# Study of Si(111) Surfaces by Optical Second-Harmonic Generation: Reconstruction and Surface Phase Transformation

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Optical second-harmonic generation has been applied to the study of clean Si(111) $2\times 1$ and $7\times 7$ surfaces. By an analysis of polarization dependences of the two reconstructions, the symmetry properties of the surfaces have been determined. The $2\times 1$ to $7\times 7$ surface phase transformation during thermal annealing has also been monitored in real time by the second-harmonic technique.

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Optical second-harmonic generation (SHG) is electric dipole forbidden within the bulk of centrosymmetric media. Consequently, in such materials the SH signal is very strongly affected by the surface layer where the lowered symmetry makes the SHG process allowed. The SHG technique has recently attracted considerable attention because as an optical probe with intrinsic surface sensitivity it is useful at interfaces between two dense media where the conventional tools of surface science are not generally applicable. This laser-based method also holds the promise for measurement of surface dynamics down to the femtosecond time scale. SHG has already been used to probe a variety of properties of adsorbed monolayers,[1] but the technique has not yet been applied to the important problem of clean, well-defined crystalline surfaces. In this Letter, we report the results of such a study for the case of the Si(111) surface,[2] both in its metastable $2\times 1$ reconstruction and in its equilibrium $7\times 7$ reconstruction.

For each of the reconstructed Si(111) surfaces, we have measured distinctive polarization dependences and have explained these patterns in terms of the symmetry properties of the surface.[3] Our results indicate that the $7\times 7$ surface has the full $3m$ symmetry of the terminated bulk structure, while the $2\times 1$ surface has only a single mirror plane. The existence of this mirror plane, for the $2\times 1$ reconstruction, is consistent, with the currently favored $\pi$-bonded chain model of the surface, in either its ideal[4] or buckled[5] form, but does not appear to be compatible with the dimerized chain[6] or $\pi$-bonded molecule structures.[7] This finding confirms and strengthens a conclusion of linear optical measurements.[8] Using the fact that the SHG is forbidden for a certain arrangement of input and output polarizations in the presence of a mirror plane, we have established the existence of the mirror planes in both reconstructed surfaces to a higher degree of accuracy than in previous measurements with other techniques. We have also performed what we believe is the first time-resolved measurement of the surface phase transformation from the $2\times 1$ to the $7\times 7$ reconstruction. During thermal annealing the additional mirror planes of the $7\times 7$ structure were seen to appear on a time scale of seconds at a temperature of $\sim 275\,°C$.

Our experiments were carried out in an ion-pumped ultrahigh vacuum chamber at a base pressure of $\sim 5\times 10^{-11}$ Torr. The Si(111) surfaces were formed by *in situ* cleaving of a bar of hyperpure silicon (Wacker) doped with $10^{15}$ $cm^{-3}$ of boron. These surfaces were examined by LEED and only those samples exhibiting a sharp pattern with a single domain of $2\times 1$ reconstruction oriented along the $[2\bar{1}\bar{1}]$ cleavage direction were retained. By heating the cleaved samples to $\sim 600\,°C$, we obtained well-defined $7\times 7$ surfaces. For the SHG measurements, we used laser excitation at 1.06 $\mu$m from a *Q*-switched Nd:YAlG (neodymium-doped yttrium aluminium garnet) laser producing 8 ns pulses at a 10-Hz repetition rate. A pump energy of $\sim 10$ mJ pulse in a 1-mm-diam spot was found to be sufficiently low to avoid any laser-induced changes in the surface morphology while still generating $\gtrsim 10^3$ photons per pulse in the reflected SH beam. The symmetry properties of the Si surfaces were probed by measuring the intensity of the reflected SH beam as the polarization of the normally incident pump beam was varied. Experimental data for the $2\times 1$ and $7\times 7$ reconstructions are displayed in Figs. 1(a) and 1(b), respectively. The top panels show the total SH intensity, while in the lower panels the SH radiation is resolved into orthogonal components along the $[2\bar{1}\bar{1}]$ and $[01\bar{1}]$ directions. Before discussing these results in detail, we remark that the observed SH signals do in fact arise from the surface layer of the sample. By oxidizing and disordering the Si surfaces, we have verified that the observed SH radiation does indeed arise almost entirely from the surface layer of the sample and that the higher-order magnetic dipole and electric quadrupole terms in the bulk[3,9] are not significant for the chosen pump wavelength.

In order to interpret the experimental data of Fig. 1, we introduce the surface nonlinear susceptibility $\chi_s^{(2)}$ describing the relation between the pump electric field and the nonlinear polarization $\mathbf{P}_s^{NLS}$ induced in the surface layer. A quantum-mechanical expression for $\chi_s^{(2)}$ involving matrix elements with occupied states and two unoccupied intermediate states can be derived from second-order perturbation theory. For our

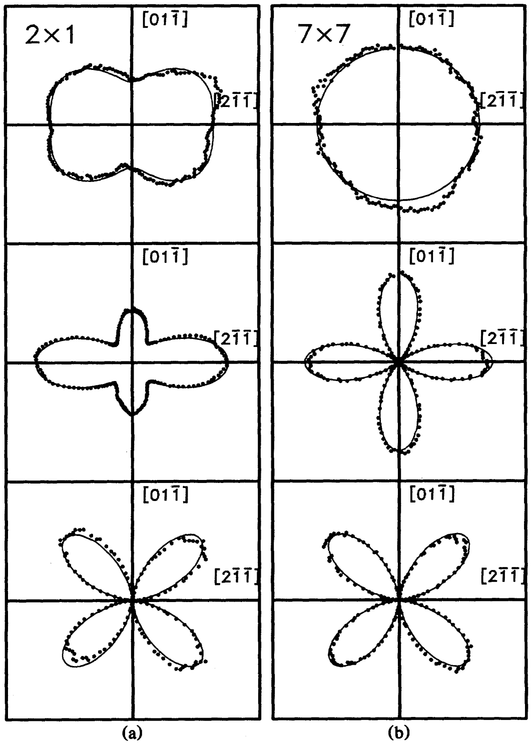


FIG. 1. SH intensity from (a) Si(111) 2×1 and (b) Si(111) 7×7 surfaces as a function of the polarization of the normally incident pump beam. The top panels display the total SH signal; the middle and lower panels show, respectively, the SH signal polarized along the [2$\bar{1}\bar{1}$] and [01$\bar{1}$] directions. The dotted curves represent the experimental data, while the solid curves show the result of the symmetry analysis discussed in the text.

present purposes, let us note that this third-rank tensor will reflect the symmetry of the surface through the symmetry properties of the surface electronic states. In terms of $\chi_s^{(2)}$, we can express the intensity of the coherently generated SH radiation as $I_{2\omega} = A\,|\hat{\mathbf{e}}_{2\omega}\cdot(\chi_s^{(2)}\cdot\hat{\mathbf{e}}_\omega)\cdot\hat{\mathbf{e}}_\omega|^2$, where $\hat{\mathbf{e}}_\omega$ and $\hat{\mathbf{e}}_{2\omega}$ are polarization vectors for the beams at the fundamental and harmonic frequencies and $A$ is a (frequency-dependent) constant determined by a full solution of the Maxwell equations. From this equation, we can predict the form of the SH polarization dependence for a given surface symmetry.[10] If we assume that the 2×1 reconstruction has a single mirror plane passing through the [2$\bar{1}\bar{1}$] direction and that the 7×7 reconstruction has the full $3m$ symmetry of the bulk crystal, we find that the nonzero components of $\chi_s^{(2)}$ relevant for our measurements are $(\chi_s^{(2)})_{xxx}$, $(\chi_s^{(2)})_{xyy}$, and $(\chi_s^{(2)})_{yxy} = (\chi_s^{(2)})_{yyx}$, where $x$ and $y$ denote, respectively, the [2$\bar{1}\bar{1}$] and the [01$\bar{1}$] directions in the surface plane. For the 2×1 reconstruction, all three of these tensor elements are independent; under the higher symmetry of the 7×7 reconstruction, $(\chi_s^{(2)})_{xxx} = -(\chi_s^{(2)})_{xyy} = -(\chi_s^{(2)})_{yxy}$. The variation of the SH intensity polarized along the $y$ direction then takes on the same form for both of the surface reconstructions:

$$I_y = A\,|(\chi_s^{(2)})_{yxy}|^2 \sin^2 2\theta, \qquad (1)$$

with angle $\theta$ of the pump polarization measured with respect to the $x$ direction. For the orthogonally polarized component of the SH signal, we obtain

$$I_x = A\{|(\chi_s^{(2)})_{xxx}|^2\cos^4\theta + |(\chi_s^{(2)})_{xyy}|^2\sin^4\theta + \tfrac{1}{2}\mathrm{Re}[(\chi_s^{(2)})^*_{xxx}(\chi_s^{(2)})_{xyy}]\sin^2 2\theta\},$$

which for the 7×7 reconstruction simplifies to $I_x = A\,|(\chi_s^{(2)})_{yxy}|^2\cos^2 2\theta$. The total SH intensity, obtained by summing the orthogonal polarization components, will in general exhibit an angular dependence for the 2×1, but not for the 7×7 reconstruction.

With the assumed symmetries, the forms derived above agree well with the experimental results. Least-squares fits of the theory to the data are indicated by the solid lines in Fig. 1. The magnitude of the tensor elements of the surface nonlinear susceptibility for the 2×1 reconstruction are found to be

$$|(\chi_s^{(2)})_{xxx}|^2 = 1.10, \quad |(\chi_s^{(2)})_{xyy}|^2 = 0.62,$$
$$|(\chi_s^{(2)})_{yxy}|^2 = 0.58,$$

where these values are referred to $|(\chi_s^{(2)})_{xxx}|^2 = |(\chi_s^{(2)})_{xyy}|^2 = |(\chi_s^{(2)})_{yxy}|^2 = 1$ for the 7×7 reconstruction.[11]

The data of Fig. 1 imply the existence of one mirror plane for the 2×1-reconstructed surface and three mirror planes for the 7×7 surface. We have verified the presence of these mirror planes in a more direct and accurate manner by measuring the nonlinear susceptibility component for polarizations of both the fundamental and harmonic beams perpendicular to the plane in question. If the surface does indeed exhibit mirror symmetry with respect to this plane, the associated nonlinear susceptibility should vanish. We find no departure from this prediction within our experimental accuracy. For the 2×1 surface, we have established an upper bound on the symmetry-forbidden tensor element of $|(\chi_s^{(2)})_{yyy}/(\chi_s^{(2)})_{yxy}|^2 < 3\times10^{-3}$. The same ratio also applies for all three mirror planes of the 7×7 reconstruction. We conclude that no significant breaking of these reflection symmetries exists for the reconstructed surfaces, at least as far as the surface electronic structure is concerned. While the null result has been obtained only for a particular wavelength excitation, it is an unambiguous sign of the mirror symmetry since the SHG process, in contrast to the linear absorption, includes contributions from both resonant and off-resonant transitions.

We now consider the implications of our measurements for the structure of the Si(111) surfaces. First, the high efficiency of the surface SHG from the clean Si(111) 2×1 and 7×7 surfaces can be understood as a consequence of rebonding of the surface atoms to produce neighboring dangling bonds. This behavior would be expected to increase the oscillator strengths of the surface-state transitions in resonance or near-resonance with the 1.17-eV pump or the 2.34-eV SH photons. For the 2×1 reconstruction, various models have been proposed in which a rearrangement of the surface atoms occurs. The original $\pi$-bonded chain model of Pandey[4] and the buckled form of this model[5] are consistent with all of our observations, including the existence of a mirror plane. The $\pi$-bonded molecular model proposed by Chadi,[7] however, violates the observed mirror-plane symmetry.[12] A dimerization of the $\pi$-bonded chain[6] would also be incompatible with the presence of a mirror plane.[12] Within the context of the $\pi$-bonded chain model, the predominance of the *xxx* component of $\chi_s^{(2)}$ is reasonable in view of the high joint density of states for transitions polarized along the *x* direction at energies in the 1–2-eV range.[13]

We shall not attempt to discuss here the diverse models proposed for the 7×7 reconstruction in light of the 3*m* symmetry of the surface seen in our measurements. Let us just remark that our observation agrees with the threefold symmetry indicated by scanning tunneling microscopy[14] and LEED.[15] These latter techniques are more sensitive to the atomic positions than to the electronic structure of the surface and show an approximate sixfold symmetry for the topmost layer of atoms. This symmetry is clearly lacking in the electronic structure since the SHG process would then be forbidden at normal incidence.[10] Note that linear optical measurements, described by a lower-rank tensor than the nonlinear process, will not be capable of distinguishing between threefold and sixfold symmetry.

We have utilized the sensitivity of the SHG process to the existence of mirror planes to monitor the surface phase transformation from the 2×1 to the 7×7 reconstruction in real time. By adjusting the input and output polarizations to a position 120° from the $[01\bar{1}]$ axis, we observed a strong SH signal from the 2×1 reconstruction, but no signal from the 7×7 reconstruction which with its higher symmetry exhibits a mirror plane perpendicular to this direction of polarization of the light. The results in Fig. 2 trace the creation of the additional mirror plane during a heating cycle. These data, constituting the only real-time measurement of the surface phase transformation known to us, indicate that the conversion from the metastable 2×1 reconstruction to the equilibrium 7×7 reconstruction occurs in a few tens of seconds at a temperature of ~275°C. As in previous studies in which the surface was examined after a prescribed heating cycle,[16] we noticed a correlation between high transition temperatures and high surface step density. We attribute the small SH signal persisting to relatively high temperature to the presence of regions of the surface with high local step density. In none of the measurements of the SH signal did we find any evidence of the existence of intermediate phases between the 2×1 and 7×7 structures.

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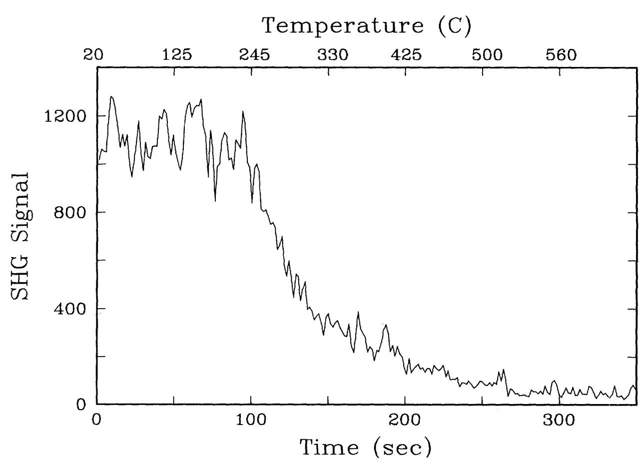


FIG. 2. SH signal monitoring the establishment of a mirror plane during the 2×1 to 7×7 surface phase transformation. The horizontal axis is calibrated both in elapsed time (below) and in sample temperature (above).

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[10]Details of the analysis presented here will be published elsewhere.

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faces, we found some variation in the numerical values for the components of $\chi_s^{(2)}$. We attribute this effect to the influence of steps on the surface.

[12]The SH signal is produced by an average nonzero polarization over a macroscopic distance. Thus the presence of many microscopic domains on the surface each indivdually lacking a mirror plane could still be consistent with our measurements provided a certain asymmetric structure and its mirror image occur with equal weight.

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