OPTICAL PICOSECOND STUDIES OF CARRIER THERMALIZATION IN AMORPHOUS SILICON

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

C. J. Fang**
Max-Planck-Institut, Stuttgart, FRG

ABSTRACT

Thermalization of photogenerated hot carriers in a-Si, a-Si:H and a-Si:H:F was studied using the pump and probe method with sub-picosecond resolution. The process is optically observable because the absorption cross-section of the hot carriers depends on their excess energy. It was found that the energy dissipation rate to phonons is the maximum possible in a-Si while in a-Si:H it is slower and can be described by Fröhlich interaction with polar phonons.

EXPERIMENTAL RESULTS

We used the pump and probe technique (Fig. 1a) with a passively mode locked dye laser for studying the ultrafast dynamics of photogenerated carriers in a-Si, a-Si:H (C_H = 4 to 24 at %), a-Si:F (C_F = 12 at %) and a-Si:H:F (C_F = 10 to 18 at %). The dye laser and experimental set up have been described elsewhere[1,2]. The laser produces linearly polarized light pulses of t_p = 0.6 to 0.8 ps duration at $\hbar\omega_p$ = 2eV, with about 2 nJ per pulse, and repetition rate of $10^6 s^{-1}$. The probe beam was passed through a polarization rotator and its polarization was either parallel (∥) or perpendicular (⊥) to that of the pump beam. The photoinduced carrier densities were estimated to be about $10^{19} cm^{-3}$ and 1 to 4 x $10^{18} cm^{-3}$ per pulse in a-Si and a-Si:H respectively.

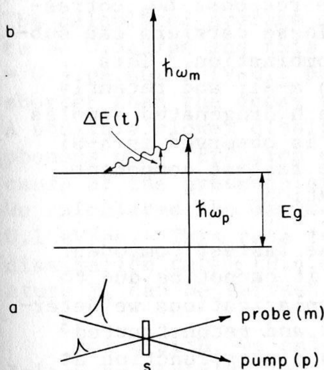

Fig. 1 - a) Pump and probe technique. b) Proposed mechanism for photo-induced absorption.

The observed changes ΔT in the transmission T_r correspond to induced absorption $\Delta\alpha = \Delta T/T_r d$ where d is the sample thickness (in the range of 0.3 to 2.5μm). Typical results for ∥ polarizations are shown in Fig. 2. Most a-Si:H and a-Si:H:F samples show an initial nonsymmetric response around t = 0 that decays fast to a lower value $\Delta\alpha_s$ persisting over 50ps independently

ISSN:0094-243X/81/730243-05$1.50 Copyright 1981 American Institute of Physics

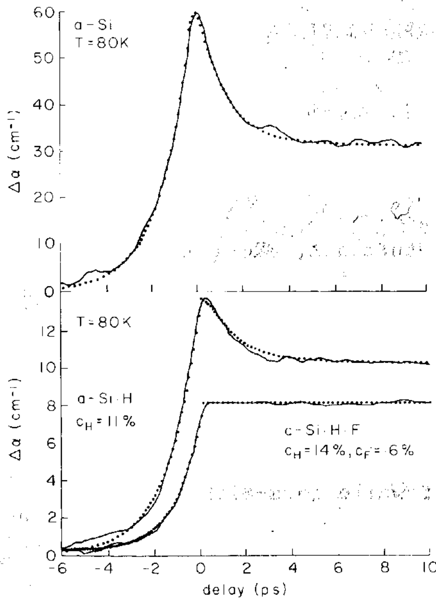

Fig. 2 - Time dependence of the photoinduced absorption in a-Si, a-Si:H (C_H = 11% and a-Si:H:F (C_H = 14%, C_F = 16%), for parallel polarization. Solid curves - experimental, dotted curves - calculated.

of temperature: this behavior is observed in a-Si only at low T. When ⊥ polarization is used the peak in $\Delta\alpha$ is reduced: this is ascribed to the reduction of the coherent artifact component[3]. The depolarization ratio at long times (up to 30 ps at least) $\Delta\alpha_s(\perp)/\Delta\alpha_s(\parallel)$ is equal to 1 in non-hydrogenated samples at 300K but is between 0.6 and 0.8 in hydrogenated samples at all T[3].

The proposed mechanism for explaining the data shown in Fig. 2 is described in Fig. 1b. Hot carriers (with excess energy ΔE) are excited across the band gap E_g by the pump pulse of energy $\hbar\omega_p$. These carriers thermalize to the bottom of the band by loosing their energy due to the electron-phonon interactions. During this process they can absorb light ($\hbar\omega_m$). The optical cross-section σ for the absorption of hot carriers depends on the instantaneous excess energy of the carriers[4]. This makes the thermalization process observable by optical methods. The response $\Delta\alpha_s$ corresponds to carriers at the bottom of the band. These carriers can subsequently be removed either by trapping or recombination. This effect has been observed at room temperature in a-Si[2] and recently we observed it also in a-Si:F. However, in the hydrogenated samples $\Delta\alpha_s$ persists over 50ps at all T; this behavior is observed in a-Si at low T. In this paper, we concentrate on the fastest component of the decay which we associate with thermalization.

We can exclude some possible origins of the fastest component of the observed decay. It is easy to see that it cannot be due to coherent artifact alone. Using the ∥ and ⊥ polarizations we determined the contribution of the coherent artifact and reconstructed[3] the true impulse response function A(t). It is a step function at t = 0 followed by a fast decay down to $\Delta\alpha_s$ which can be approximated by a linear function of time. The fast decay cannot be due to two photon absorption which would give a symmetric peak, should not depend on C_H and at our light intensity of 0.3 GW/cm^2 is estimated[5] to give $\Delta\alpha$ two orders smaller than observed.

The relative height of the measured peak at t = 0 is closely related to the average initial excess energy $\overline{\Delta E}(0) = (\hbar\omega_p - E_g)/2$.

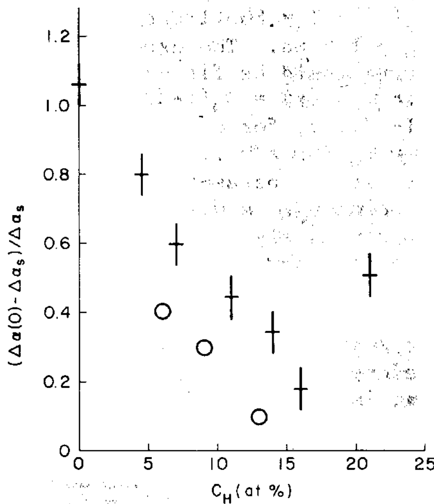

Fig. 3 - Variation of the relative height of the induced absorption peak at t = 0 with hydrogen concentration. Crosses for a-Si:H, circles for a-Si:H:F.

This is seen in Fig. 3 where $\Delta = (\Delta\alpha(0) - \Delta\alpha_s)/\Delta\alpha_s$ is plotted against C_H. Δ decreases with C_H until $C_H = 16\%$; this can be related to the increase of E_g produced by increasing the hydrogen content. In a-Si:H:F Δ is smaller than in a-Si:H with the same C_H, in agreement with the higher E_g of a-Si:H:F[6].

We can explain the fast component as well as the residual one by phonon assisted free carrier absorption (FCA). The generation of free carriers in these materials was demonstrated by the picosecond photoconductivity studies of Johnson et al[7]. In addition, $\Delta\alpha_s$ scales with the density of photogenerated carriers (Fig. 2). The optical absorption cross-section σ_o calculated from $\Delta\alpha_s$ is $3 \times 10^{-18}\text{cm}^2$ which is close to σ of free carriers in a-Si[5] ($2 \times 10^{-18}\text{cm}^2$ at 2eV and 80K).

The data indicate that the excess energy dissipation rate by interaction of electrons with phonons $d\Delta E/dt$ is the fastest possible[8] $h\nu^2$ in a-Si while it is slower in hydrogenated samples. The calculated average of $h\nu^2$ over the phonon spectrum was found to be 0.5eV/ps and this gives in a-Si a thermalization time t_o = 0.6 ps but only 0.2 ps in a-Si:H with $C_H = 11\%$, which is much shorter than the decay time seen for this sample in Fig. 2. A possible slower dissipation mechanism is by coupling to polar phonons only (Fröhlich coupling)[9]. This coupling is possible because of the presence of ir active vibrations in these materials[10]. We calculated the maximum $d\Delta E/dt$ for this interaction and found 0.1 eV/ps. This rate is smaller than the carrier-carrier energy dissipation rate[9] (0.3 eV/ps) and, therefore, a hot carrier temperature T_e can be defined in this case but not in a-Si.

For a-Si:H, we calculated the average $(d\Delta E/dt)\text{pol}$ using a Boltzmann distribution $\exp(-\Delta E/kT_e)$ integrated over the ir active phonon spectrum[10]; the dependence of $(d\Delta E/dt)\text{pol}$ on T_e is shown in Fig. 4. The rate increases sharply with T_e up to $T_e \simeq 1500\text{K}$, suggesting that in this region the thermalization time t_o and the thermalization radius r_o depend only weakly on the excitation photon energy. The time dependence of T_e was obtained by numerically solving the equation $(3/2)kdT_e/dt = -[d\Delta E(T_e)/dt]\text{pol}$ with $T_e(0) = 2/3\overline{\Delta E}(0)/k = 800\text{K}$ in a-Si:H with $C_H = 11\%$, T = 80K.

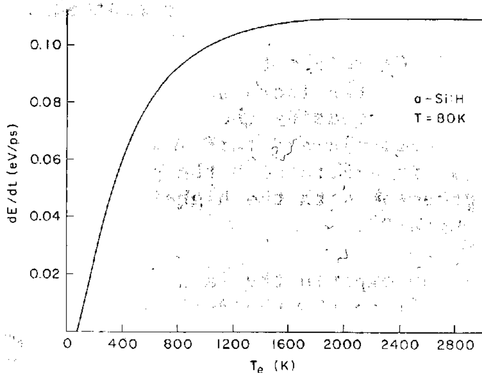

Fig. 4 - Calculated hot carrier excess energy dissipation rate $(d\Delta E/dt)_{pol}$ due to Fröhlich interaction with polar phonons in a-Si:H (T = 80K) as a function of carrier temperature T_e.

$T_e(t)$ could be approximated as $T_e(t) - T = 800(1-t/t_o)$ with $t_o = 1.2$ ps. The experimental curve could be fit by taking $A(t) \sim \sigma(t) = \sigma_o[1+aT_e(0)(1-t/1.2)]$ for $t < 1.2$ ps, and $\sigma = \sigma_o$ for $t > 1.2$ ps, with one adjustable parameter a (enhancement). a was found to be approximately independent of C_H; its value $1.7 \times 10^{-3}K^{-1}$ is close to the theoretical value of $1.3 \times 10^{-3}K^{-1}$ for FCA at 2eV assisted by optical deformation potential scattering in crystals[4].

A different approach was used for a-Si where T_e is not defined. We replace the Boltzmann distribution by an initial non-equilibrium distribution $f_i(\Delta E) \sim \sqrt{\Delta E}\sqrt{\hbar\omega_p - E_g - \Delta E}$ which was assumed to be proportional to the product of the densities of states of the initial and final states during generation. We assumed that the enhancement in the absorption cross-section of hot carriers depends linearly on the excess energy $\Delta\sigma = b\Delta E$ and calculated $\Delta\sigma(t)$ using the distribution $f_i(\Delta E)$ in which ΔE decreases with time according to $d\Delta E/dt = 0.5$ eV/ps. We could approximate $\Delta\sigma(t)$ by a linearly decreasing function of 0.7 ps duration. The fit shown in Fig. 2 was obtained with $b = 1.2 \times 10^{-3}K^{-1}$ (to be compared with $a = 1.7 \times 10^{-3}K^{-1}$ for the hydrogenated samples).

The general agreement with the data, self-consistency and reasonable values for the adjustable parameters point out the plausibility of the proposed explanation of the ultrafast decay of the photoinduced absorption as due to hot carrier phonon-assisted mechanism.

We thank J. Strait for his help with computer calculations.

*The work at Brown was supported in part by NSF grant DMR79-09819 and the NSF-MRL program at Brown University.

**On leave from Chinese University of Science and Technology, Beijing, People's Republic of China.

REFERENCES

1. E. P. Ippen and C. V. Shank, in Ultrafast Light Pulses (ed. by S. L. Shapiro) Springer, NY, 1977, p. 83.
2. D. E. Ackley, T. Tauc and W. Paul, Phys. Rev. Lett. 43, 715 (1979).
3. An explanation of polarization effects will be given in a forthcoming paper.
4. K. Seeger, Semiconductor Physics, Springer, New York, 1973, p. 374.
5. T. F. Reintges and T. C. McGroddy, Phys. Rev. Lett. 30, 901 (1973).
6. A. Madan and S. R. Ovshinsky, J. Non-Cryst. Sol., 35, 171 (1980).
7. A. M. Johnson, P. H. Auston, P. R. Smith, J. C. Bean, J. P. Harbison and D. Kaplan, in Picosecond Phenomena II (ed. by R. M. Hochstrasser et al.) Springer, NY, 1980, p. 71 and 285.
8. D. M. Pai and R. C. Enck, Phys. Rev. B11, 5163 (1975).
9. E. M. Conwell, Solid State Physics, Supp. 9 (ed. by F. Seitz et al.) Acad. Press, NY, 1967.
10. M. H. Brodsky and A. Lurio, Phys. Rev. B9, 1646 (1974).