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RESEARCH PAPER

CONDUCTION MECHANISM IN AMORPHOUS As_2S_3

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ABSTRACT

The conduction mechanism in amorphous As_2S_3 has been studied by investigating the variation of the electrical resistivity over the temperature range 300 – 450 K. The electrical resistivity is characterised by a mobility gap of 2.15 eV over the temperature range investigated. The dc conductivity provides evidence of conduction by excitation of charge carriers into the band edges near the mobility edges. The results also give the possibility of conduction by a phonon-assisted hopping of polarons between localised states.

Keywords: *Amorphous semiconductor, hopping, mobility edge*

INTRODUCTION

Discovery and study of different chalcogenide materials, whose properties can be tailored, constitute the base of development of the solid state technology. Electronic conduction in amorphous solids has received considerable attention in recent years because of its importance in electronic devices (Anwar et. al., 2005). Arsenic sulphide, As_2S_3, and arsenic selenide, As_2Se_3, are typical representatives of chalcogenide glassy semiconductors, with a wide range of applications in optoelectronics, information storage and acoustic-optics (Seddon, 1977; Madan and Shaw, 1988; Popescu et al., 1996; Andriesh, 1998). Charge transport measurements in disordered semiconductors and insulators can provide information about the electronic structure of these materials. The disorder in the atomic configuration is thought to cause localised electronic states or groups of states within the material.

Amorphous semiconductors are materials with particularly low mobility. This feature certainly can be assigned to the lack of long-range order typical for these substances, but the details of the transport mechanism are not yet well understood. One reason for this state of knowledge is the difficulty in obtaining reliable information about the mobility for certain amorphous semiconductors. Measurements of Hall effect are not only experimentally difficult, but interpretation is problematic (Stuke, 1971). Another method of determining the mobility is the combination of thermoelectric power and conductivity measurements. This is better suited for

the type of determination of the type of carrier involved. First hand information on the mobility, however, is obtained by measurement of the drift mobility. Unfortunately, these are restricted to rather low conductivity values, and, therefore, such results exist only for a few amorphous materials and here also in a restricted temperature range. Moreover, the temperature dependence of the mobility obtained by this non-equilibrium method is strongly influenced by traps which are irrelevant for the equilibrium conductivity one is mostly interested in.

There have been two basic approaches towards an understanding of the electrical transport in non-crystalline systems. The first approach is appropriate for cases in which the mean free path between scattered events is large compared to the average interactomic spacing, first developed for the calculation of electrical conductivity of liquid crystals (Ziman, 1961, 1966). This approach, though successful for many liquid metals, breaks down in situations where the mean free path is short and appears inappropriate for amorphous and liquid semiconductors. Another approach, which has been used in calculating conduction via the random array of centres found in a heavily doped crystalline semiconductor (impurity conduction), starts with a localised description of the charge carriers. Transport between localised states occurs by a phonon-assisted tunnelling process and at the absolute zero, the conductivity is zero. A case intermediate between these two extremes is that of conduction in delocalised or extended states with a mean free path of the order of the average inter-atomic spacing (Davis, 1971).

The concept of localised states is used extensively for crystalline semiconductors in which impurity atoms and point defects give rise to localised levels or traps in the forbidden energy gap. What is less familiar is the concept of a continuous range of energies in which all electronic states are localised. Localisation can occur for a variety of reasons:

(i) Strong interaction between a carrier and a polar lattice can lead to localisation by polaron formation (Adler, 1971).

(ii)In molecular solids a similar localisation can be achieved by distortion of a molecule.

(iii) A third cause of localisation is disorder, the effects of which on the electronic states have been discussed by Anderson (1958) and Mott (1968, 1969, 1970). It is this type of localisation which seems most appropriate in amorphous and liquid semiconductors.

In this work, the resistivity variation with temperature over the temperature range 300-450 K for amorphous As_2S_3 has been investigated and the mode of conduction discussed. The mobility gap of the material has also been studied.

MATERIALS AND METHODS

The method of sample preparation is similar to that described in an earlier work (Nkum, 1999). Arsenic oxide, As_2O_3, of 99.99 % purity was dissolved in hydrochloric acid (with some heating). Hydrogen sulphide gas was passed through the solution and a yellowish precipitate of arsenic sulphide, As_2S_3, was formed. The precipitate was washed, filtered out and dried. 15 gm of the As_2S_3 thus prepared was put into a quartz vial, which was evacuated at a pressure of about 10^{-3} torr and sealed. The vial was placed in a furnace for 5 hr at 500 ^oC, and then at 600 ^oC for 3 h. At this temperature the vial was rotated continuously to ensure a good homogeneity of the melt. Quenching was done by immersing the vial in iced water. The sample formed could be identified as glass by a simple visual examination. This was confirmed by X-ray diffraction examination in which the diffraction pattern showed no lines.

A piece of the arsenic sulphide prepared as described above was cut off and shaped into a thin rectangular form of dimensions 1 mm x 1 mm x 6 mm. Four electrodes were made at the ends. Silver amalgam was used in making the

contacts to avoid polarisation.
A wheatstone bridge method is not suitable for determining high resistances as it becomes insensitive at high resistances. High resistances are determined either by methods of substitution provided other resistance of that order is available or by the method of leakage. The substitution method was applied in this experiment.

The resistance of amorphous As_2S_3 was found by measuring the voltage across the sample and the current through it. By adding a very high resistance (10^9 - 10^{13} Ω) of known value in series with the sample, the current (~ 10^{-9} A) could be found by measuring the voltage across the series resistance using a valve voltmeter. The voltage across the sample and the series resistance was measured with a vernier potentiometer.

RESULTS AND DISCUSSION

The temperature dependence of the electrical resistivity of amorphous As_2S_3 is demonstrated in Fig. 1. In order to interpret the electrical data obtained on the amorphous As_2S_3 sample, it is necessary to assume a model for the electronic density of states in amorphous semiconductors. Until now much contradiction exits about the fundamental question whether the salient characteristic of the band structure of crystalline solids, i.e. the sharp edges in the density of states forming the well-defined energy gap between valence and conduction bands, is also valid for the amorphous case. One of the current models of the band structure of disordered lattices assumes that, due to the absence of long -range order, there is a range of localised states at the extremities of the bands (Mott, 1969). The densities of localised states decrease gradually into the forbidden gap, destroying in this way the sharpness of the valence and conduction bands. Since these localised states have lower energies than the band states, carriers will tend to fall into them and become 'trapped'; the trapped carriers then cannot take part in conduction unless activated (thermally or optically) into the band states or unless they hop directly to neighbouring localised states (Owen, 1970; Nagel et al., 1974). Hopping of carriers in the localised states takes place at lower temperatures (Davis, 1971).

The semiconducting behaviour of the ρ-*T* curve of amorphous As_2S_3 follows the equation

$$\rho = \rho_o \exp\left[(T_o / T)^n\right]$$

where T_o and *n* are constants. The value of the exponent *n* determines the nature of the conduction mechanism in the semiconducting sample.

Over the temperature range 300 – 450 K, the resistivity of amorphous As_2S_3 is found to obey the semiconductor equation

$$\rho = \rho_o \exp(T_o / T) = \rho_o \exp(E_g / 2kT)$$

as demonstrated by the lnρ vs 1/*T* plot in Fig. 2, with $T_0 = Eg/2$. *Eg* is the mobility gap and has the same value (2.15 Ev) over the whole measured temperature range. This indicates that the conduction in amorphous As_2S_3 is intrinsic over the temperature range, and may therefore be assumed that the Fermi level is pinned very close to the middle of the forbidden gap. The resistivity due to excitation of carriers into the band states is described by the exponential temperature dependence (Davis, 1970) found also for amorphous As_2S_3. There is therefore evidence that conduction in amorphous As_2S_3 over the temperature range considered is due to excitation of charge carriers into the band edges.

The dynamical electron-phonon interactions in amorphous As_2S_3 cause the formation of polarons which once localised also contribute to conductivity by means of hopping between equivalent sites. The conductivity of such a hopping process is also described by the exponential temperature dependence observed experimentally for amorphous As_2S_3 (Adler, 1971). Thus conduction by a phonon assisted hopping of polarons may also be possible in amorphous As_2S_3. It is reasonable, therefore,

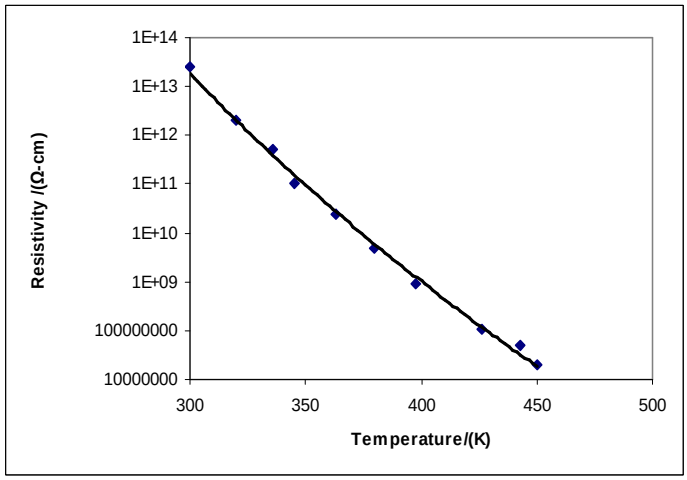


Fig. 1 : Temperature dependence of resistivity for amorphous As_2S_3

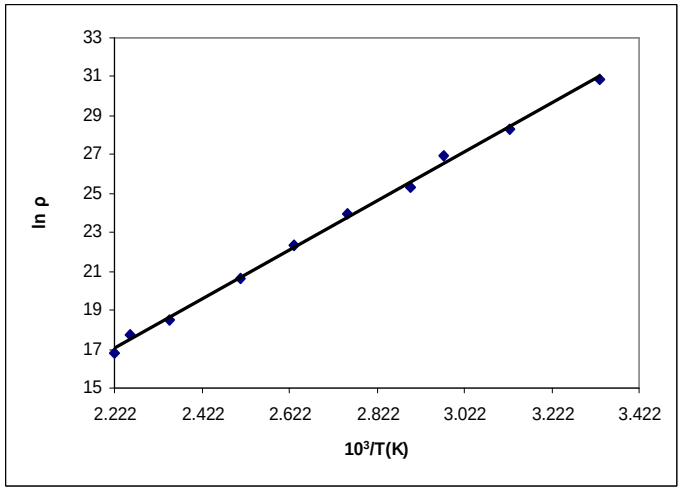


Fig. 2 : lnρ as a function of reciprocal temperature for amorphous As_2S_3

to suppose that the conductivity in amorphous As_2S_3 results from a combination of excitation of carriers into the band edges and phonon assisted hopping of polarons in the localised states.

According to Mott (1986d)

$$\rho_o = \frac{hl}{2\pi Ae^2}$$

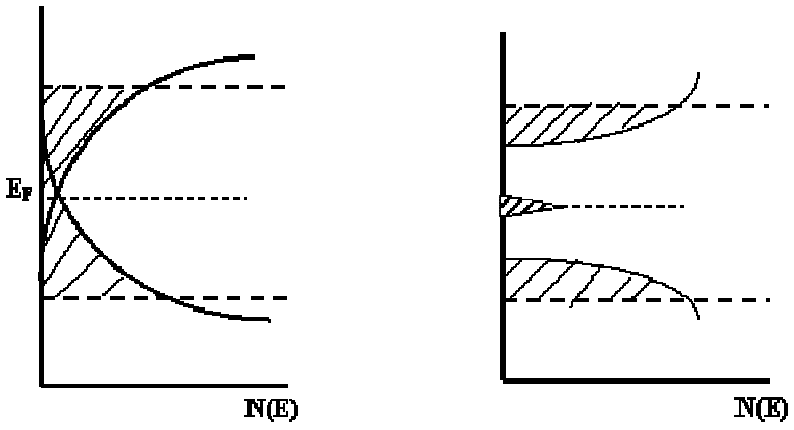
where l is the inelastic diffusion/localisation length, and A is a constant of the order of 0.1. From Fig. 2, ρ_o = 2.89 x 10^{-5} Ω cm. Thus the value of l is 0.07 Å. This value is quite small compared to the value of the diffusion/ localisation lengths obtained for other non-crystalline materials (Nkum and Datars, 1992; Nkum, 1994). It has been observed by Nkum

(1994) that the localisation length of non-crystalline solids decreases with increasing amount of impurity.

It appears that disorder leads to some tailing of the bands into the forbidden gap. Opinions vary as to the extent of this tailing. Cohen et al. (1969) have proposed a model for multicomponent systems in which the valence and conduction bands overlap in the middle of the gap (Fig. 3a). A nice feature of this model is that it ensures self compensation and a Fermi level pinned close to the centre of the gap. David and Mott (1970) have suggested a much smaller degree of tailing and proposed the existence of a 'defect' band, near the gap centre (Fig. 3b). Both models, however, use the concept of localised states in the band tails leading to the existence of mobility edges.

Amorphous As_2S_3 is found to be so resistive (resistivity at 300 K ~ 10^{11} Ωm) that measurements are only possible over a limited range of high temperature. Similar observations have been made by Owen (1970) for amorphous As_2Se_3 and some sulphide glasses. The high resistivities of sulphide glasses may be attributable to the very low electronic mobilities of sulphur group glass formers such as arsenic sulphide, germanium sulphide, and phosphorous sulphide. It may therefore be possible to obtain ion conducting chalcogenide glasses in systems in which ionisable elements combine with the sulphur glass formers. In fact, sulphide glasses exhibiting predominantly ionic conduction have been found by Plumat (1968) in the systems GeS_2-Na_2S and others by Kawamoto et al (1974, 1976) in the systems As-S-Ag, Ge-S-Ag and P-S-Ag.

The mobility gap is found to be 2.15 eV. This value agrees quite well with the range of values 2.1 eV to 2.3 eV found by Owen (1970). The mobility gap is less than the optical energy gap of 2.4 eV and 2.36 eV observed by some workers (Kolomiets, et al., 1972; Tauc and Menth, 1972). This is possibly due to the fact the mobility rises abruptly in a region of energy where



(a) (b)

Fig. 3: (a) Density of states in multicomponent glasses according to Cohen et al. (1969), (b) density of states according to Davis and Mott (1970). The ordinate in all cases is electron energy.

the states are not completely delocalised, whereas the optical absorption occurs between delocalised bands (Weiser, 1969).

CONCLUSION

The electrical resistivity of bulk glassy As_2S_3 has been found be characterised by a single activation energy, E_a, equal to 1.08 eV ($E_a = E_g/2$) over the temperature range 300 – 450 K. The dc conductivity provides evidence of conduction by excitation of charge carriers into the band states near the mobility edges and conduction by a phonon assisted hopping of polarons. It is reasonable, therefore, to suppose that the conductivity in amorphous As_2S_3 results from a combination of excitation of carriers into the band edges and phonon assisted hopping of polarons in the localised states.

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