

Keywords. K-Sb-S film; photoelectrochemical behaviour.

1. Introduction

Photoelectrochemical behaviour of many ternary semiconductors has been studied earlier (Russak and Creter 1985; Scrosati *et al* 1985). Pamplin and Feigelson (1979) reported the preparation of thin films of $A^{I}B^{III}C_2^{VI}$ semiconductors where C^{VI} is either S or Se and of quarternary and quinary (i.e. penternary) alloys based on these ternary chalcopyrite semiconductors. The potential of ternary chalcopyrites as the active semiconductors in photovoltaic solar cells was first described by Shewchun *et al* (1975) and for alloys of ternaries by Loferski *et al* (1978). In the present investigation K-Sb-S films were produced by spray pyrolysis on heated conducting and non-conducting glass substrates and studied for their compositional, electrical and optical properties. PEC cells formed with these films were studied for the photovoltaic output characteristics. The effect of substrate temperature on the properties of the film and the performance of the PEC cells have been studied and are described in this paper.

2. Experimental

Polycrystalline thin films of K-Sb-S were deposited onto ultrasonically cleaned conducting (20 Ω/cm^2 fluorine doped tin oxide) and non-conducting glass substrates (3·9 cm × 0·9 cm) by spray pyrolysis technique. Substrate temperature was varied at an interval of 25°C, from 150 to 250°C. Solutions of antimony potassium +(−) tartrate ($KSbO \cdot C_4H_4O_6$) and thiourea with $KSbS_2$ concentration of 0·1 M were prepared by dissolving appropriate amounts of AR grade compounds in deionized water. The starting solution thus prepared by mixing the above two solutions was sprayed (at 15·4 c.c/min) through a specially designed glass nozzle. The air pressure was 0·8 kg/cm^2 and the height of the solution below the tip of the nozzle was 13·5 cm. The K-Sb-S film was formed by pyrolytic decomposition of sprayed droplets on the surface of the substrate. The films were annealed in air for 30 min at the deposition temperature.

The thickness of the films deposited at various deposition temperatures was determined by the weight difference method. The resistivity of the films was measured using a nanoammeter (Aplab FET TEM-13) and TPSU model 7111. The optical absorption was measured in the wavelength range 400 to 760 nm by a monochromator (Carl Zeiss, Jena). Compositional analysis of the films deposited at various substrate temperatures was determined by the energy dispersive X-ray spectroscopy technique. A voltage of 15 kV was applied and the magnification used was 9·25 × Area. Thermoelectric power was measured to determine the type of conductivity of the film.

PEC cells were formed using these films as photoelectrodes, 0·5 M ferrocene in dimethylsulphoxide as the electrolyte and the carbon as the counterelectrode. The distance of the photoelectrode from the cell window was 1 mm and 500 W tungsten filament lamp was used to illuminate the cells.

Variation of short circuit current (I_{sc}) and open circuit voltage (V_{oc}) of the PEC cells formed with K-Sb-S photoelectrodes deposited at various substrate temperatures was noted. Current voltage (I-V) characteristics of the PEC cell in dark and in light for the optimized substrate temperature were studied using a nanoammeter and a high input impedance digital d.c. voltmeter. The series resistance (R_s) was computed from the variation of I_{sc} and V_{oc} with light intensity (F_L).

3. Results and discussion

The K-Sb-S ternary films prepared by pyrolytic decomposition of sprayed droplets on the heated substrates adhered to the substrates and were homogeneous in appearance. X-ray diffraction spectra showed that the films are polycrystalline. Variation of the thickness with substrate temperature (figure 1) shows that as temperature increases thickness also increases, then attains a maximum and finally decreases with further increase in substrate temperature. This may be explained as follows: Initially the substrate temperature is not sufficient to decompose the sprayed droplets of the solution which yields films of low thickness. At some critical temperature the

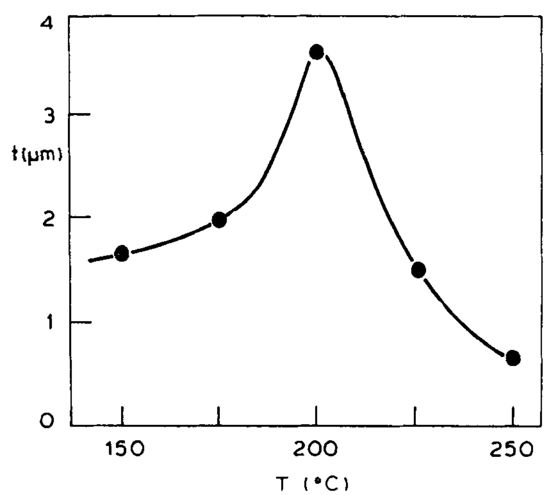

Figure 1. Variation of thickness with substrate temperature.

decomposition starts and the deposition rate increases with temperature. Decrease in film thickness at higher substrate temperature can be attributed to the large evaporation of initial ingredients (Ugai *et al* 1978).

The compositional analysis of the films deposited at various substrate temperatures has been carried out by the energy dispersive X-ray spectroscopy technique and a typical plot is shown in figure 2. It is seen that the main constituents in all the films are K, Sb and S; however, the substrate temperature affects their magnitude. The variation of the magnitude with substrate temperature is listed in table 1.

Thermoelectric power measurement shows that films produced at different temperatures are of p-type. The measurement of dark electrical resistivity films reveals that they are highly resistive ($= 10^{12}$ ohm/cm) at room temperature and the resistivity decreases with increase in temperature indicating the semiconducting nature of the film.

Variation of the optical absorption coefficient (α) with wave-length (λ) for the films deposited at various substrate temperatures is shown in figure 3. It is seen that for samples deposited at 200°C and above, the absorption edge is steep and the α value is of the order of 10^4 cm^{-1} which predicts the band gap of the material to be the direct one. The data were further analysed by plotting the graph of $(\alpha h\nu)^2$ versus $h\nu$

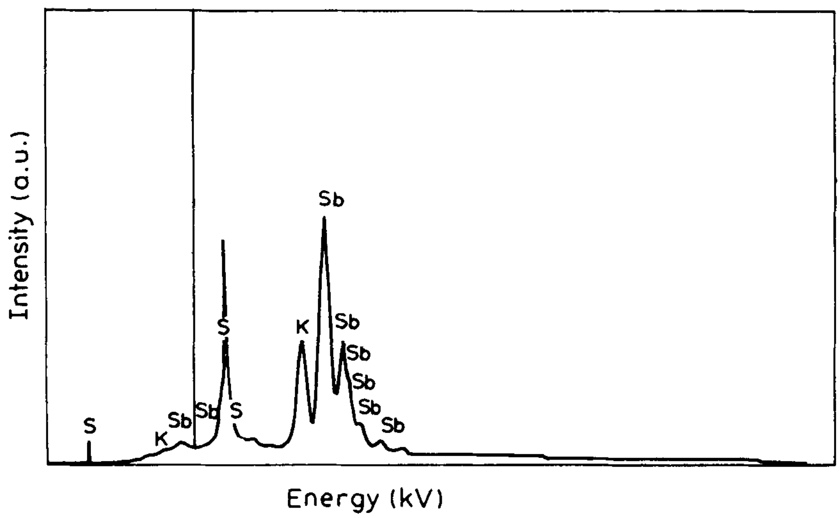

Figure 2. Compositional analysis of the film deposited at 200°C.

Table 1. Substrate temperature and film composition.

Substrate temperature (°C)	Composition of the film (%) K	Sb	S
150	50·52	36·37	13·11
175	50·05	37·90	12·05
200	32·14	42·14	25·72
225	48·08	37·32	14·60

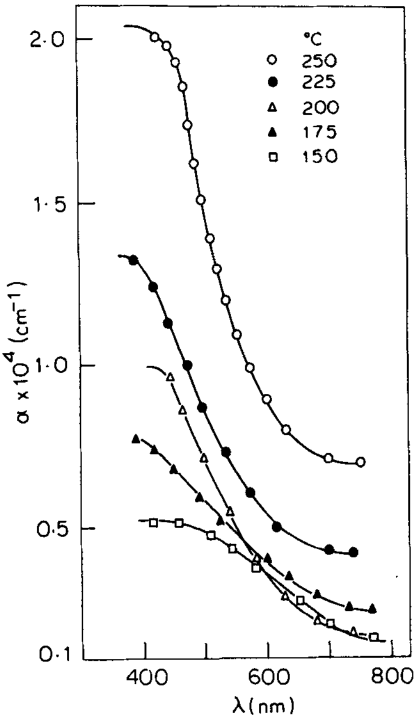

Figure 3. Variation of optical absorption coefficient with wavelength.

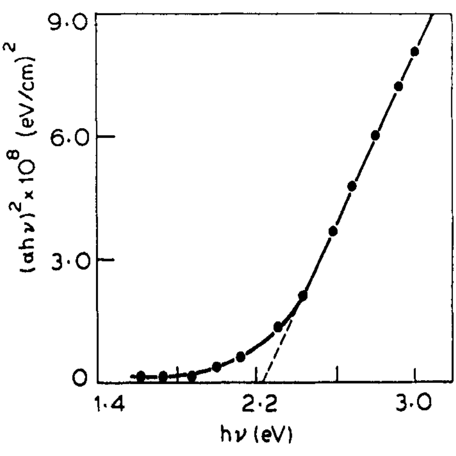

Figure 4. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for the K-Sb-S films deposited at 200°C.

(figure 4) which gives straight lines confirming that the material is of direct gap with the band gap energy equal to 2·22 eV, obtained by extrapolating the straight portion to the energy axis.

Variation of I_{sc} and V_{oc} with substrate temperature (figure 5) shows that both I_{sc} and V_{oc} increase with substrate temperature, attain a maximum at 200°C and then decrease with further increase in temperature. The variation of I_{sc} with substrate temperature may be similarly attributed to a variation of film thickness

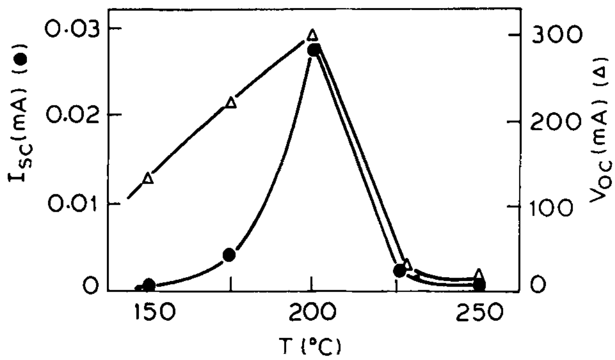

Figure 5. Variation of short circuit current and open circuit voltage with substrate temperature.

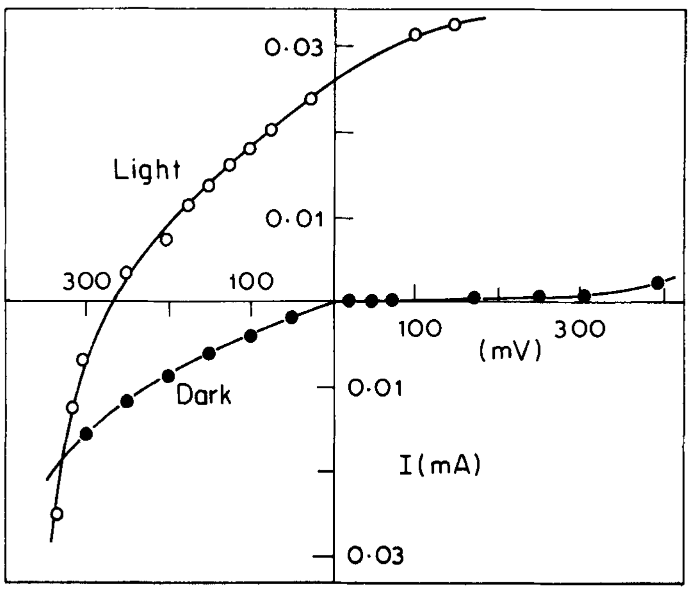

Figure 6. Current voltage characteristics in dark and in light for the PEC cell formed with K-Sb-S photoelectrode produced at optimised substrate temperature.

with substrate temperature. The decrease in film thickness reduces the absorption of light in the film and hence the decrease of I_{sc}.

The variation of V_{oc} with substrate temperature can be represented by the relation (Rajeshwar *et al* 1981)

$$V_{oc} = (nKT/q) \ln (I_{sc}/I_0), \tag{1}$$

where n is the ideality factor, I_0 the reverse saturation current. The other terms have their usual meaning. From equation (1) it is seen that V_{oc} mainly depends on I_0. The dynamic I-V characteristics studied in dark and in light for a typical PEC cell formed with K-Sb-S film electrode deposited at optimised substrate temperature (200°C) are shown in figure 6. The non-symmetric nature of the I-V curve in dark indicates that the junction formed is of a rectifying nature. The shifting of the I-V curve in the fourth quadrant under illumination indicates that the PEC cell formed with K-Sb-S photoelectrode works as a generator of electricity. Cross-over of the two curves indicates the photoconductive nature of the film (Shirland 1966).

Figure 7 depicts the variation of I_{sc} and V_{oc} as a function of light intensity (F_L). It is observed that V_{oc} increases with F_L and approaches a saturation value beyond 40 mW/cm^2 of light intensity. The saturation of V_{oc} at higher light intensities can be attributed to the increased recombination rates. I_{sc} varies linearly up to a certain light intensity beyond which non-linearity can be observed. The linear nature of the I_{sc} with F_L obeys the relation (Lokhande and Pawar 1984)

$$I_{sc} = C \cdot F_L, \tag{2}$$

where C is the constant of proportionality which depends on the fraction of light utilized for the generation of the number of charge carriers. The deviation from the linearity beyond critical intensity is attributed to the series resistance effect in the photovoltaic cell and increased recombination rates. This observation, using the

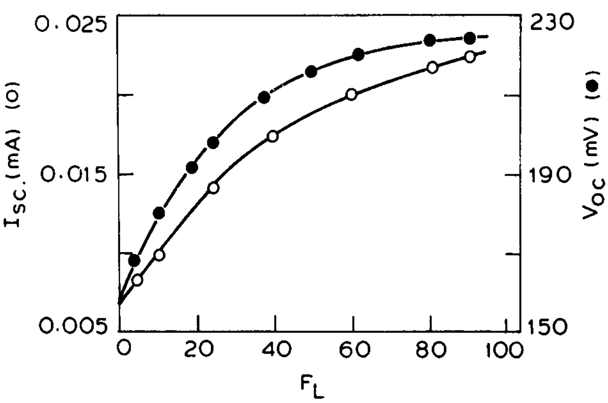

Figure 7. Variation of I_{sc} and V_{oc} with intensity of incident light.

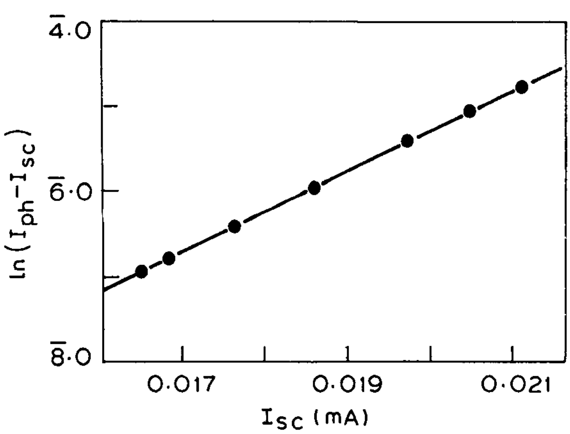

Figure 8. Plot of ln $(I_{ph} - I_{sc})$ versus I_{sc}.

relation (Agarwal *et al* 1981)

$$I_{sc} = I_o\left[\exp\left(-\frac{e \cdot I_{sc}R_s}{nKT}\right) - 1\right] - I_{ph}, \tag{3}$$

where the terms have their usual significance, is used to find the series resistance R_s of the PEC cell. A plot of ln $(I_{sc} - I_{ph})$ versus I_{sc} is depicted in figure 8. The linear nature of the plot observed agrees with the theory. The slope of this plot gives the value of series resistance R_s and is found to be 123 M.ohm.

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