Ultrafast Carrier Dynamics in Silicon: A Two-Color Transient Reflection Grating Study on a (111) Surface

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The dynamics of excited carriers generated near a silicon surface were characterized on femtosecond time scales using the transient grating technique in the reflection configuration. For electrons in the energy range 1.4 ± 0.6 eV above the conduction band edge and their corresponding holes, the lifetime for relaxation through phonon scattering at carrier densities below 10^{20} cm^{-3} was determined to be 240 fs. This relaxation time increased sharply for carrier densities higher than 5×10^{20} cm^{-3}, providing the first direct evidence for charge screening of carrier-phonon scattering in Si. [S0031-9007(98)07978-2]

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Quantitative characterization of carrier dynamics in semiconductors is important to the understanding and modeling of many physical and chemical problems involving hot carriers. For example, the relaxation rate of hot carriers depicts how fast energy is deposited into phonons and subsequently induces processes involving atomic motion such as ablation [1], etching, melting, and phase transitions [2]. For Si, the dynamics information would be particularly useful for understanding and designing Si processing with photons. The relaxation rate of photoexcited carriers determines the yield in surface photochemical reactions and the efficiency of using light in materials processing. Furthermore, accurate fundamental carrier relaxation rates are important for the correct modeling of state-of-the-art Si devices [3].

In fundamental physics, at high carrier densities, many body interactions and dynamic screening become important in carrier dynamics. Previous ultrafast experiments at very high carrier densities on Si have focused on lattice melting and heating dynamics [2]. In this Letter, we report hot carrier dynamics directly probed using transient reflection grating scattering at carrier densities from 10^{19} to 10^{21} cm^{-3}, which are below the threshold for laser-induced order-disorder transitions [2], but significantly higher than those accessed in previous time-resolved photoemission experiments [4]. This carrier density region is where screening is expected to be important in electron-phonon interactions [5]. However, despite the importance to fundamental physics and photochemical processing of Si, no data on the carrier dynamics exist for Si in this density region. Transient grating (TG) techniques have been used effectively for characterizing rate processes of carriers in Si such as ambipolar diffusion on pico and nanosecond time scales [6,7]. To understand the carrier relaxation dynamics the studies must be extended into femtosecond time scales.

In a TG experiment a pump pulse is split into two equal intensity parts and recombined on the surface at a small angle, producing a sinusoidal modulation in light intensity through interference. As the pump photons are absorbed, an excited carrier concentration modulation is generated, resulting in a refractive index grating. A variably delayed probe pulse is then scattered off the grating and the first order diffracted signal is monitored as an indication of the grating strength. The latter is directly influenced by the hot carrier concentration and can be used for the extraction of the carrier relaxation rate.

Our experiments were performed with a 1 kHz Ti:sapphire regenerative amplifier laser system that operated at 800 nm with 100 fs pulse widths and <1 mJ pulse energy. The probe beam at 400 nm was generated by doubling the laser output in a LiB_3O_5 crystal. The 800 nm pump was split into two equal intensity beams, focused, and recombined to the same spot with a diameter of 3×10^{-2} cm on the Si sample. The probe beam was greatly attenuated and focused to a diameter of 1.5×10^{-2} cm. The sample was a p-doped Si(111) surface with a resistivity of 20–30 Ω cm and a naturally grown oxide layer. The pulse widths of the pump and probe, determined by cross-correlation measurements, were 90 ± 10 fs and 120 ± 10 fs, respectively.

A diagram of the beam configuration is shown in the inset of Fig. 1. The crossing angle of the two pump beams, 1 and 2, was 3.5°, producing a grating with a 13 μm period. The probe beam incidence angle was ~8° from surface normal. The pump and probe beams had orthogonal polarizations to minimize coherent coupling effects. The first order diffracted signal at ~10° was detected by a photomultiplier tube, integrated and averaged by a boxcar and recorded using a personal computer.

TG scattering traces taken at different pump powers, normalized to the same maximum intensity, are shown in Fig. 1. The reported pump fluences are defined as the peak fluence in the interference pattern, since the diffraction strength is proportional to the grating's peak carrier density. All data were collected below the observed

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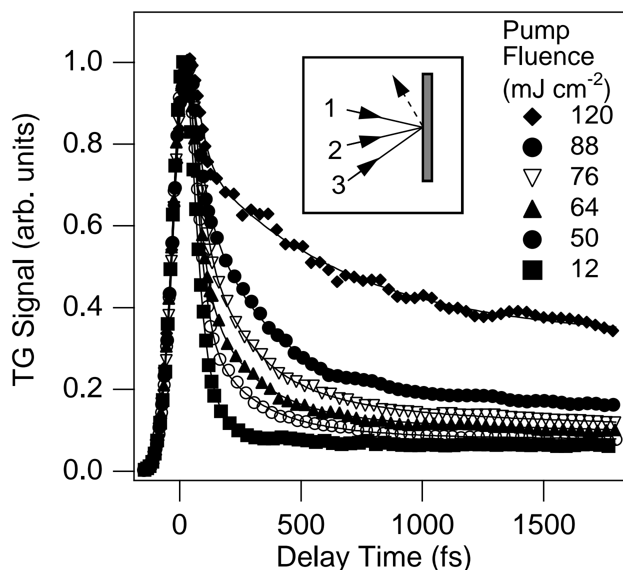

FIG. 1. Normalized TG signal versus pump-probe delay time. The solid lines are fits using the model described in the text. Inset: Experimental geometry. 1 and 2 are the pump beams, 3 is the probe beam, and the dashed line is the diffracted signal.

damage threshold of ~ 140 mJ cm^{-2}. The TG traces indicate three decay processes: the first appears to mimic the pump-probe pulse overlap; the second grows in nonlinearly with the pump fluence and decays within 500 fs; the third occurs on a much longer time scale in comparison with the maximum pump-probe delay time of 2 ps. These observations manifest the anticipated physical processes of excited carriers in Si.

A schematic illustration of the excitation and relaxation of carriers for this 800 nm pump, 400 nm probe TG experiment is shown in Fig. 2. Indirect one-photon absorption creates excited electrons in the X valley and holes near Γ. However, at high pump intensities, two-photon absorption through direct transitions creates highly excited electron-hole pairs along Λ to Γ. Initially, the photoexcited carriers thermalize electronically via carrier-carrier scattering, producing a hot carrier distribution with an elevated temperature compared to the lattice. Time-resolved photoemission experiments indicate this thermalization occurs much faster than 100 fs [4], and therefore its effect in TG scattering, if there is any, is convoluted into the first process. However, a TG signal at 400 nm probe will result from the bleaching of the absorptivity due to state filling, which refers to the presence of hot carriers in states of the conduction and valence bands optically coupled to the probe. The bleaching decays as the hot carriers cool, relaxing to the band-edge minimum via carrier-phonon scattering, and depositing their excess energy into the lattice. This hot carrier energy relaxation time over a wide carrier energy range appeared in time-resolved photoemission to be ~ 1 ps at low carrier densities [4]. Concurrently, the presence of holes at the band edge will lead to a TG signal due to bleaching from band filling (the Burstein-Moss effect [8]). Band filling refers to the presence of carriers in the states near the band edge that are optically coupled to the probe. The TG signal due to band-edge carriers will decay as the excited carrier population near the surface is reduced by recombination and diffusion. As the hot carriers relax, a TG signal may also arise from heating induced changes in the optical constants.

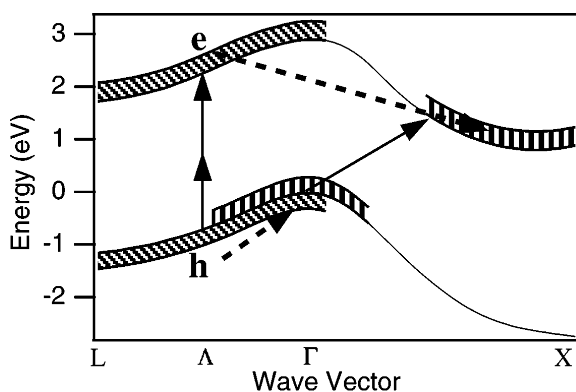

FIG. 2. Schematic diagram of the excitation processes and relaxation dynamics in Si. The energetically allowed regions for indirect one-photon transitions are indicated by the vertical lined shades. The regions for direct two-photon transitions are indicated by slanted-lined shades. The energy relaxation of the excited carriers toward the band edge is represented by a dashed arrow.

The TG signal, $S(t)$, is proportional to the square of the change of the complex index of refraction, i.e., $S(t) \propto |\Delta\tilde{n}(t)|^2$. The pump pulse induced change of the refractive index can be expressed as $\Delta\tilde{n}_{12}(t) = \Delta\tilde{n}_N(t) + \Delta\tilde{n}_T(t)$, where $\Delta\tilde{n}_N$ is due to excited carriers and $\Delta\tilde{n}_T$ is from lattice heating. As bleaching induced change of the refractive index manifests itself through the absorptivity, $\Delta\tilde{n}_N$ is purely imaginary $[\Delta\tilde{n}_N(t) = i\Delta k_N]$. To calculate the change of the index of refraction due to photoinduced bleaching, Δk_N, we phenomenologically model Δk_N as

$$\Delta k_N = (ae^{-t/\tau_c} + b)\Delta N(t), \qquad (1)$$

where $\Delta N(t)$ is the grating's peak surface carrier density, τ_c is the time constant for hot carrier energy relaxation, and a and b are constants giving the relative contributions of state and band filling. As the hot carriers cool and heat up the lattice, the $\Delta\tilde{n}_T(t)$ induced can be described by $\Delta n_T = \theta\Delta T_l(t)$, where θ is the thermo-optical coefficient, and $\Delta T_l(t)$ is the peak lattice temperature.

We have used a Boltzmann equation approach from Ref. [9] to describe carrier and heat transport following excitation, and we solved the differential equations in this model numerically. Added in this model is the fact that the lattice temperature change is correlated to the excited carrier density and the carrier energy relaxation rate.

Both the indirect one-photon and the direct two-photon absorption contributions are included in generating the

excited carriers in the model. The value of the two-photon absorption coefficient, β, has not been measured at the two-photon energy of 3.1 eV. We have extrapolated a value of 10 cm GW^{-1} from the β measured below the direct band gap at the two-photon energy of 2.3 eV [10] and above it at 4.0 eV [11]. Over the range of 5–100 mJ cm^2, carrier excitation is dominated by linear absorption at lower intensities and by two-photon absorption at higher intensities. The two contributions are equal at a fluence of ~40 mJ cm^{-2} ($\Delta N = 2.3 \times 10^{20}$ cm^{-3}). The decay of ΔN due to diffusion can be neglected in the 2 ps of pump-probe delay time due to the large grating spacing and pump absorption length.

Besides the population grating produced by the interference of pump pulses 1 and 2, a polarization grating can be produced by the interference of pump pulse 1 with probe pulse 3 [7]. Pump pulse 2 can scatter off of this additional grating, producing an additional diffracted signal. This coherent coupling gives an additional contribution to the index of refraction while the pump and probe pulses are temporally overlapped and are responsible for the initial TG signal. The total $\Delta\tilde{n}(t)$ is then given by a linear sum of all induced refractive index changes described above.

From the theoretical model, $\Delta N(t)$ and $\Delta T_l(t)$ are calculated and then used to generate a time dependent TG signal. A fit to the experimentally measured TG decay traces, shown in Fig. 1, yields the carrier relaxation time, τ_c, and the magnitude of a and b constants. A single pulse width used for both pump and probe was also treated as an adjusted parameter in the fit, instead of using the values obtained by the correlation measurements. For the fits shown in Fig. 1, the fitted pulse width was 77 ± 4 fs, somewhat shorter than the correlation measurements for the pump and probe pulses, but consistent with expectations [12]. The fitted pulse width is determined primarily by the initial coherent coupling TG signal.

In Fig. 3, the amounts of various components contributing to the TG signal at a pump fluence of 76 mJ cm^{-2} are shown. The peak surface carrier density generated is 5.7×10^{20} cm^{-3}. Near time zero, the TG signal is dominated by the coherent coupling component. As the hot carriers are excited, signal amplitude due to state filling becomes apparent. From the decay of this component, which occurs within 500 fs, the hot carrier energy relaxation lifetime is obtained. As the hot carriers relax to the band edge, the calculated lattice temperature increases almost 100 K, producing a TG signal that rises with τ_c but decays on a much longer time scale. The band-filling amplitude, from the band-edge carriers, decays by Auger recombination, also on a long time scale. Both bleaching components due to state and band filling are observed to vary linearly with the calculated carrier density.

The hot carrier energy relaxation lifetime obtained from the fit is shown as a function of the peak surface carrier density in Fig. 4. Within the estimated uncertainty of the measurements, the relaxation lifetime is constant at 240 fs

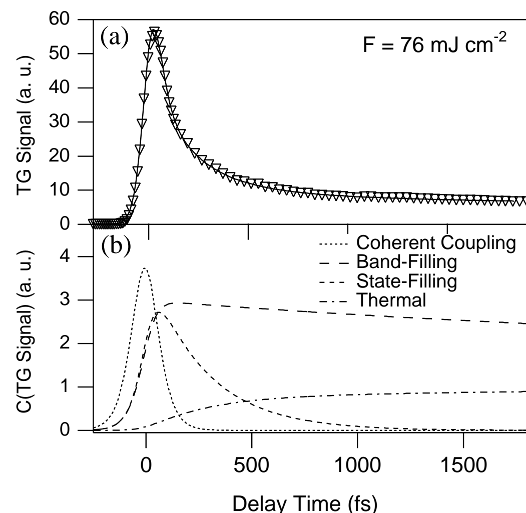

FIG. 3. (a) TG Signal (▽) versus pump-probe delay time at the pump fluence of 76 mJ cm^{-2}. The solid line is a fit to the model described in the text. (b) The various components contributing to the TG signal calculated from the model analysis.

for carrier densities up to 2×10^{20} cm^{-3}. The relaxation time's dependence on the carrier density appears to highlight the effect of screening in the carrier-phonon interaction. Yoffa's calculation [5] predicted that the hot carrier energy relaxation time depends on the carrier density as

$$\tau_c = \tau_o[1 + (N/N_{\mathrm{crit}})^2], \tag{2}$$

where τ_o is the carrier density independent relaxation time, and N_{crit} is the critical carrier density for screening. A fit of the data to Eq. (2) gives $\tau_o = 240 \pm 30$ fs and $N_{\mathrm{crit}} = (6.0 \pm 0.7) \times 10^{20}$ cm^{-3}. The latter is very close to the theoretical value of 2×10^{21} cm^{-3} [5].

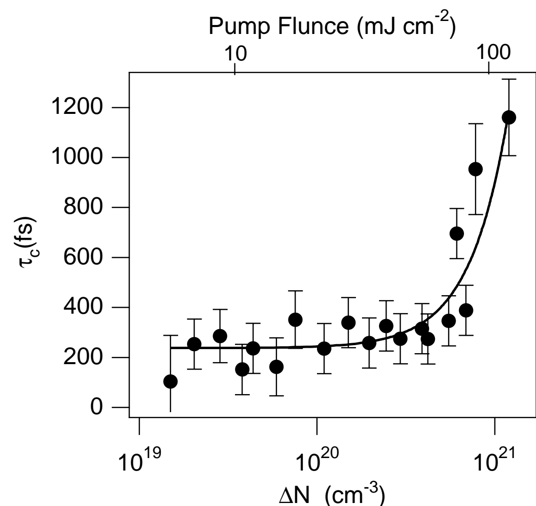

FIG. 4. Carrier relaxation time τ_c versus surface carrier density. The solid line is a fit to the screening model [5].

Figure 4 gives the first experimental evidence of screening of the carrier-phonon scattering in Si.

The hot carrier energy relaxation time obtained clarifies previously reported values. The relaxation times derived from time-resolved photoemission spectroscopy [4] were observed to be shorter than a picosecond and to be a strong function of excess energy, with faster relaxation observed for higher energies. Our TG measurement gives an average value of τ_c of hot electrons in the energy range of 1.4 $\pm$ 0.6 eV above the conduction band edge and their corresponding holes. Also, the TG signal is a function of both the electron and hole dynamics whereas incoherent time-resolved photoemission measurements are sensitive only to the electron dynamics. Doany and Grischkowsky [13] using differential reflectivity on thin silicon films on sapphire measured a relaxation time of 350 fs for carriers generated using 2 eV pump photons at low carrier densities ($\sim 10^{17}$ cm^{-3}). They attributed this time to the relaxation of electrons in the X valley. Our TG experiment is more sensitive to the presence of holes in the Γ valley; as they relax they remain in the probe's optically coupled region.

The carrier relaxation time is indispensable in calculating the quantum yield in hot-electron mediated surface photochemical reactions. Hot-electron induced desorption and photochemistry have been observed on metal and semiconductor surfaces [14]. The increase in τ_c at high carrier densities may imply an increase in yields of reactions induced by photoexcited carriers. Also, the relaxation time is important to further the understanding of the ultrafast laser-induced phase transitions [2], which occur at carrier densities higher than 10^{22} cm^{-3}. At these high densities, screening plays an important role in determining the energy transfer rate between the carriers and the lattice. The dramatic increase in the relaxation time at high carrier densities will increase the time required for the lattice to reach the melting temperature.

By using the transient grating technique on ultrafast time scales we were able to measure the hot carrier energy relaxation time as a function of excited carrier density. The use of a probe at twice the pump frequency enables bleaching effects due to hot carriers to be directly observed while the reflection configuration provides sensitivity to the near surface region. This technique should be generally applicable to other indirect band-gap semiconductors or wide band-gap materials.

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