

it is selective for the slope of the dispersion curve.<sup>4</sup> In the present case this high resolution made possible the investigation of the temperature dependence of the roton energy and line-width at low enough temperatures, where the line-width is much less than the energy. This was earlier found to be a necessary condition for unambiguous data reduction, and it is in fact assumed in the existing theories. Thus the present work is the first really meaningful direct neutron-scattering study of this problem.

It appears to me that the present results convincingly show both the feasibility of the NSE method for the high-resolution study of elementary excitations (lifetime and energy-shift effects, crossing branches and hybridization, etc.) and the physical interest of such experiments.

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## Raman Measurement of Lattice Temperature during Pulsed Laser Heating of Silicon

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The ratio of Stokes-to-anti-Stokes phonon Raman scattering of a probe laser pulse at 405 nm is used to obtain a direct measure of the lattice temperature in silicon within 10 nsec after a heating pulse at 485 nm. A lattice temperature rise of only 300°C is found with a heat pulse power density of  $\sim 1$  J/cm<sup>2</sup>. Since silicon melts at 1412°C, this result is direct evidence that strictly thermal melting models of laser annealing are inappropriate.

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Pulsed laser annealing has recently shown great promise for repairing the damage introduced by ion-implantation doping of semiconductors.<sup>1,2</sup> However, the mechanisms responsible for annealing a micron thick layer on time scales

of tens of nanoseconds are not well understood. Strictly thermal models of the annealing can begin to explain the processes only if the semiconductor is assumed to melt.<sup>2,3</sup> Alternative non-thermal-equilibrium models,<sup>1,4-7</sup> on the other hand,

require justification for how the electron system can remain out of equilibrium with the lattice for periods as long as tens of nanoseconds. We report here a direct measurement of lattice temperature by Raman scattering which shows that the lattice temperature rises by only 300 °C in silicon within 10 nsec after a heating pulse of energy density equivalent to that used for laser annealing. Since silicon melts at ~1400 °C, the inescapable conclusion is that the lattice does not melt under these conditions and laser annealing must involve nonthermal mechanisms.

The ratio of counting rates for Stokes-to-anti-Stokes Raman scattering is given by

$$\frac{R_S}{R_{AS}} = \frac{(\alpha_L + \alpha_{AS})\omega_S^3 \sigma(\omega_L, \omega_S)}{(\alpha_L + \alpha_S)\omega_{AS}^3 \sigma'(\omega_L, \omega_{AS})} \exp(\hbar\omega_0/kT), \quad (1)$$

where  $\omega_L$ ,  $\omega_S$ ,  $\omega_{AS}$ , and  $\omega_0$  are the laser, Stokes, anti-Stokes, and phonon frequencies, respectively.  $\sigma(\omega_L, \omega_S)$  and  $\sigma'(\omega_L, \omega_{AS})$  are the Stokes and anti-Stokes Raman-scattering cross sections and the term  $\exp(\hbar\omega_0/kT)$  follows directly from the ratio  $[n(\omega_0) + 1]/n(\omega_0)$ , where  $n(\omega_0)$  is the phonon occupation probability at the lattice temperature,  $T$ .

For Raman scattering with laser frequencies above the band gap in semiconductors it is essential to include the frequency dependence of the cross sections  $\sigma$  and  $\sigma'$  and furthermore to correct for the reduced scattering volume due to strong absorption of the laser and scattered beams.<sup>8,9</sup> If the absorption length  $\alpha^{-1}$  is small compared to the length of the crystal this introduces the correction  $(\alpha_L + \alpha_S)^{-1}$  for the Stokes scattering rate  $R_S$ , where  $\alpha_L$  and  $\alpha_S$  are the absorption coefficients at  $\omega_L$  and  $\omega_S$ , respectively. A similar correction occurs for anti-Stokes scattering. The Stokes Raman cross section in silicon shows considerable resonance enhancement in the region from 2 to 3.5 eV,<sup>10</sup> which therefore affects a Raman temperature measurement. Although data are published only for the Stokes cross section,<sup>10</sup> symmetry of the cross section under time reversal<sup>8,9</sup> may be used to show that for a backscattering geometry the anti-Stokes cross section  $\sigma'(\omega_L, \omega_{AS})$  for laser frequency  $\omega_L$  is equal to the Stokes cross section  $\sigma(\omega_{AS}, \omega_L)$  for laser frequency  $\omega_{AS}$  and scattered (Stokes) frequency  $\omega_L$ . Thus, we can obtain corrections to our Raman ratios from the data of Ref. 10.

We have recently used Stokes-anti-Stokes ratios to obtain lattice temperatures in silicon dur-

ing cw laser heating.<sup>11</sup> The Raman data indicated surface temperatures at the center of the laser spot as high as 1500 K. Excellent agreement was obtained with the nonlinear heat diffusion calculation of Lax<sup>12</sup> provided that the temperature dependence of the absorption coefficient of silicon was included. These cw measurements provide support for the validity of Raman ratios as a reliable measure of lattice temperature over the range from 300 to 1500 K in silicon.

Lattice temperatures may in principle be obtained from the Raman-scattered light of the heating or annealing laser pulse itself. However, in this case the Stokes-anti-Stokes ratios would average over the rising lattice temperature during the heating pulse. Furthermore, spatial variations in the power density would be reflected in spatial temperature variations so that the fringes of the beam would presumably sample a much lower lattice temperature than the beam center. Finally the exponential attenuation of laser intensity into the crystal would produce a strong temperature gradient that would be reflected in the Raman signal. To minimize these three averaging effects we chose to use a two-beam configuration with an intense heating beam and a weak probe beam which was delayed by slightly more than the ~5 nsec pulse width of the heating beam. In addition the probe was focused to a diameter at half-power points of 50  $\mu\text{m}$  and centered inside the heating beam of diameter 90  $\mu\text{m}$ . Spot overlap was repeatedly checked with a 50- $\mu\text{m}$  pinhole placed at the exact position of the silicon sample. The use of a probe beam also allowed us to select a shorter wavelength ( $\lambda_p = 405 \text{ nm}$ ) which is more strongly absorbed in silicon ( $\alpha = 6 \times 10^4 \text{ cm}^{-1}$ ) than the heating laser wavelength ( $\lambda_H \approx 485 \text{ nm}$ ) where  $\alpha = 1.2 \times 10^4 \text{ cm}^{-1}$ . With the heat-probe configuration as described above, we estimate that any spatial or temporal averaging of temperature can affect the results by no more than  $\pm 50 \text{ }^\circ\text{C}$ .

A Molelectron UV-1000 pulsed nitrogen laser was used to excite simultaneously two dye lasers. Maximum power for the heating pulse was obtained from a broadband dye laser ( $\Delta\lambda \approx 10 \text{ nm}$ ) with no dispersive element in the cavity while the probe pulse was obtained from a Molelectron DL-200 dye laser. Spectrally broad dye super-radiance was eliminated from the probe beam with a 10-nm bandwidth three-cavity interference filter. An optical delay line was used to obtain the 10-nsec delay for the probe beam. Signal detection through a Spex 1401 double spectrom-

eter was performed with a photomultiplier and gated photon counting performed with a time-to-pulse-height converter and a multichannel analyzer operated in the multichannel scaling mode.<sup>13</sup> Spectrometer throughput was measured using a calibrated tungsten lamp and the data were appropriately corrected. To maximize signal, spectrometer resolution of  $10 \text{ cm}^{-1}$  was used (1-nm slits). The spectrometer was stepped in increments of  $10 \text{ cm}^{-1}$  and four data points spanning the  $520\text{-cm}^{-1}$  peak were added to obtain an approximate integral of the peak area.

The corrections to the Raman ratio due to laser and scattered beam absorption and due to the Raman cross section were obtained from published measurements<sup>10,14</sup> of these values. These corrections are

$$\sigma(\omega_L, \omega_S)/\sigma'(\omega_L, \omega_{AS}) = 0.67 \pm 0.15 \quad (2)$$

and

$$(\alpha_L + \alpha_{AS})/(\alpha_L + \alpha_S) = 1.2. \quad (3)$$

The spectrometer throughput ratio was  $\epsilon(\omega_{AS})/\epsilon(\omega_S) = 1.11$ . A direct check of these corrections was made by defocusing the probe beam and with the heat pulse off we obtained a Raman ratio which indicated a lattice temperature of  $23 \pm 30^\circ \text{C}$  without applying any of the corrections discussed above. The fact that this agrees well with the ambient temperature of  $27^\circ \text{C}$  may be taken as an excellent verification of the technique but it does suggest that the correction factors above are slightly in error. All of the temperatures we present in this Letter have been obtained directly from the Stokes-anti-Stokes ratio with no corrections applied. The effect of applying the factors given above would be to lower the indicated temperature by  $\sim 100^\circ \text{C}$ .

The lattice temperature rise as a function of heating laser power density is shown in Fig. 1. The left-most point was taken with the heating beam blocked; it indicates the presence of some heating due to the probe pulse. However, the need to focus the probe to  $\sim 50 \mu\text{m}$  made data acquisition at lower probe power densities very difficult. Note that the average-probe power at a repetition rate of 15 pulses/sec was typically  $60 \mu\text{W}$ . To check for nonlinear effects due to heating from the probe beam, data were obtained at a probe power density of  $0.2 \text{ J/cm}^2$  in addition to the  $0.06 \text{ J/cm}^2$  shown in Fig. 1. The results indicated  $\sim 80^\circ \text{C}$  greater lattice heating from the probe but otherwise were qualitatively similar to the results shown in Fig. 1.

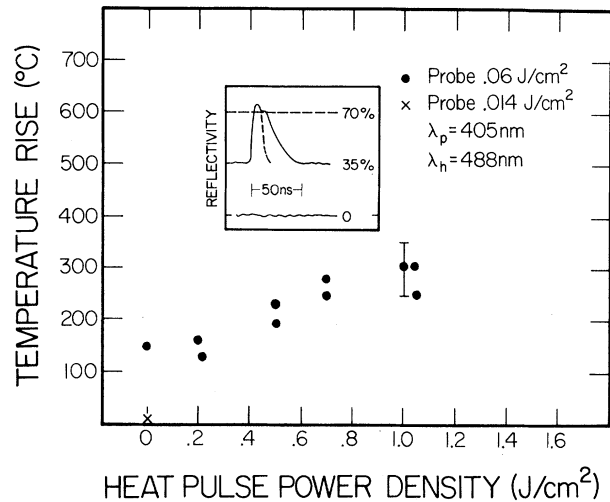


FIG. 1. Temperature rise, inferred from Stokes-anti-Stokes ratios, as a function of heating laser power, with probe delay of 10 nsec. Inset shows reflectivity signal observed with a He-Ne laser for a heat pulse power density of  $1 \text{ J/cm}^2$ . The leading pulse  $\sim 10 \text{ nsec}$  wide is scattered light from the 485-nm heating beam which conveniently serves to time the onset of the reflectivity rise.

The power densities indicated in Fig. 1 represent the power density at the center of the heating beam and were obtained with a  $50\text{-}\mu\text{m}$  pinhole positioned at the center of each focused spot and average power determined by a Scientech disk calorimeter. Pulse-to-pulse amplitude stability at the center  $50 \mu\text{m}$  of each laser spot was checked with a *p-i-n* photodiode and was  $\pm 7\%$  for the probe beam and  $\pm 10\%$  for the heating beam. The larger fluctuation in the heating pulse arise from transverse mode instability. Power fluctuations of the full heating beam were only  $\pm 5\%$ .

The temperature rise shown in Fig. 1 is anomalously low when compared with the energy deposition per unit volume. Van Vechten *et al.*<sup>5</sup> have estimated, from measured heat-capacity data,<sup>15</sup> that the energy per unit volume required to melt crystalline silicon is  $\sim 7 \times 10^3 \text{ J/cm}^3$ . For the highest power data point of Fig. 1, the energy deposition per volume is  $\sim 6 \times 10^3 \text{ J/cm}^3$  averaged over one skin depth,  $1/\alpha = 10^{-4} \text{ cm}$ , and assuming an average reflectivity during the pulse of 40%. Thus, if this energy has been transferred to the lattice within 10 nsec, the lattice temperature should be essentially at the melting point,  $1412^\circ \text{C}$ , provided little energy has diffused into the bulk material. A crude estimate of the importance of thermal diffusion may be obtained

by taking a thermal diffusivity  $D \approx 0.5 \text{ cm}^2/\text{sec}$  intermediate between that of room-temperature silicon and that at the melting point.<sup>16</sup> Thus for the 10-nsec delay  $(D\tau)^{1/2} = 0.5 \times 10^{-4} \text{ cm}$  which is significantly less than the laser absorption length of  $1/\alpha = 1 \times 10^{-4} \text{ cm}$ . Since the lattice temperature is observed to rise insignificantly compared to  $T_m = 1412 \text{ }^\circ\text{C}$ , the energy must (1) still be residing primarily in the electronic system and/or (2) the electronic system has already carried the laser energy over a length much greater than  $1/\alpha$ . The calculations of Yoffa<sup>6</sup> and Van Vechten *et al.*<sup>5</sup> show that if the carriers can retain a large fraction of the absorbed energy for 10 nsec, then carrier diffusion can easily remove much of the energy from the laser-heated regions.

The most direct evidence which has been presented to date to substantiate a melting model for laser annealing is the sudden jump in reflectivity<sup>17</sup> of the silicon surface at power densities of the order of  $0.5 \text{ J/cm}^2$ . The reflectivity typically reaches a value nearly the same as for molten silicon<sup>18</sup> within 5 nsec of the laser peak. However, we observe a similar reflectivity jump under exactly the same conditions as for the Raman data which are plotted at  $\sim 1 \text{ J/cm}^2$ . The reflectivity observed with a He-Ne laser focused to  $\sim 30 \text{ }\mu\text{m}$  at the center of the heating spot is sketched in the inset of Fig. 1. Our Raman measurements under the same conditions show conclusively that lattice melting is not responsible for the reflectivity jump.

The Stokes-anti-Stokes ratios reported here show unequivocally that the lattice temperature rise is far less than necessary to melt the silicon. Yet this small temperature rise ( $300 \text{ }^\circ\text{C}$ ) is observed simultaneously with a reflectivity jump observed with a He-Ne laser. The plausible explanation is that this reflectivity rise is caused by a dense solid-state plasma and is not an indication of lattice melting as previously believed. The observed lattice temperature rise within 10 nsec accounts for only a small fraction of the laser-deposited energy. Hence the bulk of the energy apparently remains in the electronic systems which then has sufficient time to allow ambipolar diffusion<sup>6</sup> to spread the energy over a depth much larger than the laser absorption length.

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