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Vicinal Si(111) surfaces studied by optical second-harmonic generation: Step-induced anisotropy and surface-bulk discrimination

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By modifying a Si(111) surface through the introduction of a variable number of steps, the anisotropic surface and bulk contributions to the optical second-harmonic generation could be determined separately and were found to be of the same order of magnitude for a Si-SiO₂ interface. This approach is based on the lowering of the surface symmetry by the steps and by the apparent enhancement of the nonlinear susceptibility at the step edges.

The importance of interfaces for material science and electronic devices has stimulated great interest in the development of surface analytical tools. Optical laser techniques have attracted much attention recently because of their high temporal, spatial, and spectral resolution and because of the fact that they are applicable to all interfaces accessible by light. Optical second-harmonic generation (SHG) has particularly been noticed as a versatile and sensitive interface probe for clean surfaces as well as buried interfaces and for atomic and molecular adsorbates on all kinds of different interfaces.^{1,2} The fact that SHG is described by a third-rank tensor $\chi_S^{(2)}$ makes it very suitable for the study of the symmetry of interfaces and therefore also for the study of changes in these symmetries as occur at phase transitions.^{3,4} However, though SHG derives its surface sensitivity from the dipole-allowed surface term to the SHG, that is forbidden in the bulk of centrosymmetric media, higher-order (quadrupole) bulk terms are allowed and show up as effective surface contributions. Experimentally these two contributions cannot be separated in a single experiment.⁵ This is a problem of fundamental importance if one wants to employ SHG to study intrinsic surface effects like surface phase transitions, for example. Also, for a wider application of SHG to probe microscopic interface properties, a better understanding of the different sources of the nonlinear polarizability is essential. In order to discriminate between bulk and surface SHG some authors have used the application of electric fields to the surface (in an electrolytic solution)⁶ or compared signal intensities and phases from different crystalline faces.^{5,7} We propose a way to separate bulk and surface contributions by modifying the surface by a well-defined step structure. Results on oxidized Si wafers show this to be a successful scheme.

Our samples were optically flat standard silicon wafers, Syton etched and polished, and cut with a small offset angle in the [11 $\bar{2}$] direction. It is well known that such a vicinal Si surface exhibits a regular step structure, with steps that are multiples of the double-layer spacing of 3.14 Å for Si(111).⁸ In air the sample is oxidized, and the interface will have a region where the stoichiometry changes from pure Si to pure SiO₂.⁹ However, the interface between Si and this amorphous silica overlayer is sharp within an atomic dimension, as shown by high-resolution transmission electron microscopy (TEM) pictures^{10,11} and

photoemission experiments.¹² The interface sharpness and reproducibility of such Syton-etched Si wafers is also seen in various SHG experiments: despite the different sample sources, very similar SHG responses from such samples have been observed.^{3,7,13,14} This suggests that the etching process leaves only a narrow disordered Si layer that is totally consumed by the oxidation process, producing a Si-SiO₂ interface showing the bulk Si symmetry.¹⁵ Consequently, for the oxidized vicinal surface, the Si-SiO₂ interface is also expected to exhibit a regular and sharp step structure. The contribution to the SHG of the air-silica interface and the bulk silica layer is negligible,^{5,7} because of their low nonlinearity,¹⁶ as has also been checked experimentally.

For the SHG experiment we used the frequency-doubled output at 532 nm of a seeded Q-switched neodymium-doped yttrium aluminum garnet (Nd-YAG) laser. The laser beam was incident at an angle of 45° on the sample, which was mounted on a rotation stage. The fluence of the 8-ns pulses was limited to ~50 mJ/cm², well below the damage threshold, and stable within 2%. The reflected SHG intensity was recorded while the samples were rotated about their normal at a constant rate. Three samples were studied, one precisely cut perpendicularly to the [111] direction, and two samples cut with small offset angles of 3° and 5°, respectively, towards the [11 $\bar{2}$] direction to get a regular step structure with two different step concentrations. The orientation of the samples was identified with x-ray pictures. The rotation angle ψ was defined as the angle between the plane of incidence and $\hat{\xi}$, the projection of the crystallographic [100] axis on the surface. Figure 1 displays the SH anisotropy of these samples, observed by rotating the sample about its normal while detecting the reflected s-polarized SHG signal under s-polarized excitation. The results show a very strong effect of the offset angle on the observed anisotropy: for the vicinal surfaces the threefold (111) symmetry is clearly broken. A more detailed analysis of the experimental results (see below) shows the interference of a step-induced C_{1v} symmetry with the underlying C_{3v} symmetry of the Si(111).

The dipole-allowed surface contribution to the induced nonlinear polarization $\mathbf{P}(2\omega)$ can be written as

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

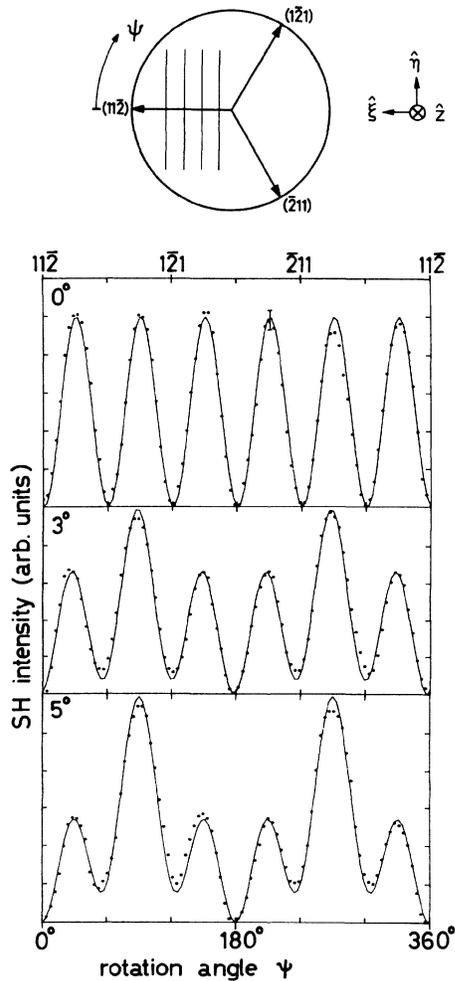


FIG. 1. s -polarized SHG intensity from Si(111) surfaces for s -polarized excitation as a function of the sample rotation angle ψ . The top trace (0°) shows the perfect C_{3v} symmetry, while the results for the two vicinal surfaces (offset angles 3° and 5°) show the interference of C_{3v} and C_{1v} symmetry. The circles are the experimental points, and the solid lines a fit to Eqs. (4) and (5). On top, a sketch of the sample geometry is given, indicating the directions of the mirror planes and the steps.

where $\overline{\chi}_S^{(2)}$ is a third-rank tensor and $\mathbf{E}(\omega)$ the incident laser field. The symmetry of $\overline{\chi}_S^{(2)}$ reflects the symmetry properties of the surface layer. For the highest symmetry, i.e., an isotropic surface, $\overline{\chi}_S^{(2)}$ has only three independent nonzero elements: $\chi_{\perp\perp\perp}$, $\chi_{\perp\parallel\parallel}$, and $\chi_{\parallel\perp\parallel} = \chi_{\parallel\parallel\perp}$, where \perp and \parallel denote directions perpendicular and parallel to the surface respectively. The top two or three layers of a Si(111) surface, responsible for the surface SHG, exhibit C_{3v} symmetry. This leads to one additional, and anisotropic, nonzero component $\chi_{\xi\xi\xi} = -\chi_{\xi\eta\eta} = -\chi_{\eta\xi\eta} = -\chi_{\eta\eta\xi}$, originating from the nonlinear response of the highly directional bonds in silicon. Here the $\hat{\eta}$ axis is 90° from $\hat{\xi}$ in the surface plane. The i th component of the lowest-order bulk contribution to the nonlinear polarization can be expressed as

$$P_{B,i}(2\omega) = \gamma \nabla_i E^2(\omega) + \zeta E_i(\omega) \nabla_i E_i(\omega), \quad (2)$$

where γ and ζ are the only nonzero bulk terms and the \hat{i} directions are along the principal crystallographic axes. The first term gives rise to an isotropic contribution and the second term provides an anisotropic contribution that depends on the crystal symmetry. The total effective nonlinear polarization is then given by

$$\mathbf{P}_{\text{eff}}(2\omega) = \mathbf{P}_S(2\omega) + \frac{i\mathbf{P}_B(2\omega)}{2k_z(\omega) + k_z(2\omega)}, \quad (3)$$

where the wave vectors are defined in the medium (Si). From this polarization, the generated SHG fields can be calculated. We will concentrate on the s -polarized SHG response for an s -polarized pump beam, because that signal only contains anisotropic terms and will be most sensitive for the surface symmetry. For a crystalline surface of C_{3v} symmetry, excited by a single s -polarized plane wave at frequency ω , the s -polarized SHG field can then be written as^{7,14}

$$E_{s,s}(2\omega) \sim [\chi_{\xi\xi\xi} - a\zeta] \sin(3\psi), \quad (4)$$

where ψ is the angle between $\hat{\xi}$ and the plane of incidence and a is a complex number containing the Fresnel coefficients. For our geometry $a = 0.062e^{-i36^\circ}$. In Eq. (4) we observe the simultaneous appearance of bulk and surface anisotropic terms, which therefore cannot be separated in a single measurement.

Equation (4) indicates that the s -polarized SHG intensity will be proportional to $\sin^2(3\psi)$ and thus show six equally spaced maxima and minima, which is in perfect agreement with the top trace of Fig. 1. The other two traces for the two vicinal surfaces with offset angles of 3° and 5° clearly deviate from this picture. From the original three mirror planes along the $[11\bar{2}]$, $[1\bar{2}1]$, and $[\bar{2}11]$ directions, the experimental results show that only the first one is preserved. This is in perfect agreement with what one would expect for these vicinal surfaces, cut with an offset angle towards the $[11\bar{2}]$ direction: as the steps will be perpendicular to $[11\bar{2}]$, the $[11\bar{2}]-\hat{z}$ (or $\hat{\xi}-\hat{z}$) plane will be the only real mirror-symmetry plane present (see also sketch on top of Fig. 1). For a C_{1v} symmetry, with $\hat{\xi}-\hat{z}$ being the mirror plane, the s -polarized SHG signal under s -polarized excitation in principle contains three independent nonzero susceptibility tensor elements: $\chi_{\xi\xi\xi}$, $\chi_{\eta\xi\eta} = \chi_{\eta\eta\xi}$, and $\chi_{\xi\eta\eta}$ (for the C_{3v} symmetry $\chi_{\eta\xi\eta} = \chi_{\eta\eta\xi} = \chi_{\xi\eta\eta} = -\chi_{\xi\xi\xi}$). The induced macroscopic nonlinear polarization in Eq. (1) results from a summation over the beam area of the microscopic nonlinear response of the medium to the local electric field and in that way reflects the local symmetry. Cutting a Si(111) surface with a small offset in the $[11\bar{2}]$ direction leads to one broken bond per atom at the step edge.¹⁷ At the Si-SiO₂ interface this bond is of course oxidized. Because of this broken bond the C_{3v} symmetry of the surface is reduced to C_{1v} at the step edges, with the only mirror plane along the broken bond, normal to the steps. Ascribing the step SHG response to the Si-O bonds is not in contradiction with the negligible response of the silica overlayer. In silica the orientation of the Si-O bonds is isotropic, whereas at the steps there is a net orientation normal to the steps, leading to an anisotropic contribution to the SHG. Because of this net orientation, the nonlinear response along

the $\hat{\xi}$ axis is expected to dominate the SHG response of the steps. Under this assumption, $\chi_{\xi\eta\eta}^{\text{step}}$, $\chi_{\eta\xi\eta}^{\text{step}}$, and $\chi_{\eta\eta\xi}^{\text{step}}$ will be small compared with $\chi_{\xi\xi\xi}^{\text{step}}$, and we will neglect them. The total SHG response of the vicinal surface will then be a sum of the step contributions, showing C_{1v} symmetry leading to a term $\chi_{\xi\xi\xi}^{\text{step}} \sin^3(\psi)$, and the terrace and bulk contributions, showing C_{3v} symmetry according to Eq. (4). Since the steps leave the bulk unchanged, the s -polarized SHG response of the vicinal surface for an s -polarized pump beam can now be written as

$$E_{s,s} \sim [(1-x)\chi_{\xi\xi\xi} - a\zeta] \sin(3\psi) + x\chi_{\xi\xi\xi}^{\text{step}} \sin^3(\psi), \quad (5)$$

where $\chi_{\xi\xi\xi}^{\text{step}}$ is the step component and x denotes the fraction of steps relative to the terraces, which depends on the offset angle θ . For perfectly sharp step edges x can be estimated to be the ratio of an atomic dimension to the size of the terrace. For $\theta=3^\circ$ and 5° we determined x to be 0.026 and 0.048, respectively. Using Eq. (5) the experimental data can now be fitted by $E_{s,s} = A \sin(3\psi) + B e^{i\Phi} \sin^3(\psi)$, where Φ denotes the phase difference between the step and terrace contributions. By Fourier decomposing the data it was further checked that no other symmetry components were present. Because we can determine A/B for the two different values of the step concentration x , we can now find values for $\chi_{\xi\xi\xi}^{\text{step}}$ and $a\zeta$ relative to the surface component $\chi_{\xi\xi\xi}$. The results are $\chi_{\xi\xi\xi}^{\text{step}} = -7.0e^{i100^\circ} \chi_{\xi\xi\xi}$ and $a\zeta = 1.0e^{-i22^\circ} \chi_{\xi\xi\xi}$. This last result is in reasonable agreement with the result of Tom *et al.*, who found $a\zeta = 0.28e^{-i22^\circ} \chi_{\xi\xi\xi}$ by comparing SHG signals from (111) and (100) surfaces.⁵ Note that in our way, though we need different samples with different x values, the results totally depend on the relative values we find for A and B for each sample independently (so we do not need to compare intensities from different samples). The possible and even likely presence of some randomly distributed steps on the 0° sample will only affect the absolute SHG intensity from the surface and will therefore have no effect on our results and conclusions.

Of course, our results do depend on the values of the parameter x , which is determined by the offset angle θ . Though θ can be measured very accurately from x-ray pictures, the values for x depend on the sharpness of the interface, or more precisely on the extension of the surface electronic states. However, a doubling of the values for x leads to $\chi_{\xi\xi\xi}^{\text{step}} = -7.0e^{i100^\circ} \chi_{\xi\xi\xi}$ and $a\zeta = 1.1e^{-i43^\circ} \chi_{\xi\xi\xi}$, i.e., the results are not extremely sensitive for the values of x . Here, it should be noted that the observed changes in the SHG anisotropy of the vicinal surfaces cannot be explained by the fact that the reflected light obeys Snell's

law with respect to the macroscopic surface, which has an offset from the (111) plane. Both the change in Fresnel coefficients for reflection from the (111) plane and the effect of the changed orientation of the crystalline bonds with respect to the incoming electric fields can be calculated and are very small for the offset angles we used.

Our results show that SHG is indeed very sensitive to the microscopic structure and symmetry properties of surfaces. The presence of steps on vicinal Si(111) surfaces leads to a very strong effect on the observed rotational anisotropy of the SHG signal, that is consistent with a very regular step structure exhibiting C_{1v} symmetry. This step structure must extend and be regular over large distances, as our optical probing beam had an area of about 0.5 cm^2 . The fact that such a small percentage of steps has such a measurable effect is due to the fact that $\chi_{\xi\xi\xi}^{\text{step}}$ appears to be an order of magnitude larger than $\chi_{\xi\xi\xi}$ for the normal Si(111) surface. This large signal can be understood by the very anisotropic environment of the atoms at the step edges. This enhancement could also be partly due to the presence of surface states localized on these steps, if they are in near resonance with the 2.34-eV pump or the 4.7-eV SHG photons. The tendency of surface states to localize on these steps has been observed on vicinal metal surfaces.¹⁸ To examine this problem, one should do spectroscopic measurements, by scanning the pump wavelength while observing the SHG response. This and experiments on clean vicinal Si(111) surfaces are presently in progress.

In conclusion, the presence of a regular step structure on vicinal Si(111) surfaces leads to a very pronounced effect on the rotational anisotropy of the SHG from these surfaces. By varying the offset angle, we could vary the step concentration and in this way the surface properties of Si(111) could be modified without affecting the bulk and without introducing any additional effects. In this way we could determine the relative surface and bulk contributions to the SHG signal in a straightforward way. The observed anisotropic contribution from the steps appears to be strongly enhanced relative to the normal surface nonlinear susceptibility. The very high sensitivity of SHG to the presence and symmetry properties of steps indicates that SHG should be a very useful probe to study these technologically very important vicinal semiconductor surfaces.

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