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Time-Resolved Optical Transmission and Reflectivity of Pulsed-Ruby-Laser Irradiated Crystalline Silicon

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The time-resolved optical transmission and reflectivity of n-type crystalline silicon has been observed during and after pulsed-laser irradiation. The transmission goes to zero, and remains at zero, during the period of enhanced reflectivity, contradicting reports of earlier experiments. Our measurements are in quantitative agreement with results of thermal melting model calculations and with known optical properties of molten silicon.

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The effects of pulsed-laser irradiation on semiconductors has recently become a topic of widespread interest, both because of practical applications in device fabrication, and because of a controversy which has arisen regarding the new physical phenomena involved. The thermal-melting model[1-3] of pulsed-laser effects assumes that the absorbed laser energy is transferred from the electronic system to the lattice in a time less than or of order of the pulse duration ($\tau_l \sim 10$ nsec) and that thereafter normal heat transfer and melting occur. This model is supported by an impressive array of experimental and theoretical results.[1-5] Recently, however, Compaan and co-workers have presented results which they claim provide conclusive proof that the thermal-melting model cannot be correct.[6,7] In particular, they observed[6] both the time-resolved reflectivity, R (at $\lambda = 0.633$ μm), and transmissivity, T (at $\lambda = 1.15$ μm), of ~400-μm-thick semi-insulating crystalline Si (c-Si) during pulsed-laser irradiation ($\lambda = 0.485$ μm). They found that, although T showed a sudden drop as R rose and a recovery when R fell, the T at minimum (duration ~50 nsec) did not go to zero, as would be expected if the layer of molten Si (skin depth ~100 Å) implied by the melting model were present. Instead, they observed that (i) about 25% of the full T recovered only with a very long time constant (~400 nsec), and (ii) the minimum T had a continuously decreasing rather than a flat bottom. They interpreted their results as arising from a laser-induced transition of Si to a new "fluid phase," arising from formation of a high-density, hot plasma, as suggested by Van Vechten *et al.*[8]

In this Letter, we present results of time-resolved T and R measurements during pulsed-laser irradiation of silicon, which contradict the results of Lee *et al.*[6] We find that when the measurements are differently carried out, the transmissivity drops to zero, and remains at zero throughout the high-reflectivity phase (HRP); other features of the T and R "signatures" are also in agreement with each other, with the results of melting-model calculations,[9] and with known optical constants for molten silicon.[10]

Experiments were carried out with use of a pulsed ruby laser ($\lambda = 0.69$ μm) operated in TEM_{00} mode with 14 ± 1 nsec full width at half maximum (FWHM) pulse duration. The samples, which were ~400-μm-thick c-Si wafers (n type, P doped, 2–7 Ω cm), polished on both sides to eliminate scattering of the 1.15-μm probe laser beam, were located 9.8 m beyond the second amplifier stage of the pulsed laser and 75 cm beyond a $f_L = 100$ cm converging lens; this resulted in good homogeneity of an ~4-mm-diam central part of the laser beam. The irradiated area was limited to a 2-mm-diam region in initial experiments (later 3 mm) by a thin mask placed directly over the sample.

Initial T measurements were carried out with an unfocused 2-mW cw He/Ne probe laser ($\lambda = 1.15$ μm, $1/e^2$ diam = 0.97 mm) incident at 14° to the sample normal, and detected without the use of collection optics. An extensive series of T and R experiments were carried out later with this beam incident at 4.7°, focused to an ~230-μm-diam ($1/e^2$) spot on the sample, and refocused onto the detector with various image/object distances and collection optics. Our observation of a period of zero T was found to be entirely independent of probe-beam focusing and/or the use of collection optics; thus, the zero-T result is not an experimental artifact resulting from scattering, deflection, and/or self-defocusing of the probe beam off the detector, due, for example, to a change in index of refraction during the HRP.[6]

Both a Si avalanche photodiode (APD; active region 1.5 mm diam, 2-nsec rise and fall times) and a Ge p-i-n photodiode were used in the T experiments. However, the Ge p-i-n diode was discarded because its responsivity is ~10 times less than that of the Si APD at 1.15 μm, and because it exhibited both a zero-baseline overshoot on a falling light signal and a very long recovery time (~600 nsec time constant). Similar detector problems may be a factor in the results obtained by Compaan and co-workers.[6,7] A 1.15-μm band-pass filter (10-nm bandwidth and ~40% T) was necessary directly in front of the Si APD detector, in order to prevent intense near–band-gap photoluminescence (NBG PL, see below) emitted by the sample from swamping the detector when it was close to the sample.

The initial (later) R measurements at $\lambda = 0.633$ μm were carried out using the Si APD detector and a 3.4-mW cw He/Ne probe laser, which was unfocused (focused to ~140 μm $1/e^2$ diam) and incident at 10° (4.7°) to the sample normal. The APD's high red sensitivity made it necessary to use three 0.633-μm 1% bandwidth (FWHM) filters in front of it, to block the ruby light pulse.

Three separate storage oscilloscope recordings, on successive ruby laser shots, with (a) both probe beam and ruby beam present, (b) probe beam blocked, and (c) both beams blocked, allowed a clean separation of the T or R signal from NBG PL and radiated electromagnetic noise (associated with firing the pulsed laser). The measured quantities are ratios of T or R during the HRP to the initial T_0 or R_0; these are converted to absolute T or R values using separate measurements of T_0 and R_0.

The transient R signals observed were similar in shape to those reported elsewhere,[4,5] consisting of a flat-topped period of maximum R followed by a decaying R tail. However, we found that the R in the HRP at 0.633 μm with both focused and unfocused probe beams (at 1.15 μm with unfocused probe beam) was 2.05 (2.1) times the initial R, corresponding to reflectivities of (71± 1.5)% [(82± 5)%]. Both values are in good agreement with R values calculated from the wavelength-dependent optical constants for molten Si,[10] $R = 72\%$ and 78% at 0.633 and 1.15 μm, respectively. Some earlier R experiments[4, 6, 7] did not demonstrate that R rises in the HRP to the values expected for molten Si; this has been cited[6] as evidence for the possible inapplicability of a thermal-melting model. The present R experiments would seem to remove this objection.

Figure 1 shows typical results of a series of T measurements with the unfocused 1.15-μm probe for pulsed-laser energy densities, E_l, both below and above the threshold (~ 0.8 J/cm^2) for the HRP. The probe-beam transmission drops to zero, and remains at zero, for a period of time that increases with increasing E_l. The maximum transmitted signal that could be present and remain undetected is ~ 1%. The linearity of the detector was checked over a wide dynamic range; the background signal and subtraction procedure were found to be highly reproducible on successive shots; and, the presence of weak NBG PL during part of the zero-T period verifies that the detector is responding during this time. Thus, our result of zero T during the HRP contradicts the large, finite T obtained by Lee *et al.*[6]

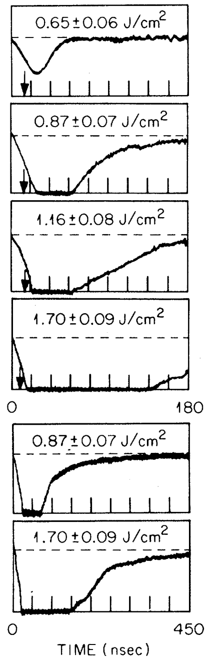

FIG. 1. Transmission of the unfocused 1.15-μm probe beam through c-Si, at a series of pulsed laser E_l and viewed on two different time scales (20 and 50 nsec/div.). The dashed horizontal lines indicate the initial T_0. The top figure is for E_l *less* than the threshold for the HRP. The arrows mark the position of the peak of the ruby-laser pulse (plus or minus a few nanoseconds).

We have also carried out detailed calculations of the time-dependent T and R signals, using the thermal-melting model. These calculations will be published elsewhere[9]; however, comparison of the main features of the T and R signatures with each other and with these calculations is given in Table I. We define τ_m (τ_0) as the duration of maximum reflectivity (zero transmission), τ_f as the fall time to the change in slope of the falling-R signal (thought to represent the transition from molten to hot, solid silicon at the sample's surface[4]); and $\tau_{\mathrm{tot}} = \tau_m + \tau_f$ is then the total surface melt duration, all measured with focused probe beams. (The spatial averaging effect of a large, unfocused probe beam results in some lengthening of rise and fall times for R and T transitions. However, measured R rise times with a focused beam were $\lesssim 2$ nsec, the 10%–90% rise time of our Si APD detector.) As Table I demonstrates, there is excellent agreement between measured and calculated values for τ_{tot}, as there is also between the measured (0.86±0.05 J/cm^2 unfocused, 0.80±0.03 J/cm^2 focused) and calculated (0.8 J/cm^2) threshold E_l for the HRP. The calculations,[9] as well as simple wavelength-dependent skin depth[10] considerations, also show that the measured τ_0 at 1.15 μm should be slightly shorter than τ_m at 0.633 μm, as is observed (Table I).

TABLE I. Comparison of characteristic times (in nanoseconds) from T (1.15 μm) and R (0.63 μm) signatures of c-Si obtained with focused probe beams, with results of thermal-melting-model calculations. The rms error in time measurements, estimated from several successive measurements, is $\lesssim \pm 10\%$.

E_l (J/cm^2)	$\tau_m(R)$	$\tau_0(T)$	Surface melt duration R	Surface melt duration Model
0.9	17	6.5	26	23.5
1.1	33.5	26	44	45
1.3	52	45	63.5	67.5

T measurements were also carried out *without* the cw probe beam and 1.15-μm bandpass filter, and with the Si sample mounted directly on the Si APD detector enclosure, ~ 9 mm from the detector chip. Intense NBG PL was detected in this case. The radiation was separated into two components, a sharp initial peak and a long slowly decaying tail. The initial NBG PL peak occurs $\lesssim 4$ nsec after the peak in the ruby-laser pulse and, although it was not completely resolved, had a FWHM comparable to the ruby pulse width. A semilog plot of the slowly decaying tail revealed that several decay processes may be involved, with time constants ranging from $\lesssim 100$ nsec to ~ 1 μsec. The initial, short-lived PL peak is easily distinguished from any leakage of the ruby pulse to the detector, since this peak increases as a fractional power of the ruby-laser intensity and eventually saturates. The PL intensity also falls off rapidly with increasing sample-detector separation, as expected from solid-angle considerations. Similar intense recombination radiation emitted by pulsed-laser–excited silicon was reported by Svantesson, Nilsson, and Huldt and by Nilsson, who ascribed the initial very rapid recombination to a third-order process.[11] It should be noted that the 2-mW, 1.15-μm probe-laser intensity corresponds to only $\sim 1.5\%$ of the peak PL intensity, with the sample ~ 9 mm from the detector chip; i.e., it would be completely swamped by the NBG PL signal, until nearly 1 μsec after the ruby-laser pulse, unless the bandpass filter is in place.

T measurements were also carried out using a Ge p-i-n diode (as was used in the measurements of Lee *et al.*[6]). It was possible by mounting the silicon sample directly on the detector enclosure, and also focusing down the 1.5-μm probe laser beam, to detect simultaneously both the NBG PL and probe-beam signals (with no bandpass filter being used). By carrying out T measurements both with and without the probe beam, and then taking the difference of the two measurements, we were able to obtain the T signal while NBG PL was also incident on the detector. A period of zero T (or even slightly below zero T, a result of detector baseline overshoot) was observed, in rough agreement with the results in Table I. However, transmission recovery was very slow, with a $1/e$ time constant >600 nsec, similar in this respect to the behavior reported by Lee *et al.*[6] In contrast, *full* transmission recovery occurred within 450 nsec in T signatures obtained with the bandpass filter/Si-APD combination (Fig. 1). Thus, it appears that the slow recovery of full transmission described by Compaan and co-workers may be an artifact of the use of a Ge p-i-n photodiode.

In summary, we have used time-resolved T and R measurements to probe the optical behavior of silicon during and immediately after pulsed-laser irradiation. The optical transmission goes to zero during the HRP, and corresponding features of the T and R signatures are in good agreement. These results contradict those of Lee *et al.*[6] As is shown in more detail elsewhere, our T and R experiments are also in quantitative agreement with the results of thermal-melting-model calculations.[9]

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Far-Infrared Emission from Population-Inverted Hot-Carrier System in *p*-Ge

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Experimental evidence is presented for radiative transitions of light holes accumulated in a limited area in momentum space to the heavy-hole band. Also reported is the observation of cyclotron resonance emission from the accumulated light holes. The possibility of far-infrared amplification is discussed.

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Streaming motion[1] and population inversion[2] of hot carriers in crossed electric and magnetic fields have been established in Hall-effect measurements on silver halides[3-5] and *p*-Ge[6,7] at 4.2 K. Here I report the first observation of far-infrared emission from the population-inverted hot-carrier system.

The experiments are performed on *p*-Ge crystals doped with In of concentration $1.2\times10^{14}/\mathrm{cm}^3$. Specimens are of simple rectangular shape ($0.4\times3\times12\ \mathrm{mm}^3$) with end contacts prepared by alloying with Au-In (2 at.%). Prior to the radiation experiment, Hall-effect measurements are carried out to confirm streaming motion and carrier accumulation. A pulsed electric field E with an amplitude $5\ \mathrm{V/cm} < E < 1\ \mathrm{kV/cm}$ and a duration 40 nsec–2 μsec is applied at a repetition rate of 30 Hz as in previous experiments.[8] Sample heating is confirmed to be insignificant by Hall-effect measurements. The magnetic field B is applied perpendicularly to the current. The specimen and a far-infrared detector are mounted at either end of a metal light pipe of 30 cm length in a similar configuration to that described in Refs. 9 and 10. The whole system is immersed in liquid helium. Two types of detector are used; a Ge/Ga photoconductive detector and an *n*-InSb cyclotron resonance detector. The Ge/Ga detector,[11] containing Ga of $\sim1\times10^{15}/\mathrm{cm}^3$ density, is used to investigate integrated radiation intensities. The *n*-InSb detector ($n\sim2\times10^{13}\ \mathrm{cm}^{-3}$ at 77 K), used under magnetic field B_d, yields a sharp spectral response at $\epsilon\sim\hbar\omega_c\equiv\hbar eB_d/m^*$ with the effective mass of electrons $m^*=0.013m_0$.[10] The spectral resolution is determined to be typically 1 meV by the observation of H_2O laser lines.

At $B=0$, far-infrared emission is observed in the whole range of E and is interpreted as due to transitions of hot light holes to the heavy-hole band. The radiation spectrum consists of a single broad peak which shifts towards higher energies with increasing E until the shift is saturated to give the maximum intensity point around $\epsilon\sim18$ meV above $E\sim100$ V/cm. The saturation of shift indicates the onset of streaming motion of light holes above 100 V/cm. This interpretation is supported by the following consideration. The collision time $\bar{\tau}_{\mathrm{imp}}$ of light holes due to ionized acceptor scattering averaged over the energy range below the optical-phonon energy $\epsilon_{\mathrm{op}}=37$ meV is estimated to be ~12 psec. For $E>100$ V/cm this $\bar{\tau}_{\mathrm{imp}}$ is longer than the traveling time, $T_{\mathrm{op}}^{1}\equiv(2m_1^*\hbar\omega_{\mathrm{op}})^{1/2}(eE)^{-1}$, for light holes initially at $\epsilon=0$ to reach $\epsilon=\hbar\omega_{\mathrm{op}}$, where $m_1^*=0.043m_0$ is the light-hole effective mass. ($T_{\mathrm{op}}^{1}\sim12$ psec at $E=100$ V/cm.) Thus streaming motion is expected above 100 V/cm. No indication is found at any levels of E for recombination radiation from impact-ionized impurities,[12-14] which would yield a sharp emission at $\epsilon\sim10$ meV. This fact can be explained by the relatively low concentration of acceptors in the specimen used.

To explore the effects of light-hole accumulation on radiation, the total radiation intensity is studied as a function of B at different levels of dissipative electric field E_x. Typical results are