Picosecond Relaxation of Optically Induced Absorption in Amorphous Semiconductors

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Picosecond relaxation of optically induced absorption in a-Si, a-Si:H, and $As_2S_{3-x}Se_x$ $(0.25 \leqslant x \leqslant 0.75)$ was studied with a passively mode-locked cw dye laser. In silicon, the results can be described in terms of trapping by defects. The fast recovery of absorption in chalcogenides indicates that recombination of highly localized excitons is the dominant mechanism in the decay of carriers excited at the Urbach edge.

We report the first observation of induced absorption with picosecond time resolution in amorphous Si (a-Si), amorphous hydrogenated Si (a-Si:H), and chalcogenide glasses $As_2S_{3-x}Se_x$ $(0.25<x<0.75)$. The subpicosecond laser techniques pioneered by Ippen and Shank[1,2] were used to study the dynamics of excited states in these materials. Our measurements showed that the relaxation processes are different in silicon and chalcogenide glasses. We suggest a model that explains these differences, and is also consistent with the observation by Fork *et al.*[3] of picosecond induced absorption in As_2S_3.

The experiments were performed with use of a passively mode-locked dye laser which produced 0.6–0.8-ps pulses at 6150 Å. The laser was cavity dumped to provide repetition rates of 10^4–10^6 pulses per second with peak pulse power of 1.5 kW. About 3% of the pulse was split off and used to probe the excited sample with variable delay that was repetitively cycled to allow use of signal-averaging techniques. The delay-line zero was set by second-harmonic generation in potassium dihydrate phosphate (KDP) or by two-photon absorption in As_2S_3 with accuracy $\simeq 0.1$ ps. The pump and probe pulses were focused with a lens to overlapping spots of 25-μm diameter on samples in a cryostat. Incident intensities of $\simeq 10^8$ W/cm^2 produced incremental transmission changes of $\Delta T/T = \Delta I/I \simeq 10^{-3}$. The laser pulses were monitored periodically for pulse width and peak power by background-free second-harmonic generation in KDP and average power measurements. The pump beam was chopped at 1050 Hz and the induced probe modulation was detected by a Si photodiode and lockin amplifier.

Samples of a-Si:H (about 1 μm thick) were prepared on transparent substrates at various hydrogen concentrations by sputtering and glow discharge. The peak carrier density produced by illumination was estimated to be $\simeq 10^{18}$ cm^{-3}; the pulse repetition rate was $\simeq 10^6$ s^{-1}. Films of a-Si prepared by sputtering were thinner (~ 0.3 μm) and typical peak carrier densities were $\simeq 10^{19}$ cm^{-3}.

The chalcogenide glasses were prepared by quenching from the melt and polished to a thickness of 0.2–0.5 mm. Carrier densities of 10^{15}–10^{16} cm^{-3} were excited as an increasing function of Se content. Illumination may produce photostructural changes in these materials. To minimize this effect, the repetition rate was reduced to $\simeq 10^4$ s^{-1} and the position of the spot was frequently changed.

The time dependence of induced absorption in a-Si and a-Si:H is shown in Fig. 1; the coherent coupling artifact[2] has been removed analytically. All samples showed instantaneous (faster than 0.5 ps) absorption that persisted in a-Si:H beyond 200 ps with no change when the sample was cooled to 85 K. The induced $\Delta\alpha_{\text{peak}} \simeq 30$ cm^{-1} corresponds to a cross section of $\sigma \simeq 3\times10^{-17}$ cm^2. Nonhydrogenated samples exhibited an initial rapid temperature-dependent decay of induced absorption. After this initial relaxation no further decay was observable to our maximum delay ($\simeq$ 100 ps). The data were analyzed with use of simple response theory.[2] The decays were fitted to exponentials; the relaxation times ranging from $\tau = 5$ ps at 300 K to $\tau = 120$ ps at 85 K are shown in Fig. 2. Cross sections are similar to a-Si:H suggesting the same absorption mechanism.

The chalcogenide alloys showed two absorption mechanisms. Two-photon absorption (one pump photon and one probe photon) was observed in pure As_2S_3; $\alpha_1 = 2.9\times10^{-10}$ cm/W compares favorably with previous results.[3] However, in a-As_2S_3 we could not induce any absorption extending to longer times because the pump-pulse intensity is too small for significant carrier generation by a

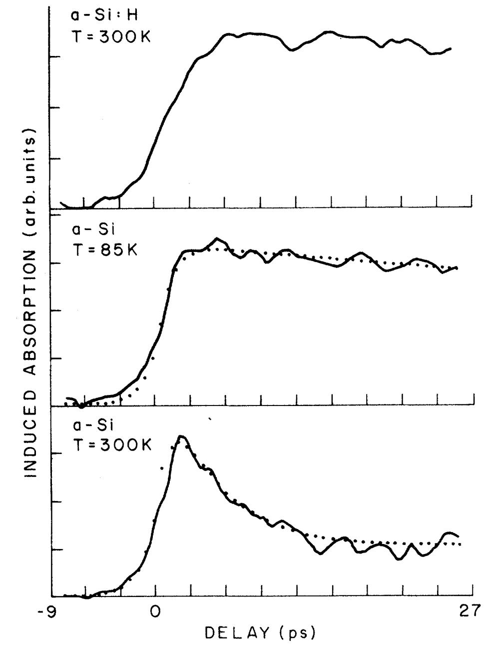

FIG. 1. Induced absorption $\Delta\alpha$ vs delay for a-Si:H at 300 K and a-Si at $T=85$ K and 300 K. Full lines are experimental data; dotted lines are fits.

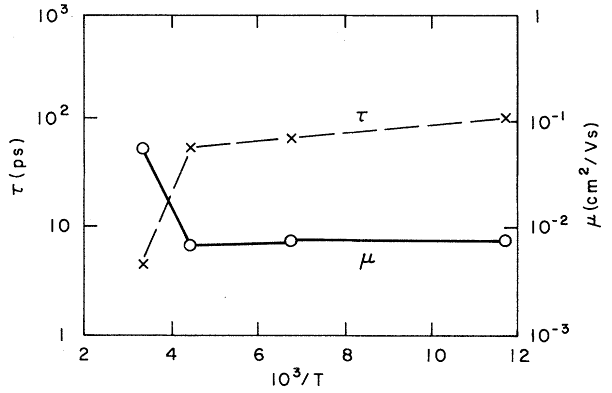

FIG. 2. Decay time τ and mobility μ vs inverse temperature for a-Si.

two-photon process. As Se was added to As_2S_3 and the linear absorption increased, a longer-lived absorption appeared in addition to the two-photon absorption. Results are shown in Fig. 3 with the two-photon component removed. The decay time increases with Se content from $\tau \simeq 4$ ps at $x=0.25$ to $\tau=12$ ps for $x=0.75$, and decreases from 12 ps to 3 ps as the sample is cooled to 85 K. The observed values of $\Delta\alpha \simeq 10^{-2}$ to 1 cm^{-1} give a constant absorption cross section of $\sigma \simeq 10^{-17}$ cm^2, independent of composition and temperature.

Our data indicate that carriers probably thermalize in times less than our resolution (0.5 ps). This is particularly evident in a-Si:H where the instantaneously induced absorption does not show any fast decay. The thermalized carriers which are probably localized absorb light by transitions to high-energy states in the same band where the density of states is large. These states are accessible because the k-conservation rule does not apply. The absorption decays when the carriers recombine or fall into deep traps where their absorption cross section is smaller at the probe wavelength.

There is a substantial difference in the behavior of the two kinds of amorphous semiconductors, in particular with respect to the temperature dependence of the decay times. We propose a model that explains the nature of the relaxation processes and the origin of the differences. It is based on the idea that the relaxation mechanism is different if the carriers are excited into the band states (silicon, $\alpha \simeq 5 \times 10^4$ cm^{-1}) or into the states giving rise to the Urbach edge (chalcogenides, $\alpha \simeq 10^2$ cm^{-1}). A critical parameter is the Onsager radius $r_e = e^2/4\pi\epsilon k_B T$. If during thermal-

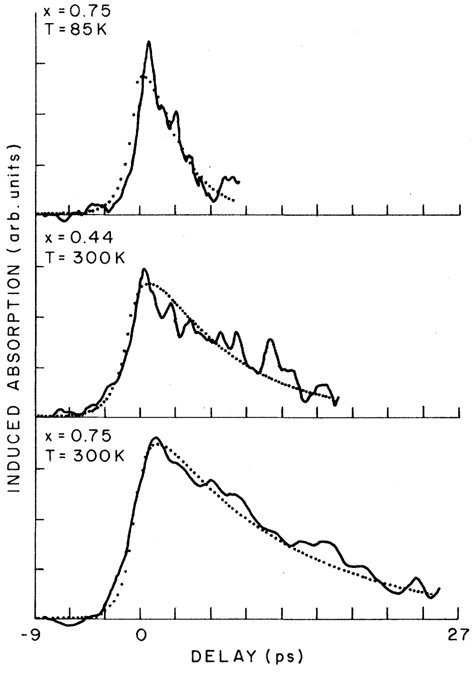

FIG. 3. Induced absorption $\Delta\alpha$ vs delay for $As_2S_{3-x}Se_x$ at 85 K and 300 K. Full lines are experimental data; dotted lines are fits.

ization the electron and hole drift apart by a distance r_0, they behave as independent carriers if $r_0 > r_e$ or as trapped excitons if $r_0 < r_e$.[4] We propose that the first case applies to amorphous Si, the other to the chalcogenides. We will discuss silicon first.

The relaxation process in systems dominated by defects may be described by

$$dn/dt = -bnN_t, \tag{1}$$

where n is the concentration of excess carriers, N_t is the concentration of deep traps or recombination centers, $b = 4\pi r_t D$, D is the diffusion constant $(= k_B T\mu/e)$, and r_t is half the average distance between traps $(r_t = \frac{1}{2}N_t^{-1/3})$.[5] The decay described by Eq. (1) is exponential with $\tau = (bN_t)^{-1}$.

We applied Eq. (1) to a-Si, assuming that N_t is equal to the concentration of spins $(\simeq 10^{20}\ \mathrm{cm}^{-3})$[6] and calculated the mobility μ from the measured relaxation times (Fig. 2). At temperatures above 225 K, μ is a strong function of temperature and may be activated, while at low temperatures μ is practically temperature independent. A similar behavior of mobility was observed by Moustakas and Paul[7] in a-Ge and interpreted as evidence for polaron formation.

In a-Si:H ESR data show that the concentration of spins is substantially smaller $(\simeq 10^3$ times).[8] Under the plausible assumption that N_t changes with the spin density we expect that the relaxation times will be at least 100 times longer and probably more because the traps are saturated at high illumination levels.

The data on chalcogenides can be understood if we assume that during thermalization the electron and hole diffuse to a distance r_0 which is substantially smaller than the Onsager radius r_e ($\simeq 80$ Å at 300 K, $\simeq 300$ Å at 85 K), and behave as trapped excitons.[4,9,10] The distance r_0 is given by

$$r_0 = (D_{\mathrm{hot}}t_0)^{1/2} = [D_{\mathrm{hot}}(\Delta E + e^2/4\pi\epsilon r_0)/h\nu^2]^{1/2}, \tag{2}$$

where ΔE is the excess kinetic energy of the hot carriers, ν is the frequency of vibrations $(\simeq 7.5 \times 10^{12}\ \mathrm{s}^{-1})$. We assumed a hot-carrier diffusion constant $D_{\mathrm{hot}} = 0.1\ \mathrm{cm}^2/\mathrm{s}$ and calculated r_0 as a function of $\Delta E = \hbar\omega_p - E_g$ ($\hbar\omega_p = 2$ eV is the pump beam energy and E_g is the band gap taken to be the energy where $\alpha = 10^4\ \mathrm{cm}^{-1}$ which shifts with composition and temperature). The calculated r_0 was in the range 3–5 Å.

It appears plausible to assume that the observed induced absorption is due to thermalized carriers and the decay is produced by their geminate recombination. This recombination process may be described by a tunneling mechanism with a rate[11]

$$\tau^{-1} = \nu e^{-2\beta r_0}, \tag{3}$$

where β^{-1} is the extent of the wave function. The dependence of our experimental values of τ on r_0 is seen in Fig. 4; from the fit to the data we find $\beta^{-1} = 1.9$ Å and $\nu = 1.3\times 10^{13}\ \mathrm{s}^{-1}$. These are plausible parameters for a localized carrier wave function and the phonon frequency.

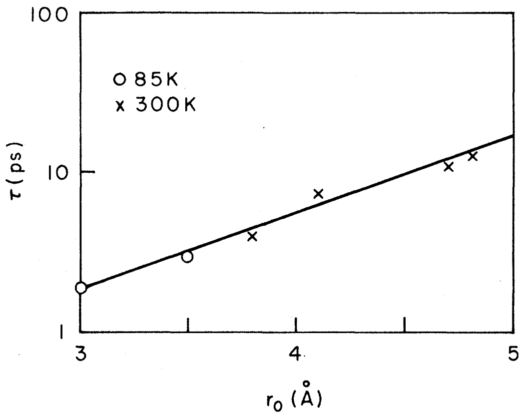

FIG. 4. Decay time τ vs r_0 calculated from Eq. (2) in a-$As_2S_{3-x}Se_x$.

This model is consistent with the results of Fork *et al.*,[3] who observed a long-lived induced absorption excited by two-photon absorption in a-As_2S_3. The carriers in their experiment were energetic enough $(\Delta E \simeq 1.5$ eV) that $r_0 > r_e$ and the probability of geminate recombination was low. In this case the recombination mechanism is similar to that proposed above for amorphous Si, in particular a-Si:H where N_t is comparable to N_t in a-As_2S_3.

In conclusion, we observed two substantially different decay mechanisms of induced absorption in amorphous semiconductors depending on the excess energies of photogenerated carriers. This result suggests that a detailed study of the excitation spectra and time-resolved induced absorption spectra could yield important information about the dynamics of carriers close to the mobility edge.

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Possible Explanation of Nonlinear Conductivity in Thin-Film Metal Wires

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We introduce the idea of an incoherence length L_2 at which inelastic collision broadening equals electronic energy-level separation. The two-dimensional conductance crosses over at L_2 from a $\ln L$ dependence suggested recently by Abrahams *et al.* to Ohmic behavior. These ideas and plausible relaxation and heating models are used to explain the nonlinear conductivity observations of Dolan and Osheroff.

Dolan and Osheroff, in the following Letter,[1] note a logarithmic dependence of conductivity on current in thin-film wires of which a typical one is about a micron wide by one or two millimeters long, with conductivity of about 5000 Ω per square, for currents in the neighborhood of 10^{-9} A and temperature 10–1000 m mK. They observe that this behavior saturates at low fields giving a linear I-V curve with a logarithmic dependence of conductivity on T at zero field as well.

In a recent Letter, Abrahams *et al.*[2] proposed a scaling theory of localization based on ideas of Thouless.[3] The essential idea is that the conductance $G = ge^2/\hbar$ of small samples of metal scales with sample size L. For one dimension the conductance scales rapidly to zero as $L \to \infty$ in all cases,[4] and for three dimensions, it approaches σL for large enough samples and large enough σ. But in two dimensions our theory predicted that

$$g(L) = g_0 - (\alpha/\pi^2)\ln L \quad \text{when } g \gg \pi^{-2}, \tag{1}$$

and for small g it predicted exponential localization. A preliminary perturbation treatment gave $\alpha = 1$ for two noncommunicating gases of electrons with spins up and down, or $\alpha = \frac{1}{2}$ if the elastic spin-flip scattering length is short compared to the other lengths in the problem.

The meaning of conductance at a finite scale is described by Thouless[3] in a number of ways. One way is to define it in terms of a time t_D to diffuse a finite distance L, which gives one

$$t_D(L) = L^2/D(L),$$

and one may measure t_D by allowing a wave packet localized in a length somewhat less than L to spread. The conductivity is then determined in