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# Time-Resolved Optical Absorption and Mobility of Localized Charge Carriers in $a$-$As_2Se_3$

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(Received 16 February 1979)

The first measurements are reported of simultaneous, transient, photoinduced optical absorption (PA) and photoconductivity (PC) in an amorphous semiconductor ($a$-$As_2Se_3$). Measurements in the time range 100 ns to 1 ms show that the same density of excited carriers gives rise to both effects. PA is observed only when carriers are in localized states, whereas PC is observed for both hot carriers ($\mu\tau\simeq 7\times10^{-12}$ cm$^2$ V$^{-1}$) and localized carriers.

The concept of localized states with an effective negative correlation energy[1] has explained a long-standing puzzle in the study of chalcogenide glasses, namely the pinning of the Fermi level in the absence of electron spin paramagnetism. Recent models[2,3] have applied this concept to specific bond-coordination defects in the glass structure in order to explain not only the diamagnetic ground state but a wide variety of excited-state phenomena as well. Of these phenomena, carrier transport and photoinduced ESR and optical absorption are thought to be direct probes of the density, structure, and charge of these defects.

In $a$-$As_2Se_3$, the best characterized of the compound chalcogenide glasses, a trap-limited carrier transport mechanism has been proposed[4,5] to account for the large, ~0.6 eV, activation energy of the hole drift mobility. The defect models identify this hole trap with the singly coordinated defect which is negatively charged in its ground state. The ESR signal and optical absorption band which appear together during illumination at low temperatures[6] are thought to result from photoionization of the bound electron pair at this same localized state. In recently reported experiments,[7] however, measurements of carrier transport and photoinduced ESR and absorption failed to show the expected correlation.

The drift mobility and photoinduced spin density were measured in samples of $a$-$As_2Se_3$ which were doped with a variety of impurities. Several elements (e.g., Tl, I) changed the hole mobility while leaving its activation energy the same as that in the undoped material, strongly suggesting

that they modulate the concentration of negatively charged intrinsic gap states. However, measurements of the metastable photoinduced ESR in the same doped samples yielded a surprising and confusing result. Although trap densities as deduced from transport measurements were found to vary by more than three orders of magnitude, the photoinduced spin density remained essentially independent of impurity concentration.

In order to make further progress toward an understanding of the chalcogenide glasses, a knowledge of the relationship between the various probes of localized levels is clearly required. We report in this Letter the first experiment which demonstrates a correlation between the electronic states involved in transport and those detected by excited-state absorption. By making the first observations of transient photoinduced absorption (PA) in $a$-$As_2Se_3$ together with simultaneous measurements of transient photoconductivity (PC) we show that the number of density of photocarriers is equal to that of PA centers at all times following pulsed laser excitation.

The measurements were performed at room temperature on a sample of melt-quenched $As_2Se_3$ of 1.5 mm thickness. Two coplanar graphite electrodes with a separation of 2 mm provided electrical contact to the material. In this configuration, space-charge screening of the applied field is negligible. The PA and PC were excited by a pulsed dye laser, of pulse width 10 ns and typical repetition rate 20 Hz, whose beam was defocused and then apertured to ensure uniform illumination transverse to the electrodes.

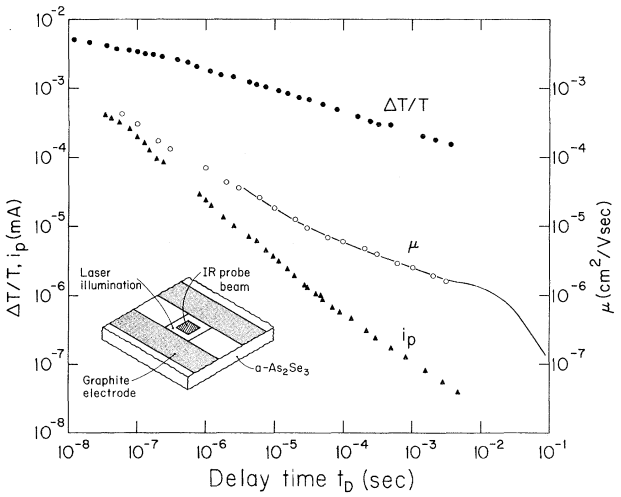


FIG. 1. Fractional change in transmission, $\Delta T/T$, (solid circles) and photocurrent $i_p$ in milliamperes (triangles) as a function of time delay $t_D$ after pulsed laser excitation (left scale). Mobility $\mu$ as derived from $\Delta T/T$ and $i_p$ (open circles) and as measured in drift experiment (solid curve, Ref. 4) as a function of $t_p$ (right scale).

Photogeneration and subsequent decay of the midgap absorption band were detected by monitoring the transmission of a probe beam from a W lamp incident on the region between the electrodes. The probe beam was passed through a colored glass filter to exclude visible light and focused to a ~ 1 mm square so that it lay entirely within the excited area defined by the laser illumination (see sketch in Fig. 1). Time-resolved measurements of transmission were performed using a Si photodiode, wide-band preamplifier, and boxcar integrator whose overall time constant was ~ 10 ns as deduced from its transient response to the excitation pulse. The transient absorption represents the average response to a band of probe photon energies extending from the onset of sample transmission at 1.5 eV to the cutoff of the Si detector at 1.1 eV. Earlier measurements[8] with a scanning monochromator and PbS detector have shown that the transient absorption band is fairly flat from the absorption edge down to a sharp cutoff at 0.65 eV, establishing that it results from the same excited states originally observed as metastable at 10°K.

The photocurrent, generated simultaneously by the laser pulse, was detected as a voltage drop across a series resistor, the value of which could be adjusted so that the bandwidth of the measurement circuit was sufficiently wide to resolve the transient signal. In Fig. 1 the fractional change in transmission, $\Delta T/T$, and the photocurrent, $i_p$, are plotted versus the delay time, $t_D$, after the laser pulse, on logarithmic scales. Each pulse corresponds to a time-integrated flux of $2\times 10^{15}$ cm$^{-2}$ photons of energy 2.14 eV.

As can be readily seen, the photocurrent decays much more rapidly than the induced absorption for the same excitation. However, we will now show that *both effects result from the same density of photoexcited carriers at all times after the laser pulse.*

The photocurrent, $i_p$, and the fractional change in transmission, $\Delta T/T$, are given by

$$i_p = N_p we\mu E, \quad \Delta T/T = N_\alpha \sigma,$$

where $N_p$ and $N_\alpha$ are the area density of charge carriers giving rise to the photocurrent and absorption, respectively, $w$ is the width of the excited region (1.5 mm), $e$ the electronic charge, $E$ the applied electric field (675 V/cm), $\mu$ the

average mobility, and $\sigma$ the absorption cross section of the excited center. The cross section is $\simeq 10^{-16}$ cm$^2$ as determined from low-temperature measurements[6] of induced absorption and ESR, where a $\Delta\alpha \sim 10$ cm$^{-1}$ is found to correspond to a spin density of $\sim 10^{17}$ cm$^{-3}$. This value is in agreement with an estimate of $\sigma \simeq (0.3\text{–}3)\times 10^{-16}$ cm$^{-2}$ with use of the sum rule for the integrated cross section.[9]

By *assuming* $N_p(t)$ to be equal to $N_\alpha(t)$ we calculate a *time-dependent mobility* which is also plotted in Fig. 1. The fact that the average mobility decreases with time following pulsed carrier excitation is a consequence of the broad distribution of event times governing the transport mechanism in $a$-$As_2Se_3$ and has been clearly demonstrated by studies of drift mobility.[4] These experiments utilize photoinjection near a blocking electrode of a sandwich-cell configuration to observe the current transient due to the motion of the mobile (hole) carriers in the absence of bulk recombination. For times shorter than the transit time, $t_T$, the number of carriers in motion through the sample is constant; the observed decrease of the photocurrent in this time regime is a direct measure of the time dependence of the mobility.

Plotted as a solid curve in Fig. 1 is a typical room-temperature current transient ($t_T = 24$ ms) from such a drift measurement showing clearly that the time dependence of the mobility is in excellent agreement with that obtained from our experiment. For ease of comparison, the mobility from the drift experiment was normalized to our result at one time. However, the absolute magnitudes agree at any time to within a factor of 2.[10] The remarkable agreement confirms the hypothesis that, at all times, $N_p(t) = N_\alpha(t)$.

The decay of the PA is not understood at this time. We have shown previously[8] from steady-state measurements that the recombination is bimolecular, however, the decay is clearly not proportional to $t_D^{-1}$ as predicted for a simple bimolecular process. The very slow decay suggests that the recombination is diffusion limited since the mobility decreases with time. An understanding of the decay kinetics might be gained through an analysis of diffusion-limited bimolecular reaction which takes into account the non-Gaussian transport.

Having established the one-to-one correlation of PC and PA in $a$-$As_2Se_3$, we proceed to examine the details of the photogeneration process. The upper part of Fig. 2 shows the magnitude of the PA at $\lesssim 100$ ns after the excitation pulse, as a function of pulse intensity, $I_{ph}$, for two different energies. The directly measured quantities, $\Delta T/T$ and $I_{ph}$ (photons/cm$^2$ pulse), have been converted to mean densities by multiplying by $\alpha/\sigma$ and $\alpha$, respectively, where $\alpha$ is the absorption coefficient at the excitation wavelength. The values obtained for 1.88 eV excitation energy have been multiplied by a factor 2.1 so that they coincide with the 2.14-eV data in the region of linear intensity dependence. This vertical adjustment corrects for a change in quantum efficiency, which we find to be a monotonically increasing function of photon energy between 1.7 and 2.5 eV. (The excitation spectrum will be published separately.) It is clear from the figure that the observed crossover to nonlinearity depends only on the mean excitation density, $\alpha I_{ph}$, and not on the photon energy.

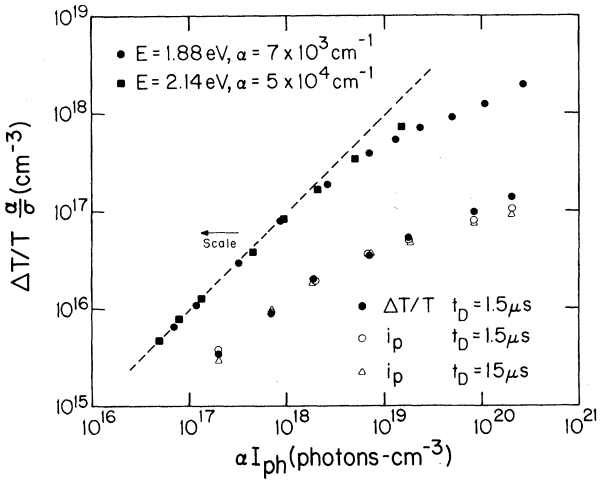


FIG. 2. Mean density of photoinduced absorption centers $(\Delta T/T)\alpha/\sigma$ vs density of photons absorbed in a single pulse, $\alpha I_{ph}$, for two different photon energies. The 1.88 eV data has been multipled by a factor 2.1. Also shown are $\Delta T/T$ and $i_p$ in arbitrary units as a function of $\alpha I_{ph}$ showing that these quantities are proportional for all delay times.

It should be noted that the intensity dependence above the crossover cannot be explained by a saturation effect which proceeds further into the sample than $\alpha^{-1}$ as the intensity is increased. For an optically thick sample ($\alpha d \gg 1$) the depth of the saturated region, and therefore $\Delta T/T$, would increase as $\ln I_{ph}$, whereas we observe a much more rapid growth in the sublinear region, roughly at $I_{ph}^{1/2}$. Furthermore, the same intensity dependence was found in a 3300-Å-thin film for which the absorption coefficient of the inducing light was chosen so that $\alpha d \lesssim 1$.

Having ruled out saturation, we conclude that the sublinear intensity dependence is the result of a recombination process whose rate depends upon the excitation density. Although this recombination process is not well understood, several pertinent facts are known. (1) The process is distinct from that leading to the time dependence of the PA seen in Fig. 1. For, although the latter recombination becomes more rapid with increasing excitation density, there is no component of the PA which tracks the laser pulse even at the highest intensity. (2) Recombination does not take place until carriers thermalize to energies near the mobility edge. The evidence for this is our observation of a PC transient ($\mu\tau_0 \gtrsim 7 \times 10^{-12}$ cm$^2$/V),[11] which *does* track the laser pulse, and remains *linear* at the highest intensities available. This suggests that the carrier, immediately after photogeneration, is in a high-mobility state[12] ($\mu \sim 1-10$ cm$^2$/V sec) whose lifetime, $\tau_0$, ($\sim 10^{-12}$ sec) is density independent and therefore corresponds to a thermalization, or localization, not a recombination, time. It appears, then, that the recombination which limits the photogeneration of PA takes place after thermalization of hot carriers but before transition to the low-mobility ($\mu \sim 10^{-4}$ cm$^2$/V sec) state responsible for both PA and the dispersive PC transient.

Although our understanding of the recombination mechanism is incomplete, several points emerge from measurements of the intensity dependence in the recombination-limited regime. The lower part of Fig. 2 shows the magnitude of the PA ($t_D$ = 1.5 $\mu$sec) and PC ($t_D$ = 1.5, 15 $\mu$sec), in relative units. We note that the observed proportionality of PA and PC, at a fixed time, confirms our contention that both processes are a manifestation of the same set of states. The proportionality constant, $\mu(t = 1.5\ \mu\text{sec})$, is seen to remain independent of intensity up to the highest photoexcited carrier density of $\gtrsim 10^{18}$ cm$^{-3}$. Furthermore, measurements for which the initial carrier concentration, $n(0)$, is $\sim 10^{16}$ cm$^{-3}$ (regime of linear intensity dependence) show that $\mu(t)$ for $10^{-7}$ sec $< t_D < 10^{-2}$ sec is essentially the same as Fig. 1 (data to be presented in a more lengthy publication).

These observations are puzzling in view of the trap concentration of $10^{16}-10^{17}$ cm$^{-3}$ deduced[4] from the analysis of a model of transport by trap-controlled hopping. This estimate is supported by measurements,[7] referred to earlier, of $t_T$ in $a$-$As_2Se_3$:Tl which show that the hole mobility begins to decrease with Tl concentration for additive densities $\sim 3\times 10^{16}$ cm$^{-3}$. We note, however, that the hopping transport is proposed to take place through a manifold of localized levels of density $\sim 10^{19}$ cm$^{-3}$. The $10^{16}-10^{17}$ cm$^{-3}$ deep levels required to account for the large activation energy of the mobility may, for example, be a feature at the low-energy tail of this larger set. We suggest the possibility that the PA results from carriers localized in any state within this continuum of levels. Furthermore, the lack of a dramatic "threshold" effect as $n(0)$ is swept through the range $10^{16}-10^{18}$ cm$^{-3}$ can perhaps be understood in the following way. Since the "intrinsic" hopping mobility of carriers is expected to be low, a significant delay is expected before photoexcited carriers encounter a dilute density ($10^{16}-10^{17}$ cm$^{-3}$) of special centers. On the basis of the observed mobility at small $t_D$ we estimate this time to be $\sim 10-100$ $\mu$sec. However, after 100 $\mu$sec recombination has lowered the carrier density by more than an order of magnitude. This can explain why $\mu(t)$ is unchanged at high $n(0)$, and leads to the prediction that the activation energy of the mobility is smaller at times $< 100$ $\mu$sec since the carriers have not yet been trapped at the deepest levels. Such a decrease in activation energy of $\sim 0.1$ eV has already been seen in drift mobility experiments with room-temperature transit times $\sim 100$ $\mu$sec.[5] A detailed study of the temperature dependence of $\mu(t)$ with use of our technique, particularly for 10 nsec $< t_D <$ 100 $\mu$sec, along with time-resolved measurements of the PA spectrum, is underway to test these ideas.

This work was supported by National Science Foundation Grants No. DMR78-00836 and No. DMR76-80895.

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[11]From our data we determine $\mu\tau_0 \simeq (7\times10^{-12}\ \mathrm{cm^2/V})y^{-1}$, where $y$ is the quantum efficiency for generating free carriers at 2.14 eV. A value $\sim 0.5$ has been obtained for $y$. See C. Main and A. E. Owen, in *Electronics and Structural Properties of Amorphous Semiconductors*, edited by P. G. LeComber and J. Mort (Academic, New York, 1973), p. 527.

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# Extended X-Ray-Absorption Fine Structure of Small Cu and Ni Clusters: Binding-Energy and Bond-Length Changes with Cluster Size

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(Received 23 April 1979)

Extended x-ray–absorption fine-structure measurements have been made on metal clusters of Cu and Ni which were formed by vapor deposition on amorphous carbon substrates. Small clusters of both elements show a substantial contraction of the nearest-neighbor metal-metal distance and an increase in binding energy for the onset of the $K$ absorption edge. The results are explained by the increasing surface-to-volume ratio as the cluster size decreases resulting in a more free-atom–like configuration of the metal atoms.

Because of the importance of supported metallic microclusters as commerical catalysts,[1] model studies which elucidate their physical and electronic properties are highly desirable. Experimental data of the past two decades have conflicted as to the existence of bond-length changes in small particles.[2] All experiments we know of have determined lattice contractions or expansions as a function of particle size (or thin-film thickness or crystallite dimension) by the displacement of x-ray or electron Bragg-diffraction peaks.[2] The diffraction measurements were analyzed by referencing the observed pattern to an assumed lattice (i.e., the bulk) structure. Recently, a theoretical modeling study by Briant and Burton[3] has cast doubt on the so-determined values for nearest-neighbor distance contractions in small clusters. Thus, to elucidate whether the structures of small metallic particles or thin films are different from the bulk ones, a new method of small-cluster analysis is needed.

We have chosen the extended x-ray–absorption fine-structure technique (EXAFS)[4] to study the interatomic distances of atoms in small clusters of Cu and Ni. The advantage is that the analysis of EXAFS data is independent of crystal structure and is applicable to materials with no long-range order. In this Letter, we report the first direct evidence for bond-length contractions as a function of decreasing cluster size of Cu and Ni and extend measurements to sizes smaller than possible by other techniques. The preparation method and the substrate employed allow the study of the inherent characteristics of the metal particles in contrast to conventional small metal catelysts where interaction between the metal and substrate atoms may be significant.[5]

Experiments were done at the Standord Synchrotron Radiation Laboratory (SSRL) on the storage ring SPEAR. The EXAFS spectra were recorded with use of fluorescence detection[6] to enhance the signal-to-background ratio. Cluster

 