from curve 1 of Fig. 2.

[13] From this point of view the linewidth broadening could also be treated as an unresolved Davydov splitting.

[14] This behavior of the linewidth is not directly related to the more common effect of exchange narrowing of magnetic resonance spectra for several reasons, the foremost being the absence of another large interaction that exchange can average out or narrow.

[15] K. A. Wickersheim, Phys. Rev. 122, 1376 (1961); R. S. Meltzer and H. W. Moos, Phys. Rev. B 6, 264 (1972).

Evidence for Percolation-Controlled Conductivity in Amorphous As_xTe_{1-x} Films

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The compositional dependence of the dc conductivity of As_xTe_{1-x} films with $0.3<x<0.78$ was measured. The resistivity over the entire compositional range investigated could be described with an effective-medium percolation theory. No adjustable parameters enter into this first analytical description of the compositional variation of a transport property in an amorphous multicomponent semiconductor.

Over the last decade, the electronic transport properties of amorphous semiconducting chalcogenides have been studied extensively. However, in spite of measurements of dc and ac conductivity, thermopower, Hall coefficient, photoconductivity, and high-field conductivity over a wide temperature range, no agreement exists on the theoretical description of the conduction process. In respect to As-Te based glasses, a controversy has recently developed between the Cohen, Fritzsche, and Ovshinsky (CFO)[1] model on the one hand and the small-polaron model[2] on the other. This paper reports the results of a study of the compositional dependence of the dc conductivity of As_xTe_{1-x}. The choice of this system was based on the following considerations: Relative to other arsenic chalcogenides,[3,4] As_xTe_{1-x} exhibits few tendencies for chemical ordering since like bonds (As-As, Te-Te) and unlike bonds (As-Te) have similar bond energies[5]; absence of short-range order is also indicated by thermodynamic data on liquid As_2Te_3,[6] and by the smooth monotonic compositional variation of both the glass transition temperature[7,8] and the nearest-neighbor separation[9]; and finally, the electrical conductivities of the pure components differ by 3 orders of magnitude, which, as discussed by Landauer,[10] allows sensitive tests of various possible mathematical descriptions of the compositional dependence of the conductivity.

Generally, an evaporated specimen has a more random structure than a quenched one, since the latter retains the short-range order of the liquid. Because of this and the reported difficulties in quenching As_xTe_{1-x},[9] steady-state sublimation of As_2Te_3 was chosen to prepare the samples. Small changes in the substrate temperature were used to vary the composition which in each case was analyzed with an electron microprobe. More details are reported elsewhere.[11]

In order to check for the absence of contact and layering effects, specimens with two and four coplanar electrodes, as well as with sandwich configurations, were evaporated onto one and the same wafer. In almost all evaporation runs, the resistivity computed from devices of various geometries agreed within the experimental error of 15% in determining dimension and resistance. Wafers containing specimens outside this range were discarded. The conductivity σ was found to be independent of thickness, which together with the absence of contact effects indicated that true bulk resistivities were measured.

Most specimens showed a slight curvature in the $\ln\sigma$ versus $1/T$ plot. The room-temperature activation energy varied approximately linearly with composition and ranged from about 0.38 eV (30 at.% As) to 0.48 eV (80 at.% As). These values are about 0.03 eV lower than those reported for bulk specimens in this composition range.[12] In the so-called Stuke plot,[13] the specimens fell within the experimental scatter on the line measured for quenched As-Te-I specimens (Quinn and Johnson[14]). The room-temperature resistivity —on a *linear* scale— as a function of composition is shown in Fig. 1. The open circles denote experimental results. The dotted lines represent calculations based on effective-medium

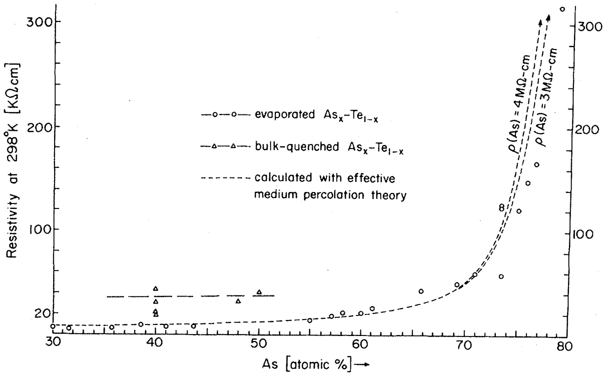

FIG. 1. Dc resistivity of evaporated $As_x Te_{1-x}$ as a function of composition.

percolation theory (EMPT).

In its original form, EMPT considers the overall conductivity of a random mixture of particles of two different conductivities under the assumption that the inhomogenous surroundings of a particle can be replaced by an effective medium.[10,15] An originally unrelated problem, the flow of a fluid through a porous medium, was first considered by Broadbent and Hammersley,[16] who introduced a lattice-percolation model in which the fluid was assumed to flow through randomly arranged bonds connecting nearest neighbors in a regular lattice of sites. In the so-called bond- or site-percolation problem, a fraction of these bonds or sites is assumed to be blocking. It can be shown rigorously that no fluid will flow through the network unless a minimum, nonzero, critical fraction x_c of conducting bonds or sites is present. Above x_c, the percolation threshold, the conductivity increases rapidly.

Kirkpatrick[17] demonstrated by means of computer calculations that EMPT provides an extremely accurate solution to the bond-percolation problem, except in the vicinity of the percolation threshold, where it deviates by a few percent. If the blocking bonds are correlated the deviation in the vicinity of the percolation threshold increases somewhat, but otherwise EMPT still applies. EMPT gives the following expression for the effective resistance ρ_m of a random mixture of particles of two different resistivities ρ_1 and ρ_2:

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

where X_1 is the volume fraction of component 1 and X_2 is the volume fraction of component 2. The expression is independent of particle size.

For X_1 or $X_2 = 1$, the above expression reduces to the resistivity of the individual component which, in this case, is the resistivity of amorphous Te or As. These resistivities are known and hence Eq. (1) can be used to predict the compositional dependence over the entire range between As and Te. The resistivities of evaporated amorphous elements depend somewhat on the annealing state of the material, and this fact was taken into account in the numerical calculation displayed in Fig. 1.

Amorphous Te films, at about room temperature, are fully annealed. The resistivity is then 5.1 kΩ cm and the activation energy of conduction is 0.435 eV.[18] Evaporated As films are characterized by room-temperature resistivities between 3.6 and 4.2 MΩ cm and activation energies of 0.57–0.60 eV.[19] The conversion between volume fraction—the parameter used in Eq. (1) —and composition was made by taking into account the specific densities and the atomic weights of Te and As.

A comparison of the prediction of EMPT and the experimental results shows excellent agreement in the frame of the experimental uncertainties (see Fig. 1). (The reader should remember that the accuracy of the composition determination of the films is at best ±2% and that this leads to more obvious scatter in the steeper regions of the curve.) The agreement can be interpreted in two ways: (1) The system is phase separated into randomly arranged amorphous As and Te clusters, or (2) the system is an atomistic mixture of As and Te atoms in which a bond-percolation process controls the conductivity. The following points can be made against the first interpretation: (a) Lack of driving forces for primary and secondary phase separation as discussed by de-Neufville.[20] (b) Lack of electron-microscopic evidence for phase separation.[21] (c) The smooth compositional dependence of T_g.[7,8] (A phase separated system would tend to exhibit two T_g's, at fixed temperature locations but of various relative magnitude.) (d) In annealing experiments, crystalline Te is formed in Te-rich As_xTe_{1-x} at surprisingly high temperatures (143°C for As_{30}-

Te_{70}) which vary strongly with composition.[9] Both effects, in our opinion, argue against the existence of separate amorphous Te clusters. (e) Raman scattering from evaporated As_xTe_{1-x} films indicates a distribution of As-As, As-Te, and Te-Te bonds compatible with a random network, rather than the relative scarcity of As-Te and the preponderance of As-As and Te-Te which one would associate with a phase-separated system.[22] (f) The compositional dependence of the apparent activation energy does not agree with a phase-separated model. The last point deserves elaboration.

If one writes the resistivities ρ_1 and ρ_2 in Eq. (1) as thermally activated resistivities and calculates with numerical methods the apparent activation energy of the system, one finds that these calculated values vary for As $\lesssim 60$ at.% more slowly and for As $\gtrsim 65$ at.% more rapidly with composition than observed.[23] The deviations are not large (about 0.03 eV) but appear to be outside the experimental scatter. The discrepancy is indicative of bond percolation since, while EMPT adequately describes the resistivity of a bond-percolation model, it is not expected to give a correct account of the apparent activation energy.[24] The sign and magnitude of the slight curvature in the experimental $\ln\sigma$ versus $1/T$ plots, on the other hand, are compatible with the predictions of EMPT. Clarification of this point requires detailed percolation calculations not currently available.

Points (a) through (f) argue against phase separation and favor the explanation that the conductivity in amorphous As_xTe_{1-x} is controlled by a bond-percolation process. The latter is not necessarily restricted to a nearest-neighbor model, since percolation thresholds also occur in systems where sites several lattice constants apart are considered to be connected. The results obtained on correlated-bond models[17] indicate that details of the bond topology play a significant role only in the vicinity of the percolation threshold. For this reason, one expects that Eq. (1) will still provide a good approximate solution to a more complex bond-percolation problem with the possible exception of the vicinity of the percolation threshold. There are indications of some deviations in the vicinity of the percolation threshold (see Fig. 1), but the precision of the data is insufficient to permit any firm conclusions.

As in the case of other phenomenological theories, the physical nature underlying the conduction process is difficult to deduce from EMPT. It is obvious, however, that amorphous chalcogenides cannot be treated as homogenous conductors on the scale on which conduction takes place. For this reason it appears difficult to reconcile the present results with conduction in extended states as envisioned in the original CFO model.[1]

The question whether an amorphous material is homogenous or inhomogenous on a microscopic scale is a fundamental one since it frequently enters into the analysis of transport measurements. The question was first raised by Fritzsche,[25] who proposed that chalcogenides were electronically diphasic and divided into random regions of electron and hole traps. In the region of the mobility edge, the regions are assumed to be in the order of the screening length or about 150 Å.

From the viewpoint of percolation theory, Fritzsche's model contains several attractive features, but the scale over which the inhomogeneities occur, ~150 Å, seems incompatible with the present results. If phase separation is absent, the local chemical composition must fluctuate on the scale of a few angstroms and the conduction process must sample these fluctuations. For this reason, it appears difficult to tie the above-mentioned regions in a systematic way to composition unless an impurity concentration is linearly related to one component. Hopping, including variable-range hopping, corresponds to a bond-percolation model in which the conductivity σ_i of an individual link depends on the site energy E_i and distance d_i. If the spread of the conductances is sufficiently large (a condition frequently fulfilled since σ_i usually is assumed to depend exponentially on E_i and d_i), it can be shown that the system behavior is similar to the single-value bond-percolation model discussed before.[26] For As_xTe_{1-x}, variable-range hopping between localized states has been proposed by Weiser, Grant, and Moustakas,[27] who, from high-field measurements, derive a hopping distance of about 100 Å. From this they deduce that potential fluctuations, as well as structural disorder, occur over comparable distances; a conclusion which, for the same reasons as discussed before, makes it very difficult to link the conductivity in a systematic way to the chemical composition.

The small-polaron model[2] assumes that the hopping carrier deforms its local environment sufficiently to become self-trapped. Of the proposed conduction mechanisms, the small-polaron model is the only one which involves hopping on an atomic scale, i.e., the scale over which the chemical composition is likely to fluctuate. The present results can be understood with small-polaron theory under the assumption that the small polaron is associated with selected bonds. This idea of a "dominant constituent" is supported by other observations on As-Te-containing glasses.[14] Further strong experimental evidence supporting the small-polaron model has recently been reviewed.[2] Computer calculations analogous to those for Fermi-level hopping[26] but based on the exact jump-rate calculations of Emin[28] are needed urgently to establish the model further and to understand the observed compositional variation of the activation energy.

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[1] M. H. Cohen, H. Fritzsche, and S. R. Ovshinsky, Phys. Rev. Lett. 22, 1065 (1969).

[2] C. H. Saeger, D. Emin, and R. K. Quinn, Phys. Rev. B 8, 4746 (1973).

[3] A. J. Leadbetter and A. J. Apling, J. Non-Cryst. Solids 15, 250 (1974).

[4] M. D. Rechtin, A. L. Renninger, and B. L. Averbach, J. Non-Cryst. Solids 15, 74 (1974).

[5] L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, N. Y., 1961), 3rd ed.

[6] M. B. Myers and E. J. Felty, J. Electron. Chem. Soc. 117, 819 (1970).

[7] J. P. deNeufville, J. Non-Cryst. Solids 8–10, 85 (1972).

[8] J. A. Savage, J. Non-Cryst. Solids 11, 121 (1972).

[9] J. Cornet and D. Rossier, Appl. Phys. Lett. 20, 304 (1972).

[10] R. Landauer, J. Appl. Phys. 23, 779 (1952).

[11] D. G. Ast, Mater. Res. Bull. 8, 1443 (1973).

[12] For a recent summary of these data see D. G. Ast, J. Vac. Sci. Technol. 10, 748 (1973).

[13] J. Stuke, J. Non-Cryst. Solids 4, 1 (1970).

[14] R. K. Quinn and R. T. Johnson, J. Non-Cryst. Solids 7, 53 (1972).

[15] D. A. Bruggeman, Ann. Phys. (Leipzig) 24, 636 (1935).

[16] S. R. Broadbent and J. M. Hammersley, Proc. Cambridge Phil. Soc. 53, 629 (1957).

[17] S. Kirkpatrick, Rev. Mod. Phys. 45, 574 (1973).

[18] These values have been deduced from Fig. 14 in Ref. 13.

[19] According to T. S. Moss, *Photoconductivity in the Elements* (Butterworths, London, 1952), p. 166, the resistivity of amorphous As at 40°C is 10^6 Ω cm. From his measured activation energies (0.57–0.605 eV) follows a room-temperature resistivity of between (3.6 and 3.92) × 10^6 Ω cm.

[20] J. P. deNeufville, Final Technical Report, Contract DA HC 15-70-c-0187, prepared by Energy Conversion Devices, Inc., for the Advanced Research Projects Agency (Order No. 1570; Program Code 0D10) (unpublished), p. 14 ff.

[21] D. G. Ast, unpublished.

[22] J. Smith, private communication.

[23] The compositional dependence of the apparent activation energy can be accounted for by EMPT if the actual temperature of the system is replaced by a fictitious temperature. Within the experimental uncertainties, this temperature agrees with T_0 introduced by K. Weiser, A. J. Grant, and T. Moustakas, in *Proceedings of the Fifth International Conference on Amorphous and Liquid Semiconductors* (Taylor and Francis Ltd., London, 1974), p. 326, to describe the temperature dependence of the high-field conductivity in a modified Cutler-Mott model in which both the hopping distance as well as the hopping activation energy vary with carrier energy.

[24] S. Kirkpatrick, private communication. See also K. Maschke, H. Overhof, and P. Thomas, Phys. Status Solidi (b) 62, 113 (1974).

[25] H. Fritzsche, J. Non-Cryst. Solids 6, 49 (1970).

[26] Maschke, Overhof, and Thomas, Ref. 24.

[27] A. J. Grant, T. D. Moustakas, T. Penny, and K. Weiser, in *Proceedings of the Fifth International Conference on Amorphous and Liquid Semiconductors* (Taylor and Francis, Ltd., London, 1974), p. 325; Weiser, Grant, and Moustakas, Ref. 23.

[28] D. Emin, Phys. Rev. Lett. 32, 303 (1974).