PHYSICAL REVIEW B VOLUME 17, NUMBER 10 15 MAY 1978

Percolation-controlled conduction in chalcogenide glass semiconductors

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(Received 1 December 1977)

The applicability of effective-medium percolation theory (EMPT) to the composition dependence of the electrical conductivity is discussed for binary and multicomponent chalcogenide glasses. Calculations assuming a random mixture of atoms, which are applied to explain the experiment for As-Te films by Ast, do not agree with experiments on all the systems considered. By assuming a strong chemical ordering which forms microscopic molecular species, the conductivity over the measured compositional range can be well described with EMPT in the As-Se, As-S, and As_2Se_3-Sb_2Se_3 systems, except for Te-Se, As_2Se_3-As_2Te_3, and $As_2S_{2.63}$-Te which contain the isomorphous Te, Se, and S atoms. Chalcogenide glasses can be classified roughly into three groups: a "random mixture of atoms" type, a "strong chemical ordering" type, and an "isomorphous-atom" type. It is suggested that EMPT has broad application in structural studies of chalcogenide glasses.

I. INTRODUCTION

The influence of inhomogeneities on amorphous semiconductors has been the subject of a variety of recent papers. In a number of cases the effect of inhomogeneities on electronic transport is treated in terms of percolation treatment using the classical approach[1-5] or computer simulations.[6-8] For example, dc hopping conductivity (Mott relation) in group-IV amorphous-semiconductor films was interpreted very well in terms of percolation treatment.[9,10]

Recently, Ast[11] has discussed the compositional dependence of the electrical conductivity for As_xTe_{1-x} films in terms of effective-medium percolation theory (EMPT). He obtained close agreement between experiment and calculation by assuming a random mixture of As and Te atoms. EMPT calculates the conductivity of a random mixture of particles of two different conductivities under the assumption that the inhomogeneous surroundings of a particle can be replaced by an effective medium. It coincides with the solutions for the bond-percolation problem computed by a Monte Carlo sampling of a disordered resistor network, except in the vicinity of the percolation threshold, while its deviation is a few percent.[7] It is not clear whether EMPT is applicable to interpret the compositional dependence of the electrical conductivity in many other chalcogenide glasses. To our knowledge this problem has not yet been treated.

In this paper the applicability of EMPT to the composition dependence of the conductivity is discussed in binary (As-Se, As-S, and Te-Se) and multicomponent (As_2Se_3-Sb_2Se_3, As_2Se_3-As_2Te_3, and $As_2S_{2.63}$-Te) chalcogenide glasses prepared by quenching the melt. Calculations assuming a random mixture of atoms, in the same way as in Ast's work, disagree with the experiments for all the systems considered here. By assuming a strong chemical ordering which forms the microscopic molecular species, the conductivity compositional dependence is well explained by EMPT in the As-Se, As-S, and As_2Se_3-Sb_2Se_3 systems except for Te-Se, As_2Se_3-As_2Te_3, and $As_2S_{2.63}$-Te which contain the isomorphous Te, Se, and S atoms.

Results suggest that chalcogenide glasses are classified roughly into three groups by EMPT. The first is of a "random mixture of atoms" type, the second is of a "strong chemical ordering" type, and the third is of an "isomorphous-atom" type which is not explained by EMPT. These are discussed in Sec. III. EMPT can be applied to structural studies of binary or multicomponent chalcogenide-glass systems.

II. CALCULATION FOR EMPT

We consider an infinite regular lattice. The average effect of the random resistivities ρ_i is expressed by giving all of them a single value ρ_m which is then equal to the resistivity of the network. For a binary distribution of ρ_i, the effective resistivity ρ_m in the system is expressed by two different resistivities ρ_1 and ρ_2,[7]

$$\rho_m = \frac{4\rho_1\rho_2}{\rho_1(3X_2-1)+\rho_2(3X_1-1)+\{[\rho_1(3X_2-1)+\rho_2(3X_1-1)]^2+8\rho_1\rho_2\}^{1/2}}\,, \qquad (1)$$

where X_1 and X_2 are the volume fractions of the components. The expression is independent of particle size and shape. The conversion from volume fraction X to atomic composition (at. %) was made by using atomic or molecular weights and specific densities for the system considered.

III. RESULTS AND DISCUSSION

Figure 1 shows the compositional dependence of the resistivity of melt-quenched As_xSe_{1-x}, with data from Arai *et al.*[12] and Minami *et al.*[13] The resistivity ρ exhibits a minimum at 40-at.%-As As_2Se_3. At this composition the mobility gap is the smallest. As_2Se_3 is a relatively-well-ordered amorphous material[14] and the increase in disorder on deviating from 40-at.% As is revealed in the measurements of the density and compressibility.[12] Hurst and Davis[14] suggested that the increase in disorder tends to push the mobility edge further into the bands.

Now we use EMPT to interpret the resistivity compositional dependence in chalcogenide glasses as pointed out by Ast.[11] The resistivity and specific density used for the calculations are tabulated in Table I, in which plausible values of the specific density are adopted in measurements or empirical relations.[15] Curve (a) denoted by the dot-dashed line in Fig. 1 represents the EMPT result, assuming a random mixture of As and Se in the same manner as in Ast's work. The result does not agree with the experiment, suggesting that the assumption of a random mixture of As and Se is not applicable.

There is evidence that the structure of the amorphous As-Se system is regarded as a mixture of Se and As_2Se_3.[16,17] Assuming that the addition of As to Se forms a microscopic molecular As_2Se_3 species in Se and that the volume fraction of the As_2Se_3 species increases linearly with increasing As content, one can treat the As_xSe_{1-x} ($x < 0.4$) as a mixture of As_2Se_3 and Se species in the EMPT calculation. A well-ordered amorphous As_2Se_3 is obtained by addition of 40-at.% As to Se. It is further assumed that the addition of excess As to As_2Se_3 ($x > 0.4$) leads to the formation of a small amount of a molecular species such as realgar As_4Se_4.[16] It can be regarded as mixture of As_2Se_3 and As_4Se_4 in the As-rich region ($x > 0.4$).

TABLE I. Resistivities at room temperature and specific densities in materials used for the calculations.

Materials	Resistivity at room temperature (Ω cm)	Specific density (g cm^{-3})
As	4.0×10^6	5.7
Se	2.5×10^{15}	4.0
As_2Se_3	1.0×10^{12}	5.0
As_4Se_4	1.0×10^{13}	5.0
S	3.0×10^{15}	2.1
As_2S_3	9.0×10^{16}	3.2
Sb_2Se_3	3.0×10^8	7.0
As_2Te_3	3.0×10^3	5.4
Te_1Se_1	1.0×10^6	5.3
$As_2S_{2.63}$	8.0×10^{16}	3.4

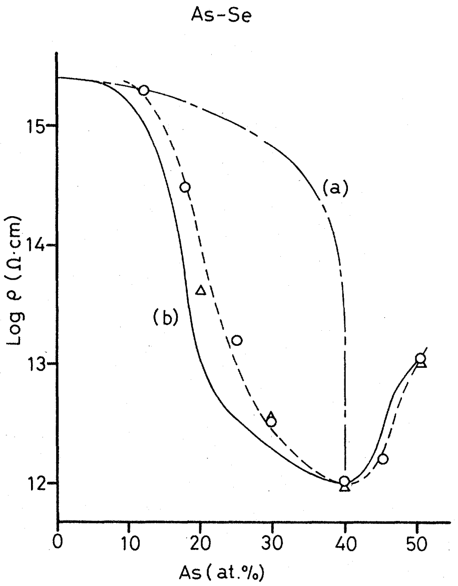

FIG. 1. Variation of the room-temperature resistivity in the As-Se system. Data from: ○, Arai *et al.* (Ref. 12); △, Minami *et al.* (Ref. 13).

Curve (b), the solid line, represents the calculated EMPT result based on the above assumptions. Close agreement with measurement was obtained in contrast to the result obtained by adopting the assumption of a random atomistic mixture of As and Se. It is suggested that the resistivity at certain As_xSe_{1-x} compositions is determined *a priori* by the resistivities of the Se, As_2Se_3, and As_4Se_4 species.

The compositional dependence of the resistivity of the melt-quenched As_xS_{1-x} system is shown in Fig. 2, with data from Minami *et al.*[13] At stoichiometric composition (40-at.% As) the resistivity exhibits a maximum contrary to what happens with the As-Se system. It is not possible to prepare the glassy As-S with more than 43-at.% As by the melt-quenched method.[16] As_4S_4 is only prepared by evaporation onto a low-temperature substrate.[18] Assuming a random mixture of As and S, the calculated resistivity decreases as the As content increases (not shown in Fig. 2), while the measured resistivity increases with increasing As content.

The solid line in Fig. 2 shows the result of the

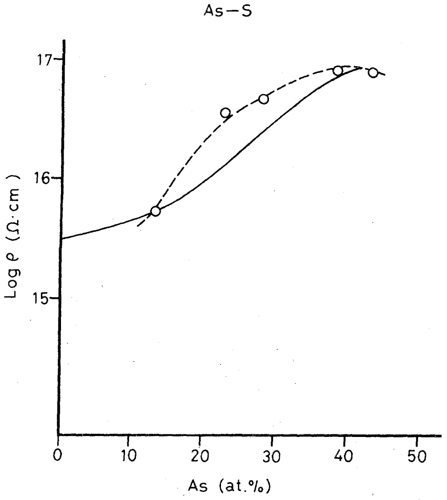

FIG. 2. Variation of the room-temperature resistivity in the As-S system, with data from Minami *et al.* (Ref. 13).

EMPT calculation. We also assumed that As-S is formed by a random mixture of S and the As_2S_3 molecular species[16] as assumed for the As-Se system. Agreement between calculation and experiment is not as good as for the As-Se system. It is known[19,20] that As_2S_3 prepared by quenching the melt contains a certain amount of the realgar As_4S_4 species and a certain concentration of As-As bonds, suggesting that a random mixture of As_2S_3 and S is not so good an assumption for the As-S system. The difference between As-Se and As-S has also been observed in the behavior of the glass-transition temperature.[16]

Next we consider the compositional dependence of the resistivity in multicomponent glasses such as As_2Se_3-Sb_2Se_3 and As_2Se_3-As_2Te_3. These are shown in Figs. 3 and 4, respectively. A value of $x \simeq 0.5$ is the limit of glass formation by quenching the melt in the $(Sb_2Se_3)_x(As_2Se_3)_{1-x}$ system. The resistivity decreases as the molecular content of Sb_2Se_3 increases, as shown in Fig. 3, with data from Platakis *et al.*[21] The solid line in Fig. 3 shows the result obtained by assuming a random mixture of As_2Se_3 and Sb_2Se_3 microscopic molecular species. It almost coincides with the experiment, suggesting that microscopic clusters of As_2Se_3 and Sb_2Se_3 are formed in the As_2Se_3-Sb_2Se_3 system, while a microscopic inhomogeneity such as phase separation has not been observed.[21] Electrical conduction in this system can be controlled by the percolation process in mixtures of As_2Se_3 and Sb_2Se_3 microscopic species.

Contrary to the As_2Se_3-Sb_2Se_3 system, the measured resistivity of As_2Se_3-As_2Te_3 is monotonically decreasing with increasing As_2Te_3 molecular content, as shown in Fig. 4 with data from Vengel *et al.*[22] The percolation threshold predicted by EMPT is not found in this system, as described by the solid line in Fig. 4, where we also assumed a random mixture of As_2Se_3 and As_2Te_3 molecules. The cause of the disagreement between experiment and calculation can be explained in two ways: (i)

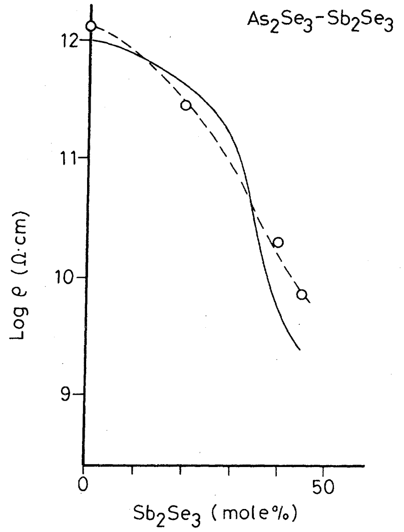

FIG. 3. Variation of the room-temperature resistivity in the As_2Se_3-Sb_2Se_3 system, with data from Platakis *et al.* (Ref. 21). A $x \simeq 0.5$ value is the limit for glass formation in the $(Sb_2Se_3)_x(As_2Se_3)_{1-x}$ system.

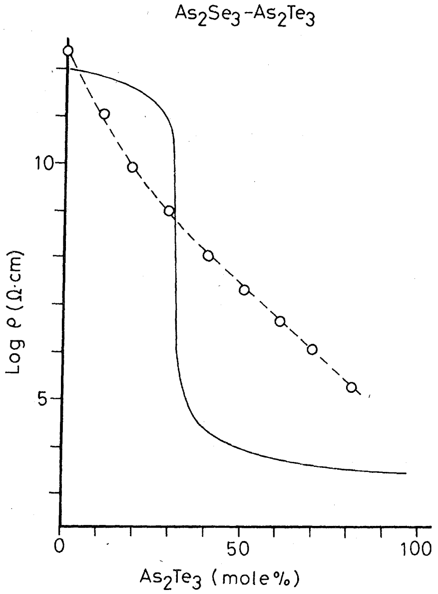

FIG. 4. Variation of the room-temperature resistivity in the As_2Se_3-As_2Te_3 system, with data from Vengel and Kolomiets (Ref. 22).

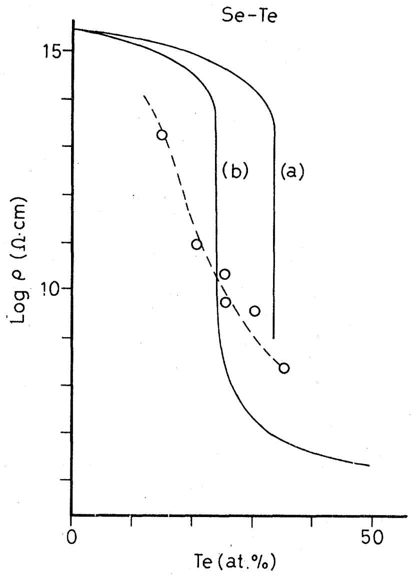

FIG. 5. Variation of the room-temperature resistivity in the Te-Se system. A value of $x \simeq 0.35$ is the limit of glass formation in the Te_xSe_{1-x} system.

The system does not exhibit any tendency to chemical ordering which causes microscopic clusters of As_2Se_3 and As_2Te_3 to form, or (ii) Another kind of microscopic clusters except for As_2Se_3 and As_2Te_3 are formed with a different composition. It is probable that Te replaces Se isomorphously, leading to no significant short-range structural change.[18] Therefore case (i) is acceptable to interpret the situation for the As_2Se_3-As_2Te_3 system.

To clarify the behavior of isomorphous Se and Te, let us consider the binary Se-Te system as shown in Fig. 5. The excess addition of 35-at.% Te to Se brings one out of the glass-forming region, in this system. The measured resistivity decreases rapidly by increasing the Te content rather than that of As_2Se_3-As_2Te_3. Curves (a) and (b), the solid lines in Fig. 5, show the calculations based on the assumption of a random mixture of Se and Te, and Se and $Te_{0.5}Se_{0.5}$, respectively. Furthermore, various arrangements, for example a random mixture of Se and $Te_{0.35}Se_{0.65}$, were considered (not shown in Fig. 5) in the Te-Se system. Calculations do not agree with experiment.

The structure of the Te-Se system prepared by quenching the melt is regarded as a mixture of Se_8 rings, Se_6Te_2 mixed rings, and Te-Se copolymer chains.[18,23,24] Se_8 rings decrease with increasing Te content and simultaneously both mixed rings and copolymer chains increase in the Te-Se system.[24] This situation may correspond to case (ii). Thus we cannot get a good solution which fits the experiments.

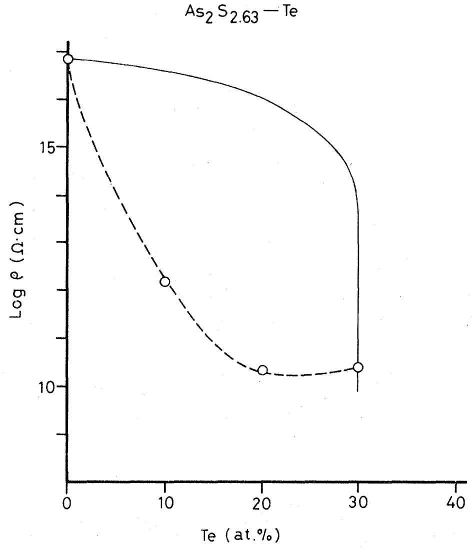

FIG. 6. Variation of the room-temperature resistivity in the $As_2S_{2.63}$-Te system, with data from Minami *et al.* (Ref. 25).

Figure 6 shows the compositional dependence of the resistivity in the $As_2S_{2.63}$-Te system, with data from Minami *et al.*[25] This system is similar to As_2Se_3-As_2Te_3. Here we assume only a random mixture of $As_2S_{2.63}$ and Te species. Calculations predict the sharp decrease of the resistivity at 30-at.% Te as described by the solid line. However, experimental results do not correspond to the prediction of the calculations. Probably Te replaces S isomorphously, as for As_2Se_3-As_2Te_3, leading to no significant microscopic structural change in this system.

IV. SUMMARY

The applicability of the effective-medium percolation theory to the composition dependence of the resistivity was discussed for melt-quenched chalcogenide glasses. The following results and conclusions were obtained.

(a) Calculations assuming a random mixture of atoms, which have been applied to explain the experiments for an As-Te film, did not agree with experiment for all the systems considered here.

(b) By assuming a strong chemical ordering which forms microscopic molecular species, agreement between calculation and experiment was obtained in the As-Se, As-S, and As_2Se_3-Sb_2Se_3 systems. The existence of microscopic inhomogeneity has been supported by various structural studies. In contrast to these systems, agreement between calculation and experiment was not obtained for As_2Se_3-As_2Te_3, Te-Se, and $As_2S_{2.63}$-Te. These systems always contain the isomorphous Te, Se, and S atoms. The disagreement was interpreted as follows: the systems exhibit few tendencies to chemical ordering, or the kinds of microscopic clusters vary with composition.

(c) The chalcogenide glasses considered in the present study can be classified into three groups in terms of EMPT: a "random mixture of atoms" type such as the As-Te film, a "strong chemical ordering" type such as As-Se, As-S, and As_2Se_3-Sb_2Se_3, and an "isomorphous-atom" type such as Se-Te, As_2Se_3-As_2Te_3, and $As_2S_{2.63}$-Te.

EMPT found broad application to describe the electrical conductivity in chalcogenide glasses. Further, it is applicable to study the structure of chalcogenide glasses.

ACKNOWLEDGMENTS

The authors wish to thank H. Yokoe for his help with the calculations. We also wish to thank Professor S. Uchida, Professor Y. Inagaki, Professor T. Arizumi, Dr. A. Yoshida, and Professor K. Morigaki for their encouragement.

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