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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-As2Se3. In a-Se and a-As2S3-Se x (0.25 < x < 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-As2Se3 and a-As2S3-Se x (0.25 < x < 0.75). We found that when the exciting photon energy \( \omega_p \) 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 \( \omega_p < E_g \), the photogenerated carriers are bound together and their geminate recombination is observed. In some of the studied amorphous semiconductors a polarization memory associated with induced dichroism was observed.

Experimental.—The dye laser and experimental set-up have been described elsewhere.4,5 The laser produces linearly polarized light pulses at \( \omega_p = 2 eV \) 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 (\( \perp \)) to that of the pump beam. All experiments were done with optically thin samples: \( d < a \) at \( 2 eV \), so that the photogenerated carrier concentration \( n \) varied from sample to sample (as \( a \)) between \( 5 \times 10^{16} \) and \( 10^{19} \) cm\(^{-3} \) per pulse.

Origins of observed relaxations.—The proposed electronic mechanisms for the transient photoinduced absorption coefficient \( \Delta \alpha(t) \) for cases: (a) \( \omega_p > E_g \) (b) \( \omega_p < E_g \) are shown in Fig. 1. In case (a) hot carriers with excess energy \( \Delta E \) are excited across the band gap by the pump pulse with energy \( \omega_p \). These carriers thermalize to the bottom of the band by losing 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 with \( \Delta E \), 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 \( r_0 \)) is larger in case (a) than the Onsager capture radius \( r_o \). Finally, the carriers move independently of each other. Eventually, the thermalized carriers

![Fig. 1 - Proposed mechanism for photoinduced absorption decay](image-url)
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.

Fig. 3 - Same as in Fig. 2 but for a-As2S2.4S0.6, a-Se and a-As2Se3.

will be removed from the bottom of the conduction band by trapping, recombination or both.1,5 In case (b) where $\omega_{\text{opt}} < E_g$, carriers are excited in the Urbach tail (Fig. 1(b)), $r_0 < r_c$ and the electron and hole are bound together. In this case the recombination is geminate and is observed as a decay of $\Delta n(t)$, since $\Delta n(t) = n(t)$.

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 $A_{\text{as}}$. The relative height of the measured peak at $t = 0$ is closely related to the average initial excess energy $\Delta E(0) = (\hbar \omega_{\text{opt}} E_p)/2$ as seen in Fig. 2 where $\Delta E(\text{Si}) > \Delta E(\text{Si:H}) > \Delta E(\text{Si:H:F})$.

When || polarization is used the peak in $\Delta n$ is reduced; this is ascribed to the reduction of the coherent artifact component.2,3 At longer times when saturation is reached $\Delta n_{\text{e}}(t) < \Delta n_{\text{g}}(t)$ and the depolarization ratio $\rho = \Delta n_{\text{e}}(t)/\Delta n_{\text{g}}(t)$ 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 $\rho$ increases with increasing the initial excess energy $\Delta E(0)$.

The data indicate that the excess energy dissipation rate by interaction of electrons with phonons $d \Delta E/dt$ is faster in a-Si than in a-Si:H. It is generally assumed6 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 $\Delta E(0) = 0.35 \text{eV}$, $t_0 = 0.7 \text{ps}$. The fit to the a-Si case shown in Fig. 2 was done using an impulse response $A(t) = c(t)$ where $c(t) = c_0 [1 + (b \Delta E(0)/K) (1 - t/0.7)]$ for $t < 0.7 \text{ps}$ and $c(t) = c_0$ for $t > 0.7 \text{ps}$ where $b$ is the enhancement parameter ($c_0 = b \Delta E$). From the fit we obtained $b = 1.2 \times 10^{-3} \text{K}^{-1}$. For a-Si:H shown in Fig. 2 $\Delta E(0) = 0.1 \text{eV}$ and the thermalization time $t_0 = 1 \text{ps}$. The fit to the observed $\Delta n_{\text{as}}(t)$ is obtained using $A(t) = c_0 [1 + a T_e(t) (1 - t/1.2)]$ for $t < 1.2 \text{ps}$ and $c_0$ for $t > 1.2 \text{ps}$ with $a = 1.7 \times 10^{-3} \text{K}^{-1}$ and $T_e = 2 \Delta E(0)/3 = 800K$. $\Delta n(t)$ for a-Si:H:F was fit with a step function impulse response $A(t) = c_0 u(t)$. The reason of why $d \Delta E/dt$ is larger in a-Si than in a-Si:H is unknown at this time; one can speculate that $d \Delta E/dt$
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 \( \Delta a(t) \) 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\(_2\)S\(_2\), a-Ge, and a-Se at all T is larger than \( \hbar \omega_p \), therefore, they represent case (b) (Fig. 1). In a-As\(_2\)Se\(_3\) \( E_g < \hbar \omega_p \) 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 Upbach tail, electron and hole are bound together as a pair with a binding energy \( e^2/4 \pi e r_0 \) (\( \varepsilon \) is the dielectric constant). The energy above the ground state is \( \Delta E^* = \hbar \omega_p - E + e^2/4 \pi e r_0 \). \( E_g \) is not well defined; we took for it the energy where \( \alpha = 10^4 \text{cm}^{-1} \). Assuming that the energy dissipation rate \( \delta E_g/\delta t = \hbar \nu/2 \) we calculate \( r_0 \) by solving the equation \( r_0 = (\hbar \omega_t t_0)^{1/2} = (\hbar \omega t_0 \Delta E^*/\hbar \nu^2)^{1/2} \). Taking \( \hbar \omega_t = 0.1 \text{ cm}^2/\text{s} \) and \( \hbar \nu = 3 \text{ eV} \) we obtain values of \( r_0 \) between 3 to 9 \( \AA \) (Table I). The values of \( \tau_r = \Delta E^*/\hbar \nu^2 \) 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 \( r_c = 80 \AA \) at 300K and \( \approx 300 \AA \) at 80K, considerably larger than \( r_0 \). Since only a fraction \( \exp[-r_c/r_0] \) of carriers escape the geminate recombination the dominant recombination process is geminate. The observed decays are exponentials \( \exp(-t/\tau_r) \) where \( \tau_r \) is longer at smaller \( E_g \). An important feature of this recombination time \( \tau_r \) 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\(^9\) to be

\[
N(t) = N_0 \exp[-r_c/r_0 \sigma/2 \text{Dt}] [1 + r_c/(\pi \text{Dt})^{1/2}].
\]

This model predicts a \( t^{-3/2} \) decay of \( \Delta a(t) \) which is slower at lower T (because of the temperature dependence of \( D \) in amorphous materials), both against the experimental data.

Another approach describes the geminate recombination as a tunneling process\(^1,9\) in which \( N(t) = N(0) \exp[-t/t_0] \) with time constant \( t_0 = \exp[2\text{D}r_0^2] \), where \( \beta^{-1} \) is the extent of the wave function. This model agrees with the observed exponential decays as well as with the temperature dependence of \( \tau_r \). This dependence is due to the temperature dependence of \( E_g \) which is larger at lower T; consequently \( r_0 \) is smaller and \( \tau_r \) is shorter. A consequence of this model is that \( \tau_r \) 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 \( \tau_r \) is plotted vs. \( r_0 \). The data lie on a straight line for almost 3 orders of magnitude of \( \tau_r \). The fit gives \( \nu = 1.1 \times 10^{13} \text{ s}^{-1} \) and \( \beta^{-1} = 2.1 \AA \); both parameters have reasonable values. In the case of a-As\(_2\)Se\(_3\) \( \hbar \omega_p > E_g \) and \( r_0 = r_c \) so that the geminate recombination time \( \tau_r \) constant becomes very long. Indeed, as shown in Fig. 3, \( \Delta a(t) \) 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 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, $r_0 << r_c$ and the diffusion is negligible at all $T$.

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References.


**TABLE I**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T$ (K)</th>
<th>$\tau$ (ps)</th>
<th>$E_g$ (eV)</th>
<th>$r_0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-As$_2$S$_2$Se$_0.75$*</td>
<td>85</td>
<td>3</td>
<td>2.58</td>
<td>3.5</td>
</tr>
<tr>
<td>a-As$_2$S$_2.56$Se$_0.44$*</td>
<td>300</td>
<td>7</td>
<td>2.51</td>
<td>4.1</td>
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<tr>
<td>a-As$_2$S$_2.4$Se$_0.6$</td>
<td>300</td>
<td>11</td>
<td>2.47</td>
<td>4.7</td>
</tr>
<tr>
<td>a-As$_2$S$_2.25$Se$_0.75$*</td>
<td>300</td>
<td>13</td>
<td>2.43</td>
<td>4.9</td>
</tr>
<tr>
<td>a-Se</td>
<td>80</td>
<td>80</td>
<td>2.20</td>
<td>7</td>
</tr>
<tr>
<td>a-Se</td>
<td>300</td>
<td>&gt;380</td>
<td>2.05</td>
<td>9</td>
</tr>
<tr>
<td>a-As$_2$Se$_3$</td>
<td>80,300</td>
<td>~</td>
<td>1.8</td>
<td>40-80</td>
</tr>
</tbody>
</table>