VOLUME 52, NUMBER 8 PHYSICAL REVIEW LETTERS 20 FEBRUARY 1984

Evidence for Thermally Generated Defects in Liquid and Glassy As_2Se_3

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(Received 31 October 1983)

Measurement of transient photoconductivity in a-As_2Se_3 through the glass transition temperature T_g gives the temperature dependence of the density of recombination centers. The activation energy of this density increases suddenly at T_g, leading to identification of the centers with negative-U defects.

PACS numbers: 71.55.Ht, 72.20.Jv

The idea that there is an effective attraction between electrons in chalcogenide glasses (the correlation energy U is negative) was proposed[1] to explain the pinning of the Fermi level in the absence of spin paramagnetism. Because this pairing of the electrons is observed only for chalcogenides and not for tetrahedral amorphous semiconductors (e.g., a-Si), models[2,3] were developed in which the negative U occurs only at defects peculiar to the chalcogenide glasses. In particular, it was proposed[3] that specific negative-U defects (valence-alternation pairs or VAP's) are present in the melt at relatively high densities because the energy required to create them is low; the defects are frozen in at the glass transition temperature T_g when the glass is quenched. In the ground state these defects are charged positively or negatively, with zero or two electrons, respectively, while in the excited state they are netural and have unpaired electrons. Unfortunately, the density of these neutral defects is too small to be measured by spin-resonance or susceptibility experiments, requiring other methods.

If the neutral defects are the dominant recombination centers for free carriers, their density can be determined from the recombination time in transient photoconductivity (TPC) measurements. Although trapping complicates this determination, Orenstein and co-workers[4] showed that for a-As_2Se_3, recombination-center densities as low as $\sim 10^{13}$ cm^{-3} could be extracted from TPC data with some confidence. In this Letter we report the first measurement of TPC of a chalcogenide semiconductor for a range of temperature T spanning T_g, that is, in the liquid as well as in the glass. We find that the density of recombination centers is thermally activated both below and above T_g but that the activation energy increases abruptly as T is increased through T_g, as predicted by the valence-alternation model.

High-purity amorphous As_2Se_3 was obtained from British Drug House. The experimental method for measuring TPC in the solid state was described by Orenstein and co-workers.[4] However, because of the long decay times for $T < 356$ K, we measured the TPC resulting from a *single* 10-ns laser pulse, whereas Orenstein and coworkers used repetitive pulses. Before the pulse, the sample was rested in the dark for a time which was sufficiently long to ensure that carriers excited by previous illumination were no longer present. For TPC measurements in the liquid a furnace was fabricated, following the design of Cutler and Peterson,[5] and we used pulsed excitation with a 10-Hz repetition rate. The light used ($\hbar\omega_x = 1.17$ eV) penetrates several millimeters into the liquid. In the glass, similar transients are observed for all excitation energies. For all measurements, the laser intensity was lowered until the observed TPC was proportional to the excitation density, and therefore only monomolecular recombination was observed.

Figure 1 shows several TPC time dependences for 295 K $< T <$ 580 K. At all temperatures, a clear change in the time dependence is evident, defining the recombination time τ. At low T, τ separates two power-law regions. At high T, the

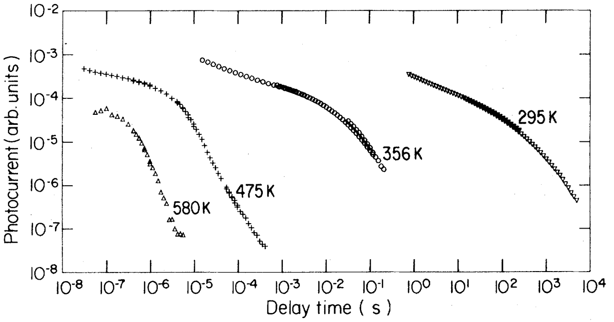

FIG. 1. Time dependence of TPC for several temperatures. For low T, TPC is composed of two power-law parts; the transition defines the recombination time τ. At high T, τ is characterized by a nearly exponential decay.

decay for $t \gg \tau$ approaches a power-law form, but for $t \sim \tau$ the decay is faster than this power law, in agreement with predictions[6] of an exponential onset for recombination when $T > T_0$. The temperature dependence of τ is strong: Over an interval of 300 K it changes by a factor of 10^9.

The time dependence of the TPC can be understood in terms of multiple trapping (MT)[4] in an exponential density of localized states (DOS):

$$g(E) = (N_L / kT_0)\exp(E/kT_0), \tag{1}$$

where kT_0 is the energy width of the distribution. If we also assume that this exponential extends all the way to the mobility edge ($E = 0$) and that the capture coefficient is independent of energy, then we have the simplified model which we refer to as MTX. N_L is then the total number of localized states in the exponential distribution. A relation between τ and the density of recombination centers, N_{th}, can be found in the following way. In the absence of trapping $\tau = (b_r N_{\text{th}})^{-1}$, where b_r is the recombination coefficient, assumed to be the same for all the centers. However, in the presence of shallow traps, which are in thermal equilibrium with the transport states, the onset of recombination is delayed[7] and τ is increased by a factor $(n + n_t)/n$, where n and n_t are the densities of carriers in transport states and in shallow traps, respectively. For a multiple-trapping system the shallow traps are those whose characteristic times for release of carriers to the transport states above the mobility edge are shorter than the time of observation. In MTX the release time is $\nu_0^{-1}\exp(-E/kT)$, and the shallow states are those above the demarcation energy $E_d = -kT\ln(\nu_0 t)$, where ν_0 is found[4] to be $\sim 10^{12}$ s^{-1} for a-As_2Se_3. The density n_t is the integral of $g(E)f(E)$ from E_d to $E = 0$, where the mean occupation number $f(E)$ is $(n/N_c)\exp(-E/kT)$; N_c is the number of extended states within kT of the mobility edge. Using these results one finds

$$b_r N_{\text{th}} = \tau^{-1}\left[1 + \frac{\alpha}{1-\alpha}\frac{N_L}{N_c}\{(\nu_0\tau)^{1-\alpha} - 1\}\right], \tag{2}$$

where $\alpha = T/T_0$. At T well below T_0, this gives a result for τ similar to that obtained previously[4,8] by a different argument.

The calculated value of $b_r N_{\text{th}}$ depends on the numerical values for three material parameters: ν_0, T_0, and N_c/N_L. In order to determine the best choice for these parameters as well as the sensitivity of our results to the values chosen, we have performed a numerical analysis of the transients, based on the formulation of Monroe and Kastner.[6] The magnitude of the exponential part in the high-T recombination transients allows us to estimate the value of N_c/N_L to be ~ 20; we find $\nu_0 \sim 10^{12}$ s^{-1} and $T_0 = 550$ K, consistent with values found by other methods.[4] Using these values in Eq. (2) we obtain $b_r N_{\text{th}}$ at each T.

Figure 2 is a semilog plot of $b_r N_{\text{th}}$ versus $1/T$. The data fall on two straight lines with an abrupt change of slope near $T \sim T_g$. The highest temperatures reached are close to T_m, the melting temperature of the crystal. At these temperatures, TPC is probably influenced by the presence of some crystalline inclusions in the supercooled liquid; samples held above 520 K crystallized completely after a prolonged period of time.

In the analysis above several simplifying assumptions were made about the microscopic origins of the dispersive behavior of photocurrent. We have considered possible deviations from this MTX model, specifically variations in the capture coefficients of the traps with energy. However, the analysis of Monroe and Kastner[6] shows that any variations can be described in terms of an *effective* DOS which determines the dynamics of TPC *and* the relation between τ and $b_r N_{\text{th}}$; as long as MTX is a good description of the temperature and time dependence of the TPC in the absence of recombination, our interpretation of the

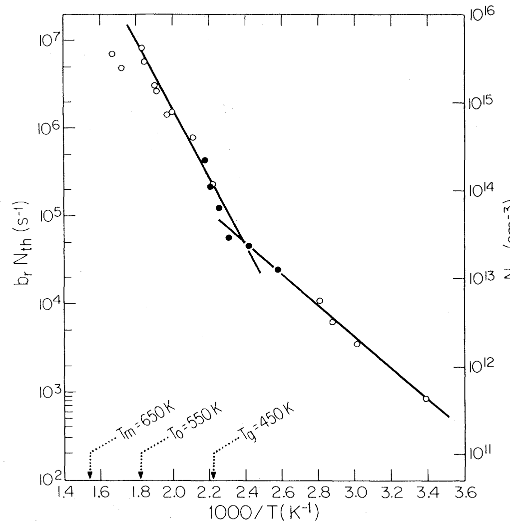

FIG. 2. Temperature dependence of $b_r N_{\text{th}}$, the capture rate of the recombination centers. The right-hand scale gives the density of recombination centers, N_{th}, with $b_r \sim 2 \times 10^{-9}$ $\text{cm}^3\,\text{s}^{-1}$. The temperatures T_m, T_0, and T_g are defined in the text. The solid points are data taken from Ref. 4 ($E_x = 1.8$ eV), and the open points are from the present work ($E_x = 1.17$ eV, except for $T = 295$ K for which $E_x = 1.4$ eV).

recombination data will be adequate. Experimentally, the simple time and temperature dependence predicted by MTX and assumed in the above discussion has been verified[4] over a large range of T, from 200 to 450 K. In addition, we have examined what changes are necessary in our interpretation of the data if the DOS near the mobility edge deviates from the exponential form, if conduction in the transport states is by hopping, or if the material parameters have weak T dependences. In all cases, we find that the general form of the plot of $b_r N_{\mathrm{th}}$ versus $1/T$ is insensitive to the details of the model used for its carrier dynamics, as long as such dynamics fall within a generalized multiple-trapping framework.

In order to determine the absolute magnitude of N_{th}, we use the intensity dependence of τ at low T to separate the factors b_r and N_{th}. At low excitation intensities τ is constant, indicating that N_{th} is the thermal-equilibrium density of recombination centers. But when the density of photoexcited electron-hole pairs becomes equal to N_{th}, τ begins to decrease because of bimolecular recombination. Orenstein and co-workers[4] used this fact to calibrate N_{th}. Assuming a quantum efficiency of 10% at $T = 295$ K, we find $b_r \sim 2 \times 10^{-9}$ cm^3 s^{-1}, corresponding to a diffusion-limited recombination radius of ~ 2 Å. We take b_r to be constant over the temperature range of the experiment (we will justify this below), and thus conclude that N_{th} is thermally activated above T_g, with an activation energy 0.8 ± 0.1 eV and a prefactor $N_0 \sim 6 \times 10^{22}$ cm^{-3}. Below T_g the activation energy is 0.35 ± 0.05 eV and the prefactor is $N_g \sim 4 \times 10^{17}$ cm^{-3}. Both prefactors have an uncertainty of about an order of magnitude, and reasonable variations of the parameters ν_0, T_0, and N_c/N_L do not significantly change the values of the quantities above.

The value for b_r is large and is at most weakly T dependent for low T [4]; it is therefore not expected to increase dramatically at higher T. If b_r were to *decrease* at higher T, it would, if anything, enhance the change of slope of $N_{\mathrm{th}}(T)$ at T_g. It would also lead to a larger prefactor N_0, which is already as large as it can be.

N_0 is of the order of the number density of atoms in the solid. This strongly suggests that the recombination centers seen at high T are indeed defects: Above T_g almost any atom can become a defect. The change of activation energy in our data occurs near T_g. It is therefore reasonable to assume that the dominant recombination centers at low T are frozen-in defects of the same chemical nature as those created above T_g. These centers could in principle have a different origin, e.g., impurities, but it would then be fortuitous that the recombination rates for the two types of recombination centers were equal at T_g.

These observations are easily understood in terms of the valence-alternation model. According to this model pairs of positively and negatively charged defects are thermally generated in the melt, with an activation energy E_{VAP}. Below T_g the density of VAP's is constant, because they are frozen in. However, an energy $|U|$ must be supplied to unpair electrons, so that the density of neutral defects, which can act as recombination centers, is predicted to be a thermally activated fraction of the density of VAP's, with an activation energy $|U|/2$. The factor $\frac{1}{2}$ arises from the fact that two neutrals are created for every separated pair of electrons. Above T_g the activation energy of neutral defects is then predicted to be $(|U| + E_{\mathrm{VAP}})/2$. Our experiment, therefore, provides the first direct measurement of the negative correlation energy: $U = -0.7 \pm 0.1$ eV, in agreement with indirect estimates.[3] The energy to create defect pairs is also obtained directly for the first time: $E_{\mathrm{VAP}} = 0.9 \pm 0.35$ eV. Previously, this energy could only be estimated from the density of frozen-in defects which is found by many methods[3] to be near the value we find here: $N_g \sim 4 \times 10^{17}$ cm^{-3}.

Additional evidence that the recombination centers are indeed negative-U defects comes from the T dependence of the dark conductivity: It shows very little change in activation energy through T_g,[9] indicating that the Fermi level E_{F} remains pinned at the same energy below and above T_g. Since the density of defects, as measured in this experiment, becomes very high above T_g, the pinning of E_{F} strongly suggests that the defects detected here have negative U and are the same as those which pin E_{F} below T_g.

In summary, we have found that the density of recombination centers in a-As$_2$Se$_3$ has precisely the T dependence predicted by the valence-alternation model for the neutral negative-U defects. Previous studies by Abkowitz and co-workers[10] indicated that defects could be thermally generated. They found that the density of certain defects can be modified by thermal cycling through the glass transition, and even that electron and hole traps in a-Se tend to be created in pairs. In this experiment we have succeeded in measuring the density of centers over a range of T well into the liquid and thereby demonstrating the thermal generation of defects above T_g and the freezing in of the same defects below T_g. This also provides the first direct measurement of the negative correlation energy in a chalcogenide glass, and of the low energy to create defects explained by the valence-alternation model.

This work was supported by National Science Foundation Grant No. DMR81-15620. One of us (D.M.) acknowledges receipt of a National Science Foundation Predoctoral Fellowship and an IBM Corporation Predoctoral Fellowship.

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