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Hot-Carrier Thermalization in Amorphous Silicon

Z. Vardeny and J. Tauc
Division of Engineering and Department of Physics, Brown University, Providence, Rhode Island 02912

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Thermalization of photoinduced carriers in a-Si and a-Si:H was studied with use of subpicosecond-pump and probe techniques with parallel and perpendicular polarizations. The underlying process was identified as hot-carrier absorption whose cross section increases with the carrier excess energy. The energy dissipation rate in a-Si is $\simeq 0.5$ eV/ps ($\simeq \hbar\nu^2_{\text{phonon}}$) and is less than 0.1 eV/ps in a-Si:H; Fröhlich interaction with polar phonons can explain this smaller rate. A photoinduced dichroism associated with polarization memory was observed.

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We report the first observation of hot-carrier thermalization in amorphous semiconductors obtained from time-resolved studies of photoinduced absorption (PA) in the subpicosecond time domain. We could identify the underlying process as phonon-assisted hot-carrier absorption whose strength increases with increasing carrier excess energy ΔE. We found that the energy dissipation rate in a-Si is significantly higher than in a-Si:H and show that the difference can be understood if the energy dissipation in a-Si:H occurs via polar phonons while in a-Si all phonons are involved.

We used the pump and probe technique with a cavity-dumped passively mode-locked dye laser[1,2] producing 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 of 10^6 s^{-1}. The probe beam passed through a polarization rotator and its polarization was either parallel (∥) or perpendicular (⊥) to that of the pump beam. We studied thin films of sputtered a-Si (thickness $d \simeq 0.3$ μm) and reactively sputtered a-Si:H and a-Si:H:F ($d \simeq 1$ μm); hydrogen and fluorine concentration (C_H and C_F) varied from 4 to 22 and from 10 to 18 at.%, respectively. The photogenerated carrier densities per pulse were estimated to be 10^{19} cm^{-3} in a-Si and $(2-4)\times 10^{18}$ cm^{-3} in a-Si:H.

The PA responses for ∥ and ⊥ polarizations are shown in Figs. 1 and 2 ($\Delta\alpha = \Delta T/Td$). All samples show an initial nonsymmetric response around $t=0$ that decays fast to a lower-value $\Delta\alpha_s$ persisting at 80 K for over 50 ps; the peak is larger in a-Si than in a-Si:H. This component is partially reduced in the ⊥ case relative to the ∥ case. The ratio $\Delta\alpha_\perp/\Delta\alpha_\parallel$ at $t>t_p$ is seen to be 0.75 in the a-Si and 0.7 in the a-Si:H samples.

In the linear response theory,[1] $\Delta\alpha(t)$ is the sum of two terms: $\gamma(t)$, given by the convolution of the impulse response function $A(t)$ with the pump and probe intensities, and $\beta(t)$ ("coherent artifact"), given by the convolution involving pump and probe electric fields; $\beta(t)$ is a sharply decreasing symmetric function around $t=0$. If $A(t)$ is given by a step function then for ∥ polarizations $\beta(0)=\gamma(0)=\frac{1}{2}\gamma(t>t_p)$; therefore, the observed peaks around $t=0$ shown in Figs. 1(a) and 2(a) cannot be explained by coherent artifact, with $A(t)$ a step function.

An evaluation of the coherent artifact contribution is essential for the determination of $A(t)$ close to $t=0$. This can be done by measuring both $\Delta\alpha_\parallel$ and $\Delta\alpha_\perp$. $A(t)$ is related to the imaginary part of the third-order nonlinear susceptibility tensor $\chi_{ijkl}^{(3)}$. For isotropic media only two elements are independent and the relation $\chi_{xxxx} = \chi_{xxyy} + 2\chi_{xyxy}$ holds.[3] It can be shown[4] that in the ∥ case both β and γ are determined by χ_{xxxx}, while in the ⊥ case γ is associated with χ_{xxyy} and β with χ_{xyxy}. Defining the depolarization factor[3] $\rho = \chi_{xxyy}/\chi_{xxxx} = \gamma_\perp/\gamma_\parallel$, one obtains $\beta_\perp/\beta_\parallel = \chi_{xyxy}/\chi_{xxxx} = \frac{1}{2}(1-\rho)$. For $t>t_p$ the contribution of $\beta(t)$ is negligible, and $\Delta\alpha_\perp/\Delta\alpha_\parallel = \gamma_\perp/\gamma_\parallel$, which in our case $\simeq \frac{3}{4}$ (Figs. 1 and 2). Using the same ρ for $t<t_p$, we obtain $\beta_\perp/\beta_\parallel \simeq \frac{1}{8}$; this explains the observed reduction of $\Delta\alpha_\perp$ relative to $\Delta\alpha_\parallel$ for $t<t_p$. Curves (c), shown in Figs. 1 and 2, are $\Delta\alpha - \rho^{-1}\Delta\alpha_\perp$, which is equal to $(3\rho-1)\,\beta_\parallel/2\rho$ and therefore directly related to the coherent artifact. Curves (c) were found to be similar to the pulse autocorrelation functions measured by background-free second-harmonic generation in potassium dihydrogen phosphate, as expected for transform-limited pulses used in our experiments.

The depolarization factor $\rho<1$ shows that a polarization memory associated with photoinduced dichroism can exist in the studied amorphous materials for surprisingly long times. We observed that ρ increases with increasing initial excess energy.

We can exclude some other possible origins of the fastest PA component, such as the polarization grating effect[5] (which would give $\Delta\alpha<0$) and two-photon absorption. (Two-photon absorption would give a symmetric response around $t=0$, should not depend on C_H, and should give two orders smaller $\Delta\alpha$ with our intensity of 0.3 GW/cm^2

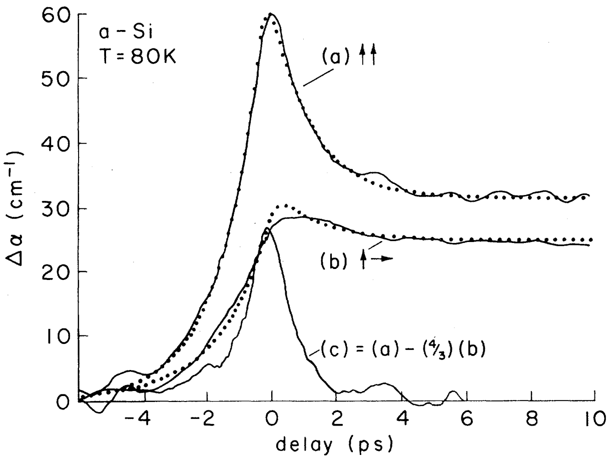

FIG. 1. Time dependence of the photoinduced absorption in a-Si for ∥ and ⊥ polarizations. Solid curves, experimental; dotted curves, calculated.

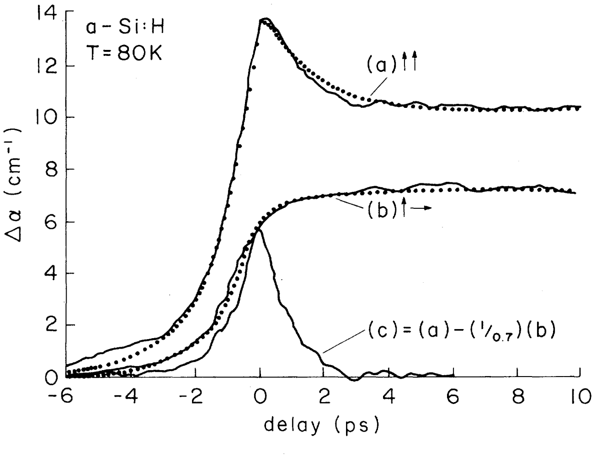

FIG. 2. Same as Fig. 1, but for a-Si:H with hydrogen concentration $C_H = 10\%$.

if we use the cross section[6,7] for c-Si.) We can explain the fast component as hot-carrier absorption and $\Delta\alpha_s$ as absorption by thermalized carriers whose transport is probably influenced by interaction with shallow traps. The generation of such carriers in these materials was demonstrated by the picosecond photoconductivity studies of Johnson *et al.*[8] From $\Delta\alpha_s$ in Figs. 1 and 2 we estimate the absorption cross section $\sigma_s = 3\times 10^{-18}$ cm^2, which is close to free carrier σ in c-Si (2×10^{-18} cm^2 at 2 eV and 80 K).[6] We attribute the enhancement of $\Delta\alpha$ close to $t=0$ to the larger σ of carriers with higher excess energy. A theory of this effect has been derived before[9] and gives reasonable agreement with the data in a-Si:H and with some modifications, discussed below, for a-Si as well.

A further support for the proposed explanantion is provided by the observed dependence of the relative height of PA at $t=0$, $\Delta = [\Delta\alpha(0) - \Delta\alpha_s]/\Delta\alpha_s$, on the average initial excess energy $\overline{\Delta E}(0) = \frac{1}{2}(\hbar\omega_p - E_g)$. We varied this energy by changing E_g in a series of a-Si:H and a-Si:H:F samples of different composition since it is known that E_g increases with increasing $C_{\rm H}$ and $C_{\rm F}$. Figure 3 shows that Δ decreases with increasing $C_{\rm H}$ until $C_{\rm H} = 16\%$ and further with adding F, in agreement with the decrease of $\overline{\Delta E}(0)$.

The enhancement of hot-carrier σ is related[9] to the carrier effective temperature T_e. T_e can be defined if the energy dissipation rate due to phonons $(d\overline{\Delta E}/dt)_{\rm ph}$ is smaller than the carrier-dissipation rate which depends on carrier density and excess energy.[10] A typical value for this rate in our case is $(d\overline{\Delta E}/dt)_{\rm car} \simeq 0.3$ eV/ps. In a-Si:H ($C_{\rm H} = 10\%$), $\overline{\Delta E}(0) \simeq 0.1$ eV and the thermalization time t_0 is over 1 ps (Fig. 2); consequently $(d\overline{\Delta E}/dt)_{\rm ph}$ is smaller than 0.1 eV/ps and therefore smaller than $(d\overline{\Delta E}/dt)_{\rm car}$. In this case T_e can be defined and the standard theory[9] can be used. On the other hand, in a-Si we obtain from data analysis $(d\overline{\Delta E}/dt)_{\rm ph} \simeq 0.5$ eV/ps which is larger than $(d\overline{\Delta E}/dt)_{\rm car}$; therefore T_e cannot be defined and the theory[9] has to be modified.

It is generally assumed[11] 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 since $h\nu^2$ averaged over the phonon spectrum[12] gives 0.5 eV/ps. However, $(d\overline{\Delta E}/dt)_{\rm ph}$ is considerably slower in a-Si:H. A slower dissipation rate is provided by Fröhlich coupling to polar phonons[10]; the existence of Fröhlich electron-phonon interaction in noncrystalline semiconductors was suggested[13] before. The total phonon oscillator strength $S = \epsilon_0 - \epsilon_\infty$ was determined from the ir absorption spectrum[14] to be 0.5 (as compared with $S \simeq 2$ in c-GaAs). For a-Si:H, we calculated the average $[d\overline{\Delta E}(T_e)/dt]_{\rm pol}$ using a Boltzmann distribution[10] $\exp(-\Delta E/kT_e)$ integrated over the ir active phonon spectrum[14] with $dS(\nu) = n\alpha(\nu)d\nu/\pi^2\nu^2$ [n is the refraction index and $\alpha(\nu)$ the ir absorption coefficient]. The rate increases sharply with T_e and around 2000 K reaches a broad maximum of 0.1 eV/ps. This value can be compared with the measured[15] $(d\overline{\Delta E}/dt)_{\rm pol} \simeq 0.4$ eV/ps for very hot carriers in c-GaAs.

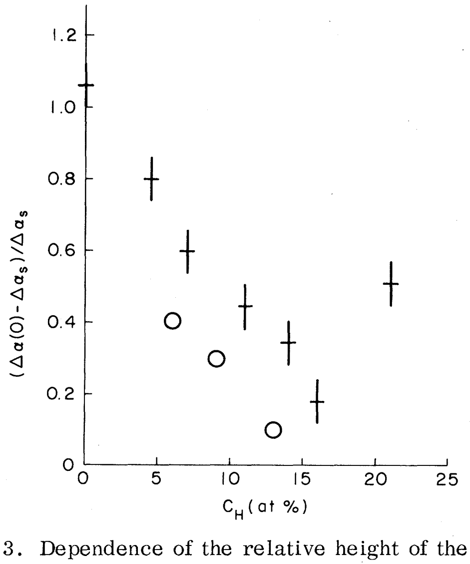

FIG. 3. Dependence of the relative height of the induced absorption peak at $t=0$ on hydrogen concentration. Crosses, a-Si:H; circles, a-Si:H:F. ($C_{\rm F} \simeq 14$ at.%) $T = 300$ K.

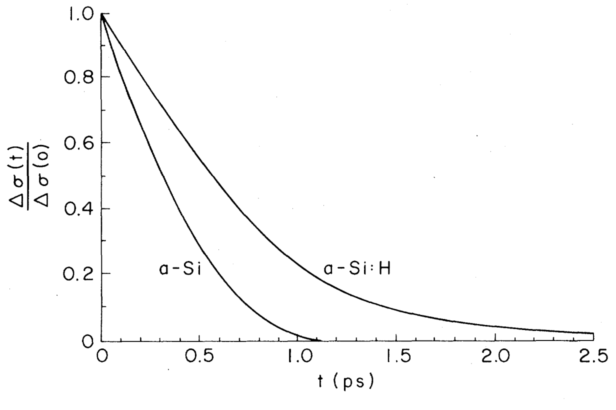

FIG. 4. Time dependence of the normalized hot-carrier absorption cross section $\Delta\sigma = \sigma - \sigma_s$ in a a-Si and a-Si:H at 80 K.

The time dependence of T_e for a-Si:H ($C_{\mathrm{H}} = 10\%$) was obtained by numerically solving the equation $\frac{3}{2} k\, dT_e/dt = -[d\overline{\Delta E}(T_e)/dt]_{\mathrm{pol}}$ with $T_e(0) = 800$ K and is shown in Fig. 4 [$\Delta\sigma(t)/\Delta\sigma(0)$ plotted in this figure is equal to $T_e(t)/T_e(0)$]. For fitting the PA data, we disregarded the long tail and approximated $T_e(t)$ with a linear decay over $t_0 = 1.2$ ps. We could simultaneously fit curves (a) and (b) in Fig. 2 with the impulse response $A(t) \sim \sigma(t) = \sigma_s + \Delta\sigma(t) = \sigma_s[1 + aT_e(0)(1 - t/1.2)]$ for $t < 1.2$ ps, and $\sigma = \sigma_s$ for $t > 1.2$ ps, with one adjustable parameter a (enhancement). In calculating the convolution for $\gamma(t)$ the intensity autocorrelation function was taken from curve (c); the magnitude of β in the $\perp$ case was reduced by a factor of 8 compared to the $\parallel$ case for reasons discussed above. The value of $a \simeq 1.7 \times 10^{-3}\ \mathrm{K}^{-1}$ is close to the value of $1.3 \times 10^{-3}\ \mathrm{K}^{-1}$ calculated for hot-carrier absorption at 2 eV assisted by optical deformation potential scattering in crystals.[9]

In a-Si where T_e cannot be defined we assumed that $\Delta\sigma(t)$ is proportional to the average carrier excess energy $\overline{\Delta E}(t)$ ($\Delta\sigma = b\overline{\Delta E}$). In calculating this average, we assumed a nonequilibrium distribution function $f(\Delta E) \sim (\Delta E)^{1/2}(\hbar\omega_p - Eg - \Delta E)^{1/2}$ in which ΔE changes with time according to $d\overline{\Delta E}/dt = 0.5$ eV/ps. The reason for assuming this distribution is that at $t = 0$, $f(\Delta E)$ is proportional to the product of the initial and final densities of states during the photogeneration. The result is shown in Fig. 4. Again we disregarded the tail and fit the curves in Fig. 1 using $A(t) \sim \sigma_s\{1 + [b\overline{\Delta E}(0)/k](1 - t/0.7)\}$ for $t < 0.7$ ps and σ_s for $t > 0.7$ ps. From the fit we obtained $b = 1.2 \times 10^{-3}$ K^{-1}.

In conclusion, our results show that ultrafast photoinduced absorption measurements can be used to study the hot-carrier thermalization process in amorphous semiconductors. We found that the excess energy dissipation rate in a-Si is considerably larger than in a-Si:H. We show that the slower rate can be explained by Fröhlich interaction with polar phonons; in this model the initial sharp increase of the dissipation rate with excess energy suggests that the thermalization time and thermalization radius depend rather weakly on the excitation energy in the range $1.85 < \hbar\omega_p < 2.3$ eV. We observed a polarization memory which persists beyond the thermalization process.

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