JOURNAL OF MATERIALS SCIENCE 23 (1988) 3636–3639

Electrical resistivity of amorphous antimony trisulphide films

KH. A. MADY
Physics Department, National Research Centre, Dokki, Cairo, Egypt
M. M. EL-NAHAS, A. M. FARID, H. S. SOLIMAN
Faculty of Education, Ain Shams University, Heliopolis, Cairo, Egypt

The electrical resistivity of amorphous antimony trisulphide films was investigated in the temperature range from 0 to 200° C. The temperature dependence of the resistivity follows the ordinary semiconducting behaviour above room temperature. The electrical band gap was found to be consistent with a mobility gap. By annealing the conductivity reduces and the slope of the conduction is increased indicating that the mobility gap is appreciably enhanced by annealing.

1. Introduction

Antimony trisulphide corresponds to the stoichiometric binary semiconducting compounds which are of great interest as amorphous and crystalline materials. Problems may arise from decomposition during the process due to the preparation technique. The conditions of creating stoichiometric Sb_2S_3 films on substrates are highly dependent on vacuum conditions, deposition rate and the substrate.

The properties of thin films of Sb_2S_3, such as photoelectric properties [1, 2], the conduction and charge carrier transport mechanism [3, 4] and various types of contacts given by metal electrodes to Sb_2S_3 films [5] have been investigated. In all these cases the films were prepared by the vacuum evaporation of the compound Sb_2S_3 which may cause some departures in the stoichiometry of the compound film formed. The temperature dependence of the conductivity of coevaporated films of Sb_2S_3 prepared at different substrate temperatures was also studied [6].

In the present paper the electrical resistivity of amorphous films of Sb_2S_3 vacuum deposited on optically plane glass slides was investigated in the temperature range from room temperature up to 200° C. The behaviour was studied for as-deposited and pre-annealed films.

2. Experimental techniques

Thin films of antimony trisulphide were obtained by conventional thermal evaporation of the original material (industrially grade lead-grey of purity 99.9%, Balzers, Germany) using molybdenum boats in 133.3×10^{-6} Pa vacuum. All the films were prepared on optically plane microscope glass substrates; cleaned and subjected to ion bombardment in the vacuum system. The thicknesses of the films were measured using multiple beam interferometric methods and a quartz crystal film thickness monitor. Structural studies were made using an X-ray diffractometer (Philipps D500) with CuKα radiation and a transmission electron microscope (EM 10, Zeiss).

The two-point probe technique was employed for measuring the electrical resistivity with some modification to eliminate the effect of the contact resistance given that the specimen cross-section is relatively uniform. The film resistors are commonly characterized by a normalized parameter, called the sheet resistance R, which is related to the resistivity ϱ by

$$R = \varrho/d = rw/l$$

Hence,

$$\varrho = r\frac{wd}{l}$$

where w, d and l are the film width, thickness and length, respectively, and r is the resistance of the film. The film resistance was measured in darkness in the temperature range from room temperature to 200° C. The temperature was determined to an accuracy of ±0.5° C using a chromel–alumel thermocouple. During measurements the body of the furnace was earthed to avoid the effect of external stray fields. A high impedance electrometer (Keithley, type 610 C) was used for measuring the resistance directly.

3. Results and discussions

An X-ray diffraction study of the bulk showed that the material was crystalline (Fig. 1a). Vacuum-deposited films were amorphous in nature and featureless. A typical X-ray diffractogram is shown in Fig. 1b compared to that of the bulk. Even after temperature cycling (< 200° C) these films did not show any significant grain growth or crystallinity when observed by transmission electron microscopy or the selected area diffraction method.

The current–voltage characteristics of Sb_2S_3 film contact with vacuum-deposited aluminium electrodes

0022-2461/88 $03.00 + .12

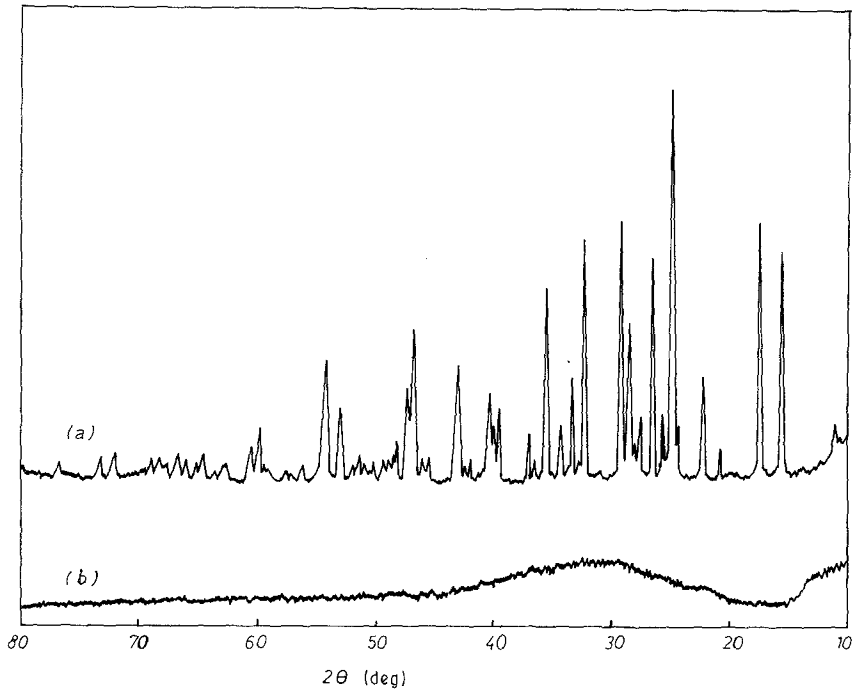

Figure 1 X-ray diffraction pattern of vacuum-deposited Sb_2S_3 film compared to the powder pattern.

are linear (Fig. 2) in the case of positive or negative polarity and also at high temperatures ($< 200°C$), indicating an ohmic contact, i.e. no hysteresis or rectification occurred.

The temperature dependence of the electrical resistivity of amorphous Sb_2S_3 films of thickness varying between 200 nm and 700 nm is shown in Fig. 3. Above room temperature the resistivity changes according to the ordinary semiconducting relation

$$\varrho = \varrho_0 \exp(\Delta E/KT)$$

where ΔE represents the activation energy of the conduction mechanism. The activation energy deduced from the experimental data was found to be 0.93, 0.85, 0.84 and 0.79 eV for 200, 300, 430 and 700 nm thick films, respectively. The activation energy decreased on increasing the film thickness (Fig. 4). The decrease of the activation energy might be attributed to the fact

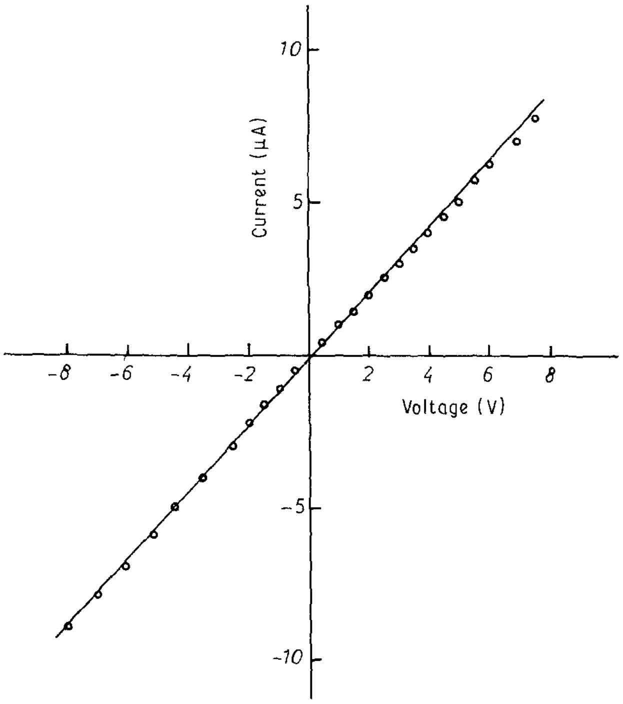

Figure 2 Current voltage characteristics of Al–Sb_2S_3 film contact.

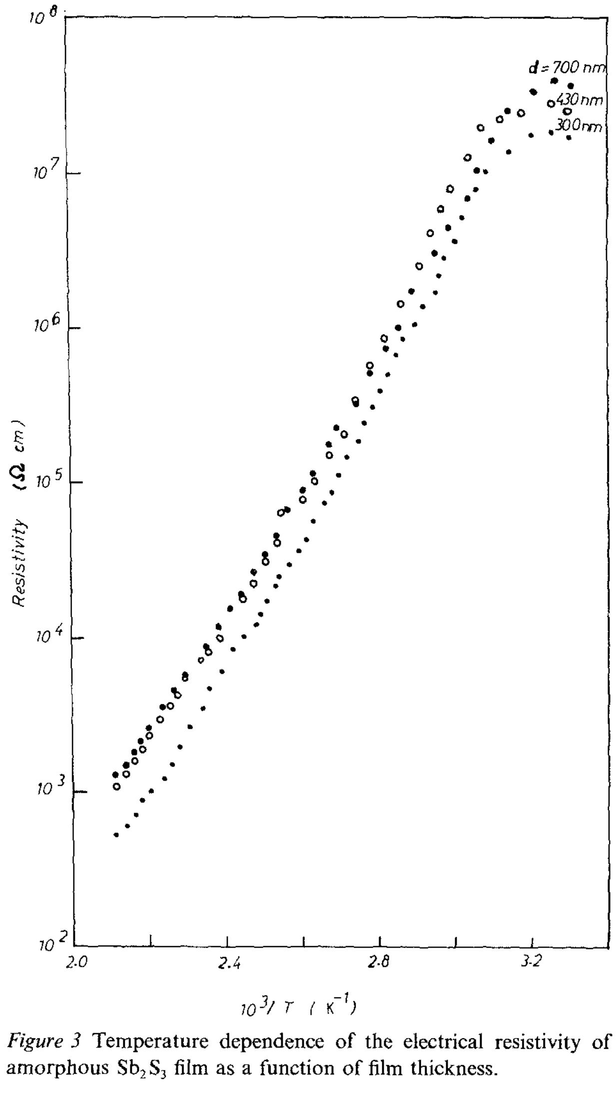

Figure 3 Temperature dependence of the electrical resistivity of amorphous Sb_2S_3 film as a function of film thickness.

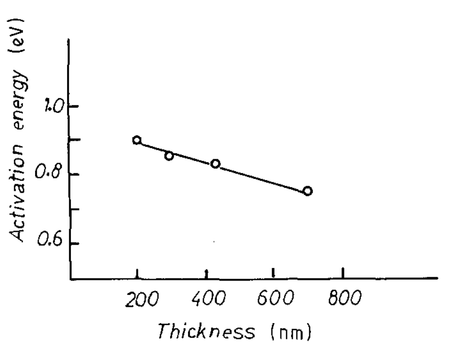

Figure 4 Activation energy plotted against film thickness.

that the surface states are becoming less involved in the carrier matrix (hopping motion). It should be noted that the activation energy determined from the dark conductivity of Sb_2S_3 crystals lies between 0.5 and 0.6 eV [7]. However, films prepared at substrate temperatures below 250° C showed separate values of the activation energy in the range 0.9 to 1.1 eV [6]. In the case of such films the condensation of excess sulphur on the substrate was possible [8], and might also result in the non-stoichiometry in the film formed.

The forbidden band determined by optical methods [9] is larger than the value of E_g obtained from the temperature dependence of resistivity. This fact is in agreement with Mott's view, namely that the position of the Fermi level in amorphous materials does not occur precisely in the middle of the forbidden band due to a difference in the smearing of the valence and conduction bands [10].

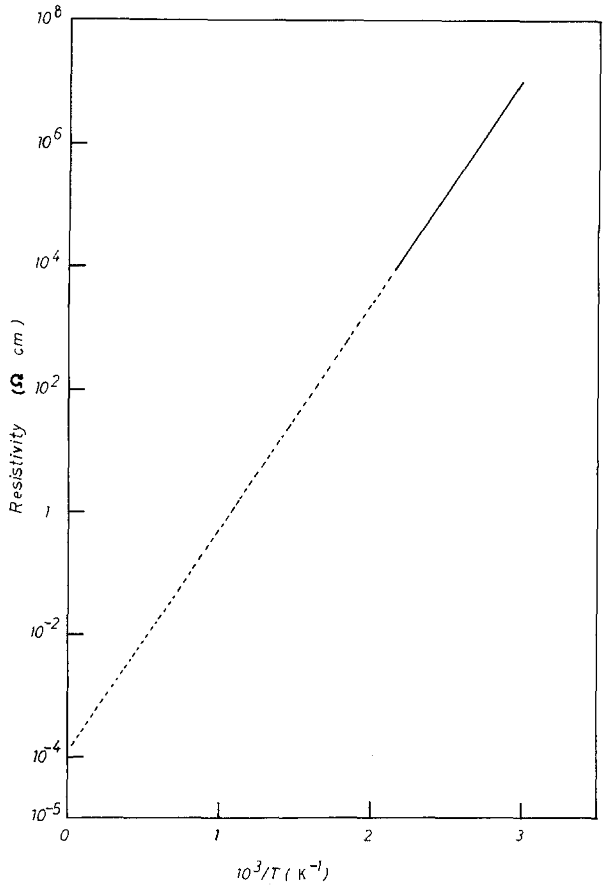

Figure 5 Extrapolation of the intrinsic conduction to $1/T = 0$ for the amorphous semiconductor Sb_2S_3.

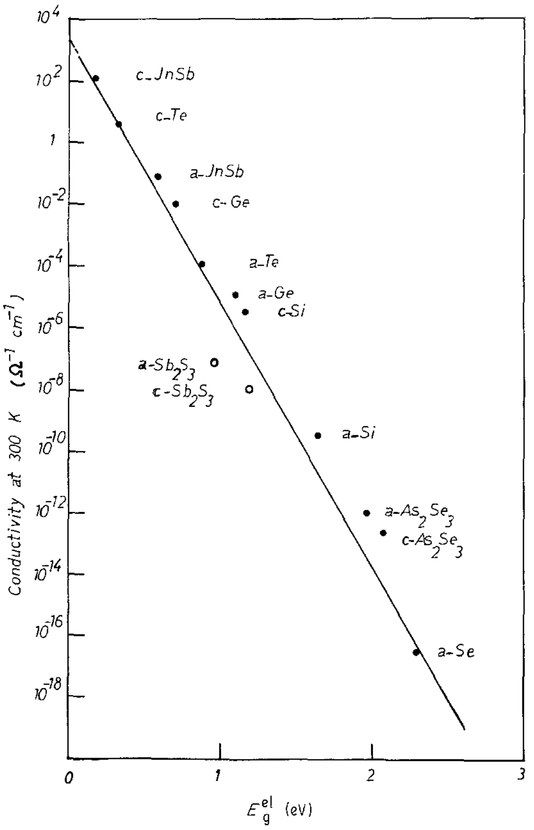

Figure 6 Relation between electrical conductivity at room temperature and electrical band gap for a number of semiconductors, a = amorphous, c = crystalline [18] (The corresponding values of antimony trisulphide are shown as depicted from the present work).

The relatively large distance between the absorption edge and electrical gap indicates that at the band edges of amorphous Sb_2S_3 a large number of energy states over a relatively broad energy range contribute only very weakly to conductivity. This feature can be understood by the well known model of Gubanov [11], Banyai [12] and Mott [13], that due to the disorder, the states near the band edges become localized, whereas only beyond a certain energy do they become non-localized or extended. The measured electrical band gap, therefore, is not a density of states gap as in crystals but is actually a mobility gap as has been pointed out by Cohen, Fritzsche and Ovshinsky [14].

The non-linearity of the resistivity curve in the $\log \varrho - (1/T)$ plot at low temperatures indicates that here the activation energy is not constant. It is thought worthwhile to test whether the cause of this finding could be the predominance of thermally activated hopping conduction in which case the mobility would behave following the relation [15]

$$\mu = A \exp(-B/T^{1/4})$$

where A and B are constants. The non-linearity can also be explained by a slow shift of the Fermi level with temperature due to a high density of localized states.

A significant feature of the intrinsic conduction of amorphous and also of crystalline Sb_2S_3 is that the extrapolation of all curves to $1/T = 0$ lead to approximately the same value of the resistivity, ϱ_0 here (Fig. 5). The value of ϱ_0 for other materials is also only slightly changed by the transition to the amorphous

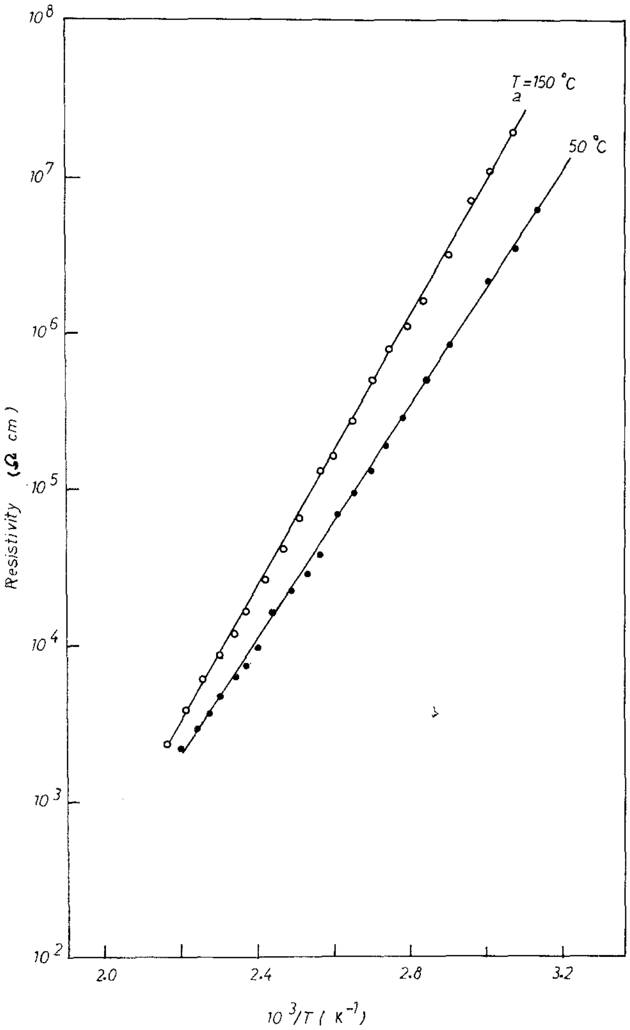

Figure 7 Temperature-dependence of the electrical resistivity of amorphous Sb_2S_3 films (310 nm) annealed for 1 h at 50 and 150° C.

phase [16]. A relation between the conductivity at a certain temperature (e.g. at room temperature) and the corresponding activation energy was found [17] for amorphous semiconductors. Fig. 6 shows such a relation, where each point corresponds to a temperature dependence of a certain material in the amorphous or in the crystalline state. Therefore, it seems to be a general rule that σ_0 for most amorphous semiconductors amounts to about 10^3–$10^4\,\Omega^{-1}\,\mathrm{cm}^{-1}$ and that it is only slightly changed in going to the crystalline state [18]. To explain this result we note that the value of σ_0 for crystals is essentially determined by the product of the effective density of states and the microscopic mobility. The small change of σ_0 at the transition to the amorphous state shows that this product is not strongly changed for the energy states at the mobility edge. Böer [19] has estimated that with a reasonable density of states the mobility here is about 50–$100\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{S}^{-1}$. This value is much larger than the value in the mobility gap [20]. Obviously here a serious problem exists, which for a more detailed understanding of the transport mechanism in amorphous semiconductors at the mobility edge probably is of great importance.

The as-deposited films were annealed inside the vacuum chamber at certain temperatures for 1 h and thereafter the annealed film was left to cool gradually to room temperature. The resistance of each film was then measured as a function of temperature. The temperature dependence of the resistivity of amorphous films of the same thickness (310 nm) annealed for 1 h at 50 and 150° C is shown in Fig. 7. On increasing the annealing temperature the resistivity increases, i.e. the conductivity reduces. By annealing not only the conductivity reduces, but the slope of the conduction is increased. Therefore, the mobility gap is appreciably enhanced by annealing. Possibly this interesting result can be interpreted by the assumption that the disappearance of a number of dangling bonds leads to a stronger distortion of most other bonds.

References

1. M. J. CHOCKALINGAM, K. NAGARAJA RAO, N. RANGARAN and C. V. SURYANARAYANA, *J. Phys. D.* **3** (1970) 1641.
2. A. A. MOSTAVSKII, L. G. TIMOFEEVA and O. A. TIMOFEEV, *Sov. Phys. Solid State* **6** (1964) 389.
3. T. BUDINAS, P. MACKUS, A. SMILGA and J. VISCAKAS, *Phys. Status Solidi* **31** (1969) 375.
4. E. MONTRIMAS and A. PAZERA, *Thin Solid Films* **34** (1976) 65.
5. J. P. MITCHELL and D. G. DENURE, *ibid.* **16** (1965) 285.
6. J. GEORGE and M. K. RADHAKRISHNAN, *Solid State Commun.* **33** (1980) 987.
7. R. H. BUBE, *J. Appl. Phys.* **31** (1960) 315.
8. J. DE KLERK and E. F. KELLY, *Rev. Sci. Instrum.* **36** (1965) 506.
9. C. GHOSH and B. B. VARMA, *Solid State Commun.* **31** (1979) 683.
10. N. F. MOTT, *Festkorperprobleme* **9** (1969) 22.
11. A. T. GUBANOV, "Quantum Electron Theory of Amorphous Semiconductors", Consultants Bureau, New York (1965).
12. L. BANYAI, "Physique des Semiconducteurs", Dunod, Paris (1964) p. 417.
13. N. F. MOTT, *Adv. Phys.* **16** (1967) 49.
14. M. H. COHEN, H. FRITZSCHE and S. R. OVSHINSKY, *Phys. Rev. Lett.* **22** (1969) 1065.
15. N. F. MOTT, *Phil. Mag.* **19** (1969) 835.
16. J. STUKE, in Proceedings of Conference on Low Mobility Semiconductors, Sheffield (1966) (unpublished).
17. H. FRITZSCHE, Lecture at Gordon Research Conference, "Electrons and Phonons in Disordered Systems, Meriden, NY (1968).
18. J. STUKE, *J. Non-cryst. Solids* **4** (1970) 1.
19. K. W. BOER, *Phys. Status Solidi* **34** (1969) 721.
20. M. H. COHEN, Lecture at Gordon Research Conference, "Electrons and Phonons in Disordered Systems", Meriden, NY (1968).

Received 22 September 1987
and accepted 28 April 1988