Energy Transfer during Silicon Irradiation by Femtosecond Laser Pulse

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Measurements of the total energy reflected from crystalline and amorphous silicon illuminated by a femtosecond laser pulse are reported, for wavelengths of 0.62 and 0.31 μm. The results are interpreted by use of a highly nonlinear regime of light propagation in the dense plasma of electrons and holes (e-h). Densities higher than 10^{22} cm^{-3} are reached. We demonstrate that free-carrier absorption is dominated by e-h collisions.

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Recently, femtosecond techniques have been demonstrated[1,2] to be a valuable method for the analysis of the initial events following the irradiation of semiconductors by intense optical pulses. In their work, Shank and co-workers used 90-fs pulses to create a high-density electron-hole (e-h) plasma in silicon and measured the time-dependent reflectivity over a 20-ps time scale,[1] at various laser energies, below and above the apparent threshold of melting. These experiments, as well as those on second-harmonic generation,[2] were directed towards elucidating the nature of the involved phase transitions. The use of pulses so short and intense raises the possibility of reaching an e-h density high enough to break so many covalent bonds that the crystal becomes fluid, even at $T=0$ K. The density of a few 10^{21} cm^{-3} necessary for this mechanism,[3] as first proposed by Van Vechten,[4] cannot be reached with longer pulses, because the e-h creation becomes then less efficient than Auger recombination.

The understanding of the exact nature of the melting induced by very short pulses relies on a good knowledge of the energy transfer from the laser pulse to the sample. The femtosecond laser is a very unique tool to study the conversion of photons into electronic excitations since all the other characteristic times—e-h recombination, plasma expansion, electron-phonon interaction, and lattice heating—are longer. The spatial distribution of e-h at the end of the pulse is not trivial because the optical properties of the silicon sample strongly change in space and time during the pulse itself, the laser penetration depth decreasing by a factor of 100 when the plasma frequency passes the optical frequency. Moreover, the exact absorption processes involved in very dense e-h plasmas have never been studied in detail up to now.

In this Letter, we address that problem by measuring the *total* amount of energy of the 100-fs pump pulse reflected by the Si sample and its variation with pulse intensity. The reflectivity which is closely related to the change of the optical properties *during the pulse* is compared with a calculation based on a model for the absorption, which allows us to determine the variation with space and time of the e-h plasma density and the resulting instantaneous dielectric constant and penetration depth.

Hundred-femtosecond pulses generated at 620 nm in a passively mode-locked cw ring dye laser were further amplified in a four-stage dye amplifier pumped by a Q-switched frequency-doubled Nd-doped yttrium aluminum garnet laser.[5] Temporal broadening due to group-velocity dispersion in the dye solvents and the optics is compensated by a grating pair introduced at the output of the second amplifier stage. To insure a *very uniform spatial profile,* we added a doubled spatial filtering at the expense of some loss. The beam was then focused on the nondoped silicon (1,0,0) surface to a diameter of 40 μm (corresponding to a maximum energy density of about 2 J/cm^2), and its reflection was directed through an aperture of a photodiode (No. 1), while a small part taken before the sample was

directed to another diode (No. 2). In the case of uv excitation, the second harmonic at 0.31 μm was generated in a 3-mm potassium dihydrogen phosphate crystal and focused to a 300 μm spot, yielding a maximum energy density of about 10 mJ/cm^2.

Both diode signals (S_1 and S_2) are sent through an electronic chain to a computer. To improve the linearity of the detection, only a small range of variation for the pulse energy was allowed on the detectors, and the response of the chain was carefully calibrated, so that any small remaining nonlinearity could be automatically corrected. The experimental procedure to obtain accurate measurements in an important range of variation of the incident intensity was as follows: (1) We switched one by one a set of 0.3-optical-density calibrated filters from the beam before the sample to the beam after the sample reflection, to obtain factor-of-2 steps of variation (the filters were introduced in a section where the beam diameter was large, to avoid any bleaching); with this technique, the variation of energy on diode No. 1 was due to the change of reflectivity. (2) We filled the gap between the discontinuous sets of measurements of taking advantage of the pulse-intensity variation of 50% from shot to shot. (3) The sample was moved so that each pulse could irradiate a fresh region of silicon.

All of these operations were driven by the computer which, for each shot, recorded the reflection coefficient (S_1/S_2) as a function of the incident pulse (S_2T, where T corresponds to the transmission of the filters removed from before the sample) and averaged over 0.03-optical-density steps of energy variation. About 30 000 laser shots have been taken into account to obtain the reflectivity curves in Fig. 1.

This Fig. 1 shows the change in total reflectivity for crystalline silicon under a 0.62-μm excitation and for amorphous silicon under 0.31 μm (inset), when the laser intensity was varied by over two orders of magnitude. The reflectivity first decreases by about 5% and then increases, with some indication of saturation, 70% higher than the unexcited value R_0, i.e., still well below the usual liquid value.

Let us first develop a qualitative understanding of what happens during the laser pulse, i.e., when the electronic system is excited. The leading edge of the pulse finds a virgin silicon sample, part (R_0) of the light being reflected while the rest of the beam is absorbed, through interband excitation, over a penetration depth of $d \simeq 3$ μm, creating an e-h plasma with a decreasing density profile. The silicon sample keeps reacting that way until the surface density reaches a fraction of N_p, the plasma-

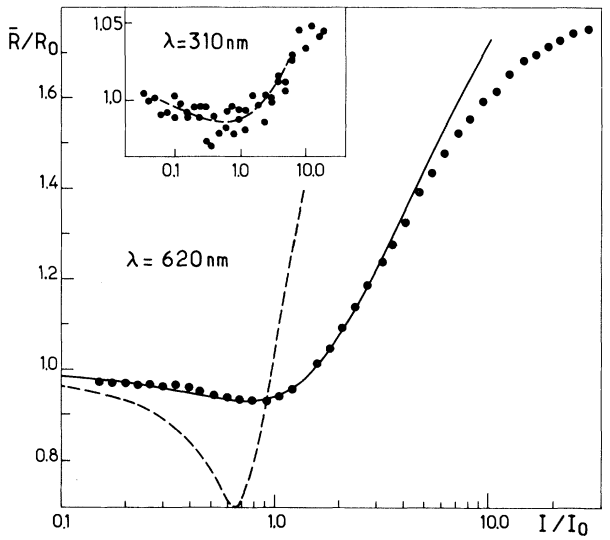

FIG. 1. Total reflectivity $\bar{R}$ vs pulse intensity for $\lambda = 0.62$ μm: The dots are the experimental data. The solid line is the calculated value for $\omega_0\tau = 1$, while the dashed line is for $\omega_0\tau = 10$. The inset gives similar data for $\lambda = 0.31$ μm on amorphous silicon (the dashed line is just a guide to the eyes).

frequency density. The reflectivity and penetration depth then fall, because of the decrease of the real part of the dielectric constant, as well as the increase of the induced free-carrier absorption. If the power is high enough, the surface density goes beyond N_p within the pulse, yielding an instantaneous reflectivity larger than R_0. At the same time, the beam transmitted into the sample, now a vanishing wave, can create e-h pairs only very close to the surface (i.e., over a few hundred angstroms).

A quantitative determination of the reflected energy $R(t)$ during the pulse requires a general resolution of the Maxwell equations, taking into account the change at any time of the dielectric constant, via the modification of the e-h plasma density profile $N(z,t)$. This dielectric constant at frequency ω_0 and for e-h density N reads

$$\epsilon = \epsilon_0\left[1 - \frac{N}{N_p(1 + i/\omega_0\tau)}\right] + i\epsilon_0'. \quad (1)$$

$\epsilon_0 + i\epsilon_0'$ is the static dielectric constant of virgin silicon at frequency ω_0, ϵ_0' leading to interband absorption (i.e., e-h creation). τ is a relaxation time which describes dissipative processes in the previously created plasma.

Within such an extremely short pulse, one can neglect e-h pair motion and recombination, so that the density variation comes only from e-h creation.

If we take only the contribution coming from interband processes in the absorbed energy $\frac{1}{4}(E+E^*)\partial(D+D^*)/\partial t$ (where $\vec{D}=\epsilon\vec{E}$), this variation reads reads

$$\hbar\omega_0\partial N/\partial t=\tfrac{1}{2}\epsilon_0''|E|^2\omega_0. \quad (2)$$

Adding Eq. (2) to the Maxwell equation $c^2\partial^2E/\partial^2z=-\omega_0^2\epsilon E$, where dispersion has been neglected (as $\partial E/\partial t \ll \omega_0 E$), one can calculate numerically the electric field $E(z,t)$ inside the sample at any time during the pulse, using the two boundary conditions $E(\infty,t)=0$ and

$$2E_0=E(0,t)-(ic/\omega_0)\partial E/\partial z|_{z=0}. \quad (3)$$

The second condition comes from the continuity of the electric and magnetic fields at the irradiated surface, E_0 being the electric field of the incident beam. The instantaneous reflectivity is then easily obtained as $R(t)=|E(0,t)-E_0|^2/|E_0|^2$, and its averaged value $\bar{R}$ over the pulse duration is just the quantity to compare with the experiment.

The experimental data can be very well fitted (Fig. 1) over a large range of energy variation by taking a relaxation time $\tau=3\times10^{-16}$ s. Figure 2 gives the corresponding e-h surface density and profiles at the end of the pulse for various laser intensities; the average reflectivity $\bar{R}$ starts to rise when N_s, the surface density, is of the order of N_p.

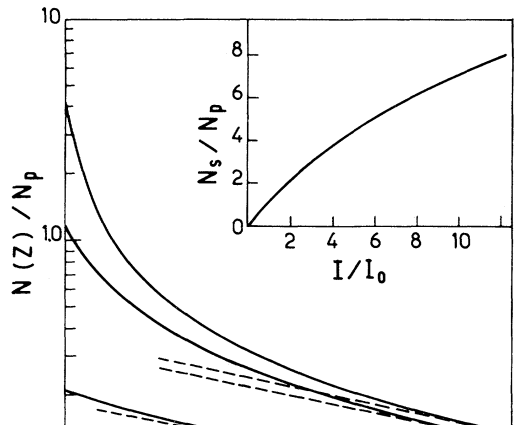

FIG. 2. Calculated electron-hole density profiles $N(z)$ at the end of the pump pulse for $I/I_0=0.2$, 1, and 5. The dashed lines show the behavior for a profile decreasing exponentially over the virgin Si penetration depth. The inset gives the surface density N_s at the end of the pulse vs pulse intensity. N_p is the plasma-frequency density.

To determine N_s, one needs an estimate of $N_p=\mu\omega_0^2\epsilon_0/4\pi e^2$, where μ is the e-h plasma reduced mass. At low density, μ and ϵ_0 are well known: $\mu=0.12m_0$[6] and $\epsilon_0=14.4$ for $\lambda=0.62$ μm and $\epsilon_0\simeq15$ for $\lambda=0.31$ μm. At very high densities, μ can go up to $0.5m_0$ if we take for m_e and m_h the free electron mass m_0, while ϵ_0 decreases but no theory has been given up to now. Using these approximates values for ϵ_0, one finds a density range for N_p: at $\lambda=0.62$ μm, 5×10^{21} cm^{-3} $<N_p<2\times10^{22}$ cm^{-3}, and at $\lambda=0.31$ μm, 2×10^{22} cm^{-3} $<N_p<8\times10^{22}$ cm^{-3}. In these experiments, we clearly go beyond N_p and indeed reach extremely high densities in view of the total number of valence-band electrons (2×10^{23} cm^{-3}).

The value for the relaxation time τ necessary to fit the experiment is extremely short, and cannot be attributed to electron-phonon interaction. The electron-phonon collision time τ_p is usually of the order of 10^{-13} s and moreover increases with plasma density as a result of screening. For very dense plasma, a new mechanism of absorption may appear, due to electron-hole collisions: Collisions between two electrons or two holes cannot lead to dissipation because, as they conserve the total particle momentum, they conserve the total current, while in e-h collisions, the total current can change although the total momentum is conserved. One can estimate the e-h relaxation time τ_{eh} using a screened Coulomb interaction and the Rutherford scattering cross section.[7] τ_{eh}^{-1} increases linearly with plasma density at low N, and saturates at high densities (for a degenerate plasma) to a value of 2×10^{15} s^{-1}. This is in good agreement with the value for τ used to fit our experimental data.

At very high incident power, the reflectivity seems to saturate when compared to theory. This can be explained by a decrease of the interband absorption and consequently a saturation of the e-h pair density due to the Burstein-Moss effect.

In conclusion, the femtosecond experiments clearly indicate that one reaches densities well above the plasma resonance for $\lambda=0.62$ μm and $\lambda=0.31$ μm, since the reflectivity, after crossing the minimum, reaches high metalliclike values. The theoretical model used to interpret these experiments takes into account the space-time evolution of the plasma during the pulse. The small value of the dip in reflectivity at the plasma resonance shows that the dissipation time inside the created plasma is very short ($\sim3\times10^{-16}$ s); we associate this free-carrier absorption to a new mechanism: electron-hole collisions. This analysis allows us also to

determine the plasma density profile at the end of the exciting pulse. This knowledge is crucial to study of the evolution of silicon after optical pulse irradiation.

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