Paramagnetic States and Hopping Conductivity in a Chalcogenide Glass: As_2Te_3

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Variable-range hopping as evidenced by a resistivity proportional to $\exp T^{-1/4}$ and by the two-dimensional behavior of thin films has been observed for the first time in a chalcogenide glass. This was accomplished by sputtering As_2Te_3 at 77°K. The localized paramagnetic hopping states have also been established by the existence of an ESR signal.

Variable-range hopping conductivity associated with localized gap states has been observed in amorphous Ge[1] (a-Ge) and amorphous Si[2] (a-Si). These localized gap states have been related to dangling bonds by electron-spin-resonance (ESR) experiments[3,4] and by susceptibility measurements[5,6] which revealed the existence of Curie paramagnetism at low temperatures. However, as recently stated by Street and Mott,[7] the situation in pure amorphous chalcogenide glasses is different: Usually there is no ESR signal[8] or Curie paramagnetism at low temperatures,[9] and variable range hopping has not yet been observed.[7,10] One should point out, however, that an ESR signal depending on thermal treatment which is larger for quenched samples has been seen in various chalcogenide glasses.[11] Localized gap states have also been inferred from the temperature dependence of the resistivity in Tl_xTe_{1-x} films.[12] A theoretical explanation for this difference was proposed by Mott and co-workers[7,13] in terms of a model developed by Anderson.[14] It was assumed that all amorphous materials contain a large number (10^{18}–10^{19} cm^{-3}) of dangling bonds, but that the neutral dangling bond, containing an unpaired electron (referred to as D^0),[7,13] which leads to an ESR signal, Curie paramagnetism, and hopping conductivity, is stable only in such amorphous materials as Ge and Si. However, in the chalcogenide glasses, the dangling bonds are either empty (D^+) or doubly occupied (D^-) because the polaron energy gained by the contraction of a bond more than compensates for the Coulomb repulsion.[14] The D^0 state should therefore exist in chalcogenide glasses only as a result of excitation as for example in the recent optically induced paramagnetic states experiments by Bishop, Strom, and Taylor.[15]

A different point of view on dangling bonds was suggested by a comprehensive study of the hopping conductivity on a-InSb[16] and other amorphous semiconducting compounds,[16,17] namely, that the presence or absence of dangling bonds depends on the type of chemical bond (covalent or ionic) which prevails between the atoms of the compound. Since this observation is based on dc conductivity,[16] ESR, and susceptibility measurements,[17] it should be restricted to the D^0 type of dangling bond. In a-Ge and a-Si where only covalent bonding is present, dangling bonds remain even after high-temperature annealing.[18] On the other hand in compounds such as InSb,[16] AlSb, and GaAs[17] where ionic bonding is also present, hopping conductivity (resistivity proportional to $\exp T^{-1/4}$) is observed only in films deposited at 77°K. Annealing at or above room temperature leads[16] to the disappearance of the dangling bonds associated with hopping conductivity (resistivity proportional to $\exp T^{-1}$). With this point of view in mind, it is not surprising that hopping conductivity has not been observed in the chalcogenide compounds since many of them (As_2Se_3, As_2S_3, etc.) can be obtained in the amorphous state by quenching the melt. Consequently, the chances to observe these metastable dangling bonds in chalcogenide glasses should be best with low temperature sputtering: sputtering, as this process is more likely than evaporation to break up the molecules, and low temperature to prevent the annealing of the metastable dangling bonds.

Most of the films under the present study were sputtered onto sapphire substrates at 77°K using a power of 2.25 W (1500 V, 1.5 mA) with an argon pressure of 3×10^{-2} Torr. The average rate of deposition was approximately 420 Å/min. In order to study the effect, if any, of the deposition parameters on the properties of the films, the sputtering conditions were varied in the following manner: The sputtering power was varied between 1 and 3 W; the rate of deposition was changed from 25 to 700 Å/min by changes in power and distance between substrate and target; the argon pressure ranged from 9×10^{-3} Torr to 1.1×10^{-1} Torr. The ESR samples were sputtered on a (6.35×10^{-4})-cm-thick Mylar sheet stretched over a copper table kept at 77°K. After deposition of

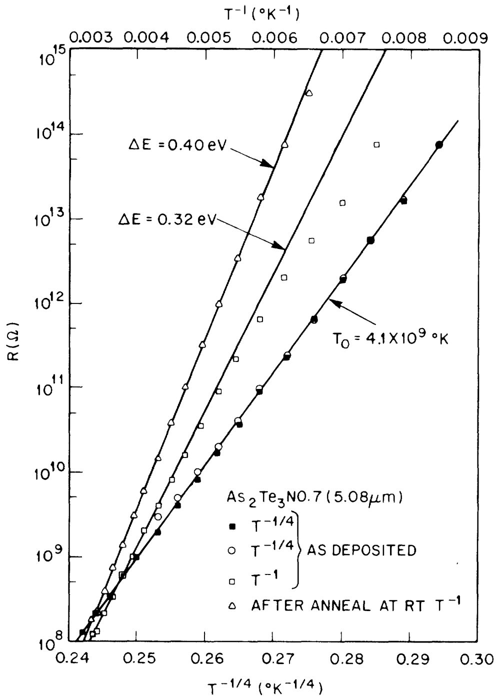

FIG. 1. Temperature dependence of the resistance (R) for an As_2Te_3 film as deposited at 77°K and after room temperature anneal. The solid squares represent raw data, while the open circles represent data obtained after subtraction of the band-conduction contribution (see text).

the film, the Mylar sheet was transferred under liquid nitrogen into a capillary quartz tube and the tube was then cooled to 5°K without ever warming up the sample above 77°K.

The temperature dependence of the resistance measured in the Ohmic regime without warm-up on a film deposited at 77°K is shown in Fig. 1. It is clear from Fig. 1 that the as-deposited data are well fitted from 130°K to near room temperature (most films anneal around 150°K) by the relationship characteristic of a variable-range hopping conductivity[10]:

$$\rho = \rho_0 \exp(T_0/T)^{1/4}, \tag{1}$$

where

$$T_0 = 16\alpha^3/kN(E_F), \tag{2}$$

k is Boltzmann's constant, α^{-1} is the radius of the localized state wave function, and $N(E_F)$ is the density of localized states. In view of the very high value for the exponential constant T_0 (4×10^9 °K), one may wonder whether the data could be fitted just as well by an exponential dependence of R on T^{-1}. It is obvious from Fig. 1 that such a fit is not possible over the whole range of data. However, after annealing at room temperature, the hopping conductivity disappears and the resistance now depends exponentially on T^{-1} with an activation energy (ΔE) of about 0.4 eV, which is in very good agreement with the data of Weiser and Brodsky[19] obtained on films evaporated at 77°K and annealed at room temperature. The value of the parameter T_0 is constant, within a factor of 2, for films ranging in thickness between 18 μm and 1000 Å (thinner films show a two-dimensional behavior discussed below) and for all the variations in deposition conditions described above. This implies, via Eq. (2), that the number of localized states is fairly independent of all deposition parameters except for the temperature of deposition. The resistivity, however, which under similar variations changes by about a factor of 10 is inversely proportional to the argon sputtering pressure and was as low as 1.4×10^4 Ω·cm at 300°K which is close to the value reported for evaporated films.[19]

The deviation observed in the as-deposited films from a strict exponential behavior, which has been attributed to variable range hopping, could have alternative explanations. It may be caused by a small temperature dependence of the exponential prefactor or by the fact that phonon-assisted hopping conduction in states between E_F and the respective mobility edge occurs. If indeed the conduction is in extended states at high temperatures and by variable-range hopping near E_F at low temperatures, then the former has to be subtracted from the total conductivity in a calculation for the latter. If one assumes that the conductivity of the annealed film yields the band conduction, subtracting the conductance of the annealed film from that of the as-deposited film should yield the hopping conductance, which is shown as hopping resistance by the open-circle data points of Fig. 1. It is obvious that in the temperature range 130 to 240°K, the corrected data are quite close to the raw data for the as-deposited films, suggesting that the band-conduction contribution is small in the as-deposited films. The deviations from the $T^{-1/4}$ behavior above 240°K in the corrected data are to be expected as the films anneal around this temperature and the correction can no longer be used since the film is not anymore an as-deposited film but a partially annealed film. Consequently, the $T^{-1/4}$ behavior at low temperatures is certainly consistent with variable-range hopping.

A further proof for variable-range hopping is

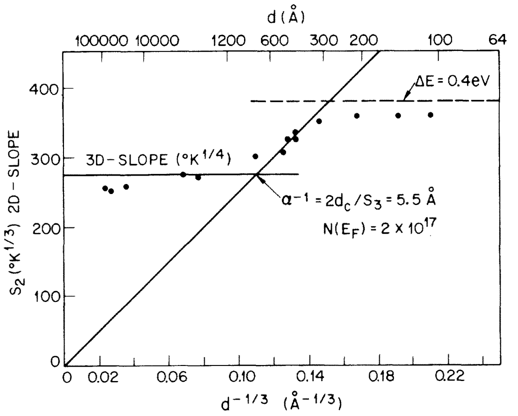

FIG. 2. Slopes of ln$R$ versus $T^{-1/3}$ plotted as a function of $d^{-1/3}$.

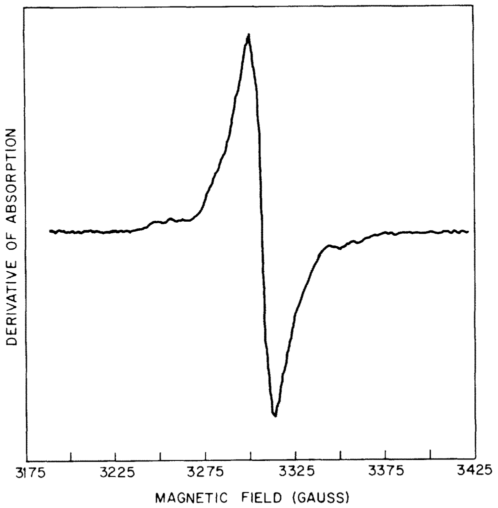

FIG. 3. ESR spectrum obtained at 9.26 GHz and 5°K on a-As$_2$Te$_3$ (0.01 cm^3) deposited at 77°K and cooled to 5°K without warmup.

provided by the two-dimensional behavior of thin films where the resistivity should obey[20,21] Eq. (1) with the exponent $\frac{1}{4}$ replaced by $\frac{1}{3}$, where

$$T_0 = 8\alpha^2/kdN(E_F) \tag{3}$$

and d is the film thickness. Consequently, the resistivity should depend exponentially on $d^{-1/3}$. The slopes of lnρ versus $T^{-1/4}$ (S_3) or $T^{-1/3}$ (S_2) are plotted as a function of $d^{-1/3}$ in Fig. 2; although there are few pertinent data points, they are consistent with the two-dimensional model. The reasons for the limited data are twofold: First, the three-dimensional slope (S_3) is high, reflecting most probably a low density of localized states [see Eq. (2)]; second, as one enters the two-dimensional regime, one loses states and soon there are so few states left that the two-dimensional dependence (exp$T^{-1/3}$) becomes undistinguishable from an exponential dependence on T^{-1}. This explains why the data saturate for thin films approaching asymptotically the dashed line labeled with $\Delta E = 0.4$ eV (this dashed line means that data plotted as lnρ versus T^{-1} with $\Delta E = 0.4$ eV can be plotted as well as lnρ versus $T^{-1/3}$ with a slope S_2 of about 380°K$^{1/3}$). If one defines the critical thickness (d_c) as the thickness where the two-dimensional and three-dimensional slopes are equal, one obtains by combining Eqs. (2) and (3)

$$\alpha^{-1} = 2d_c/S_3. \tag{4}$$

Using the data of Fig. 2 in Eq. (4) one obtains $\alpha^{-1} \simeq 5.5$ Å which after substitution in Eq. (2) yields $N(E_F) \simeq 2\times10^{17}$ states (eV cm^3)$^{-1}$.

The ESR spectrum obtained on an a-As$_2$Te$_3$ sample deposited at 77°K and cooled to 5°K without warmup is shown in Fig. 3. The linewidth is about 16 G and the inflection point of the resonance line corresponds to a g value of 2.002. The signal, using a strong pitch calibration, corresponds to 2×10^{16} spins in a sample of 0.01 cm^3. The calibration was checked to be accurate to within a factor of 2 by comparing the ESR signal and the susceptibility on an a-GaAs sample. Consequently, the ratio of the total density of spin states for As$_2$Te$_3$ (2×10^{18} cm^{-3}) to the density of states at the Fermi level deduced from electrical measurements is about 10 which is similar to the results previously reported on a-Ge[3] and a-Si.[4] But most importantly, the signal decreases by almost two orders of magnitude after annealing at room temperature. The total density of states present after annealing (3×10^{16} cm^{-3}) is consistent with the fact that hopping conductivity can no longer be observed. It is tempting at this point to speculate whether the metastable states obtained here by low temperature deposition are similar to those induced optically.[15] On the one hand, the narrow linewidth is again consistent with a spin localized on the chalcogen atom.[15] On the other hand, the near-free-electron value for g would point to electrons rather than the holes[15] suggested by optical experiments.

Although the present technique may not produce hopping conductivity in every glass, it has already been seen in GeTe, As$_2$Se-As$_2$Te$_3$ mixtures (which will be discussed in a more complete report) suggesting that this is indeed a general phenomenon.

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ing the possibility of ESR experiments.

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[1] P. A. Walley and A. K. Jonscher, Thin Solid Films $\underline{1}$, 367 (1968).

[2] P. A. Walley, Thin Solid Films $\underline{2}$, 327 (1968).

[3] M. H. Brodsky and R. S. Title, Phys. Rev. Lett. $\underline{23}$, 581 (1969).

[4] M. H. Brodsky, R. S. Title, K. Weiser, and G. D. Pettit, Phys. Rev. B $\underline{1}$, 2632 (1970).

[5] F. J. Di Salvo, Jr., B. G. Bagley, R. S. Hutton, and A. H. Clark, to be published.

[6] S. J. Hudgens and H. Fritzsche, Bull. Am. Phys. Soc. $\underline{20}$, 392 (1975).

[7] R. A. Street and N. F. Mott, Phys. Rev. Lett. $\underline{19}$, 1293 (1975).

[8] S. C. Agarwal, Phys. Rev. B $\underline{7}$, 685 (1973).

[9] F. J. Di Salvo, Jr., A. Menth, J. V. Waszczak, and J. Tauc, Phys. Rev. B $\underline{6}$, 4574 (1972).

[10] N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, England, 1971).

[11] R. E. Smith, J. Non-Cryst. Solids $\underline{8-10}$, 598 (1972).

[12] R. P. Ferrier, J. M. Prado, and M. R. Anseau, J. Non-Cryst. Solids $\underline{8-10}$, 798 (1972).

[13] N. F. Mott, E. A. Davis, and R. A. Street, Philos. Mag. $\underline{32}$, 961 (1975).

[14] P. W. Anderson, Phys. Rev. Lett. $\underline{34}$, 953 (1975).

[15] S. G. Bishop, U. Strom, and P. C. Taylor, Phys. Rev. Lett. $\underline{34}$, 1346 (1975).

[16] J. J. Hauser, Phys. Rev. B $\underline{8}$, 2678 (1973).

[17] Similar results to those observed on InSb (Ref. 16) were obtained on AlSb and GaAs (ESR and susceptibility measurements were performed as well in the latter case).

[18] A. Lewis, Phys. Rev. Lett. $\underline{29}$, 1555 (1972).

[19] K. Weiser and M. H. Brodsky, Phys. Rev. B $\underline{1}$, 791 (1970).

[20] E. M. Hamilton, Philos. Mag. $\underline{26}$, 1043 (1972).

[21] M. L. Knotek, M. Pollak, T. M. Donovan, and H. Kurtzman, Phys. Rev. Lett. $\underline{30}$, 853 (1973).

Experimental Evidence for the Existence of an Electron-Hole Liquid in II-VI Compounds

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Measurements of optical absorption and gain in CdS and gain in CdSe show that for high excitation density optically excited carriers form an electron-hole liquid with binding energy of 13 meV for CdS and 2 meV for CdSe. The measurements are compared to a recent theory for electron-hole liquid formation in polar semiconductors.

We report measurements of optical absorption and gain for CdS in the presence of high-intensity optical pumping. The results of these measurements are in agreement with the expected behavior of a degenerate electron-hole liquid (EHL),[1] rather than with an interpretation based on exciton interactions.[2,3] We conclude that for conditions of high excitation density (HED), optically excited electrons and holes in CdS form a liquid with a binding energy of ~13 meV measured with respect to the free exciton.[4] In addition we present gain spectra, measured by the method of Shaklee and Leheny,[5] for a second II-VI compound, CdSe, where we find the data are also best described by an EHL bound by less than 2 meV. The magnitude of the binding energies for the liquid state as well as the spectral widths of the measured gain are in agreement with the theoretical predictions for EHL formation in polar compounds recently developed by Beni and Rice.[6]

Our measurement for CdS is made using two lasers, one as a pump and the other as a tunable probe. We find that there is a transition from gain to loss occurring at ~4883 Å for incident power density of $\sim 5\times10^5$ W/cm^2. Examination of the sample reflectivity indicates that the exciton contribution to the index of refraction is negligible under HED conditions. From these results we conclude that excitons do not contribute to the recombination kinetics. A similar conclusion has been drawn by Lysenko *et al.*,[4] using measurements of gain determined by the variation of luminescence intensity with excitation length similar to the measurement for CdSe reported here, but this measurement technique provides no information on changes in absorption resulting from HED. Goto and Langer[7] have investigated HED transmission for CdS and found an increase in absorption at longer wavelengths with increasing pump intensity. However, these investigators made use of an incoherent fluorescence source as a probe making measurements of amplification difficult, if not impossible, since the spectral brightness of the probe beam cannot be expected to exceed that of the sample luminescence. By using a tunable laser probe we have overcome this difficulty and we will show here that an accurate determination of *both* the gain and loss