JOURNAL OF MATERIALS SCIENCE **21** (1986) 46–50

Electrical properties of Bi_2S_3 thin films prepared by the dip–dry method

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Bi_2S_3 thin films have been prepared by the dip–dry method and their electrical properties such as conductivity, thermoelectric power and spectral response of photoconductivity were investigated. Some uncommon findings, such as a simultaneous increase in conductivity and thermoelectric power with thickness of film, are explained by Seto's model for polycrystalline silicon film duly modified for inhomogeneities.

1. Introduction

Compound semiconductors like bismuth telluride and bismuth selenide have been extensively investigated because of their use in thermoelectric coolers [1]. However, bismuth sulphide (Bi_2S_3), another important member of this class of chalcogenides, has been the subject of only a few investigations [1–10] and there are also large deviations in the reported electrical properties. Loferski [11] and Schoijet [12] pointed out that since Bi_2S_3 is characterized by a favourable band gap (~ 1.3 eV) it may be a prospective candidate material for solar photovoltaic converters. With the object of using the material in thin-film solar cells, thin films of Bi_2S_3 have been prepared by the dip–dry process [13] and the electrical, thermoelectric and photoelectronic properties have been investigated.

In this paper experimental results for electrical conductivity, thermoelectric power and spectral response of photoconductivity are reported. The results are understood by making use of Seto's theory of polycrystalline films [14] along with the analysis of Kwok [15] for calculating the thermoelectric power of an inhomogeneous semiconductor.

2. Experimental details

Bi_2S_3 thin films were deposited on pyrex glass substrates employing the dip–dry method, the details of which have been reported elsewhere [13]. Greyish-black films were grown on glass slides (area 6 cm × 2.5 cm) by baking a thin layer of the bismuth–thiourea complex at a temperature of about 220° C. Microstructural characterizations were carried out by X-ray diffraction and scanning electron microscopy (SEM) in order to determine the lattice constants and study the surface topography of the films [13]. The grain size of the film for different thicknesses was determined from SEM micrographs by taking the arithmetic mean.

Electrical conductivity and thermoelectric power (TEP) measurements were carried out in a specially designed cryostat which could maintain temperature in the range 80 to 370 K at a vacuum of 10^{-4} torr. Ohmic contacts were made by applying an alcoholic solution of colloidal graphite to the films. Electrode separation was maintained at 1 cm with electrode width of 0.5 cm. The current flowing through the sample by an application of 9 V from a dry battery was measured by determining the voltage drop across a series resistance ($r_{\text{series}} \ll r_{\text{sample}}$). To measure the TEP, a small heating element was placed at one end of the sample to maintain a temperature gradient of 10 K between the two opposite ends of the sample. The TEP for the films was measured by employing an ECIL EA–815 electrometer amplifier having an input resistance of $10^{14}\,\Omega$. The spectral response of the photoconductivity of films was studied by illuminating the samples with monochromatic light from a Hilger monochromator (D 246302) using a tungsten halogen lamp (Philips, 600 W) which was fitted in a CEL lamp housing with a focusing facility. The light output of the monochromator was chopped by a PAR chopper (33 Hz, 220 V a.c. operated, built-in silicon photodiode for reference signal). The voltage across a small resistance in series with the sample was measured using a lock-in amplifier (EMCO–EE 201). The response was normalized.

3. Results

The temperature variation of dark conductance of the Bi_2S_3 films was studied for five different thicknesses. Fig. 1 shows the typical nature of variation of the conductance (G) in the range 80 to 370 K. The non-exponential nature of the curves can be considered exponential over a small range of temperature; hence activation energies can be assigned to the straight portions of the curves. The curves can be divided into two regions: (a) 370 to 280 K and (b) 280 to 80 K. E_1 and E_2 are the respective activation energies attributed to these regions. The experimental values of E_1 along with impurity concentration N calculated for five different thicknesses from Seto's formula [14] (for $LN > Q_t$ where L = grain size and Q_t = density of surface states) are given in Table I. It is observed that with increase in thickness of film while E_1 decreases,

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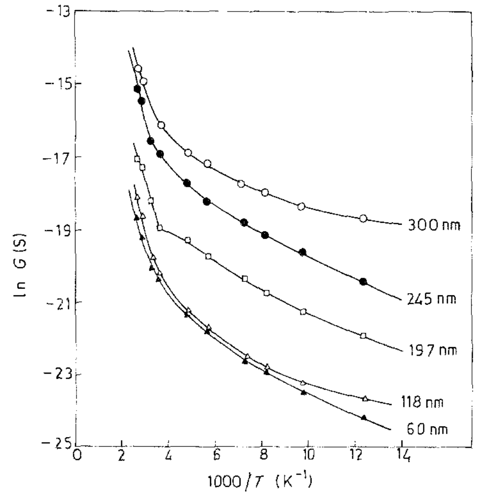

Figure 1 Variation of dark conductance with temperature of Bi_2S_3 films prepared by the dip–dry method.

conductivity increases at the same time. Major attention is focused here on E_1 only, as the validity of Seto's model is restricted to the higher temperature region ($E_B > kT$).

The high sample resistance of the films ($\sim 10^7\,\Omega$ and more) did not make it possible to measure the Hall voltage by the set-up available in the laboratory. TEP measurements however made it possible to confirm the n-type conduction in the films. TEP is found to increase with increase in thickness, and its room temperature (300 K) values for different thicknesses are shown in Table I. As temperature decreases TEP is observed to increase and maintains a negative character throughout the temperature range 80 to 370 K. Fig. 2 exhibits such a variation for a typical sample. The a.c. spectral response of photoconductivity at room temperature has been studied for five different thicknesses of Bi_2S_3 films. As seen from Fig. 3, the half-width of the spectral response curve decreases with increase in thickness.

4. Discussion

The experimental results on Bi_2S_3 thin films can be summarized as follows:

(a) The activation energy of the electrical conductivity in the temperature range 280 to 370 K decreases with increase in thickness/grain size.

(b) The magnitude of the electrical conductivity of the films increases with increase in thickness/grain size.

(c) TEP increases with increase in thickness.

(d) TEP decreases with increase in temperature.

(e) The half-width of the spectral response curve is thickness dependent.

The dependence of activation energy on thickness/grain size suggests that the polycrystalline nature of the film is responsible for such behaviour.

The grain size of the films as observed by SEM is found to increase with increase in thickness and is shown in Table I. Slater [16] worked out a relationship between grain size and activation energy for PbS films. Seto [14] put forward a one-dimensional theory to explain the activation energy of silicon films in terms of grain size, impurity concentration etc. Recently Kazmerski [17] and Orton *et al.* [18] have reviewed and studied the various formulations on electrical transport properties of polycrystalline films. Although the two-dimensional formulation of Orton *et al.* is a more realistic approach the qualitative features of the one- and two-dimensional formulations are the same with certain numerical changes in the results. It will therefore not be very inappropriate to use the simplistic one-dimensional approach of Seto [14] to explain the experimental findings in this work.

According to Seto, the activation energy/barrier height is given by

$$V_B = \frac{qL^2N}{8\varepsilon}, \qquad LN < Q_t \tag{1a}$$

$$V_B = \frac{qQ_t^2}{8\varepsilon N}, \qquad LN > Q_t \tag{1b}$$

where q = electronic charge, ε = electric permittivity, V_B = barrier height; $E_B = qV_B$ is the energy of the barrier between crystallites formed due to trapping of carriers in the surface states; L = grain size, Q_t = density of surface states and N = dopant concentration. All energy values are measured with respect to the intrinsic Fermi level. Since the values of N and Q_t are not known, it is not possible to say whether $LN > Q_t$ or $LN < Q_t$. In the first case of Equation 1 the barrier height will increase with increase in grain size even if N is constant. Thus the observed decrease in V_B with increase in thickness rules out the probability of the condition $LN < Q_t$. The decrease in barrier height with increase in thickness suggests that the doping concentration N increases with increase in thickness because Q_t is not likely to decrease significantly with increase in grain size. The increase in doping concentration is also corroborated by the

TABLE I Variation of different parameter values with thickness for Bi_2S_3 films prepared by the dip–dry method

No. of dips	Thickness of film (nm)	Grain size determined from SEM (μm)	Dark conductivity σ determined at 300 K ($\Omega^{-1}\,cm^{-1}$)	Activation energy E_1 (E_B) determined from graph of G against $1/T$ (eV)	Dopant concentration N per cm^3 (n_2) calculated from Seto's formula for $LN > Q_t$ ($\times 10^{18}$)	TEP at 300 K ($\mu V\,K^{-1}$)
5	60	2.2	6.643×10^{-4}	0.26	5.792	350
10	118	2.7	4.561×10^{-4}	0.24	6.275	380
15	197	3.9	1.224×10^{-3}	0.23	6.547	435
20	245	10.6	5.212×10^{-3}	0.22	6.845	465
25	300	11.08	1.118×10^{-2}	0.21	7.171	480

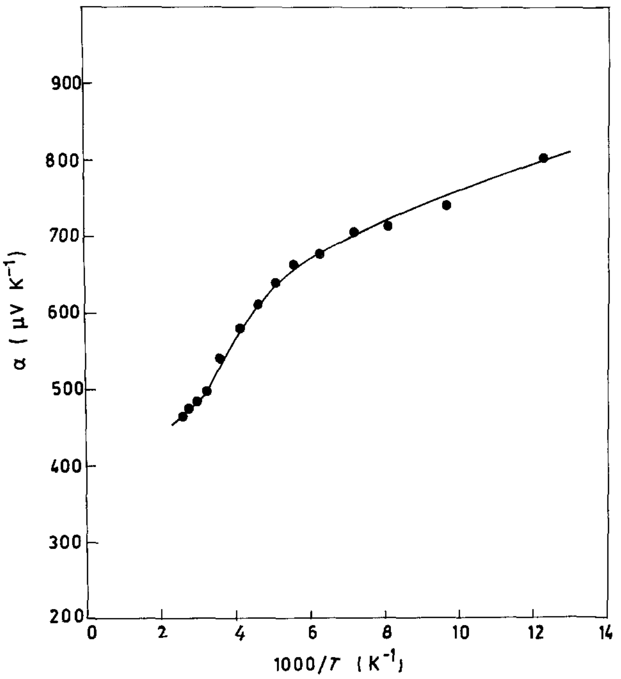

Figure 2 Variation of TEP with temperature of Bi_2S_3 (~300 nm) prepared by the dip–dry method.

observed increase in the absolute magnitude of conductivity of the films as the thickness increases.

The increase in doping concentration with the increase in thickness is quite feasible in the dip–dry process of film preparation. It has been reported [13] that the films are prepared by dipping glass slides in a methanolic solution of bismuth chloride and thiourea and baking the resulting coating in air (this is intentionally done to reduce the resistance of the film so that it can be used for photovoltaic cell manufacture). When baked in air at about 500 K, the coating turns dark grey. During this process of baking the following reaction is likely to take place as happens in the case of antimony [19]:

$$2\,Bi_2S_3 + 9O_2 = 2Bi_2O_3 + 6SO_2 \qquad (2a)$$

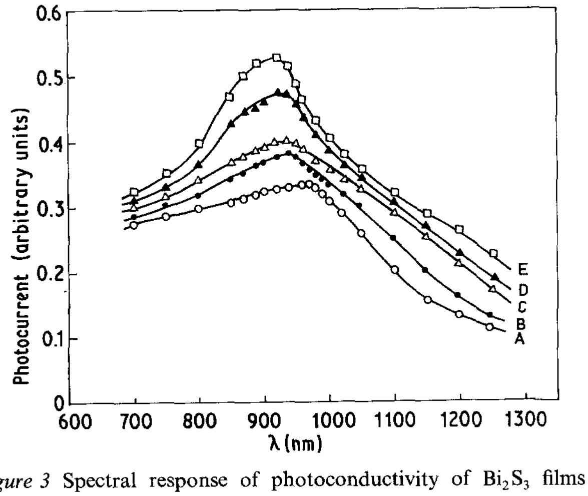

Figure 3 Spectral response of photoconductivity of Bi_2S_3 films prepared by the dip–dry method: thickness (A) 60 nm, (B) 118 nm, (C) 197 nm, (D) 245 nm, (E) 300 nm.

Since this reaction would be exothermic [20] the generated heat may be sufficient to raise the local surface temperature of the film to the order of 1240 K even though the environment is at 500 K. At 1240 K Bi_2O_3 reduces to bismuth as follows [21]:

$$2\,Bi_2O_3 + Bi_2S_3 = 6\,Bi + 3\,SO_2 \qquad (2b)$$

The excess bismuth formed by this reaction will be mostly lying on the surface of the Bi_2S_3 grain. On further deposition which involves baking, bismuth would diffuse in and increase the average doping of the grain; the outer region of the grain will be characterized by more doping compared to the interior. As the number of dips increases, this process repeats and the average dopant concentration of the grain increases. The grain is likely to be surrounded by a more conducting layer. The n-type behaviour of the films as confirmed by TEP measurements corroborates the presence of excess bismuth. However, there is no direct evidence to conclude the presence of excess bismuth.

As mentioned earlier, it is interesting to note that as the magnitude of TEP increases with increase in thickness/grain size, the conductivity increases. Since doping concentration increases with increase in thickness, the increase in conductivity looks contradictory, but for an inhomogeneous sample it is quite feasible. The Bi_2S_3 grain prepared by the dip–dry process constitutes an inhomogeneous system where an inner core of carrier concentration n_2 and length L_2 is surrounded by an outer layer of carrier concentration n_1 ($n_1 > n_2$) and length L_1. Using Kwok's formula [15] the measured TEP of such a structure can be given as

$$\alpha_{av} = -\frac{k}{q}\left(A + \ln N_c - \frac{1}{1 + L_2/L_1}\ln n_1 - \frac{1}{1 + L_1/L_2}\ln n_2\right) \qquad (3)$$

where N_c stands for the effective density of states in a conduction band, calculated by taking the effective mass of an electron equal to its rest mass; A is a constant whose value lies between 2 and 4 depending on the scattering mechanism and k is Boltzmann's constant. The value of A is chosen here to be 4. The method of film growth suggests that as the thickness grows, the ratio L_1/L_2 will decrease. Fig. 4 shows a plot of variation of TEP (α) with L_1/L_2 for an assumed value of n_1 (the surface dopant concentration has been assumed to be 10^{20} per cm^3 to make α_{calc} agree with α_{meas} or α_{av}) and for various expected values of n_2 (the bulk doping). The expected bulk doping has been estimated by using Equation 1b which connects the conductivity activation energy with dopant concentration and is shown in Table I. The value of Q_t has been assumed to be 10^{13} per cm^2. It is evident from the plot of Fig. 4 that as the thickness of film increases the TEP increases for a constant n_2 value (Curve A). In the dip–dry method, as explained earlier, since the increase in thickness is also likely to be accompanied by an increase in doping concentration, one can go to Curve D or E and find that for certain values of L_1/L_2 the measured TEP has increased with increase in thickness although n_2 has also increased at the same time.

The average carrier concentration n_{av} for such an

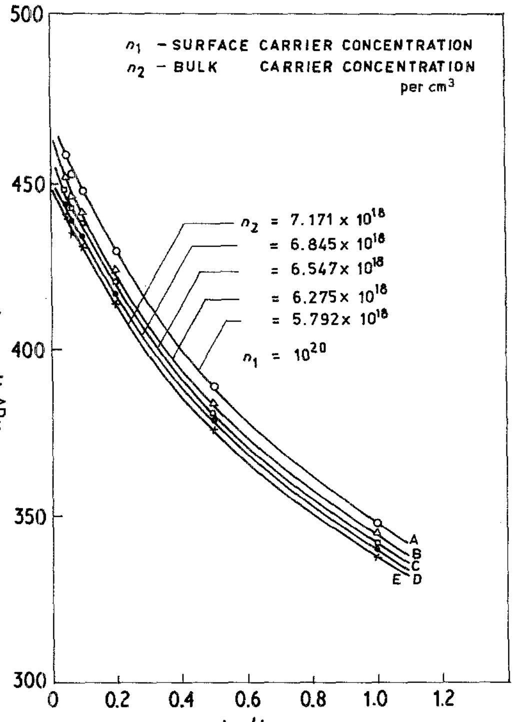

Figure 4 Variation of theoretically calculated TEP with L_1/L_2 for different values of n_2 and a fixed n_1 value.

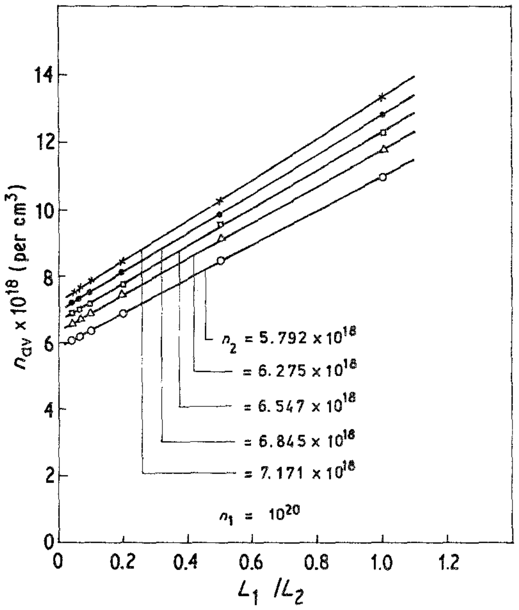

Figure 5 Variation of average carrier concentration n_{av} with L_1/L_2 for different values of n_2 and a fixed n_1 value (per cm^3).

inhomogeneous structure is given by Kwok [15]:

$$n_{av} = \frac{L_1 + L_2}{L_1/n_1 + L_2/n_2} = \frac{1 + L_2/L_1}{1/n_1 + (L_2/L_1 \times 1/n_2)} \qquad (4)$$

The theoretical plot of n_{av} with L_1/L_2 as exhibited in Fig. 5 shows that for an assumed value of n_1 (10^{20} per cm^3), the effective value of n_{av} increases with increase in n_2 for any thickness. Such expected variation in n_{av}, coupled with the decrease in barrier height with increase in grain size, explains the increase in absolute magnitude of conductivity with thickness. This is quite clear from the expression of conductivity derived by Seto [14]:

$$\sigma = Lq^2 n_{av} \left(\frac{1}{2\pi m^* kT}\right)^{1/2} \exp\left(\frac{-qV_B}{kT}\right) \qquad (5)$$

where m^* stands for the effective mass of electron.

Using the theory of nondegenerate semiconductors, the decrease in TEP with increase in temperature can be understood. For a nondegenerate semiconductor the TEP is given [22] by

$$\alpha = -\frac{k}{q}\left(A + \ln\frac{N_c}{n_b}\right) \qquad (6)$$

where n_b denotes the effective carrier concentration. The average value of carrier concentration in the grain is modified by two effects: inhomogeneity in doping and the band bending at the surface. The average value of carrier concentration in the grain due to doping variation along the grain can be calculated using Equation 4. Since the value of L_1 is likely to be of the order of 20 nm and L_2 as measured from SEM for the typical sample (thickness 300 nm) is about 11 μm, the value of n_{av} will thus be approximately n_2 only. The effective carrier concentration including the effect of band bending is given by Seto's expression

$$n_{eff} = n_b\left\{\left(1 - \frac{Q_t}{LN}\right) + \frac{1}{qL}\left(\frac{2\varepsilon kT\pi}{N}\right)^{1/2} \times \operatorname{erf}\left[\frac{qQ_t}{2}\left(\frac{1}{2\varepsilon kTN}\right)^{1/2}\right]\right\} \qquad (7)$$

For $Q_t = 10^{13}$ per cm^2, $N = 10^8$ per cm^3, $\varepsilon/\varepsilon_0$ (dielectric constant) $= 15$ for Bi$_2$S$_3$, the values of the argument of the error function in the above equation, are 6.869 and 7.896 for $T = 370$ and 280 K, respectively. In both cases the values of error function tend to unity: when $T = 370$ K,

$$n_{eff} = n_b\,[(1 - 0.0111) + 1.433 \times 10^{-3}\operatorname{erf}(6.869)] \qquad (8a)$$

and when $T = 280$ K,

$$n_{eff} = n_b\,[(1 - 0.0111) + 1.246 \times 10^{-3}\operatorname{erf}(7.896)] \qquad (8b)$$

Since the second terms in the above equations are negligible, Equation 7 can be written as

$$n_{eff} \approx n_b = N_c \exp\left(\frac{E_c - E_f}{kT}\right) \qquad (9)$$

where E_c and E_f are energy levels of the conduction band and Fermi level respectively, measured with respect to the intrinsic Fermi level. Substituting the value of n_b from Equation 9 into Equation 6 we can write

$$\alpha = -\frac{k}{q}\left(A + \frac{E_c - E_f}{kT}\right) \qquad (10)$$

It is evident from this expression that α should vary inversely with temperature. An experimental plot of α against $1/T$ shown in Fig. 2 for a typical sample gives a straight line in the region 280 to 370 K, which is in

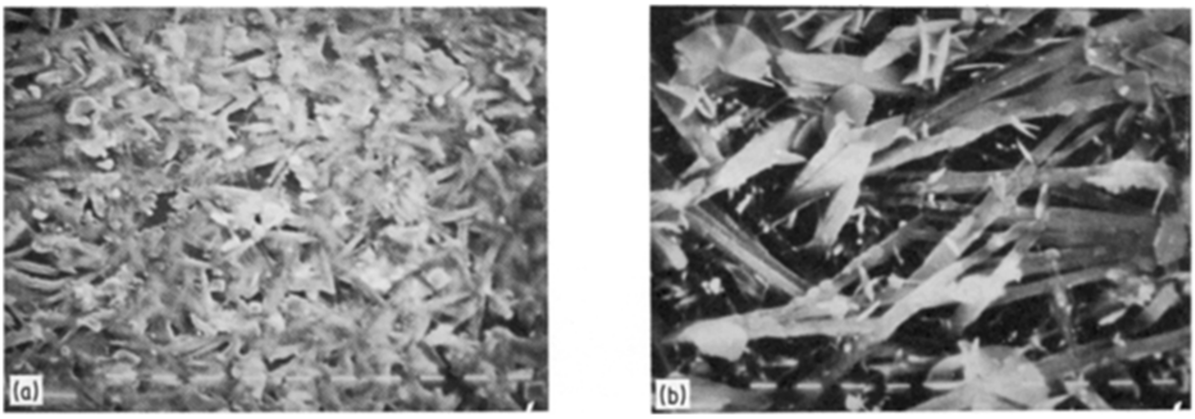

Figure 6 SEM micrographs of Bi_2S_3 films prepared by the dip–dry method: (a) 5 dips, thickness 60 nm; (b) 25 dips, thickness 300 nm. Marker size 1 μm.

the range where the Seto model is valid. The slope of experimental curve gives $E_c - E_f = 0.09$ eV.

The thickness dependence of the spectral response of photoconductivity (Fig. 3) can be understood if one considers the crystal perfection in the films. The SEM photographs shown in Fig. 6 reveal that crystal size and perfection increase with increase in thickness of film. The increase of half-width of the photoconductivity spectral response as the film thickness decreases can therefore be accounted for by the decrease in crystal perfection for thinner films.

5. Conclusion

Seto's model of polycrystalline silicon films can be applied to explain the electrical properties of Bi_2S_3 films prepared by the dip–dry method, provided that the roles played by inhomogeneities are taken into account.

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*Received 21 September
and accepted 18 December 1984*