Femtosecond-Time-Resolved Surface Structural Dynamics of Optically Excited Silicon

C. V. Shank, R. Yen, and C. Hirlimann
Bell Telephone Laboratories, Holmdel, New Jersey 07733

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The dynamics of the structural changes that take place on a silicon surface following excitation with an intense optical pulse are observed with 90-fs time resolution. The threefold rotational symmetry of the silicon ⟨111⟩ surface becomes rotationally isotropic within a picosecond after excitation consistent with a transition from the crystalline to the liquid molten state.

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In one of the first investigations of second-harmonic generation in reflection from media with inversion symmetry, Bloembergen *et al.*[1] proposed that this process could provide structural information. Unlike reflectivity, the process of second-harmonic generation is governed by a tensor quantity that can contain elements of the crystal symmetry. Recently, Guidotti, Driscoll, and Gerritsen[2] have observed the orientational dependence of second-harmonic generation in reflection from Ge and Si. In the work reported here, we use a 90-fs pulse to optically excite a silicon surface and then measure the second-harmonic generation from a weaker probe pulse that is delayed in time, in order to measure the time evolution of the crystalline order following excitation. These experiments provide new structural information which we were unable to obtain in our recently reported[3] measurements of time-resolved reflectivity from highly excited silicon with femtosecond time resolution. Determination of the structural dynamics will assist in elucidating the nature of phase transitions in Si induced by intense optical pulses.[3-7]

Second-harmonic generation from the surface of a medium with inversion symmetry, such as silicon, was first reported by Bloembergen and Chang.[8] In general the nonlinear response of a medium with a center of inversion symmetry requires the consideration of higher-order nonlocal contributions to the susceptibility. For a medium with cubic symmetry we can write the ith component of the nonlinear source polarization as[1,9]

$$P^{\mathrm{NLS}}(2\omega) = (\delta-\beta)[\vec{\mathbf{E}}(\omega)\cdot\nabla]E_i(\omega) + \beta E_i[\nabla\cdot\vec{\mathbf{E}}(\omega)] + (2i\omega/c)\gamma[\vec{\mathbf{E}}(\omega)\times\vec{\mathbf{B}}(\omega)]_i + \xi E_i(\omega)\nabla_i E_i(\omega), \quad (1)$$

where δ, β, γ, and ξ are frequency-dependent constants. The first three terms give rise to an isotropic contribution to the second-harmonic polarization and the last term provides an anisotropic contribution which is determined by the crystal symmetry.

Driscoll and Guidotti[10] have performed extensive measurements of second-harmonic generation as a function of polarization, crystal surface, and angle of rotation of the sample about the surface normal. Their conclusion is that the above description does not describe the generation of second-harmonic radiation from Si but that an optically excited electron-hole plasma alters the local crystal symmetry which gives rise to a dipolar bulk contribution to the nonlinear polarizability. In contrast, Shen and Heinz[11] have found that by varying the angle of incidence, θ, interference occurs between the isotropic and the anisotropic contributions to the generated second-harmonic radiation. By properly including this information they have been able to describe the second-harmonic generation from Si in reflection without induced dipolar contributions to the susceptibility. Both groups agree that second-harmonic radiation is generated in a layer near the surface of the silicon. In our experiment the depth of this layer is 70 Å corresponding to the escape depth of the second-harmonic radiation.

In the experiments described in this communication we direct our attention to the ⟨111⟩ surface of silicon. The projection of the bulk symmetry onto the ⟨111⟩ surface is threefold symmetric. In accord with Shen and Heinz[11] we can describe the second-harmonic radiation from this surface with p-polarized fundamental and second-harmonic radiation by

$$I(2\omega) = KI^2(\omega)[\cos 3\varphi + A(\theta)]^2, \quad (2)$$

where φ is the angle of rotation about the surface normal, K is a constant, and $A(\theta)$ is the isotropic

contribution to the nonlinear polarization which is a function of the angle of incidence, θ. For $A(\theta) = 0$ the generated second-harmonic radiation is sixfold symmetric and for $A(\theta) = 1$ a threefold symmetry is expected. In the experiments to be described here the angle of incidence is 45° and the second-harmonic radiation is observed to have nearly threefold symmetry indicating $A(\theta) \sim 1$.

In our experiments we use a pulse at 620 nm with a duration of 90 fs[12-14] to excite the $\langle 111 \rangle$ surface of a polished silicon wafer and measure the second-harmonic radiation generated by a second much weaker pulse at delayed time. The probing beam sampled the central 10% of the sample area and the probe intensity was at least an order of magnitude weaker than the weakest pump intensity. The pumping pulse was incident normal to the semiconductor surface and was 100 μm in diameter. The sample was mounted on a combination rotation and translation stage. A computer controlled the rotation and translation of the wafer so that each pulse of the laser was incident on a new spot on the silicon wafer. This was absolutely necessary because multiple shots from the laser produce cumulative damage to the surface. The laser was operated at 10 Hz. The probing pulse was incident on the surface at an angle of 45° with the polarization parallel to the plane of incidence. The primary difficulty with this experiment is isolating the second-harmonic radiation from the pumping pulse from the much weaker second-harmonic signal generated by the probing pulse. Since the second-harmonic radiation generated by the probe pulse is collinear with the reflected fundamental radiation it is possible to use spatial filtering to prevent unwanted second-harmonic light from the pump from entering the detection system. This was easily checked by noting that the detected second-harmonic signal from the probing pulse went to zero when the probe pulse was blocked.

As in our previous work[3] we observe the threshold for amorphous surface-layer formation to be at 0.1 J/cm^2 and define this intensity to be E_{th}. As we have discussed, the observed variation of the second-harmonic radiation as function of the angle of rotation φ about the $\langle 111 \rangle$ axis exhibits a nearly threefold rotational symmetry. Maxima and minima in the second-harmonic radiation from the surface are observed every 120°. In Fig. 1 we show the time dependence of the second-harmonic signal generated by the probe pulse as a function of time delay following excitation of the surface by the pumping pulse. In Fig. 2 we have plotted the second-harmonic radiation as a function of angle of rotation of the crystal, φ, in polar coordinates for two different power levels.

The data in Fig. 1(a) show the dependence of the second-harmonic intensity on the time delay, with the pumping pulse at $0.5E_{th}$ energy. The electron density at this pumping level is approximately 10^{21} cm^2. A small 15% increase in the second-harmonic radiation is observed within the first few hundred femtoseconds for $\varphi = 120°$. The polar plot in Fig. 2(a) reveals that the rotational dependence of the second harmonic shows little change. These experiments indicate that even at these high densities bonding electrons still dominate the second-harmonic generation process. The small secondary peak of the second-harmonic radiation at $\varphi = 60°$ disappears shortly after excitation, possibly indicating that the plasma causes a more perfect cancellation between the isotropic and anisotropic contributions to the

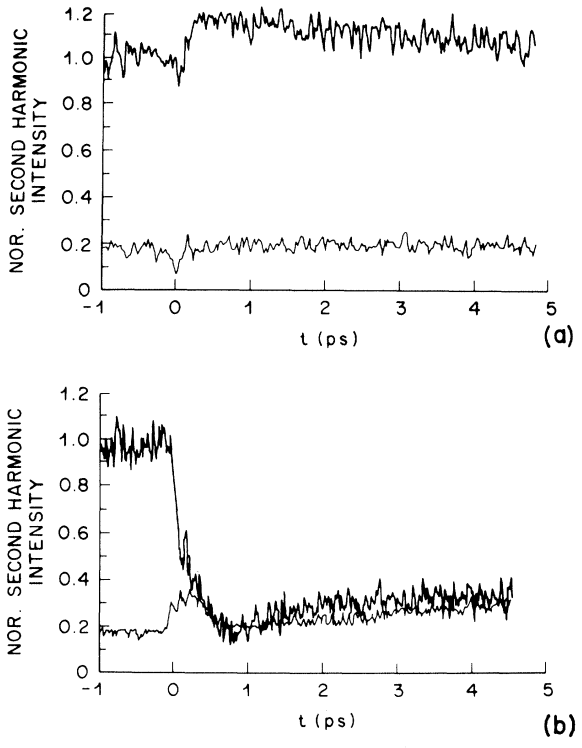

FIG. 1. (a) Normalized second-harmonic intensity as a function of time for $0.5E_{th}$ pump energy. The upper curve is for $\varphi = 120°$ (maximum) and the lower curve is for $\varphi = 60°$ (minimum). (b) Normalized second-harmonic intensity as a function of time for $2.0E_{th}$ pump energy. The upper curve is for $\varphi = 120°$ (maximum) and the lower curve is for $\varphi = 60°$ (minimum).

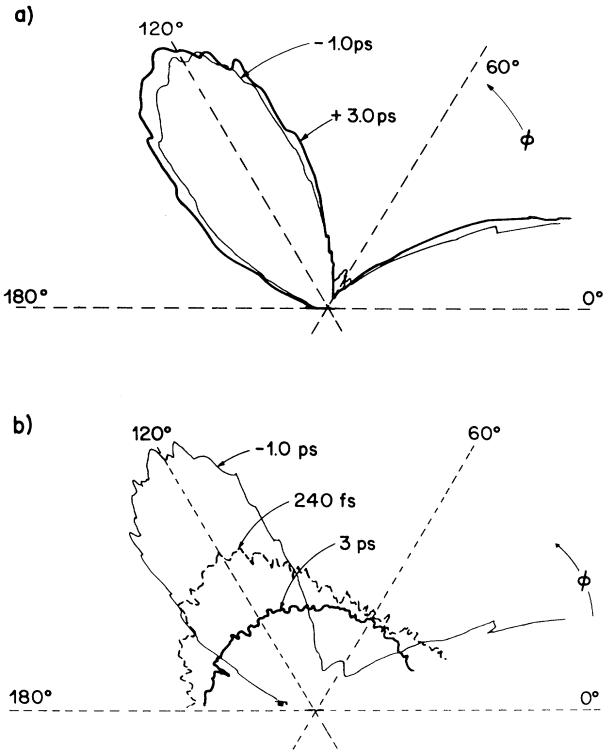

FIG. 2. (a) Polar plot of second-harmonic intensity as a function of time and angle φ for low pump energy, $0.5E_{th}$. (b) Polar plot of second-harmonic intensity as a function of time and angle φ for pump energy $2.0E_{th}$.

second-harmonic tensor.

In Fig. 1(b) the second-harmonic radiation dramatically decreases within the first 150 fs at the maximum ($\varphi = 120°$), and a slight increase in second-harmonic intensity is observed at the minimum ($\varphi = 60°$) lasting for about a half a picosecond. The polar plot reveals a large change in the symmetry of the second-harmonic radiation following excitation. Before $t = 0$ the second-harmonic radiation is clearly anisotropic. After 240 fs have elapsed, the width of the lobe at $\varphi = 120°$ broadens and the minimum becomes less distinct. Apparently the surface is beginning to lose order. Within the first picosecond, the second-harmonic light coming from the surface becomes nearly isotropic. This is precisely what would be expected if the surface order makes a transition from a crystalline structure to a disordered liquid. At a pumping level of $3.0E_{th}$ a similar process takes place but somewhat more rapidly.

In conclusion, we have been able to observe the transition from crystalline order on the $\langle 111 \rangle$ surface to disorder consistent with melting of the surface on a time scale of less than a picosecond using femtosecond pulse excitation. The large decrease in the second-harmonic intensity is probably due to the loss of resonant enhancement of the second-harmonic radiation following melting. For the crystalline material the second-harmonic energy, 4.0 eV, is very close to the sharp peak in the absorption coefficient for silicon. These results for the first time clearly demonstrate the utility of nonlinear optical processes to time resolve structural changes at a semiconductor surface.

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