Time-Resolved Reflectivity Measurements of Femtosecond-Optical-Pulse-Induced Phase Transitions in Silicon

C. V. Shank, R. Yen, and C. Hirlimann
Bell Telephone Laboratories, Holmdel, New Jersey 07733
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The reflectivity of silicon has been measured following excitation with intense 90-fsec optical pulses. These measurements for the first time clearly resolve in time the process of energy transfer to the crystal lattice and the dynamics of the phase transition to the melted state.

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Phase transitions induced by intense optical pulses on semiconductor surfaces have recently been the subject of intense interest[1-4] and controversy.[5] In this work we report the first observations of optically induced reflectivity changes in silicon with 90-fsec optical pulses. These measurements clearly resolve the process of energy transfer from an optically excited electron-hole plasma to the crystal lattice, followed by a subsequent phase change to a "melted state."

The experimental tools for performing these measurements have become available as a result of recent advances in short-optical-pulse techniques which have opened the way to making measurements in the femtosecond time domain.[6] A 90-fsec optical pulse from an amplified colliding-pulse mode-locking dye laser[7,8] is split into two pulses, forming a pump and a probe pulse. The probe pulse is focused into a cell containing D_2O to generate a white-light continuum pulse. The pump pulse is focused to about 150 μm in diameter. The continuum pulse is focused onto the sample and the central 10% of the probing area is imaged into a spectrometer with an optical multichannel-analyzer vidicon array on the output slit. The measurements are performed at a 10-Hz repetition rate. A two-axis computer-controller stepper motor moves the silicon wafer in a raster pattern so that each laser pulse sees a fresh region of the Si wafer. This is necessary to prevent artifacts that come about from cumulative excitations of the same spot. The silicon samples were undoped single-crystal $\langle 111 \rangle$ wafers.

The results of the reflectivity measurements are plotted in Fig. 1 with zero time corresponding to the overlap of pumping and probing pulses. The excitation pulse was a 90-fsec optical pulse at a wavelength of 620 nm. The reflectivity measurements were made at near normal incidence for three wavelengths: (a) 1000 nm, (b) 678 nm, and (c) 440 nm. The energy E_{th} is the apparent melting threshold defined as the energy excitation density where visual evidence of amorphous layer formation is observed. This energy corresponds to 0.1 J/cm^2.

In attempting to interpret these data, the question immediately arises as to what is meant by phase changes that take place in a fraction of a picosecond. If we discuss the process of melting using the Lindemann criterion,[9] melting is considered to have taken place when the root mean square displacement of each atom is some fraction x of the dimension of the unit cell. For most solids x is on the order of 0.2–0.25. The vibrational period for LO phonons in silicon is 70 fsec, a time on the order of the excitation pulse. Just how long it takes for the crystal lattice to disorder and what is the influence of the electron-hole plasma on the melting process remain to be determined. In view of these conceptual uncertainties we have defined melting to have taken place when the optical properties of silicon approach those for melted silicon.

With the above caveats in mind, we propose a simple model to provide a basis for understanding our experimental results. The immediate consequence of optically exciting silicon with a 2.0-eV optical pulse is the generation of a dense electron-hole plasma in a thin layer on the surface. The depth of the layer is on the order of the optical absorption depth ($\alpha^{-1} = 3$ μm). At the earliest time following excitation we expect the reflectivity to be dominated by the electron-hole plasma.[10] As we increase the pulse intensity, the e-h plasma becomes dense enough that significant energy is transferred to the crystal lattice and the crystal melts. We expect the melting to begin at the surface and move inward into the bulk with a velocity v.

We can estimate the e-h plasma contribution to the reflectivity using the simple Drude expression for the refractive index of a plasma neglecting dampening:

$$n_p = n_c(1 - \omega_p^2/\omega^2)^{1/2}, \quad (1)$$

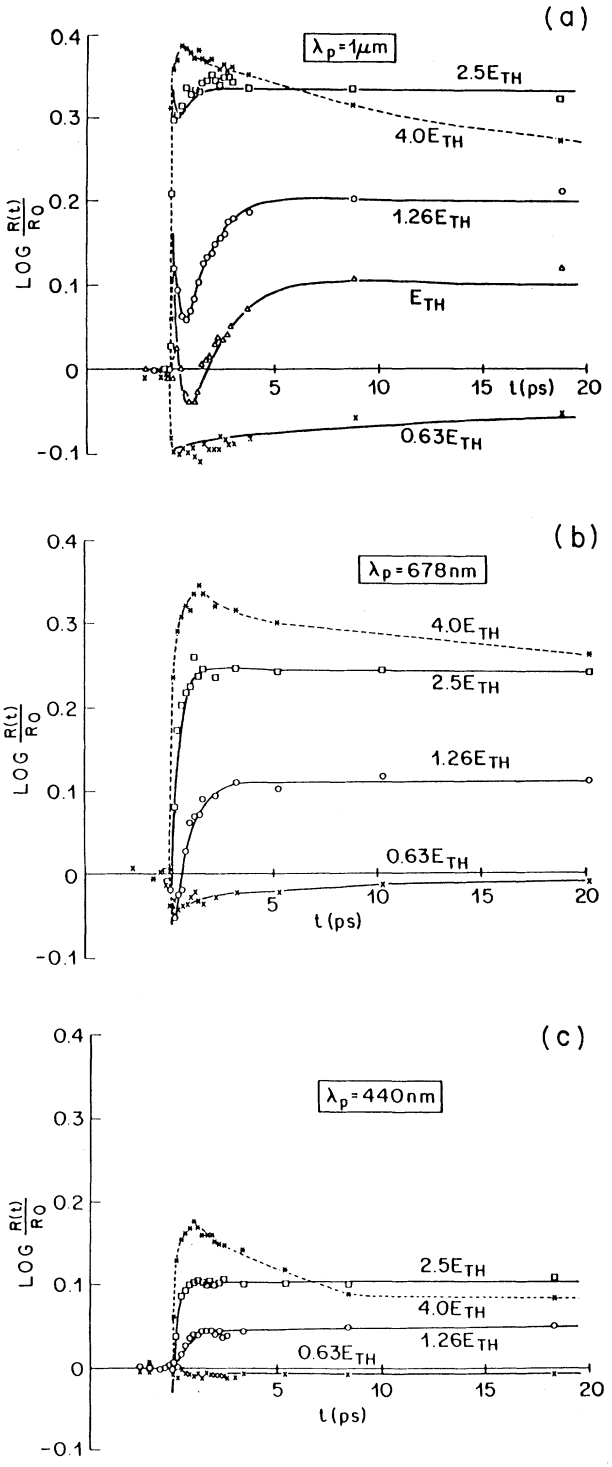

FIG. 1. Transient reflectivity data at three probe wavelengths following a 90-fsec excitation pulse at 620 nm. The solid lines for the $0.63E_{th}$ data are calculated on the basis of carrier diffusion into the bulk. The solid lines $E \geq E_{th}$ are calculated with the thin-film melting model. The dashed curves at the highest excitation are to guide the eye.

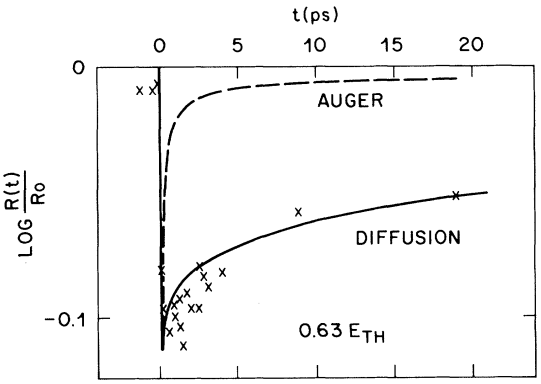

FIG. 2. Plot of the reflectivity data from Fig. 1(a) at $0.63E_{th}$ and a probe frequency of 1.0 μm. The solid curve is the calculated reflectivity accounting for diffusion and the dashed curve is the calculation based on Auger recombination.

where n_c is the crystalline silicon refractive index. At the lowest excitation level in Fig. 1(a) we observe that the reflectivity decreases immediately after excitation just as one would expect from Eq. (1) with the plasma frequency ω_p less than the probe frequency ω. We can estimate the density of the plasma from the magnitude of the reflectivity change using the expression for the plasma frequency,

$$\omega_p = (4\pi N_e e^2/m^*\epsilon_c)^{1/2}.$$

If we assume m^* to be equal to the free-electron mass, we determine $N_e = 5\times10^{21}$ cm^{-3} for an excitation density of $0.63E_{th}$. The slow decay of the reflectivity increase is due primarily to diffusion of the electron-hole plasma into the bulk. This is shown very clearly in Fig. 2, where the data from Fig. 1(a) are compared to a model based on diffusion (solid curve). Also plotted is the decay of the reflectivity change expected from Auger recombination[11] (dashed curve) with use of the previously determined Auger coefficient $\gamma = 3.8 \times10^{-31}$ cm^6/sec. Clearly the experimental data more closely fit the diffusion model. At this density and higher densities we see no evidence of Auger recombination. These observations are consistent with the prediction of Yoffa[12] that the Auger recombination rate saturates at densities above 3×10^{21} as a result of screening effects of the e-h plasma.

As the excitation density is increased above E_{th} in Fig. 1(a) we see the reflectivity increase rather than decrease just after the excitation pulse. This behavior is predicted by Eq. (1). When the plasma frequency exceeds the probing

frequency, the index of refraction becomes imaginary leading to an increased reflectivity. In Figs. 1(b) and 1(c) we see an initial decrease in reflectivity indicating that the wavelength corresponding to the plasma frequency was above 1000 nm and below 678 nm.

Thus far we have described the reflectivity during the first few hundred femtoseconds following excitation in terms of a solid-state plasma. At later times especially near and above E_{th} considerable structure is observed in the reflectivity spectrum seen in Fig. 1(a). The reflectivity change is observed to increase, then reverse sign and increase to a plateau value within the first picosecond and a half. We can explain this curious behavior if we consider a thin molten layer on the surface which expands in depth into the bulk with a velocity v. Using the optical properties of molten Si we can calculate the effect of a thin molten film on the reflectivity. We find that destructive interference between the wave reflected from the air-melt interface and the melt–solid-state-plasma interface acts to lower the intensity of the reflected beam. Since the Si melt is highly absorbing, the optical reflectivity becomes dominated by the optical properties of melted silicon when the melt front has penetrated more than an absorption depth for the probing radiation. This gives rise to an increasing reflectivity and a final plateau reflectivity value. At lower densities near threshold, the peak molten reflectivity is not observed, possibly because of nonuniform melting either due to the laser-beam spatial profile or because of some property of the melting process itself.

The solid curves shown in Fig. 1 are the result of a calculation with the thin-film reflectivity formula given by Eq. (2):

$$R=\left|\frac{(1-n_m)(n_m+n_p)\exp(-ik_ml)+(1+n_m)(n_m-n_p)\exp(ik_ml)}{(1+n_m)(n_m+n_p)\exp(-ik_ml)+(1-n_m)(n_m-n_p)\exp(ik_ml)}\right|^2, \quad (2)$$

where $k_m=(\omega/c)\,\mathrm{Im}[n_m]$, $l=vt$. We have assumed the optical constants of the thin film to be those of molten Si,[13] and the optical constants of the substrate to be those of the e-h plasma given by Eq. (1). The velocity of the melt front and the plateau reflectivity were assumed to be free parameters of the fit to the data. We find that a single melt-front velocity of 6.2×10^5 cm/sec closely matches the reflectivity for all observed wavelengths for an excitation of $1.0E_{th}$. This value is near the velocity of sound in crystalline silicon. In a similar manner we fit the data at $1.26E_{th}$ and found a melt-front velocity of 9×10^5 cm/sec. To explain the rapidly rising reflectivity at $2.5E_{th}$ a velocity of 25×10^5 cm/sec is required. It is possible that bulk melting takes place at such high excitation levels. In fact, a gradient in the *local* melting rate as a function of depth could result in a very high *effective* melt-front velocity. At the highest excitation level of $4.0E_{th}$, the rapid decay of the reflectivity is due to catastrophic damage of the sample. At this pump level a small crater is formed on the sample surface.

A unique aspect of these experiments is that by exciting the silicon surface with a short (90-fsec) optical pulse, we have been able to create a previously unobserved unstable form of highly excited silicon which persists for a fraction of a picosecond. The properties of this material with nearly 10% of the available electrons excited remain to be determined. Unlike previous measurements, we observe apparent melting to take place after excitation rather than during the exciting pulse.

In conclusion, we have observed the reflectivity of silicon using femtosecond optical techniques and have found these observations consistent with a melt that is initiated at the surface moving into a region of dense electron-hole plasma with a velocity dependent on pump intensity. In addition, we have observed the Auger recombination rate to be substantially reduced at excitation levels above 5×10^{21} cm^{-3}.

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