

## Time-Resolved Study of Laser-Induced Disorder of Si Surfaces

H. W. K. Tom, G. D. Aumiller, and C. H. Brito-Cruz

*AT&T Bell Laboratories, Holmdel, New Jersey 07733*

(Received 22 December 1987)

Optical second-harmonic studies show that the electronic structure in the top 75–130 Å of a crystal-line Si surface loses cubic order only 150 fsec after the Si is excited by an intense 100-fsec optical pulse. This suggests that atomic disorder can be induced directly by electronic excitation, before the material becomes vibrationally excited. In contrast, the electronic properties of the equilibrium molten phase are not obtained for several hundreds of femtoseconds.

PACS numbers: 78.47.+p, 61.80.Ba, 64.70.-p, 71.38.+i

With use of ultrashort laser radiation pulses, it is possible to excite the electronic states of a solid before appreciable energy is transferred to the lattice vibrational states. Here, we explore the question posed several years ago by Van Vechten, Tsu, and Saris,<sup>1</sup> whether or not crystalline Si can be driven to disorder by electronic excitation without the lattice modes' equilibrating at a temperature above the melting temperature. This possibility has obvious practical importance in laser-assisted semiconductor processing and surface photochemistry in general. It is of fundamental interest because the dynamics of electron-phonon equilibration may directly effect the evolution of the phase transition. Indeed, a recent picosecond time-resolved study of graphite after pulsed laser excitation reported observation of an intermediate nonequilibrium phase.<sup>2</sup>

The physical picture of how Si might be disordered by nonequilibrium electronic excitation is appealing. Silicon is well described by a tight-binding model, and therefore electronic excitation might directly drive disorder by a process akin to photodissociation in molecules. In a more delocalized picture, the electronic excitation might weaken the interatomic bonding and thus lower the vibrational energy required to produce disorder. However, previous linear reflection<sup>3,4</sup> and second-harmonic generation<sup>5</sup> (SHG) experiments on laser-induced disorder of silicon can be interpreted in the normal picture of cascade electron-phonon relaxation and subsequent lattice melting in  $\approx 1$  psec. Here, we report new time-resolved optical measurements. We find that the SH reflection changes abruptly in a way that is consistent with the top 75–130 Å of the silicon surface's losing cubic symmetry in <150 fsec. Because 150 fsec is less than two electron-phonon relaxation times, the result suggests that the laser induces disorder before the phonons equilibrate above the melting temperature. In addition, the data indicate that the electronic properties of the equilibrium molten phase are not obtained on this short time scale but rather with a >300-fsec time constant. This suggests that considerable vibrational excitation is required to obtain the interatomic distance and/or correlations of the liquid.

The experiments are very similar to those reported in Refs. 4 and 5. Laser pulses of 75 fsec duration (110 fsec FWHM autocorrelation) were obtained by dispersion compensation of the amplified output of a colliding-pulse mode-locked laser operating at 610 nm. To make the excitation relatively uniform over the probe spot, we used a smooth spatially filtered beam profile (central Airy spot) and focused the excitation and probe beam to diameters of 75 and 25  $\mu\text{m}$ , respectively. Our sample was a Si wafer (B-doped, 1800  $\Omega\text{-cm}$ ) with a native oxide and the experiments were conducted in air. The excitation and probe beams were incident at  $-20^\circ$  and  $30^\circ$  to the surface normal, respectively, to avoid scattered SH from the excitation pulse from dominating the much weaker probe SH signals. A different position on the sample was used for each shot of the laser.

In Fig. 1, the top two panels show the *s*- and *p*-polarized SH signals as functions of probe time delay with respect to the excitation pulse. SH was generated in reflection from the surface with the *p*-polarized fundamental probe excitation. The two SH polarizations were separated by a beam-splitting polarizer, and then detected with a pair of photomultiplier tubes and gated electronics. The third panel, Fig. 1(c), shows the sum-frequency signal obtained from mixing of the excitation pulse and probe pulse on the surface. This signal emerged near normal to the surface and was detected with a third photomultiplier tube. It measures the arrival of the pump pulse with respect to the probe and the effect of the noncollinear excitation geometry in increasing the intensity cross-correlation FWHM to 180 fsec. The dashed line is a fit with the autocorrelation of intensity  $I(t) = \text{sech}^2(t/t_p)$ , where  $t_p = 67$  fsec. Figure 1(d) shows the *p*-polarized linear reflection of the probe as a function of probe time delay. All four traces were obtained from the Si(111) surface excited at twice threshold (0.2 J/cm<sup>2</sup> peak intensity) where the after-the-fact melt spot was measured with an optical microscope to be 75  $\mu\text{m}$ .

The sensitivity of SHG to surface structural symmetry has been demonstrated.<sup>6</sup> The technique is based on the fact that the structural symmetry of the media is mani-

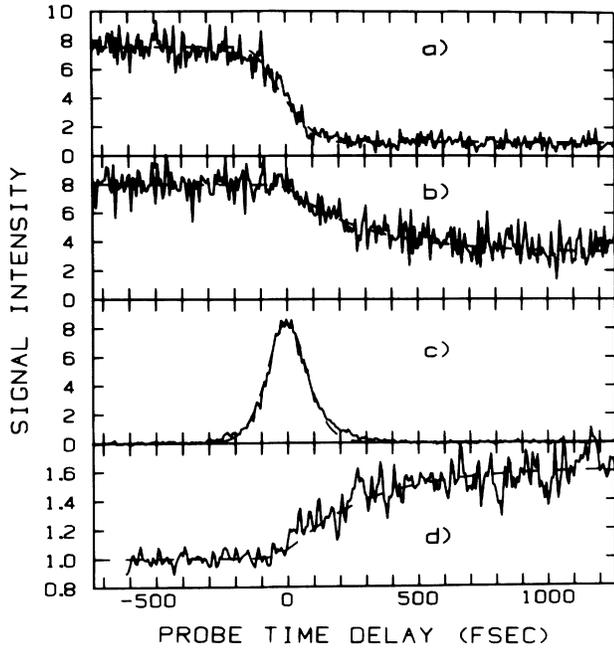


FIG. 1. Signal intensity from Si(111) surface vs probe time delay after a  $2\times$  threshold pump pulse. (a)  $s$ -polarized SH; (b)  $p$ -polarized SH; (c) pump-probe cross correlation; (d)  $p$ -polarized linear reflection. Solid line: data. Dashed line: fits explained in text.

festated in the symmetry of the nonlinear susceptibility tensor and that it is possible through careful choice of polarization and sample orientation to measure certain elements of the tensor that are only nonzero in the presence of certain low symmetries. The symmetry of the surface (top 5–10 Å layer) manifests itself in the nonlinear source polarization of the form

$$\mathbf{P}(2\omega) = \chi : \mathbf{E}(\omega) \mathbf{E}(\omega), \quad (1)$$

where  $\chi$  is a third-rank tensor and  $\mathbf{E}(\omega)$  is the fundamental field vector. For all surfaces there are three independent and nonzero elements of  $\chi$ ,  $\chi_{\perp\perp\perp}$ ,  $\chi_{\parallel\perp\perp}$ , and  $\chi_{\parallel\perp\parallel}$ , where the subscripts denote directions perpendicular and parallel to the surface. For  $3m$  symmetric surfaces there is an additional nonzero element  $\chi_{\xi\xi\xi}$ , where the direction  $\xi$  is along the  $[2\bar{1}\bar{1}]$  axis (in the mirror plane) of the surface.  $\chi_{\xi\xi\xi} = 0$  in the absence of  $3m$  symmetry. The cubic symmetry of the bulk manifests itself in the nonlinear source polarization of the form

$$P_i(2\omega) = \gamma \nabla_i E^2(\omega) + \zeta E_i(\omega) \nabla_i E_i(\omega), \quad (2)$$

where  $\gamma$  and  $\zeta$  are the only nonzero bulk susceptibility tensor elements.<sup>6</sup> The directions  $\hat{i}$  are along the principal  $\langle 100 \rangle$  axes.  $\gamma$  is always nonzero but  $\zeta = 0$  in the absence of cubic symmetry.

The data in Fig. 1 were obtained with the angle between the  $[2\bar{1}\bar{1}]$  axis and the plane of incidence equal to

$90^\circ$ . Using the equations of Ref. 6, one can show that the  $s$ -polarized field  $E_{s,111} \propto \chi_{\xi\xi\xi} + a\zeta$ , where  $a$  is a geometry-dependent constant. While it is not obvious, it can be shown that it is impossible to measure either  $\chi_{\xi\xi\xi}$  or  $\zeta$  separately. However, the combination in  $E_{s,111}$  contains only order-dependent elements and may thus be considered an order-dependent signal. It should go to zero if order is lost. In contrast, the  $p$ -polarized field

$$E_{p,111} \propto (\chi_{\perp\perp\perp} - \gamma) + b(\chi_{\perp\parallel\parallel} - \gamma) + c\chi_{\parallel\perp\parallel} + d\zeta$$

is a combination of order-independent and order-dependent elements and is thus an order-independent signal.

One sees in Figs. 1(a) and 1(b) that the order-dependent SH signal  $|E_{s,111}|^2$  disappears in less than 150 fsec while the order-independent signal  $|E_{p,111}|^2$  decreases in 500 fsec to a lower value. The data in Fig. 1(a) can be fitted with the dashed curve

$$E_{s,111}(t) = A_f + (A_0 - A_f) \exp[(t_0 - t)/t_A],$$

where  $t_0 = 53.3$  fsec and  $t_A = 100$  fsec for  $t > t_0$ .  $E_{s,111}(t)$  has been convolved with the sech<sup>2</sup> time profile of the probe pulse. An abrupt change in  $E_{s,111}(t)$  does not fit the data as well. The action seems to begin well before the excitation pulse is over. We have given  $E_{s,111}(t)$  a constant background  $A_f$  which we attribute to material at the edges of the probe beam that is excited below threshold. We can fit the data of Fig. 1(b) by

$$E_{p,111}(t) = B_f + (B_0 - B_f) \exp(-t/t_B),$$

where  $t_B = 333$  fsec. The ratio between final and initial values is  $B_f/B_0 = 0.633$ . For lower pump intensity, the SH signals change on the same time scales but to different saturation values consistent with the size of the after-the-fact damage spot decreasing. No change is seen in either SH signal for pump intensity at half the melting threshold when the damage spot is only a few micrometers in diameter. These results are consistent with the earlier work by Shank, Yen, and Hirlimann.<sup>5</sup> However, they could not distinguish the fast decrease of the order-dependent signal because they measured linear combinations of the order-dependent and order-independent elements.

To resolve whether or not the ultrafast change in the SH signal comes from changes in the Si-SiO<sub>2</sub> interface (5–10 Å layer) or in the underlying Si bulk, we have repeated the measurements on the Si(100) surface. Quite often the SHG from the surface layer dominates that from the bulk, and SHG has been used successfully to study molecular adsorption and orientation on surfaces.<sup>7</sup> However, for  $4m$ -symmetric surfaces there are no nonzero order-dependent elements of the surface  $\chi$  such as  $\chi_{\xi\xi\xi}$  and it becomes possible to measure the bulk susceptibility  $\zeta$  alone. In Fig. 2 we show the SH signals taken with the angle between the sample  $[100]$  axis and the plane of incidence equal to  $22.5^\circ$ . In this case,

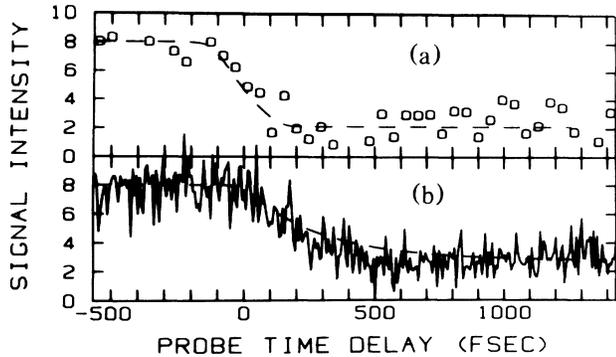


FIG. 2. SH intensity from Si(100) surface vs probe time delay after a  $2\times$  threshold pump pulse. (a)  $s$ -polarized SH; (b)  $p$ -polarized SH. Solid line: data. Dashed line: fits explained in text.

$|E_{s,100}|^2$ , shown in Fig. 2(a), is proportional to  $|\zeta|^2$ . Despite the poor signal-to-noise ratio,<sup>8</sup> it is clear that  $|E_{s,100}|^2$  decreases as rapidly as  $|E_{s,111}|^2$  in Fig. 1(a). The dashed curve is a fit with the same time dependence as that used in Fig. 1(a). Since  $\zeta$  is a bulk susceptibility, these fast changes are due to changes of the electronic properties of *bulk* Si rather than from the Si-SiO<sub>2</sub> interface. Spatially, the "bulk" means the topmost 75 to 130 Å near the surface, depending on the choice of liquid or solid values of the Si linear dielectric constants.

In Fig. 2(b) we show  $|E_{p,100}|^2$  which has the same dependence on the elements of  $\chi$ ,  $\gamma$ , and  $\zeta$  as  $E_{p,111}$  except that the coefficient  $d$  is different. The dashed line is a fit following the same form used to fit Fig. 1(b). It is probable that the order-independent signals  $E_{p,100}$  and  $E_{p,111}$  are also dominated by the bulk electronic properties, e.g., the element  $\gamma$ .

In principle, changes in the SH signals can also be produced by changes in the linear dielectric constants. However, such changes are relatively unimportant in the present case because, even if  $\epsilon(\omega)$  and  $\epsilon(2\omega)$  were to suddenly change from solid values ( $3.88+0.021i$  and  $4.95+3.63i$ ) to liquid values<sup>9</sup> ( $3.86+5.19i$  and  $1.6+3.61i$ ), the SH signals in Figs. 1(a), 1(b), and 2(b) should increase rather than decrease.

The fast decrease of  $\zeta$  implies that the top 75 to 130 Å is disordered in  $< 150$  fsec. Atomic disorder in less than two electron-phonon relaxation times requires that the atoms move out of lattice positions directly because the electronic states have been changed. This rapid configurational relaxation is observed in molecules as the Franck-Condon effect and in defects in solids as Jahn-Teller distortion. It is surprising that long-range atomic order is changed in solids by electronic excitation, however, because the electronic states are more delocalized and have shorter lifetimes. On the other hand, it is quite possible, mechanically, to disorder the atoms on this time scale. The atoms need only acquire a velocity of  $10^5$

cm/sec [ $(\frac{1}{4}$  lattice space)/(100 fsec)], which is comparable to atomic velocities in vibrational modes. In addition, the electronic potential driving the atoms to disorder could be very large. At the laser intensities used, 5% of the valence band is photoexcited if we assume linear absorption,<sup>10</sup> and even more, if nonlinear absorption<sup>11</sup> occurs due to free carrier and two-photon absorption or band-gap narrowing. At 10% promotion from the valence band there is already the equivalent of a charged defect at next-nearest-neighbor sites which could force the atoms to conform to a random configuration. At 40%, the bonding is sufficiently weakened that the lattice is predicted to be unstable to shear stress.<sup>1</sup> At less than 40%, perhaps the lattice is unstable to the small amount of vibrational energy transferred to the lattice in the first 100 fsec. In any case, if the atoms disorder this quickly, they are probably vibrationally cold compared to the equilibrium melt.

The slow decrease in  $\gamma$  shows that once threshold for disorder is exceeded, the highly excited system does not attain equilibrium ( $\gamma = \gamma_{\text{liquid}}$ ) for at least several hundred femtoseconds. This conclusion applies equally well if we model the process as occurring homogeneously in the top 130-Å layer with a 333-fsec time constant or as occurring in a thin expanding layer (as in Ref. 4) but with  $\gamma$  approaching  $\gamma_{\text{liquid}} = 0.633\gamma_{\text{solid}}$  with a 300-fsec time constant. In the latter case, we use a fit (shown as dashed line) to the  $p$ -polarized linear reflection in Fig. 1(d) to set the layer expansion rate at  $v = 2 \times 10^6$  cm/sec. The slow decrease in  $\gamma$  may be due to the disordered Si's being initially a semiconductor rather than a metal. Experiments at wavelengths appropriate to distinguish amorphous from metallic Si might allow the identification of such an intermediate phase if it exists.

We must mention one caveat to the analysis. That is that  $\gamma$  and  $\zeta$  are wavelength-dependent electronic susceptibilities and therefore only measure properties of the atomic structure indirectly. We cannot rule out the possibility that the laser excitation bleaches the valence-conduction band transition or that the high carrier density screens the cubic ionic potential. However, severe bleaching is probably unlikely because there is no large change in the dielectric constants (as evidenced by the linear reflection) nor instantaneous change in the  $p$ -polarized SH. We can argue that screening<sup>12</sup> is also unlikely to cause a complete loss of anisotropic susceptibility since for Si even the carriers in the conduction band see a fairly strong cubic potential as evidenced by the nonspherical band structure.<sup>13</sup> While these arguments are not a proof, there is convincing reason to believe that the rapid reduction in  $\zeta$  is due to atomic disorder in  $< 150$  fsec.

In summary, we have measured the order-dependent and order-independent SH reflection as well as the linear reflection of Si after an intense optical pulse with 100-fsec time resolution. We have found that the order-

dependent SH disappears after only 150 fsec, a time too short for the excited electronic states to heat the lattice to the equilibrium melting temperature. The data are consistent with the lattice's disordering in the first 100 fsec while the lattice remains relatively cold. The optical properties of molten Si are approached in the top 75–130 Å with a 0.3-psec time constant as expected from electron-phonon relaxation rates and previous measurements.

We acknowledge useful discussions with C. V. Shank, R. L. Fork, D. Chemla, Y. R. Shen, and I. Boyd, and the technical assistance of F. Beiser.

---

<sup>1</sup>J. A. Van Vechten, R. Tsu, and F. W. Saris, *Phys. Lett.* **74A**, 422 (1979).

<sup>2</sup>A. M. Malvezzi, N. Bloembergen, C. Y. Huang, *Phys. Rev. Lett.* **57**, 146 (1986).

<sup>3</sup>J. M. Liu, H. Kurz, and N. Bloembergen, *Appl. Phys. Lett.* **41**, 643 (1982); L. A. Lompre, J. M. Liu, H. Kurz, and N. Bloembergen, *Appl. Phys. Lett.* **44**, 3 (1984).

<sup>4</sup>C. V. Shank, R. Yen, and C. Hirlimann, *Phys. Rev. Lett.* **50**, 454 (1983).

<sup>5</sup>C. V. Shank, R. Yen, and C. Hirlimann, *Phys. Rev. Lett.* **51**, 900 (1983).

<sup>6</sup>H. W. K. Tom, T. F. Heinz, and Y. R. Shen, *Phys. Rev. Lett.* **51**, 1983 (1983). The form of Eq. (2) applies for SH excited by a single plane wave.

<sup>7</sup>H. W. K. Tom, C. M. Mate, X. D. Zhu, J. E. Crowell, T. F. Heinz, G. A. Somorjai, and Y. R. Shen, *Phys. Rev. Lett.* **52**, 348 (1984).

<sup>8</sup>From the equations in Ref. 6, one can show that if  $\chi_{\xi\xi\xi} \ll \zeta$ , then  $|E_{s,100}|^2/|E_{s,111}|^2 \approx \frac{1}{30}$ .

<sup>9</sup>G. E. Jellison, Jr., and D. H. Lowndes, *Appl. Phys. Lett.* **47**, 718 (1985); K. M. Shvarev, B. A. Baum, and P. V. Gel'd, *Fiz. Tverd. Tela (Leningrad)* **16**, 3246 (1974) [*Sov. Phys. Solid State* **16**, 2111 (1975)].

<sup>10</sup>M. C. Downer and C. V. Shank, *Phys. Rev. Lett.* **56**, 761 (1986).

<sup>11</sup>T. F. Bogess, Jr., A. L. Smirl, S. C. Moss, I. W. Boyd, and E. W. Van Stryland, *IEEE J. Quantum Electron* **21**, 488 (1985).

<sup>12</sup>H. M. van Driel, *Appl. Phys. Lett.* **44**, 617 (1984).

<sup>13</sup>M. L. Cohen and V. Heine, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24, p. 38.