Direct Measurement of the Hot Carrier Cooling Rate in *a*-Si:H Using Femtosecond 4 eV Pulses

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We report the first direct measurement of the hot carrier cooling rate in *a*-Si:H. The femtosecond pump and probe technique with both 2 and 4 eV pulses was used to generate and probe directly hot carriers with considerable excess energy in the extended states of this material. The unexpectedly large average energy dissipation rate of 2 eV/psec obtained from our experiments suggests that disorder-enhanced carrier-phonon interactions may play an important role in the cooling process.

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The study of nonequilibrium carrier dynamics is essential for an understanding of the electronic properties of semiconductors and the physics of semiconductor devices. While great progress has been made in the investigation of hot carrier relaxation processes in crystalline semiconductors through the use of ultrafast lasers [1], little is known about the carrier cooling rates which provide important information about the fundamental carrier-phonon interactions in the extended states of amorphous semiconductors. Most experiments have been performed on the technologically important amorphous hydrogenated silicon (*a*-Si:H) using the pump and probe technique with conventional laser systems [2–5] which operate at or below photon energies in the spectral region surrounding 2 eV. Since the optical gap of *a*-Si:H is ~ 1.7 eV, these measurements consequently probe photocarriers with little excess energy and their time evolution close to the mobility edge. The inability of these studies to directly resolve the hot carrier cooling process suggests that the cooling rate is in excess of 1 eV/psec, in agreement with the results of recent three pulse experiments of a more indirect nature [6].

In this Letter we report the first direct time-resolved measurement of the hot carrier cooling rate in *a*-Si:H. Femtosecond ultraviolet pulses of 4 eV photon energy were used in the excitation and probing of carriers with considerable excess energy in extended states required for the observation of the ultrafast cooling processes in amorphous materials. The unexpectedly high cooling rate in *a*-Si:H determined by this technique suggests that previous theoretical predictions employing a weak coupling perturbative approach are inadequate to explain our results, which offer new insight into the fundamental carrier-phonon interactions above the mobility edges in amorphous semiconductors.

The *a*-Si:H samples employed in our experiments were 300 Å films deposited by rf glow discharge on sapphire substrates at Syracuse University. The absorption length of 4 eV photons in these films was $\zeta \sim 80$ Å, as determined from measurements of the optical constants with a Cary spectrophotometer. Pulses of 2 eV photon energy and ~ 125 fsec duration were obtained from a colliding-pulse mode-locked ring dye laser and amplified to a pulse energy of 2 μJ in a Cu vapor laser-pumped amplifier. The amplified pump and probe pulses were independently frequency doubled in KDP to obtain pulses of the same duration and ~ 2 nJ pulse energy for experiments requiring 4 eV photon energies. The conventional pump and probe geometry was used. Time-resolved photoinduced changes in reflectivity ΔR and transmission ΔT were recorded for initial carrier densities between 10^{19} and 10^{21} cm^{-3} and for all possible combinations of pump and probe pulses with 2 and 4 eV photon energies. Measurements were performed for sample temperatures between 80 and 300 K. The time evolution of the changes in the complex dielectric constant $\epsilon_1 + i\epsilon_2$ in the first 6 psec was calculated from a first-order expansion of the changes in the complex refractive index $n + i\kappa$ in terms of the measured ΔR and ΔT [7]. The spatially inhomogeneous depth profile of the photoinduced changes in the dielectric function was accounted for by a first-order perturbative solution to Maxwell's equations using the sensitivity function method of picosecond acoustics [8].

Figure 1 shows the $\Delta\epsilon_2$ data for 2 and 4 eV excitation as measured with a 4 eV probe. Both $\Delta\epsilon_2$ curves exhibit a sharp negative onset at $t = 0^+$, but the initial decrease for 4 eV excitation (curve *b*) is delayed with respect to the immediate decay observed in 2 eV excitation experiments. The absolute values of $\Delta\epsilon_2$ in curves 1*a* and 1*b* are ap-

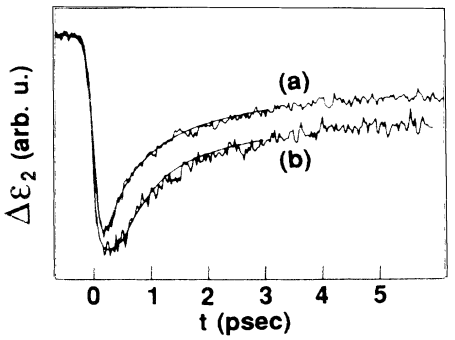

FIG. 1. Comparison of $\Delta\epsilon_2$ decays in *a*-Si:H for 4 eV probe and (a) 2 eV excitation and (b) 4 eV excitation. The carrier density is $n \sim 3 \times 10^{20}$ cm^{-3}. The fit is described in the text.

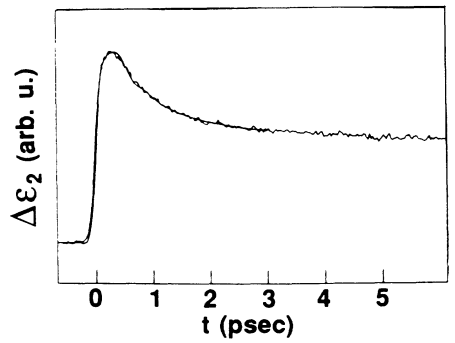

FIG. 2. $\Delta\epsilon_2$ decay in a-Si:H for 4 eV excitation and 2 eV probe. The carrier density is $n\sim 3\times 10^{20}$ cm^{-3}. The fit is described in the text.

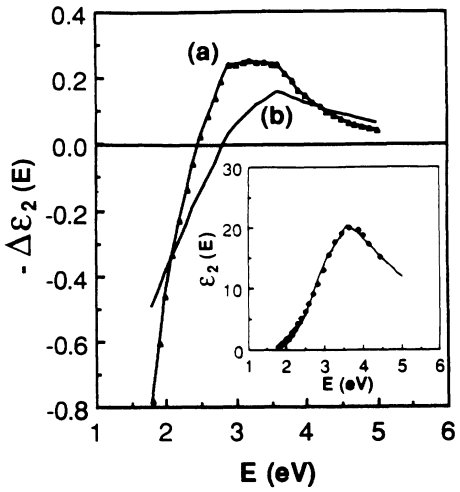

FIG. 3. Sum of the calculated band filling and intraband absorption contributions to $\Delta\epsilon_2(E)$ at $n\sim 3\times 10^{20}$ cm^{-3} for (a) 2 eV excitation and (b) 4 eV excitation. Inset: Experimental $\epsilon_2(E)$ data (diamonds) and spectrum calculated from Eq. (1) using the parameters defined in the text.

proximately equal for the same density of photoexcited carriers. A similar broadening of the decay curve is also observed in the 4 eV excitation and 2 eV probe data (Fig. 2), for which case $\Delta\epsilon_2$ is positive. All of the data obtained from experiments in which either 4 eV pump or probe pulses were employed were found to be both temperature and intensity independent over the measurable ranges of these quantities.

These results are strikingly different from previous ones reported for a-Si:H from experiments employing a probe in the spectral region around 2 eV. The positive onset in $\Delta\epsilon_2$ found in the near-band-gap probe experiments at high carrier densities has been attributed to photoinduced intraband absorption ascribable to a free carrierlike polarizability [4,6]. The negative onset in $\Delta\epsilon_2$ observed in our 4 eV probe experiments indicates that the dominant changes in the dielectric function at this photon energy are primarily associated with photoinduced bleaching of interband transitions [9] analogous to that reported in transient absorption saturation studies of GaAs [1]. These results therefore indicate the necessity of including reasonable quantitative estimates of the contributions of both interband and intraband transitions in any viable model of the photoinduced changes in the dielectric function at photon energies exceeding the optical gap in a-Si:H. We present the first such model here and use it to show that the broadening of the decay curves in Figs. 1 and 2 provide a direct measure of the hot carrier cooling rate in this material.

The inset of Fig. 3 shows the experimental $\epsilon_2=2n\kappa$ data (diamonds) as a function of photon energy E obtained from reflectivity and transmission measurements and numerical solution of the thin film equations for n and κ [10]. The dielectric function may also be calculated from the expression

$$\epsilon_2(E)=\frac{(2\pi e)^2R^2(E)}{3\rho_A}\int N_v(E')N_c(E'+E)dE', \quad (1)$$

where e is the electronic charge, ρ_A is the atomic density, and the integral represents the joint density of conduction and valence states N_c and N_v appropriate for amorphous semiconductors due to the absence of **k** conservation. This integral is performed over all transitions between conduction and valence states separated by the photon energy E with $e^2R^2(E)$ defined as the dipole matrix element squared averaged over these transitions and normalized to the **k**-conserving value for crystalline silicon [11]. Using the experimentally determined densities of states of Jackson *et al.* [11], we find that the best fit to our ϵ_2 data is obtained by employing a constant matrix element $R^2(E)\sim 7$ Å^2 for extended state transitions up to ~ 3.5 eV, with this quantity dropping off as E^{-4} at higher energies, in qualitative agreement with the experimental results of Ref. [11].

The initial change in the dielectric function associated with the photoinduced bleaching of interband transitions after illumination with a short excitation pulse may be written as

$$\Delta\epsilon_2(E)_{\rm bl}=-\frac{(2\pi e)^2R^2(E)}{3\rho_A}\int[f_h(E')+f_e(E'+E)]N_v(E')N_c(E'+E)dE', \quad (2)$$

where f_e and f_h are the nonequilibrium electron and hole distribution functions, respectively. The intraband absorption contribution to $\Delta\epsilon_2$ can be calculated from [12]

$$\Delta\epsilon_2(E)_{ab} = -\frac{(2\pi e)^2\hbar^2 P^2(E)}{3m^2E^2\rho_A}\int [f_e(E') - f_e(E'+E)]N_c(E')N_c(E'+E)dE', \quad (3)$$

with m the carrier effective mass, $P^2(E)$ the momentum matrix element averaged over all transitions separated by the energy E, and the hole contribution obtained by substituting f_h and N_v for f_e and N_c, respectively. At the high carrier densities employed in our experiments, the subband-gap intraband absorption has been found to possess a Drude-like spectral shape [5]. Using a constant matrix element $\hbar^{-2}P^2(E) \sim 0.017$ Å^{-2}, good agreement with the data of Ref. [5] can be obtained from Eq. (3) without the invocation of physically implausible subfemtosecond momentum relaxation times. Equation (3) reduces to the Drude result in the weak scattering limit, for which the mean free path L of the carriers is long ($kL > 1$) [13].

Figure 3 shows the spectra of $\Delta\epsilon_2(E) = \Delta\epsilon_2(E)_{bl} + \Delta\epsilon_2(E)_{ab}$ calculated from Eqs. (2) and (3) for 2 and 4 eV excitation. The initial mean excess energy of the carriers, assumed to be shared equally by electrons and holes, was 0.15 eV for 2 eV excitation and 1.15 eV for 4 eV excitation. The carriers were assumed to thermalize and form Fermi distributions within the temporal resolution of the experiment. This is a reasonable approximation in view of recent results in GaAs [14] and time-resolved studies of the coherent artifact in a-Si:H [15]. The calculated spectra reproduce the experimental facts that photoinduced intraband absorption dominates at 2 eV probe energy while band filling is more important at 4 eV, with the broad signature apparent in both cases indicative of the lack of $\mathbf{k}$ conservation in amorphous semiconductors. They also show that the bleaching at 4 eV and induced absorption at 2 eV are essentially unchanged by the dissipation of 1 eV of excess energy in the bands, consistent with the absolute values of the data in Fig. 1. This result indicates that the observed broadening of the decay curves in Figs. 1 and 2 for the 4 eV excitation is a direct manifestation of the hot carrier cooling process in a-Si:H.

The average carrier cooling rate may be determined from fits to the data obtained from calculations of the carrier dynamics using a model based upon the time evolution of Eqs. (2) and (3). In this model the carrier distributions are characterized by a constant average energy loss rate W until they arrive near the mobility edges. The subsequent dynamics of the surviving free carrier density are governed by the relation $n(t) = n_0/[1 + (t/\tau)^{0.9}]$, with τ defined as the characteristic time appropriate for trapping processes governed by dispersive relaxation in highly disordered media. The matrix elements for both interband and intraband transitions involving trapped carriers are reduced in proportion to the degree of localization of states below the mobility edges [16,17]. The impulse response calculated from Eqs. (2) and (3) using this model was convolved with the intensity cross correlation of the pump and probe pulses and the best fits to the $\Delta\epsilon_2$ data are shown in Figs. 1 and 2. Good agreement with all of the decay curves is achieved for an average carrier cooling rate and characteristic trapping time of $W = 2 \pm 0.2$ eV/psec and $\tau = 0.4 \pm 0.1$ psec, respectively.

This energy dissipation rate is significantly larger than that expected from previous theoretical calculations employing a perturbative approach. The hot carrier cooling rate in amorphous semiconductors has been calculated in the random phase approximation [18,19] to be the highest possible rate associated with phonon emission $W = A\hbar\omega_0^2$, where ω_0 is a mean phonon frequency obtained by averaging $\hbar\omega^2$ over the phonon spectrum and A is of order unity in the weak interaction limit for which perturbation theory applies. The performance of this averaging procedure in a-Si:H [20] results in a W of ~ 0.5 eV/psec. This discrepancy between the theoretical predictions and the experimental results suggests that disorder-enhanced carrier-phonon scattering may play an important role in the cooling process. Assuming a fractal nature of the pure electronic eigenstates close to the mobility edge, Soukoulis, Cohen, and Economou [21] have argued that the interaction of carriers with phonons is dramatically increased. A treatment of this strong coupling case has been developed by Thornber and Feynman [22] to explain the existence of energy loss rates greater than $\hbar\omega_0^2$ in Al_2O_3. Perhaps a similar theory may be applicable to a-Si:H. One may also speculate that carrier interaction with high frequency silcon-hydrogen vibrational modes, for which $\hbar\omega \sim 0.25$ eV, leads to an enhancement of the cooling rate.

The slight difference in the decay curves of Fig. 1 at longer times indicates the presence of ultrafast lattice heating arising from carrier cooling, which makes a negative contribution to $\Delta\epsilon_2$ at 4 eV [9]. This result is in broad agreement with those obtained from 2 eV excitation and near-band-gap probe experiments [4,6], in which delay times between nonradiative recombination and heat production as small as 0.1 psec [6] have been reported. Assuming that the carriers primarily interact with the optic phonon modes, the short delay between phonon emission and the lattice heating observed in our data suggests that a strong coupling between phonon branches exists in a-Si:H which is probably associated with the lack of $\mathbf{k}$ conservation in this material. This strong phonon-phonon interaction leads to a rapid decay of the optic phonons created in the cooling process, and thereby effects a suppression of nonequilibrium phonon population buildup in the optic modes, which may account for the lack of carrier density dependence to the average cooling rate found in our experiments. In addition, because the initial carrier temperature $\Theta_c \sim 11\,000$ K for 4 eV excitation is much higher than the lattice temperature Θ_L, no depen-

dence of the average cooling rate on Θ_L can be observed until the carriers cool to near this temperature [18]. The 2 eV excitation data [Fig. 1(a)], for which no significant broadening of the decay curve is found, indicate that in this case ($\Theta_c \sim 1100$ K) ultrafast trapping processes dominate the $\Delta\epsilon_2$ dynamics.

The 0.4 psec trapping time observed in our data involving 4 eV photons indicates that the density of shallow traps probed in our measurements is so large [23] that the fast nonradiative bimolecular recombination process found at high carrier densities [4,6] does not become a significant factor for any carrier density employed in our measurements, as evidenced by the lack of intensity dependence in the $\Delta\epsilon_2$ decays in Figs. 1 and 2. The fact that this ultrafast trapping process is only observed in experiments involving 4 eV photons implies that the highly defective region is primarily confined to the first 100 Å of the sample in which these photons are strongly absorbed. The temperature independence of our decays suggests that they are primarily associated with the rapid tunneling of trapped carriers to more localized states rather than thermal reexcitation and multiple trapping. Calculations of the mobility gap in *a*-Si:H [21,24] indicate that in this highly defective near-surface area of the material the mobility edges may shift into the power-law regions of the band densities by as much as 0.1 eV, creating a density of shallow localized states in excess of 10^{21} cm^{-3} and a distance R between sites of ~ 10 Å. Assuming an attempt to tunnel frequency $\nu_0 \sim (10^{12}$ to $10^{13})$/sec and wave functions of extent $\beta^{-1} \sim 50$ Å, the transition rate for downward tunneling [25] calculated from $\Gamma = \nu_0 \times \exp(-2\beta R) \sim 2 \times 10^{12}$/sec shows that this is a plausible mechanism for the decays.

In conclusion, we have presented the first direct measurement of the hot carrier cooling rate in *a*-Si:H. A quantitative model which expresses the time-dependent band filling and intraband absorption contributions to the photoinduced changes in the dielectric function in terms of the microscopic carrier dynamics has been developed and applied to the calculation of $\Delta\epsilon_2$. The unexpectedly large average cooling rate of 2 eV/psec suggests that disorder-enhanced carrier-phonon interactions play an important role in the cooling process.

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