

Symmetry analysis of second-harmonic generation in silicon

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We present observations of second-harmonic generation in Si and argue that under intense laser excitation inversion symmetry is broken, and dipolar bulk second-harmonic generation becomes possible. A mechanism is proposed for removing inversion symmetry in highly excited Si.

When an intense electromagnetic field interacts with a medium, it is convenient to treat the interaction in terms of a dipolar response by expanding the induced dipole moment (\vec{P}) in terms of higher-order contributions from the dielectric response (χ) to the incident electric field (\vec{E}):

$$P_i = E_j(\chi_{ij}^{(1)} + \chi_{ijk}^{(2)} E_k + \chi_{ijkl}^{(3)} E_k E_l + \dots) \quad (1)$$

The second term in the expansion describes dipolar second-harmonic generation (SHG) and is of primary interest to us because it is strictly forbidden in a medium with microscopic inversion symmetry and long-range order (macroscopically centrosymmetric).

Dipolar SHG, although not symmetry forbidden, is expected to be very weak in disordered crystals whose average structure is centrosymmetric even though the constituent unit cell or molecular unit lacks a center of inversion (i.e., liquids and gases). This is true since it is the long-range order of noncentrosymmetric unit cells that provides the coherence necessary for SHG. In what follows we present our observations of SHG in Si under intense laser excitation. We will argue, from its dependence on crystallographic orientation, that the observed signal is dipolar in origin and arises from within the bulk. We will argue that impurities, adsorbates, oxide layers, or surface symmetry-breaking effects do not provide an explanation for our data. We will also demonstrate that a nonlinear dipole source of the form¹ $P_i = \chi_{ijk}^{(3)} E_j \partial_k E_l$, commonly referred to as the quadrupolar source term for SHG (where ∂_k is an electric field gradient), is not capable of reproducing the SHG selection rules we observe in Si. Finally, we will suggest that a model based on the formation of highly localized (Frenkel-type) excitons provides a consistent explanation for all our observations.

The source of our 10-ps excitation pulses has been described elsewhere,² and we demonstrated earlier³ that the signal we observe in reflection is indeed characteristic of SHG by its collimation, wavelength, and quadratic power dependence.

When the incident photon energy is just below the indirect edge of Si (1.054 μm), no SHG is observed with (incident polarizer, SHG analyzer) set for (\perp , all) up to incident fluences of $5 \pm 1 \text{ J/cm}^2$ at which point the Syton-etched (111) surface damages. For the configuration (\parallel , all) only 2–3 photons per pulse were observed at fluences just below the damage threshold. This weak SH signal may be due to surface symmetry-breaking effects producing quadrupolar interactions.⁴ In contrast, a strong SH signal is observed in Si when $\lambda_0 = 527 \text{ nm}$. In fact, peak SHG from Si is weaker than peak SHG from GaP by only a factor of 10.

Over a range of doping concentrations from 10^{14} to 10^{19} cm^{-3} , SHG in Si is found to be unaffected in magnitude or angular dependence. Furthermore, a surface which has

been lapped with $\frac{1}{4}$ - μm diamond generally yields about half the SH signal of a Syton-etched surface and has, in addition, a lower damage threshold. However, dependence of SH signal on crystal orientation is unaffected by the two surface treatments. On a freshly etched (111) Si surface we measured the SH signal strength at fixed angle on a new sample spot for each incident pulse. The SH signal strength obtained in this way is the same as that observed after 50 superimposed shots, provided the sample is not damaged. The formation of amorphous spots does not affect the SH signal strength.

A useful way to determine the symmetry of the nonlinear source term is to measure the (relative) SH strength as a function of crystal orientation. In the scattering coordinates (X, Y, Z), X - Z is taken as the plane of incidence with Z normal to the crystal surface. Y is then normal to the plane of incidence. As the crystal rotates about the Z axis by a variable angle ϕ , the SH intensity varies in accordance with the symmetry of the SH tensor, which is dictated by the symmetry of the crystal.

For a (100) Si surface we find the following selection rules for average SH emission $\bar{N}_{2\omega}$: $\bar{N}_{2\omega}(\perp, \perp) = \bar{N}_{2\omega}(\parallel, \perp) = 0$ and $\bar{N}_{2\omega}(\parallel, \parallel) \sim \bar{N}_{2\omega}(\perp, \parallel) = \text{const}$, in the absence of damage. Virtually identical selection rules are found for a (110) Si surface. Representative SH emission from a (111) Si surface is displayed in Figs. 1 and 2. [See also Fig. 2(a) of Ref. 3.] Each data point in all our measurements is obtained by a log least-squares analysis of the SH signal as a function of incident fluence over 50 single-pulse laser shots. A data point then represents the relative SH signal taken at one particular (average) single-pulse energy. Because our detection scheme uses pulse-height analysis, we can only measure signals greater than one photon per pulse. This level is indicated in the figures by a short dashed line. A fresh sample area is probed when

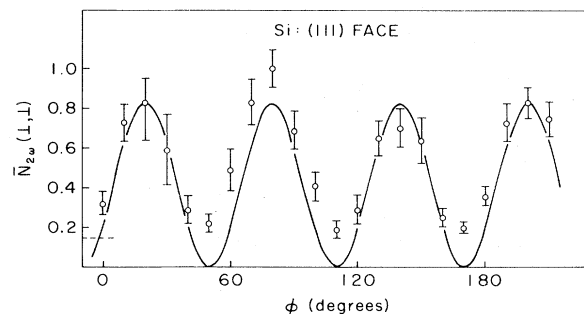


FIG. 1. Relative SH emission for a (111) Si surface for (\perp , \perp) configuration. The solid curve is a dipolar fit with symmetry D_{2d} .

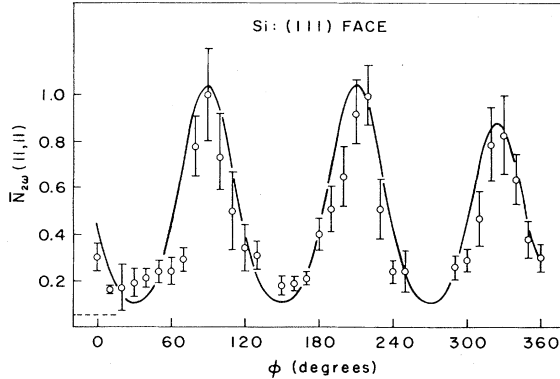


FIG. 2. Relative SH emission for a (111) Si surface for (||, ||) configuration. The solid curve represents a dipolar fit with D_{2d} symmetry.

the angle ϕ is changed.

The data displayed in these figures can be fitted with a (dipolar) second-order susceptibility tensor as though the Si has become piezoelectric. The matrix A represents a sequence of coordinate rotations which takes a vector \vec{E}_s in the (laboratory) scattering coordinate system (X, Y, Z) to a vector \vec{E}_c in the crystal pseudocubic axes (1,2,3). $E_{ci} = A_{ij} E_{sj}$. The dipole moment $P_c(2\omega)$ at the SH frequency has vector components given by Eq. (1): $P_{ci} = \chi_{ijk}^{(2)} E_{cj} E_{ck}$. In the scattering coordinates $P_{si} = A_{ij}^{-1} P_{cj}$ and the calculated SH strength ($I_{2\omega}$) is proportional to $|P_s|^2$. For a (100) surface the observed SH selection rules (given above) are consistent with tetragonal crystal class C_{4v} with no restrictions on the three independent tensor elements, or trigonal class C_{3v} with additional tensor elements small compared with those of C_{4v} . Tensors $\chi_{ijk}^{(2)}$ belonging to crystal classes C_4 , C_{2v} , C_2 , C_3 , and C_1 will also reproduce these selection rules provided we impose adequate restrictions on the relative magnitude and sign of the additional tensor elements that occur for lower crystal symmetry.

For a (111) Si surface the transformation matrix A has previously been given³ and the angular dependence in Figs. 1 and 2 and in Fig. 2(a) of Ref. 3 is very well fitted with a dipolar SH tensor belonging to crystal class D_{2d} with the two independent coefficients related by the ratio $\chi_{321}/\chi_{123} = (0.8-0.9)$. Again, with adequate restrictions, lower-symmetry classes S_4 , D_2 , C_2 , and C_1 can also be used to fit the (111) data.

Finally, for a (110) surface the observed SH selection rules given above cannot be reproduced with a $\chi_{ijk}^{(2)}$ belonging to any crystal class of symmetry higher than orthorhombic. We find that we must carefully choose relative ratios and signs of the five independent tensor elements allowed in C_{2v} symmetry if we are to reproduce the observed selection rules, at least within our experimental error bars. It is expected that monoclinic classes (biaxial) C_3 and C_2 will also account for our observations with adequate restrictions on magnitude and sign of nonvanishing tensor elements.

Because of the finite absorption depth (d) of Si ($d=1 \mu\text{m}$ at $\lambda_0=500 \text{ nm}$; $d=500 \mu\text{m}$ at $\lambda_0=1.05 \mu\text{m}$), there necessarily exists an electric field gradient normal to the surface. Quadrupolar SHG is then possible and must be considered. The third-order susceptibility tensor $\chi_{ijkl}^{(3)}$ has the same structure for the four cubic classes O_h , O , T , and T_d . We have assumed this form of $\chi_{ijkl}^{(3)}$ and have, in addi-

tion, taken ∂_k along the excitation gradient, normal to the surface. With these reasonable assumptions we find that a quadrupolar source of SHG is inconsistent with all selection rules we have observed in Si except for those at a (100) surface.

On a (110) Si surface we can find relationships among the three independent tensor elements of $\chi_{ijkl}^{(3)}$ so that $I_{2\omega}(\parallel, \perp) = 0$, as observed. This attains when (a) $\chi_{1313}^{(3)} = 0$ and $\chi_{1111}^{(3)} = \chi_{1122}^{(3)} + \chi_{1221}^{(3)} = 1$. Contrary to observation, however, condition (a) also predicts a strong oscillatory behavior for $I_{2\omega}(\parallel, \parallel)$. In order to satisfy the observed selection rule $\bar{N}_{2\omega}(\perp, \perp) = 0$, the tensor elements of $\chi_{ijkl}^{(3)}$ must be related in the following way. (b) $\chi_{1111}^{(3)} = 0$ and $\chi_{1313}^{(3)} = -\chi_{1122}^{(3)} + \chi_{1221}^{(3)} = 1$. Condition (b) predicts a strong oscillatory behavior for $I_{2\omega}(\perp, \parallel)$. Therefore, not only does a quadrupolar interaction predict SH emission from a (110) cubic surface that is strongly dependent on crystal orientation (periodic angular dependence with zero points of SHG), but conditions (a) and (b) are mutually exclusive in the sense that, taken together, these predict no SHG whatsoever at a (110) Si surface.

Finally, the data displayed in Fig. 1 can be fitted with a quadrupolar nonlinear source for any choice of independent tensor elements that is consistent with the restriction $\chi_{1111}^{(3)} + \chi_{1122}^{(3)} + \chi_{2323}^{(3)} + \chi_{2332}^{(3)} = 0$. The same choice of tensor elements does not, however, fit the data in Fig. 2 nor does it account for the angular dependence of SHG for configurations (\parallel, \perp) and (\perp, \parallel) .

It is clear that quadrupolar contributions to SHG resulting from an electric field gradient normal to the surface do not explain the observed angular dependence at a (110) or (111) Si surface, and agreement with (100) data may simply be accidental. After the systematic process of elimination outlined above, we conclude that the SH signal we observe in Si is not of quadrupolar origin, nor does it arise from extrinsic effects such as impurities, dislocations, or surface contamination. We further argue that this SH signal does not originate within the first or second atomic layer since the magnitude of SHG in Si is comparable with that from GaP where SHG is allowed by symmetry. SHG depends quadratically on the density of nonlinear oscillator sources, and restricting its origin to one or two atomic layers imparts an unrealistic oscillator strength to these sources. Finally, it is not reasonable to expect a well-defined bulklike symmetry to prevail in the very first or second layer of atoms at a surface, especially one that has been polished and etched in air. An oxide layer or any adsorbate on the surface of our Si sample would display an angular dependence that is inconsistent with observation, as well as showing similar SH signals when λ_0 is $1.054 \mu\text{m}$ or 527 nm .

We must therefore conclude that the SH signal we observe in Si is dipolar in origin ($\chi^{(2)}$) and arises from within the bulk as it does, for example, in GaAs.

A mechanism that is effective in removing the center of inversion from the Si unit cell is suggested by noting that bulk dipolar SHG in Si is directly linked to the degree of excitation. We estimate an $e-h$ (electron-hole) concentration of $10^{21}-10^{22} \text{ cm}^{-3}$ in the excitation volume for a 10-ps pulse of 0.5 J/cm^2 when $\lambda_0=527 \text{ nm}$. When $\lambda_0=1.054 \mu\text{m}$ and the incident fluence is as high as 5 J/cm^2 (where damage occurs), we estimate a peak $e-h$ concentration of $2 \times 10^{20} \text{ cm}^{-3}$. No dipolar SHG is observed from Si in this case. It is clear therefore that inversion symmetry is absent within the absorption volume where Si is highly excited by an intense laser pulse. When the $e-h$ concentration is as high as $\sim 1\%$ of the atomic density, pair separation ap-

proaches 10 \AA , and Coulomb screening then requires effective Bohr orbits significantly less than this dimension. It may then be possible for an electron to become localized on one Si atom and correlated with a hole residing on a nearest-neighbor atom⁵ (allowing exchange). One can then construct a unit cell containing two different excited-state Si atoms, one having an excess electron (e -Si), the other an excess hole (h -Si). Clearly, such a cubic unit cell will have T_d symmetry. A lattice composed of this type of excited-state Si will consist of e -Si surrounded by four nearest neighbors of h -Si and vice versa, similar in form to GaAs. A tightly bound e - h pair (Frenkel exciton) localized on one of the two Si atoms in the Wigner-Seitz cell,⁶ or along bonding directions,⁷ will also lower the crystal symmetry from O_h to T_d . Crystal classes D_{2d} , C_{2v} , and C_{3v} , which account for the observed SHG selection rules from (111), (110), and (100) Si surfaces, are all subgroups of T_d and may derive from T_d by a phase transformation that is promoted by the intense electric field of an incident laser pulse.

The existence of tightly bound excitons in covalent crystals under any excitation condition is yet to be clearly demonstrated although there is some supporting circumstantial evidence in laser-induced photoemission⁸ and dielectric constant calculations.⁹ Further, SHG selection rules in Si and Ge are most consistently explained in terms of a bulk $\chi_{ijk}^{(2)}$, which is strictly vanishing in the undistributed lattice. Given this conclusion, we are obliged to suggest a mechanism

which effectively removes inversion symmetry. The tightly bound exciton description outlined above is at least capable of providing a starting point from which we can begin to understand the origin of a nonvanishing second-order susceptibility in Si and Ge.

Finally, by modifying our Pockels cell single-pulse selector we can extract two nearly equal intensity ($\pm 20\%$) pulses from the mode-locked train. The second pulse is delayed from the first by 8 ns, well within the high reflectivity phase of Si (Ref. 10) generated by the first pulse. (The high reflectivity phase of Si after excitation by a 30-ps laser pulse has been demonstrated¹¹ to persist for at least 80 ns.) The SH signal from the second pulse is generally half that from the first and shows the same angular dependence. These characteristics were confirmed on a (111) Si surface over a range of fluences up to the damage limit. Our results indicate that (111) Si has the same well-defined symmetry (D_{2d}) 8 ns into the high reflectivity phase that it has during the interaction time of a single 10-ps pulse.

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