Second-Harmonic Reflection from Silicon Surfaces and Its Relation to Structural Symmetry

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Second-harmonic reflection from Si(100) and Si(111) surfaces exhibits a strong dependence on the angle of rotation of the sample about its surface normal. This behavior can be related directly to the structural symmetry of the crystal and of the surface. Analysis of the results shows that the surface and bulk contributions to the observed second-harmonic signals from Si are generally of the same order of magnitude.

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Recently the process of optical second-harmonic generation (SHG) has been exploited to study the spectroscopy and orientation of molecular monolayers adsorbed at interfaces between two centrosymmetric media.[1] The simple case of a bare surface of a crystalline medium is clearly also of interest. While the early work of Bloembergen *et al.*[2] indicated that the SH reflection from crystalline silicon was independent of the cut and orientation of the face, current investigations[3,4] show that this is not so. Here we report results for SHG from different silicon faces as a function of the crystal orientation. The observed variation in the SH intensity as the sample is rotated about its surface normal is governed by the symmetry of the crystal and of its surface. A theory incorporating the response of the surface layer by a sheet of polarization and of the bulk by magnetic-dipole and electric-quadrupole terms is presented and is shown to be capable of accurately reproducing the experimental data. By comparing the behavior for (100) and (111) faces of silicon, we are also able to determine directly the relative importance of the surface and of the (electric-dipole–forbidden) bulk contributions to the SHG.

Away from the surface of a centrosymmetric medium, there can be no electric-dipole (local) contribution to the SHG process. Then for a material such as silicon with $\bar{4}3m$ symmetry, the dominant nonlocal contribution to the nonlinear polarization at the SH frequency induced by an electric field $\vec{E}$ at the fundamental can be cast in the general form

$$P_i^{NB} = \beta E_i(\nabla\cdot\vec{E}) + (\delta-\beta-2\gamma)(\vec{E}\cdot\nabla)E_i + \gamma\nabla_i\vec{E}^2 + \zeta E_i\nabla_i E_i. \quad (1)$$

This expression has been written with respect to the principal axes of the crystal, and β, γ, δ, and ζ are constants describing the material's nonlinear response. The first three terms are present in isotropic media,[2] while the last term is anisotropic. For excitation of a homogeneous medium by a single plane wave, note that only the last two terms are nonvanishing.

In the surface region, the inversion symmetry of the bulk is broken and we expect a large contribution to the nonlinear polarization. We represent this term by a sheet of nonlinear polarization $\vec{P}^{NS}$ located just inside the medium. This layer of nonlinear polarization can be related to the electric field at the fundamental frequency by $\vec{P}^{NS} = \vec{\chi}^{NS}:\vec{E}\vec{E}$. The structural symmetry of the surface is, of course, reflected in the form of the nonlinear susceptibility tensor. For a (100) surface with $4m$ symmetry, $\vec{\chi}^{NS}$ turns out to be isotropic. The tensor then has three independent elements, namely, $\vec{\chi}_{\perp\perp\perp}^{NS}$, $\vec{\chi}_{\perp\parallel\parallel}^{NS}$, and $\vec{\chi}_{\parallel\perp\parallel}^{NS}$, where $\parallel$ and $\perp$ refer to directions parallel and perpendicular to the surface. In the case of a (111) surface with $3m$ symmetry, an anisotropic term appears. This term is characterized by $\vec{\chi}_{\xi\xi\xi}^{NS}$ with the ξ axis defined by the projection of the [100] crystal axis on the surface.

The SH radiation arising from the bulk and surface polarization can be calculated in a straightforward fashion.[5] Under excitation by a single plane wave, the s- and p-polarized components of the SH reflection are

$$E_s = \frac{16\pi i\omega^2}{c^2(k_{1z}+k_{2z})}P_{\mathrm{eff},y}^{NS}, \quad (2a)$$

$$E_p = \frac{16\pi i k_1\omega^2}{c^2(k_2^2k_{1z}+k_1^2k_{2z})}\times(k_{2x}P_{\mathrm{eff},z}^{NS}+k_{2z}P_{\mathrm{eff},x}^{NS}), \quad (2b)$$

with

$$\vec{P}_{\mathrm{eff}}^{NS} = \vec{P}^{NS} + \frac{i\vec{P}^{NB}}{k_{sz}+k_{2z}}. \quad (2c)$$

Here we have chosen $\hat{z}$ to lie normal to the interface between (linear) medium 1 and (nonlinear)

medium 2. The y axis is taken to be perpendicular to the plane of incidence of the pump wave. The wave vectors $\vec{k}_1$ and $\vec{k}_2$ refer to the free waves at the harmonic frequency 2ω propagating in the forward direction; $\vec{k}_s$ describes the source polarization wave vector at 2ω, i.e., twice the wave vector of the pump beam.

By considering the form of the surface and bulk source polarizations, we can show that for an isotropic medium no s-polarized SH radiation is produced by either a purely s- or p-polarized pump. Consequently, in these cases, any observed SH radiation must be attributable solely to the anisotropic terms. For a (111) surface, we expect to see a threefold symmetric pattern in the SH radiation as a function of rotation of the sample about its surface normal. Under p-polarized excitation, a complete calculation[6] leads to an electric field at the SH frequency of

$$E_s^{(111)} \propto (\chi_{\xi\xi\xi}^{NS} + a\zeta)(\cos^3\theta - 3\cos\theta \sin^2\theta). \quad (3)$$

In this expression, a is a constant determined by the linear optical properties and the angle of rotation θ is that of the ξ axis of the crystal with respect to the normal to the plane of incidence. The pattern described by Eq. (3) consists of six identical lobes which alternate in sign as θ is scanned from 0 to 2π. The SH intensity will then actually show a full sixfold symmetry.

The situation for the (100) surface is similar. In this case, only the bulk (ζ) term contributes to the s-polarized SH output, since the surface (with the assumed $4m$ symmetry) has an isotropic response. For a p-polarized pump, we find

$$E_s^{(100)} \propto \zeta \sin 4\theta. \quad (4)$$

Now θ measures the angle through which the [100] axis has been rotated away from the normal to the plane of incidence. The fourfold symmetry exhibited by $E_s^{(100)}$ gives rise to an eightfold symmetry for the observed SH intensity.

With other combinations of input and output polarizations, contributions from the isotropic terms should generally appear. Following the theory outlined above, we can, for example, calculate the p-polarized SH output with a p-polarized pump. For a (111) face, we obtain

$$E_p^{(111)} \propto b + c(\chi_{\xi\xi\xi}^{NS} + a\zeta)(\sin^3\theta - 3\sin\theta \cos^2\theta). \quad (5)$$

The corresponding result for a (100) face is

$$E_p^{(100)} \propto d + e\zeta(\sin^4\theta + \cos^4\theta). \quad (6)$$

As before, $b, c, \ldots, e$ denote constants dependent on the input beam geometry, but independent of the sample rotation. The addition of the isotropic terms causes the corresponding SH intensities to have now just the threefold or fourfold symmetry associated with the (111) or (100) face.

In our experiment, pump radiation at 532 nm was provided by the frequency-doubled output of a Q-switched Nd-doped yttrium aluminum garnet laser. The pump beam fell at a 45° angle of incidence on the optically flat surface of a standard silicon wafer cut in the desired plane. The reflected SH intensity was recorded while the sample was rotated at a constant rate. In order to minimize the effect of laser fluctuations, the SH signal was continuously normalized against that of a reference quartz plate. The fluence of the 10-ns pulses was limited to ~5 mJ/cm^2, well below the damage threshold.

Figure 1 displays the s-polarized SH signal from a Si(111) surface under p-polarized excitation.[7] As predicted, the pattern exhibits sixfold symmetry, with six peaks lying at $\theta = 0, \pi/3, \ldots, 5\pi/3$. By interfering this signal with that from a quartz reference, we could verify directly the sign change of the SH electric field in passing between adjacent lobes. The figure also shows the excellent fit of the angular function of Eq. (3) to the experimental data. From this fit we can deduce a value for $|\chi_{\xi\xi\xi}^{NS} + a\zeta|$. It would be of particular interest to compare the surface and bulk anisotropic contributions. This can be accomplished by measuring the s-polarized SH output from a (100) surface with a p-polarized input. In this case, the SH output exhibits an eightfold symmetric pattern in agreement with Eq. (4) from

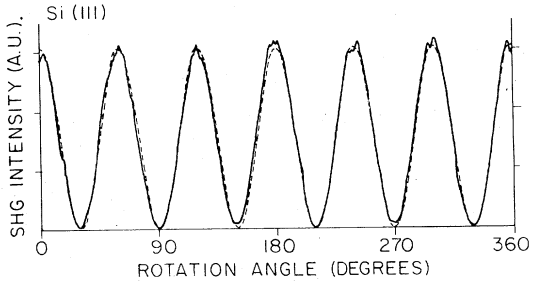

FIG. 1. Experimental data (solid line) and theoretical fit (dashed line) for the intensity of the s-polarized SH reflection from a Si(111) face under p-polarized excitation as a function of the angle of rotation of the sample about its surface normal. The zero of the angular scale (specified in the text) was determined by x-ray diffraction.

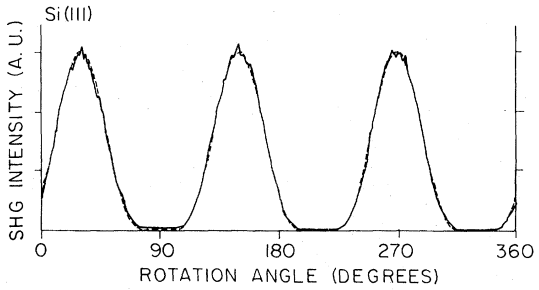

FIG. 2. Intensity of the p-polarized SH reflection from a Si(111) face under p-polarized excitation.

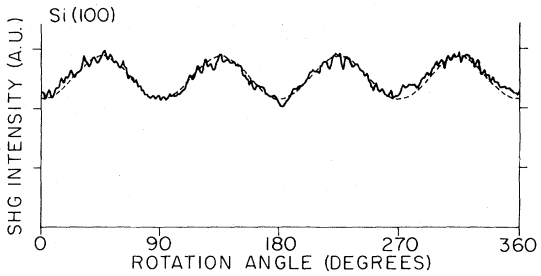

FIG. 3. As in Fig. 2 for Si(100).

which we can then deduce a value for $|\zeta|$ alone. Experimentally, we found $|\chi_{\xi\xi\xi}+a\zeta|=2.9|a\zeta|$ with $|a|=0.066$ for the specified geometry and $\epsilon(\omega)=17.0+i0.4$ and $\epsilon(2\omega)=-13.9+i15.4$.[8] Allowing for all possible phase differences between $|\chi_{\xi\xi\xi}{}^{NS}|$ and $|\zeta|$, we can conclude that $0.12|\zeta| \leq |\chi_{\xi\xi\xi}{}^{NS}| \leq 0.26|\zeta|$.

When the analyzer was rotated away from s polarization the isotropic terms were introduced. The interference between this orientation-independent part and the orientation-dependent part caused the amplitudes of alternate peaks to increase and decrease. For the (111) surface, the three minor peaks at $\theta=\pi/2$, $7\pi/6$, and $11\pi/6$ almost completely vanished in the p-polarized output as shown in Fig. 2. This indicates that the isotropic term b and the anisotropic amplitude $c(\chi_{\xi\xi\xi}{}^{NS}+a\zeta)$ in Eq. (5) must be of nearly the same magnitude. Indeed, setting $b=-c(\chi_{\xi\xi\xi}{}^{NS}+a\zeta)$, we see that the theory matches the experimental data in the figure. For the (100) surface, a similar interface effect arises between the isotropic and anisotropic terms. Since the isotropic contribution is larger in this case, the SH intensity of Fig. 3 shows a modulated form with four peaks and four valleys. The experimental data could be reproduced closely by Eq. (6) with $d=-4.3e|\zeta|$. From our analysis of the shape of these and similar curves for different polarizations, we can estimate the relative values of isotropic terms. We infer $|\chi_{\parallel\perp\parallel}{}^{NS}| \sim |\chi_{\perp\parallel\parallel}{}^{NS}-\gamma| \sim |\zeta|$, while $|\chi_{\xi\xi\xi}{}^{NS}| \sim 0.2|\zeta|$, as mentioned above. A more accurate determination of these parameters requires knowledge of the relative phases of the various terms in the nonlinear polarization.

The surface region here is defined as the surface layer between air and the centrosymmetric bulk. It includes presumably the silicon oxide layer at the surface, the disordered Si layer created in the polishing process, and the transition layer between disordered and crystalline bulk Si. Only the transition layer can contribute to the anisotropic surface susceptibility $\chi_{\xi\xi\xi}{}^{NS}$. The value of $\chi_{\xi\xi\xi}{}^{NS}$ appears to be significantly smaller than that of the isotropic part of $\bar{\chi}^{NS}$. This is understandable since $\chi_{\xi\xi\xi}{}^{NS}$ is derived from the lack of inversion symmetry in the surface plane, while the other elements of $\bar{\chi}^{NS}$ are related to the lack of inversion symmetry perpendicular to the surface. Despite the relatively small value of the anisotropic tensor element, this term still makes an appreciable contribution to the SH signal because of its higher radiation efficiency compared with the isotropic term. This higher efficiency stems from the larger Fresnel factors for electric fields in the medium lying parallel rather than perpendicular to the surface.

In summary, we have observed anisotropic response in the SHG of crystalline silicon. The SH signals as a function of rotation about the surface normal for (111) and (100) faces have been measured for different combinations of input and output polarizations. These results can be well accounted for within the framework of a simple theory relying on the material's symmetry properties. From our analysis, we find that the surface and bulk make comparable contributions to the SHG for silicon samples. In addition to the extension of this work to other simple crystalline surfaces, such measurements should permit a determination of the symmetry of ordered layers.

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