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PICOSECOND DYNAMICS OF CARRIERS IN AMORPHOUS SEMICONDUCTORS

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Abstract.- Using time resolved photoinduced absorption with subpicosecond resolution we studied hot carrier thermalization followed by deep trapping and recombination in a-Si, a-Si:H, a-Si:F, a-Si:H:F and a-As_2Se_3. In a-Se and a-$As_2S_{3-x}Se_x$ ($0.25 \leq x \leq 0.75$) the observed relaxations were attributed to geminate recombination.

Introduction.- A passively modelocked dye laser producing subpicosecond pulses was used to study the ultrafast dynamics of excess carriers by the time resolved photoinduced absorption in a-Si, a-Si:H, a-Si:H:F and chalcogenide glasses: a-Se, a-As_2Se_3 and a-$As_2S_{3-x}Se_x$ ($0.25 \leq x \leq 0.75$). We found that when the exciting photon energy $\hbar\omega_p$ is larger than the band gap E_g, the photogenerated carriers are not bound together and we could follow the hot carrier thermalization as well as the consecutive trapping and recombination processes. On the other hand, when $E_g > \hbar\omega_p$, the photogenerated carriers are bound together and their geminate recombination is observed. In some of the studied amorphous semiconductors a polarizaton memory associated with induced dichroism was observed.

Experimental.- The dye laser and experimental set-up have been described elsewhere.[1-3] The laser produces linearly polarized light pulses at $\hbar\omega_p = 2$eV with a single side exponential shape and $t_p = 0.6 - 0.8$ ps duration, 1-2 nJ energy and repetition rate 10^4-$10^6\,s^{-1}$. We used the pump and probe technique; the probe pulse is delayed by varying the length of its optical path. The probe beam passed through a polarization rotator and its polarization was either parallel (‖) or perpendicular (⊥) to that of the pump beam. All experiments were done with optically thin samples: $d < \alpha^{-1}$ at 2eV, so that the photogenerated carrier concentration n varied from sample to sample (as α^{-1}) between 5×10^{16} and 10^{19} cm^{-3} per pulse.

Origins of observed relaxations.- The proposed electronic mechanisms for the transient photo-induced absorption coefficient $\Delta\alpha(t)$ for cases: (a) $\hbar\omega_p > E_g$ (b) $\hbar\omega_p < E_g$ are shown in Fig. 1. In case (a) hot carriers with excess energy ΔE are excited across the band gap by the pump pulse with energy $\hbar\omega_p$. These carriers thermalize to the bottom of the band by loosing their energy due to the electron-phonon interaction. During this process they can reabsorb light. Since the optical absorption cross-section of hot carriers increases[4] with ΔE, it is possible to observe the fast thermalization process by optical method, providing the system's response is fast enough. The electron-hole distance after thermalization (thermalization radius r_o) is larger in case (a) than the Onsager capture radius r_c[1] and the carriers move independently of each other. Eventually, the thermalized carriers

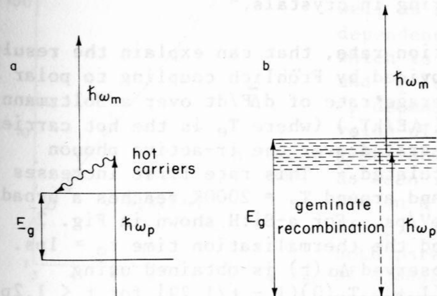

Fig. 1 - Proposed mechanism for photo-induced absorption decay (a) $\hbar\omega_p > E_g$, (b) $\hbar\omega_p < E_g$.

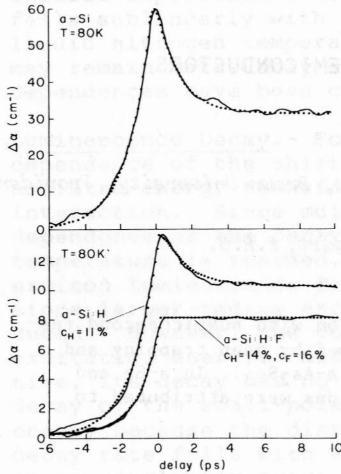

Fig. 2 - Time dependence of the photoinduced absorption in a-Si, a-Si:H and a-Si:H:F for || polarizations. Solid curves - experimental, dotted curves - calculated.

will be removed from the bottom of the conduction band by trapping, recombination or both.[1,5] In case (b) where $\hbar\omega_p < E_g$, carriers are excited in the Urbach tail (Fig. 1(b)), $r_o < r_c$ and the electron and hole are bound together. In this case the recombination is geminate and is observed as a decay of $\Delta\alpha(t)$, since $\Delta\alpha(t) \sim n(t)$.

Amorphous Silicon.- Typical results for || polarization are shown in Fig. 2; they are examples of case (a). Most samples show an initial nonsymmetric response around t = 0 that decays fast to a lower value $\Delta\alpha_s$. The relative height of the measured peak at t = 0 is closely related to the average initial excess energy $\overline{\Delta E}(0) = (\hbar\omega_p - E_g)/2$ as seen in Fig. 2 where $\overline{\Delta E}(Si) > \overline{\Delta E}(Si:H) \gtrsim \overline{\Delta E}(Si:H:F)$.

When $\perp$ polarization is used the peak in $\Delta\alpha$ is reduced; this is ascribed to the reduction of the coherent artifact component.[2,3] At longer times when saturation is reached $\Delta\alpha_s(\perp) < \Delta\alpha_s(||)$ and the depolarization ratio $\rho = \Delta\alpha_s(\perp)/\Delta\alpha_s(||)$ varies between 0.6 and 0.9.[2] This shows that a polarization memory associated with photoinduced dichroism can exist in these materials for surprisingly long times. We observed that ρ increases with increasing the initial excess energy $\overline{\Delta E}(0)$.

The data indicate that the excess energy dissipation rate by interaction of electrons with phonons $d\overline{\Delta E}/dt$ is faster in a-Si than in a-Si:H. It is generally assumed[6] that the thermalization rate in amorphous solids is the highest possible rate associated with phonon emission $h\nu^2$. Our results show that this is the case for a-Si; $h\nu^2$ averaged over its phonon spectrum gives 0.5 eV/ps in agreement with the thermalization rate extracted from the data ($\overline{\Delta E}(0) \simeq 0.35$eV, $t_o \simeq 0.7$ps). The fit to the a-Si case shown in Fig. 2 was done using an impulse response $A(t) \sim \sigma$ (t) where $\sigma(t) = \sigma_s[1 + (b\overline{\Delta E}(0)/K)(1 - t/0.7)]$ for t < 0.7ps and $\sigma(t) = \sigma_s$ for t > 0.7ps where b is the enhancement parameter ($\Delta\sigma = b\overline{\Delta E}$). From the fit we obtained $b = 1.2 \times 10^{-3} K^{-1}$ which is surprisingly close to the value of $1.3\ 10^{-3} K^{-1}$ calculated for hot carrier absorption at 2eV assisted by optical deformation potential scattering in crystals.[4]

A slower dissipation rate, that can explain the results in a-Si:H, is provided by Fröhlich coupling to polar phonons. The average rate of $d\overline{\Delta E}/dt$ over a Boltzmann distribution $\exp(-\Delta E/kT_e)$ (where T_e is the hot carriers temperature) integrated over the ir-active phonon spectrum was calculated.[2] This rate first increases sharply with T_e and around T_e = 2000K reaches a broad maximum[5] of 0.1 eV/ps. For a-Si:H shown in Fig. 2 $\overline{\Delta E}(0) \simeq 0.1$ eV and the thermalization time $t_o \simeq$ 1ps. The fit to the observed $\Delta\alpha(t)$ is obtained using $A(t) \sim \sigma(t) = \sigma_s(1 + a\, T_e(0)(1 - t/1.2))$ for t < 1.2ps and $\sigma(t) = \sigma_s$ for t > 1.2ps with $a = 1.7 \times 10^{-3} K^{-1}$ and $T_e = 2\overline{\Delta E}(0)/3$ = 800K. $\Delta\alpha(t)$ for a-Si:H:F was fit with a step function impulse response $A(t) = \sigma_s u(t)$. The reason of why $d\overline{\Delta E}/dt$ is larger in a-Si than in a-Si:H is unknown at this time; one can speculate that $d\overline{\Delta E}/dt$

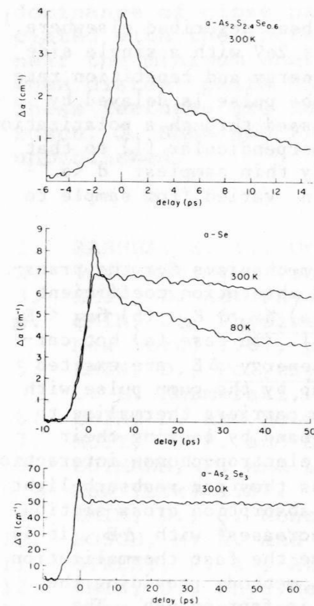

Fig. 3 - Same as in Fig. 2 but for $a\text{-}As_2S_{2.4}S_{0.6}$, a-Se and $a\text{-}As_2Se_3$.

increases with increasing disorder as other electron phonon interaction channels may open.

After thermalization, at longer time a slower decay, that cannot be described by a single exponential, of $\Delta\alpha(t)$ was observed[1] in sputtered a-Si; at lower T this decay is slower. It was attributed to trapping in deep traps or recombination centers. We observed similar decays in a-Si:F but not in hydrogenated samples. This suggests that F alone does not compensate the dangling bonds effectively.

Chalcogenide glasses.- Typical results for chalcogenide glasses are presented in Fig. 3. The gap E_g for a-$As_2S_{2.4}Se_{0.6}$ and a-Se at all T is larger than $\hbar\omega_p$, therefore, they represent case (b) (Fig. 1). In a-As_2Se_3 $E_g < \hbar\omega_p$ and it represents case (a) in the chalcogenide group. In the latter case the relaxations are similar as in a-Si:H discussed above. We will concentrate now on case (b). Excited in the Urbach tail, electron and hole are bound together as a pair with a binding energy $e^2/4\pi\varepsilon r_o$ (ε is the dielectric constant). The energy above the ground state is $\Delta E^* = \hbar\omega_p - E_g + e^2/4\pi\varepsilon r_o$. E_g is not well defined; we took for it the energy where $\alpha = 10^4 cm^{-1}$. Assuming that the energy dissipation rate $d\Delta E^*/dt = h\nu^2$ we calculate r_o by solving the equation $r_o = (D_{hot}t_o)^{1/2} = (D_{hot}\Delta E^*/h\nu^2)^{1/2}$. Taking $D_{hot} = 0.1\ cm^2/s$[6] and $h\nu = 35 meV$ we obtain values of r_o between 3 to 9Å (Table I). The values of $t_o = \Delta E^*/h\nu^2$ are less than 50 femtoseconds, too short to be observed. The observed decays are ascribed to recombination.

The Onsager capture radii[6] in these materials are $r_c \simeq 80$Å at 300K and $\simeq 300$Å at 80K, considerably larger than r_o. Since only a fraction $\exp[-r_c/r_o]$ of carriers escape the geminate recombination the dominant recombination process is geminate. The observed decays are exponentials $\exp[-t/\tau_r]$ where τ_r is longer at smaller E_g. An important feature of this recombination time τ_r is that it decreases with decreasing temperature[1] (as shown for a-Se in Fig. 3 and for other chalcogenides in Table I); this is just the opposite of the temperature dependence of the recombination time observed in a-Si after thermalization[1] mentioned above.

Geminate recombination model.- Two models for geminate recombination were considered. In the first model (usually referred to as time-dependent Onsager model[8]) the carriers diffuse towards each other. The number of pairs N(t) surviving recombination was calculated[8] to be $N(t) = N_o \exp[-r_c/r_o][1 + r_c/(\pi Dt)^{1/2}]$. This model predicts a $t^{-1/2}$ decay of $\Delta\alpha(t)$ which is slower at lower T (because of the temperature dependence of D in amorphous materials), both against the experimental data.

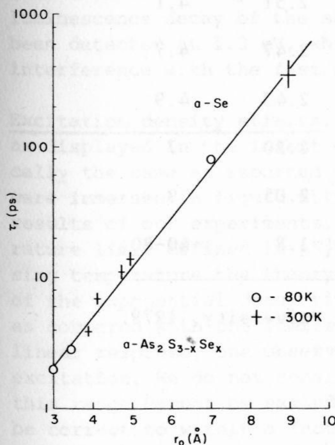

Fig. 4 - Decay time τ_r plotted vs. the thermalization radius r_o for a-$As_2S_{3-x}Se_x$ and a-Se.

Another approach describes the geminate recombination as a tunneling process[1,9] in which $N(t) = N(0) \exp[-t/\tau_r]$ with time constant $\tau_r = \nu^{-1}\exp[2\beta r_o]$, where β^{-1} is the extent of the wave function. This model agrees with the observed exponential decays as well as with the temperature dependence of τ_r. This dependence is due to the temperature dependence of E_g which is larger at lower T; consequently r_o is smaller and τ_r is shorter. A consequence of this model is that τ_r depends on E_g only, regardless of whether a certain value of E_g is obtained by changing composition or temperature. This is clearly confirmed by experiment, as seen in Fig. 4 where τ_r is plotted vs. r_o. The data lie on a straight line for almost 3 orders of magnitude of τ_r. The fit gives $\nu = 1.1 \times 10^{13} s^{-1}$ and $\beta^{-1} = 2.1$Å; both parameters have reasonable values. In the case of a-As_2Se_3 $\hbar\omega_p > E_g$ and $r_o \simeq r_c$[10] so that the geminate recombination time constant becomes very long. Indeed, as shown in Fig. 3, $\Delta\alpha(t)$ shows no apparent decay up to 60ps.

Our results do not contradict the work on the temperature dependence of the luminescence decay in GD

a-Si:H[11] in which diffusion had to be included for explaining the data on geminate recombination at high T. In our case the excitation occurs into the Urbach tail, $r_o \ll r_c$ and the diffusion is negligible at all T.

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TABLE I

Geminate Recombination Decay Parameters in Chalogenide Glasses

Sample	T(K)	τ_r(ps)	E_g(eV)	r_o(Å)
$a\text{-}As_2S_{2.25}Se_{0.75}$*	85	3	2.58	3.5
$a\text{-}As_2S_{2.56}Se_{0.44}$*	300	7	2.51	4.1
$a\text{-}As_2S_{2.4}Se_{0.6}$	300	11	2.47	4.7
$a\text{-}As_2S_{2.25}Se_{0.75}$*	300	13	2.43	4.9
a-Se	80	80	2.20	7
a-Se	300	>380	2.05	9
$a\text{-}As_2Se_3$	80,300	-	1.8	40-80

*From D. E. Ackley's Ph.D. Thesis, Brown University, 1979.