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## Circular dichroism in second harmonic generation from oxidized Si (001)

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Circular dichroism in second harmonic generation (SHG) is often related to molecules and materials with chiral structures. In this letter, we report circular dichroism in SHG from anisotropic achiral oxidized Si (001) at room temperature. The dichroism value depends on the azimuthal angles of the crystal axes. Due to the simple nonlinear susceptibility elements involved, we were able to attribute the dichroism in SHG to interference between particular terms of the bulk electric quadrupole and surface dipole contributions. The presence of a phase shift between the bulk and surface SHG is required to observe circular dichroism. © 2006 American Institute of Physics.

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Optical second harmonic generation (SHG) is often used as a noninvasive and noncontact tool to study the electronic and structural properties of surfaces and buried interfaces. Its strong sensitivity to surface properties arises from its ability to detect broken inversion symmetry. In the electric dipole approximation, SHG is forbidden in bulk crystals with inversion symmetry but is allowed at surfaces within several atomic layers. SHG generated by surfaces is usually comparable to or even stronger than that from inversion-symmetric bulk crystals, where the lowest order response arises from higher order nonlocal contributions such as electric quadrupole and/or magnetic dipole terms.<sup>1</sup>

Circular dichroism in SHG, i.e., different responses to left- and right-hand circularly polarized light, is routinely used to study chiral films, including investigations of surface-bound biomolecules.<sup>2</sup> Several possible mechanisms for such dichroism have been proposed, including interactions between electric and magnetic dipoles<sup>3</sup> and a large phase shift between different nonlinear tensor elements in the presence of spectral overlap between multiple excited states.<sup>4</sup> It was also demonstrated that nonlinear circular dichroism can occur in surface films with in-plane anisotropy, even in the case of films comprised of achiral chromophores.<sup>5</sup>

The properties of oxidized Si (001) have been extensively studied due to their enormous importance to the semiconductor industry. An ultrathin layer of oxidized Si is present in the channel region of field-effect transistors, the building blocks of very large scale integrated (VLSI) circuits. Previous SHG experiments have investigated various phenomena including charge transfer,<sup>6</sup> resonance enhancement,<sup>7</sup> and hydrogen annealing.<sup>8</sup> In this work, we investigate circular dichroism in SHG from oxidized Si (001), i.e., whether SHG is different for left-hand versus right-hand circularly polarized incident beams. We show that SHG from oxidized Si (001) exhibits circular dichroism, which has not been reported previously, to the best of our knowledge. Due to the simple nonlinear susceptibility elements involved, we were able to attribute the dichroism in

SHG to interference between particular terms of the bulk electric quadrupole and surface dipole contributions.

The experimental schematic is shown in Fig. 1(a). Ultrashort laser pulses of 100 fs duration and 76 MHz repetition rate are chosen to take advantage of the high peak intensity at a low average power. A pair of prisms precompensates for pulse spreading due to material group velocity dispersion introduced by various optics. The polarization of incident light is controlled by a liquid crystal cell that has a voltage controlled variable phase retardance. In this way, we automatically alternate the polarization of the light while ensuring that no deflection of the beam is introduced. The fundamental beam makes a 45° incident angle with respect to the surface normal. The reflected beam together with the SHG signal is collected. After passing through an analyzing polarizer and a short wavelength pass filter, only the SHG photons are counted with a photomultiplier tube (PMT). The PMT photocathode has a large work function to further suppress detection of the nondoubled fundamental photons. The average power used is about 40 mW. Both focusing and collection lenses have a focal length of ~1 cm.

Although SHG measurements are fairly straightforward, the detected signal can arise from subtle interactions between multiple nonlinear tensor elements, making the signal difficult to interpret. We chose the polarization of both the inci-

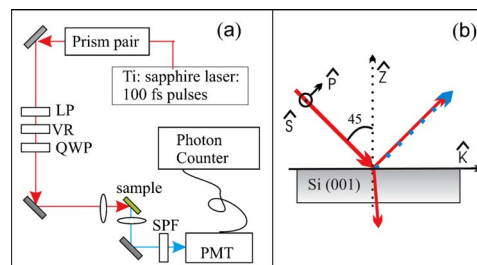


FIG. 1. (Color online) (a) The schematics of the experimental setup. LP: linear polarizer; VR: variable retarder; QWP: quarter wave plate; SPF: short wavelength pass filter; PMT: photomultiplier tube. (b) Experimental geometry and unit vector definitions.

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dent fundamental beam and the detected second harmonic light to reduce the number of contributing tensor elements. In addition, we performed azimuthal angle resolved SHG measurements, in which the sample was mounted on a rotating stage with the rotation axis along the surface normal. Azimuthal angle dependent studies help elucidate symmetry properties and provide useful information for separating different nonlinear tensor elements from bulk and surface contributions.

To relate the detected SHG signal to particular nonlinear coefficients in the bulk Si crystal and (001) surface contribution, we follow a macroscopic theory established by Sipe *et al.*<sup>9</sup> All equations below are written in the beam coordinate axes ( $\mathbf{s}$ ,  $\boldsymbol{\kappa}$ ,  $\mathbf{z}$ ) illustrated in Fig. 1(b) unless specified otherwise. Although nonlinear response coefficients of materials need to be calculated from a microscopic theory, the form they take is constrained by crystal symmetry. The lowest order nonlinear response in bulk Si has an electric quadrupole symmetry; it can be written in terms of an effective polarization as

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

If we consider the interaction of a single transverse plane wave with a medium, only the last two terms contribute. The term  $\gamma \nabla_i(\mathbf{E} \cdot \mathbf{E})$  is isotropic, while  $\zeta E_i \nabla_i E_i$  is anisotropic with respect to crystal orientation.  $\gamma$  and  $\zeta$  are phenomenological constants. In case one chooses to detect the harmonic light with  $s$  polarization, it can be shown that the isotropic bulk contribution vanishes. The anisotropic contribution can then be written as

$$P_{i,\text{anisbulk}}^{(2\omega)} = i \frac{\omega n \zeta}{c} M_{iln} E_l E_n. \quad (2)$$

For  $s$  polarized harmonic light, there are three nonzero  $M$  elements:  $M_{111} = -1/4f_s \sin(4\phi)$ ,  $M_{122} = 1/4f_s \sin(4\phi)$ ,  $M_{112} = -1/4f_s [1 \cos(4\phi)]$  where  $\phi$  is the azimuthal angle. The electric field direction of the  $p$  polarized light in the medium is  $f_s \mathbf{z}_+ + f_c \boldsymbol{\kappa}$ . The components of the fundamental field in the medium, expressed in the beam coordinate axes are  $E_s$ ,  $E_\kappa = f_c E_p$ , and  $E_z = f_s E_p$ .

At the surface of the sample, inversion symmetry is broken; therefore, a dipole contribution to the SHG becomes allowed. In addition, a discontinuity in the normal component of the electric field can induce higher order multipole terms. Both effects are modeled by an effective surface dipole polarization. If one assumes that the cubic crystal (001) surface is simply truncated, the dipole contribution takes the form in the crystal axis coordinates with only three nonzero independent parameters:

$$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 & \partial_{15} & 0 \\ 0 & 0 & 0 & \partial_{15} & 0 & 0 \\ \partial_{31} & \partial_{31} & \partial_{33} & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_y E_z \\ 2E_x E_z \\ 2E_x E_y \end{pmatrix}. \quad (3)$$

We can rewrite these nonlinear tensor elements in the beam coordinates. For  $s$  polarized harmonic light, the only nonzero element is  $\Delta_{113} = \partial_{15}$ . This surface contribution is only

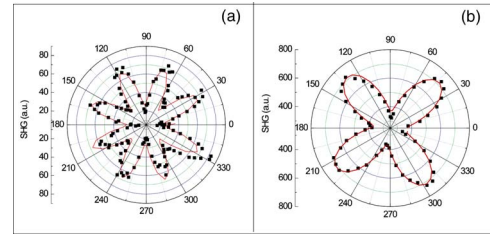


FIG. 2. Azimuthal angle dependent SHG from oxidized Si (001) surface. (a) The input (output) polarizer is set to be  $p$  ( $s$ ). The bulk quadrupole contribution is isolated, resulting in an eightfold symmetry. (b) The input (output) polarizer is set to be circular ( $s$ ). Both bulk quadrupole and surface dipole terms contribute to SHG, leading to a fourfold symmetry. Solid lines are guides to the eyes.

present when the incident fundamental beam has both  $p$  and  $s$  polarization components. In addition, the SHG from the Si (001) surface is isotropic with respect to crystal orientation; i.e., it has no azimuthal angle dependence.

There are fundamental difficulties in completely separating the bulk and surface contributions in SHG in general.<sup>10</sup> However, for oxidized Si (001), one can isolate the bulk electric quadrupole contribution by setting the output polarization to be  $s$  and the input polarization to be either  $s$  or  $p$ .<sup>11</sup> In this case, no SHG signal from the surface is allowed according to Eq. (3). The bulk SHG signal with an eightfold symmetry was observed as a function of azimuthal angle, as shown in Fig. 2(a). However, in the case of circularly polarized incident light, both the bulk electric quadrupole and surface electric dipole terms are present, resulting in a fourfold symmetric SHG signal shown in Fig. 2(b). In the case that only the bulk contribution is measured, the SHG electric field varies as  $\sin(4\phi)$  [bulk element  $M_{122}$  in Eq. (2)]. Therefore, the SHG intensity varies as  $\sin^2(4\phi)$ , which has an eightfold symmetry. When both the bulk and surface contributions are included, the SHG electric field varies as  $\sin(4\phi) + a$ , where  $a$  is constant. The SHG intensity then varies as  $(\sin(4\phi) + a)^2$ , a fourfold symmetric function.

Very generally, the second harmonic intensity generated from circularly polarized incident light can be written as

$$I(2\omega) = |fE_p(\omega)E_p(\omega) + gE_s(\omega)E_s(\omega) + hE_s(\omega)E_p(\omega)|^2 = | -f + g \pm ih|^2 I^2(\omega), \quad (4)$$

where  $E_p(\omega)$  and  $E_s(\omega)$  are the  $p$ - and  $s$ -polarized components of the fundamental field outside the sample, and  $f$ ,  $g$ , and  $h$  can be complex numbers. We have used the relation  $E_p(\omega) = \pm iE_s(\omega)$  for circularly polarized light.

We define circular dichroism as  $D_C = (I_R - I_L)/(I_R + I_L)$ , where  $I_R$  ( $I_L$ ) corresponds to SHG intensity generated with right (left)-hand circularly polarized fundamental light. The circular dichroism magnitude can be calculated in terms of  $f$ ,  $g$ , and  $h$ :

$$D_C = \frac{2 \operatorname{Re}[(-f + g)(ih)^*]}{|-f + g|^2 + |ih|^2}. \quad (5)$$

From Eq. (5), one can see that the requirements for the observation of circular dichroism are that off-diagonal terms in the second order nonlinear susceptibility  $\chi^2$  ( $h$ ) as well as diagonal terms in  $\chi^2$  ( $-f + g$ ) must be nonzero and that there must be a phase shift between them. The apparent circular dichroism arises from interference between contributions from diagonal and off-diagonal elements of  $\chi^2$ . If there is a

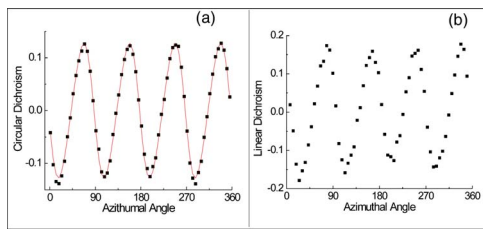


FIG. 3. Dichroism observed from oxidized Si (001) surface. An output polarization  $S$  is used for both cases. (a) The input polarization is switched between left-hand and right-hand circular polarizations. Solid line is a fit to equations discussed in the text. (b) The input polarization is switched between  $45^\circ$  and  $-45^\circ$  linear polarization. A constant offset of dichroism was removed from both plots.

phase shift between  $h$  and  $f+g$ , then their contributions are no longer in-quadrature, but rather can interfere constructively or destructively. When the incident field is changed from left-hand to right-hand circular polarization, the contribution from  $h$  changes sign. For one excitation, the interference is constructive, whereas for the other it is destructive. The presence of a bulk anisotropic resonance at  $\sim 3.3$  eV has been identified in previous SHG studies on oxidized Si (001),<sup>12</sup> and the resonance was ascribed to the  $E_1$  critical point due to the band structure of bulk silicon with a strain induced redshift at oxidized interfaces. Such a nearby resonance may lead to a phase shift between components— $f+g$  and  $h$  at the detected two photon energy  $\sim 3.26$  eV in the current study.

The measured dichroism in SHG is shown in Fig. 3(a). A fourfold symmetry is clearly observed. We note that the polarization of the fundamental beam inside of the medium is not circular due to the different Fresnel transmission coefficients for  $s$  and  $p$  polarized light. Such difference in Fresnel transmission coefficients itself cannot account for the observed circular dichroism since it should only change the values of  $f$ ,  $h$ , and  $g$ , not their relative phases. In addition, Fresnel coefficients do not change as a function of azimuthal angle in Si.

When the incident beam polarization is chosen be to  $+45^\circ$  vs  $-45^\circ$ , i.e.,  $E_p(\omega) = \pm E_s(\omega)$ , the SHG follows a similar equation:  $I(2\omega) = |f+g \pm h|^2 I(\omega)^2$ . We measured linear dichroism  $D_L = (I_{+45^\circ} - I_{-45^\circ}) / (I_{+45^\circ} + I_{-45^\circ})$  from oxidized Si (001) as shown in Fig. 3(b). In contrast to circular dichroism, the observation of linear dichroism does not require a phase shift between  $f+g$  and  $h$ .

In order to relate circular dichroism to particular nonlinear susceptibility elements in oxidized Si (001), we examine total  $s$  polarized SHG from both bulk and surface terms. One can relate  $f$ ,  $g$ , and  $h$  to the surface dipole element  $\partial_{15}$  and the phenomenological parameter  $\zeta$  in the bulk quadrupole response:

$$\begin{aligned} f &= -A\zeta \sin(4\phi) f_c^2, \\ g &= A\zeta \sin(4\phi), \\ h &= 2A\zeta [\cos(4\phi) - 1] f_c + 2B\partial_{15}, \end{aligned} \quad (6)$$

where  $A$  and  $B$  are constants related to the frequencies, wave vectors, and Fresnel coefficients of the fundamental and harmonic light. The values of both circular and linear dichroisms depend on the ratio between the bulk and surface terms. Specifically, we define parameters  $b_1$  and  $b_2$  as  $b_1 + ib_2$

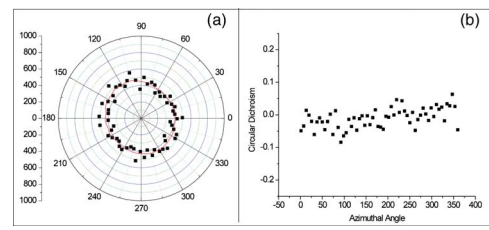


FIG. 4. SHG from sputtered Al film. (a) The input (output) polarizer is set to be  $p$  ( $s$ ). (b) The input polarization is switched between left-hand and right-hand circular polarizations.

$= 2B\partial_{15}/A\zeta$ . Parameters  $b_1 \sim 15.2 \pm 0.7$  and  $b_2 \sim 8 \pm 1$  were extracted from numerical fits to the circular dichroism data shown in Fig. 3(a). However, the values of  $b_1$  and  $b_2$  are dependent on each other, therefore, difficult to determine accurately. As we have mentioned earlier, a phase shift between  $-f+g$  and  $h$  is required for the observation of circular dichroism. Such a phase shift can be determined by the complex argument of  $h/(-f+g)$ , and it is a function of the azimuthal angle and parameters  $b_1$  and  $b_2$ .

We note that our theoretical calculation predicts that both circular and linear dichroisms should vary symmetrically around zero. In other words, the integration of dichroism value over all azimuthal angles should go to zero. In the raw data, a finite offset value of the dichroism was observed. We verified that such an offset resulted from the imperfect polarization of the incident fundamental beam, and thus removed it from Figs. 3(a) and 3(b).

For comparison, we studied a sputtered Al film in the same setup. Al is an easily prepared, nearly free-electron cubic metal. SHG on sputtered Al film has been studied thoroughly.<sup>13</sup> It is believed that surface currents both parallel and perpendicular to the surface as well as bulk contribute to the SHG signal. It was also found that total SHG is isotropic, i.e., independent of azimuthal angles. We have confirmed this result in Fig. 4(a). In addition, we observed no dichroism on the Al film, as shown in Fig. 4(b). Therefore, we ruled out the possibility that the dichroism observed from oxidized Si (001) is due to trivial experimental geometric reasons.

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