Transformation of the optical phonon spectrum of silicon during bombardment by intense picosecond laser pulses

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The spectra of an optical phonon in crystalline silicon have been measured at various excitation levels (up to the point at which the crystal melts) by coherent active Raman spectroscopy with picosecond pulses. The transformation of the spectra is evidence of a significant heating of the phonon subsystem and of the generation of a strong photostimulated stress over times on the order of 10 ps.

1. In this letter we are reporting the results of an experiment in which a transformation of the Raman scattering spectrum by surface layers of crystalline silicon has been detected for the first time with a high time resolution ($\sim$30 ps) and a high spectral resolution ($\sim 3\ \mathrm{cm}^{-1}$) during the simultaneous excitation of the Si surface by intense picosecond pulses of visible light (the intensity was varied up to the point at which the crystal melted). The spectra were measured by the method of coherent active Raman spectroscopy (CARS) in the reflection geometry. The results, examined along with the results of a numerical modelling, provide evidence of a rapid heating of optical phonons at the center of the Brillouin zone during the laser pulse and of the appearance of a strong photoinduced elastic stress in a surface layer.

2. Time-resolved Raman spectroscopy yields unique information on the dynamics of the phonon subsystem of photoexcited surface layers of crystals.[1,2] For example, measurements of the phonon spectra of Raman scattering with a nanosecond time resolution have established that the melting of the surface of silicon by "giant" laser pulses occurs at a temperature which is the same as the melting temperature under equilibrium conditions (e.g., Ref. 3). Serious technical difficulties have prevented measurements of this type in the picosecond range, although these are precisely the measurements which could provide information of fundamental importance on the excitation and thermalization of the phonon subsystem during the interband absorption of short, intense laser pulses and also on the relationship between these processes and the melting of the crystal.

3. Figure 1 shows the experimental arrangement. The sources of picosecond pulses with tunable frequencies ω_1 and ω_2 are two lasers using solutions of an organic dye which are pumped synchronously by trains of pulses of the second harmonic from a Nd:YAG laser with passive mode locking. The light with the frequency ω_1 is also used to excite the surface of the crystal. The CARS signal at the frequency $\omega_a = 2\omega_1 - \omega_2$ is detected by a photomultiplier, after a spatial and spectral filtering, as the frequency difference $\omega_1 - \omega_2$ is scanned over the region of the Raman resonance. The frequency scanning and the data acquisition are orchestrated by a microcomputer. Spectra of the optical phonon mode F_{2g} were recorded (Fig. 2) at several values of the energy density (E) of the exciting light, from $E = (0.30 \pm 0.05)E_0$ to

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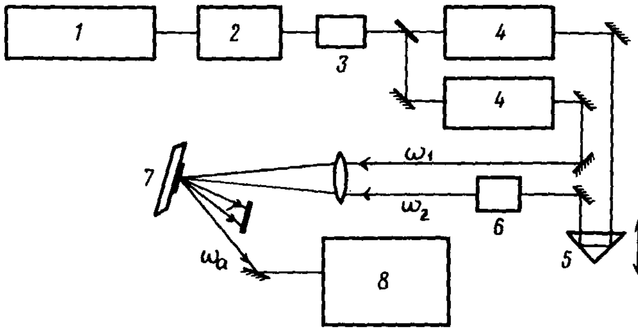

FIG. 1. Block diagram of the experimental apparatus. 1—Nd:YAG laser with passive mode locking; 2—laser amplifier; 3—frequency doubler; 4—laser using a solution of rhodamine 6G (pulse length of 30 ps); 5—delay line; 6—polarization rotator; 7—Si(100) sample; 8—microcomputer-controlled data-acquisition and control system.

$E \simeq E_0$ ($E_0 \simeq 0.2$ J/cm^2 is that energy density of light at $\lambda = 560$ nm which causes melting). The diameter of the illuminated spot on the surface of the crystal is 700 μm. At room temperature, in the absence of excitation, the spectrum of the optical phonon is a relatively narrow ($\simeq 3.5$-cm^{-1}), intense line at the frequency $\simeq 520$ cm^{-1}. It can be seen from Fig. 2 that with increasing excitation intensity we observe a significant broadening of the line and a change in its shape; its intensity also decreases in comparison with the nonresonant (electron) background. We believe that these changes are

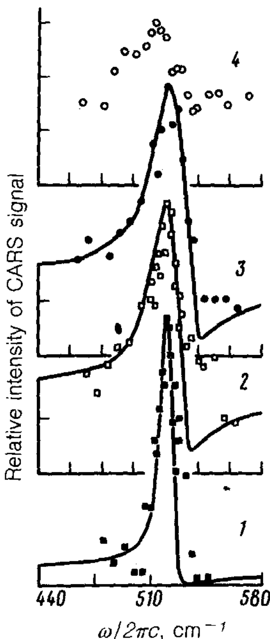

FIG. 2. Experimental (points) and calculated (solid lines) CARS spectra of silicon at various energy densities (E) of the exciting pulses. Exciting energy density, free-carrier concentration, and stress found through the theoretical fit of the experimental spectra: 1—$C = 0.3E_0$ $T = 700$ K, $n = 1.6 \times 10^{21}$ cm^{-3}, $p = 10$ kbar; 2—$E = 0.5E_0$, $T = 970$ K, $n = 2.6 \times 10^{21}$ cm^{-3}, $p = 27$ kbar; 3—$E = 0.7E_0$, $T = 1240$ K, $n = 3.5 \times 10^{21}$ cm^{-3}, $p = 40$ kbar; 4—$E \simeq E_0$.

caused by an inhomogeneous broadening of the phonon line due to a significant increase in the phonon temperature, the generation of a dense electron-hole plasma, and the strong stresses caused in the surface layer by this plasma through the mechanism of the electron-phonon strain energy.

4. For a quantitative estimate of the lattice temperature (T), the concentration (n) of photoexcited free carriers, and the stress (p) in the crystal we carried out a numerical modelling of the experimental spectra. The center of the Raman-scattering line is shifted in opposite directions by the temperature T and by the stress $p = -K(\partial U/\partial z)$ (K is the bulk modulus, U is the displacement, and z is the coordinate measured into the sample). As was shown in static experiments,[4] a compressional stress causes a high-frequency shift of a phonon line with a coefficient of 0.47 cm^{-1}/kbar, while a heating of the lattice causes a "softening" of the phonon mode and a broadening of the Raman-scattering line in the low-frequency direction.[5] The width and spectral position of a line thus carry information on the temperature of the phonon mode and on the magnitude of the stress which arises during the pulse. It should be noted, however, that T and p vary rapidly with distance into the sample, with distance along a transverse coordinate, and also in time, with the result that the observed intergral spectrum is inhomogeneously broadened. Accordingly, it is difficult to directly extract data on T and p from the spectra, and a numerical simulation is required.

The equations for T, n, and the displacement U are

$$\partial T(t,z)/\partial t = I(t,z)(\hbar\omega_1 - E_g)(1-R)/d_0\rho c_p\hbar\omega_1 ,$$

$$\partial n(t,z)/\partial t = -\gamma n^3 + I(t,z)(1-R)/d_0\hbar\omega_1 ,$$

$$\partial^2 U/\partial t^2 - c_0^2(\partial^2 U/\partial z^2) = (\theta_0/\rho)\cdot(\partial n/\partial z),$$

where $I(t,z) = I_0(t)\exp(-z/d_0)$ is the intensity of the radiation, which is in the form of a Gaussiam pulse with a length of 30 ps, d_0 is the radiation absorption depth, R is the reflection coefficient, c_p is the specific heat, ρ is the density, c_0 is the sound velocity, γ is the Auger recombination coefficient, and θ_0 is the strain energy. Figure 3

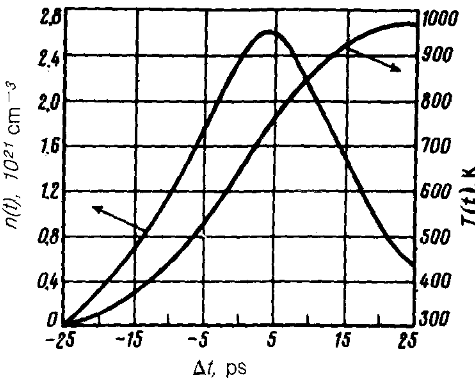

FIG. 3. Representative calculations of $n(t)$ and $T(t)$ at a silicon surface for $E = 0.5E_0$.

shows some representative curves of $n(T)$ and $T(t)$ calculated for $E = \int I(t)dt = 0.5 E_0$.

In the course of fitting the experimental spectra, we varied the strain energy θ, which determines the magnitude of the stress p at given values of n, and we also varied the depth of the probing of the surface layer, d. It can be seen from Fig. 2 that this comparatively simple model leads to a good agreement with experiment with the values $\theta_0 = 15$ eV and $d = 1000$ Å (curves 1–3 in Fig. 2). We made no attempt to numerically model spectrum 4 in Fig. 2 because of the complexity of dealing with the changes in the optical characteristics of the crystal during melting.

5. In summary, by analyzing the experimental data we have become convinced that over a time scale on the order of 10 ps there is a significant heating of the optical phonon mode at the center of the Brillouin zone. Combining this result with the well-known fact that the energy of the photoexcited electrons in silicon is transfered primarily to the short-wave parts of the phonon branches,[6] we conclude that the energy thermalization occurs at a high rate within the optical part of the phonon subsystem. In addition, we have obtained the first data on the generation of a substantial nonuniform stress (with a magnitude of tens of kilobars) in the surface layer of a crystal during the absorption of an intense picosecond pulse.

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