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Femtosecond energy transfer in *a*-Si:H

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Using femtosecond optical pulses to inject carrier density greater than 10^{19} cm^{-3}, we observe that most of the carriers disappear within a few picoseconds. We show that this phenomenon results from nonradiative recombination, a process in which each electron-hole pair heats the lattice by giving up an energy equal to the pump photon energy. The delay between carrier recombination and lattice heating is estimated to be smaller than 100 fs, which may result from a very fast coupling between optical and acoustical phonons.

The ultrafast electronic processes in hydrogenated amorphous silicon (*a*-Si:H) have been investigated by several groups in recent years[1-3] using analysis of photoinduced absorption in the picosecond time domain. While the temporal evolution of excited carriers can be monitored in crystalline materials by measuring the spectral dependence of the induced transparency, this is not possible in amorphous semiconductors, due to the lack of momentum conservation in optical transitions.[4] What is then observed is mainly an induced absorption corresponding to the intraband re-excitation of already excited carriers. The magnitude of this signal is proportional to the density of carriers $N(t)$ and to the optical cross section σ. Previously reported data[1] have been first interpreted as representative of carrier trapping leading to a change of σ. At high carrier density we have already shown[5] that when not taken into account, the thermal heating of the material can make interpretations unreliable for experiments in which pump and probe wavelengths are identical. In this work we take advantage of the fact that we optically monitor the temperature variations in hydrogenated amorphous silicon to determine the amount of energy released by the photoexcited carriers to the lattice. We show that for large carrier densities *most of the injected carriers are not trapped but recombine nonradiatively within less than 30 ps.* By comparing the induced absorption of electronic origin and the thermal contribution, we estimate *the delay between carrier recombination and lattice heating to be smaller than 100 fs.*

We monitor the dynamics of the photogenerated carriers by measuring the time-resolved complex refractive index ($\tilde{n}=n+ik$, $k=\alpha\lambda/4\pi$) in a pump-probe configuration for different probe wavelengths. When the probe photon energy is lower than the band-gap energy, the absorption is due only to intraband transitions of photoexcited carriers. For a probe energy well above the gap, both intraband and interband absorptions are present. While intraband absorption is mainly related to the carrier density, interband absorption is sensitive to lattice temperature through the band-gap renormalization. Therefore such a full analysis enables us to study simultaneously carrier recombination and lattice heating.

It is clear from previously reported data[6] that the induced intraband absorption strongly diminishes after excitation. This could originate either (i) from a decrease of the optical cross section σ due to trapping in localized states or (ii) from a decrease of the carrier density or from both. In (i) the energy released to the lattice by each carrier corresponds to the thermalization (excess energy at the creation with respect to trap energy) while in (ii) each electron-hole (*e*-*h*) pair which disappears by nonradiative recombination gives to the lattice an energy equal to the pump photon.[7] While an increase of the lattice temperature was measured previously,[5,8] no quantitative measurement of the energy released per pair has been provided. Measuring the contribution of each *e*-*h* pair to the lattice heating will then provide information on the carrier evolution and a choice between cases (i) and (ii).

Our samples are undoped *a*-Si:H thin films, deposited by rf glow discharge on glass, with a thickness of about one absorption length at 2 eV and a band gap of 1.7 eV. A colliding pulse mode-locked laser and amplifier are used to generate the optical pulses which are less than 100 fs in duration at a repetition rate of 10 Hz. The 2 eV pump pulse is focused to a spot of 1 mm^2 and its intensity is

varied so that the injected carrier density ranges from 10^{19} cm^{-3} to 10^{21} cm^{-3}. The technique of self-phase modulation is used to generate a wavelength continuum from which the probe pulse is selected with interferential filters. The measured cross correlation between the pump and the probe at 1 μm has a 300-fs full width at half maximum (FWHM). With this time accuracy, while it is not possible to follow the shape of faster variations, it is, however, possible to measure delays as low as 50 fs. We can also generate an infrared pump pulse by amplification of a part of the wavelength continuum in a three-stage dye amplifier.[9] We measure transient changes in the transmission and the reflectivity of the probe pulse, at normal incidence and room temperature. The real and imaginary parts of the refractive index are obtained by inversion of the Fabry-Pérot formulas.

At high injected carrier density ($N \sim 10^{20}$ cm^{-3}), the induced intraband absorption (as measured at 1 μm) has almost disappeared at a delay of 30 ps after excitation (it is at most a few percent of its maximum value) because of carrier trapping or e-h pair recombination. We take advantage of this experimental situation to measure at this delay the sample heating through the increase of the interband absorption. This can be performed at any probe wavelength where the interband absorption is significant. We have chosen 525 nm for which the electronic contribution at its maximum value (at zero delay) is only 40% of the maximal thermal contribution (at long delays). We can also use the change of the real part of the refractive index by assuming that trapped carriers, if any, do not contribute appreciably. When the absorption coefficient α is greater than 10^4 cm^{-1}, the Tauc relation can be used so that the absorption increase is linked to the band-gap renormalization by

$$\alpha+\Delta\alpha=C[\hbar\omega-E_g-(dE_g/dT)\Delta T]^2/\hbar\omega\,, \qquad (1)$$

where α is the absorption coefficient, $\hbar\omega$ the photon energy, E_g the Tauc gap, C a constant, ΔT the temperature rise of the sample, and dE_g/dT the variation of the Tauc gap with temperature. dn/dT and dk/dT have been determined experimentally by ellipsometry. We have found $dn/dT=2.0\times10^{-4}$ K^{-1} and $dk/dT=5.5\times10^{-4}$ K^{-1} at 520 nm. This leads to an experimental value of dE_g/dT of about -3.5×10^{-4} eV K^{-1} in agreement with other reported measurements.

We have performed two different types of experiments in order to determine the amount of energy ΔE released to the lattice by each excited e-h pair. In the first experiment, we estimate the temperature change to be $\Delta T=36$ K from the Δk measurement and $\Delta T=34$ K from the Δn measurement at 2×10^{20} cm^{-3}. We have

$$\Delta E=\rho C_p\Delta T/N\,, \qquad (2)$$

where ρ is the density, C_p the heat capacity, and N the density of initially excited carriers. N is determined from the fraction of the pump pulse absorbed in the sample. Using $\rho=0.95\rho_c$, where ρ_c is the crystalline silicon density and C_p the crystalline specific heat, we obtain $\Delta E=1.7\pm0.5$ eV, close to the 2 eV value expected if all the pairs recombine nonradiatively. The uncertainty in the absolute value of the carrier density is responsible for a large part of the error bar. We have also directly measured the specific heat of amorphous silicon by calorimetry. We find for a-Si:H, $C_p=0.62$ J/g K around $T=320$ K, compatible with the crystalline value.

We have also performed a novel type of experiment so as to measure directly ΔE, independently of the ρC_p product and of the absolute value of the incident flux. The experimental scheme is now based on the use of three different beams. As before, we excite the carriers with the $\hbar\omega_1=2$ eV pump beam and we measure the lattice-temperature increase at a fixed delay through the induced change of interband absorption at 525 nm. In addition, we heat the excited carriers, when they exist, with the help of a third ultrashort laser pulse. The wavelength of the third beam ($\lambda=860$ nm) is selected so that only intraband transitions are possible.[10] A free carrier absorbing a $\hbar\omega=1.44$ eV photon is then excited high in the band and thermalizes rapidly (less than a few picoseconds), releasing its energy to the lattice as heat. The infrared (ir) beam does not change the carrier density; its only effect is to heat the sample in a measurable way. Figure 1 shows the increase of absorption at 525 nm measured 6 ps after the e-h pair creation, as a function of the delay between the pump pulse and the ir pulse. The temperature increase reproduces well the temporal evolution of the carrier density. The quantum yield $aN(t)$ for the ir intraband absorption[11] is known from a classical pump-probe experiment with a probe wavelength at 860 nm, where $N(t)$ is the time-dependent number of excited carriers by

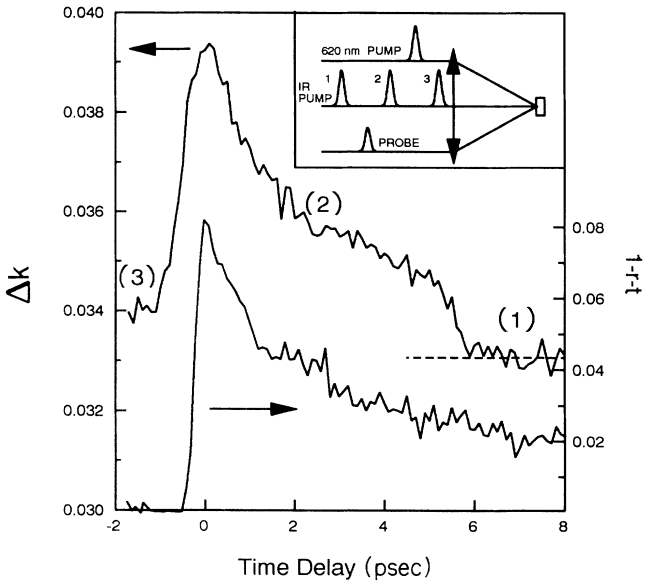

FIG. 1. Induced absorption at 525 nm (upper curve) measured 6 ps after the 620-nm pump, vs delay between the ir pump and the 620-nm pump. The inset describes the timing in regions 1-3. In region 3, the small increase of Δk results from weak interband absorption involving the band tails. The carrier density measured from $1-r-t$ at 860 nm (lower curve) follows the same dynamics after injection at 620 nm. Note that slower rise of the signal in the upper curve results from the relatively long ($\sim$500 fs) duration of the ir pump pulse.

the 2 eV pump beam. We have

$$V\rho C_p \Delta T_{ir} = aN(t)E_2, \quad (3)$$

where V is the silicon volume excited by the ir pump beam, ΔT_{ir} is the resulting lattice heating, and E_2 the ir incident energy. Using the measured values of the two pump pulse energies, we find that $\Delta E = 1.85 \pm 0.2$ eV, a value which again is equal within the experimental uncertainty to the 2 eV value expected if the e-h pairs lose all their energy to the lattice by nonradiative recombination. This result is in agreement with the one deduced from the first experiment, with a smaller uncertainty because we only need relative measurements of energy.

So far we have shown that, at least when the injected carrier density is high (a few 10^{20} cm^{-3}), the energy lost by the e-h pairs after 30 ps is the energy of the initial exciting photon. This implies that it is the disappearance of the carriers and not their trapping which is responsible for the strong decrease of the "electronic" induced absorption (intraband transitions). This result is not unexpected as long as N is larger than the density of traps in our samples ($N_t \sim 5\times10^{19}$ cm^{-3}). In order to extend the validity of this result down to $N = 10^{19}$ cm^{-3}, we have measured for a delay $\Delta T = 30$ ps the induced absorption at 525 nm as a function of pump intensity, i.e., of the excited carrier density N. As already discussed previously, this induced absorption at long delay and short probe wavelength represents almost exclusively the thermal contribution so that it is directly proportional to the lattice temperature rise.[12] Figure 2 shows that ΔT is a linear function of N between 10^{19} and 10^{21} cm^{-3}. This indicates that even when the initial density is smaller than the density of traps N_t (but larger than 10^{19} cm^{-3}), nonradiative recombination controls the time evolution of the induced absorption.

We can now check if the temperature rise follows the pair recombination. This will give us an estimate of the delay between optical phonon emission (pair recombination) and their thermalization into acoustical phonons (lattice heating). It is reasonable to assume that $N(t)$ is known through the time-dependent "electronic" induced absorption as measured at 1 μm. We have already shown[13] that this process is well described by the Drude formalism using a subfemtosecond scattering time. The band-gap renormalization due to lattice heating is obtained from the $\Delta k(t)$ curve measured at 720 nm, after subtraction of the electronic part. We have chosen a probe wavelength of 720 instead of 525 nm because the magnitude of the electronic contribution is evident at 720 nm and zero delay and it can thus be subtracted from the total contribution without the use of estimated parameters. The shape of the temporal evolution of the electronic part is deduced from the $\Delta k(t)$ curve recorded at 1 μm. Figure 3 shows the lattice heating and the amount of energy released by the carriers. This last curve was obtained assuming that carriers lose instantaneously 0.3 eV due to thermalization in the extended states, then 1.7 eV during recombination calculated from $\Delta k(t)$ at 1 μm. In this way we obtain the fastest energy release possible. The agreement between experimental and calculated curves is very good, consistent with our interpretation of nonradiative carrier recombination. Using the electronic contribution measured at 1 μm and the thermal contribution deduced from the above considerations, we have been able to reproduce the experimental data at all probe wavelengths, including 525 nm where at short delays both contributions are important. Remarkably the delay between carrier disappearance and lattice heating is experimentally at most 100 fs. It is unlikely that on this short time scale carriers emit directly acoustical phonons. Thus the delay may be interpreted as the average time it takes for an optical phonon to decay into acoustical phonons. The small

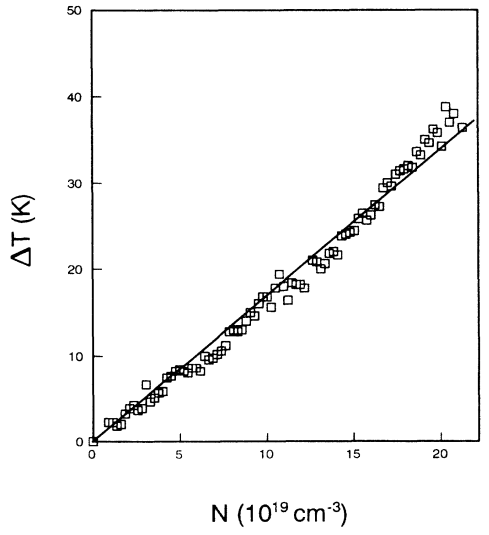

FIG. 2. Temperature rise measured at 525 nm at a delay of 30 ps after injection vs injected carrier density. The data follow a linear dependence.

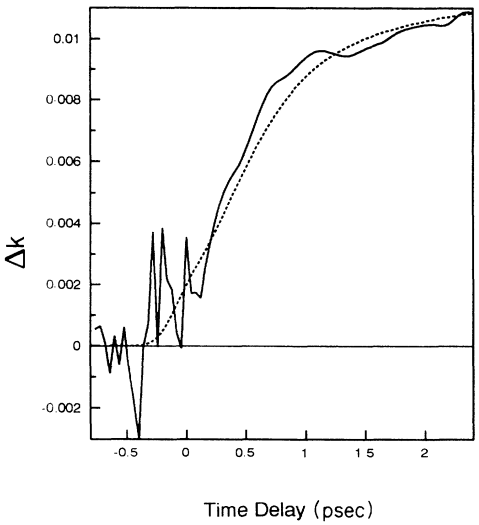

FIG. 3. Induced absorption proportional to the lattice temperature increase (solid line) and energy released by the carriers (dotted line) obtained as described in the text. The two curves have been normalized. The zero delay has been chosen to correspond at the maximum of the carrier density measured through the electronic contribution (Δk at 1 μm).

value of the decay can be related to the lack of momentum conservation in amorphous materials, unlike what happens in crystalline semiconductors.[14,15]

The concept of optical and acoustical phonons which has been used to describe the experimental results may be questionable in amorphous materials. Furthermore, localized phonons such as Si-H vibrations have to be taken into account. What is shown here is the nearly simultaneous occurrence of carrier energy release and lattice heating. Since it is likely that recombining carriers emit phonons of large energy like optical phonons in crystalline semiconductors and that band-gap renormalization proceeds from macroscopic internal fields as the one generated by acoustical phonons, we feel that the description in terms of optical and acoustical phonons is adequate.

In conclusion we have shown that in *a*-Si:H both electronic and thermal effects induce variations of the real and imaginary parts of the optical refractive index. For injected carrier density higher than 10^{19} cm^{-3}, most of the carriers recombine nonradiatively within 30 ps so that an energy of 2 eV is transferred to the lattice from each *e-h* pair created by a 2 eV photon. We have measured the temporal dependence of the lattice temperature increase and found that it follows the carrier disappearance with a delay of at most 100 fs. This small delay implies a very fast coupling between optical and acoustical phonons.

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[10]Although the unexcited sample is not completely transparent at 860 nm, the only possible absorption corresponds to band-tail transitions. These band-tail states being saturated by the already injected carriers, no interband absorption exists for the ir beam in our experimental conditions.

[11]$aN(t)$ represent the fraction of the ir beam which is absorbed inside the sample and is equal to $1-r-t$, r and t being the reflectivity and the transmission at 860 nm in the presence of injected carriers of density $N(t)$.

[12]At 525 nm the electronic contribution at its maximum is 40% of the maximum thermal contribution. Furthermore, at 30 ps, the carrier density is *never* larger than 20% of its initial value, so that the electronic contribution is always smaller than 8% of the thermal contribution at this delay.

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