

**Surface second-harmonic generation from Si(111)(1×1)H: Theory versus experiment**

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Comparing calculations of the second-harmonic generation (SHG) from the monohydride-terminated Si(111)(1×1)H surface with experimental spectra covering the two-photon energy range from 2.4 eV to 5.0 eV, we present a quantitative test of available state-of-the-art theory of surface SHG from a well-characterized semiconductor surface. We conclude that the density-functional theory within the local-density approximation approach with quasiparticle corrections leads to a semiquantitative agreement between theory and experiment and that the SHG arises from transition across bulk states which are perturbed by the surface. The calculations show that the spectra are sensitive to relaxations of the second-layer Si atoms.

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**I. INTRODUCTION**

In recent years, surface nonlinear optical spectroscopies and in particular, second-harmonic generation (SHG) have evolved as useful nondestructive and noninvasive tools to study properties of surfaces and interfaces: atomic structure, phase transitions, and adsorption of atoms.<sup>1–11</sup> The high sensitivity of SHG spectroscopy is due to the fact that, within the dipole approximation, the bulk SHG signal of centrosymmetric materials is identically zero, and thus only the surface, where the inversion symmetry is broken, can radiate. The theoretical calculations have used the semiempirical tight-binding approach,<sup>12–18</sup> and methods based on the density-functional theory (DFT) within the local-density approximation (LDA).<sup>18–20</sup> Both have yielded results in qualitative agreement with experiments and have clarified the atomic and electronic structure of different surfaces and the adsorption of foreign atoms. However, the semiconductor surfaces treated so far are reconstructed and have surface states that make the comparison between theory and experiment not so straightforward, and thus the of a simple semiconductor surface as a test case is of great importance for further development of the field.

In this paper we study SHG from the H-terminated Si(111)(1×1) surface. This surface is the most simple of all semiconductor surfaces, in that its equilibrium geometry is very close to that of the ideal bulk-terminated Si(111) surface. Also, as H saturates the surface Si dangling bond, there are no surface-related electronic states in the band gap. Experimentally, this surface can be prepared to a high degree of structural quality. Computationally, it is very simple as it has only one atom per unit surface cell. Therefore, this surface represents an ideal reference system for SHG studies of semiconductor surfaces. Previous experimental SHG work on the H-terminated Si(111) focused on the energy range of the  $E_1$  transition of Si.<sup>11</sup> For a conclusive comparison between theory and experiment it is necessary to extend this limited spectral range. We present experimental SHG spectra

with two-photon energies from 2.5 eV to 5 eV, covering both the  $E_1$  and  $E_2$  transitions. The large energy range of our experimental SHG spectra puts the test of the theory of SHG on firm ground. Moreover, our determination of absolute values for the experimental reflection coefficients allows a quantitative comparison with calculated spectra.

We carried out SHG experiments with different polarizations of the incoming and outgoing beams, and compare the results with state-of-the-art calculations of surface SHG, which are within a DFT-LDA plus scissors operator, expanding the wave function on plane waves and using norm-conserving pseudopotentials.<sup>20</sup> We find that for this surface SHG has a quite simple physical interpretation, since it is mostly due to  $2\omega$  resonances involving transitions across bulk states. Using the three-layer model for SHG, we compare three different possibilities for the screening of the external electric field that induces the nonlinear process, and we show that the spectra are very sensitive to relaxations of the back-bonded second-layer Si atoms.

The paper is organized as follows: we briefly present some of the theoretical (Sec. II) and experimental (Sec. III) aspects required in order to obtain the SHG spectra. In Sec. IV we present, compare, and discuss the experimental and calculated results, and in Sec. V we give the conclusions.

**II. THEORY**

The second-order susceptibility tensor  $\vec{\chi}$  of a bulk-terminated Si(111) surface (symmetry group  $C_{3v}$ ) has the following nonzero components:<sup>21</sup>

$$\chi_{zzz} \equiv \chi_{\perp\perp\perp},$$

$$\chi_{zxx} = \chi_{zyy} \equiv \chi_{\perp\parallel\parallel},$$

$$\chi_{xxz} = \chi_{yyz} \equiv \chi_{\parallel\parallel\perp},$$

$$\chi_{xxx} = -\chi_{xyy} = -\chi_{yyx} \equiv \chi_{\parallel\parallel\parallel}, \quad (1)$$

where we have chosen the  $x$  and  $y$  axes along the  $[1\bar{1}2]$  and  $[1\bar{1}0]$  directions, respectively. The  $\chi_{\parallel\parallel\parallel}$  component induces a second harmonic (SH) response which is anisotropic with respect to the azimuthal angle  $\phi$  that the plane of incidence makes with the  $x$  axis. Notice that  $\chi_{\parallel\parallel\parallel}$  can be selectively probed with  $pS$  (incoming  $p$  outgoing  $S$ ) or  $sS$  (incoming  $s$  outgoing  $S$ ) polarization configurations [see Eqs. (8) and (10)]. The SHG efficiency is defined as the nonlinear reflection coefficient,  $\mathcal{R} = I(2\omega)/I^2(\omega)$ , with  $I$  the intensity of the corresponding incoming linear ( $\omega$ ) field or outgoing nonlinear ( $2\omega$ ) field. In our calculation of  $\mathcal{R}$ , which also includes that of  $\vec{\chi}$ , the fundamental electric field oscillating at  $\omega$ , which induces the nonlinear response, is taken inside the surface. The spatial variation of this field near the surface and its subsequent screening is calculated through the dielectric function within the three-layer model of Ref. 12. The three-layer model assumes that the external fundamental field comes from vacuum, and that the SH is generated in a thin layer below the surface characterized by a surface dielectric function  $\epsilon_s(\omega)$ . Below this surface region we have the bulk of the system which has a bulk dielectric function  $\epsilon_b(\omega) \neq \epsilon_s(\omega)$ . The function  $\epsilon_s(\omega)$  is calculated following Ref. 22, and  $\epsilon_b(\omega)$  is the standard bulk dielectric function. From Ref. 23,  $\mathcal{R}$  can be written as

$$\mathcal{R}_{iF} = \frac{32\pi^3\omega^2}{(n_0e)^2c^3\cos^2\theta} |T_F^{vs}T_F^{sb}(t_i^{vs}t_i^{sb})^2r_{iF}|^2, \quad (2)$$

where  $i = s$  or  $p$  (lower case) indicates the polarization of the incoming photon of frequency  $\omega$ ,  $F = S$  or  $P$  (upper case) the polarization of the outgoing photon of frequency  $2\omega$ , and the superindices denote vacuum ( $v$ ), surface ( $s$ ), and bulk ( $b$ ). The Fresnel factors that give the transmitted fields at the vacuum-surface ( $vs$ ) or surface-bulk ( $sb$ ) interface, for  $s$  or  $p$  polarization are given by

$$t_s^{vs}(\omega) = \frac{2\cos\theta}{\cos\theta + k_{zs}(\omega)}, \quad (3)$$

$$t_p^{vs}(\omega) = \frac{2\cos\theta}{\epsilon_s(\omega)\cos\theta + k_{zs}(\omega)}, \quad (4)$$

$$t_s^{sb}(\omega) = \frac{2k_{zs}(\omega)}{k_{zs}(\omega) + k_{zb}(\omega)}, \quad (5)$$

$$t_p^{sb}(\omega) = \frac{2k_{zs}(\omega)}{\epsilon_b(\omega)k_{zs}(\omega) + \epsilon_s(\omega)k_{zb}(\omega)}, \quad (6)$$

where the appropriate term  $\sqrt{\epsilon(\omega)}$  from the usual definition of  $t_p$  has been taken out,<sup>24</sup> and a Fresnel factor written with a capital  $T$  means that  $T = t(2\omega)$ . Also  $k_{zj}(\omega) = (\omega/c) \times (\epsilon_j(\omega) - \sin^2\theta)^{1/2}$ , with  $j = s$  or  $b$ , is the magnitude of the wave vector perpendicular to the surface. Also,

$$\begin{aligned} r_{pP} = & \sin\theta\epsilon_b(2\omega)[\sin^2\theta\epsilon_b^2(\omega)\chi_{\perp\perp\perp} + k_{zb}^2(\omega)\epsilon_s^2(\omega)\chi_{\perp\parallel\parallel}] \\ & + \epsilon_s(\omega)\epsilon_s(2\omega)k_{zb}(\omega)k_{zb}(2\omega)[-2\sin\theta\epsilon_b(\omega)\chi_{\parallel\perp\perp} \\ & + k_{zb}(\omega)\epsilon_s(\omega)\chi_{\parallel\parallel\parallel}\cos(3\phi)], \end{aligned} \quad (7)$$

$$r_{sP} = \sin\theta\epsilon_b(2\omega)\chi_{\perp\parallel\parallel} - k_{zb}(2\omega)\epsilon_s(2\omega)\chi_{\parallel\parallel\parallel}\cos(3\phi), \quad (8)$$

$$r_{pS} = -k_{zb}^2(\omega)\epsilon_s^2(\omega)\chi_{\parallel\parallel\parallel}\sin(3\phi), \quad (9)$$

$$r_{sS} = \chi_{\parallel\parallel\parallel}\sin(3\phi). \quad (10)$$

In the above relations,  $\theta$  is the angle of incidence,  $c$  the speed of light,  $e$  the charge of the electron, and  $n_0$  the electron density of the system. The expression for  $\mathcal{R}$  is strictly valid within the dipole approximation; the isotropic and anisotropic bulk quadrupole terms in  $\mathcal{R}$  have been shown to yield negligible contributions as compared to the surface dipole terms.<sup>25</sup> We mention that the full treatment of the surface screening is still lacking, and further improvement of the present formulation can be made along this point.

With the three-layer model we can get two opposite cases, one in which the SH conversion takes place in vacuum for which we simply put  $\epsilon_s = 1$  in the above formulas, and the other case where the layer is identical to the bulk, or  $\epsilon_s = \epsilon_b$ . The former case corresponds to no screening or vacuum model and the latter to the usual Fresnel screening or Fresnel model.

We use the DFT-LDA method to find the equilibrium atomic positions. The structure that we obtain is in agreement with previous calculations.<sup>26–29</sup> The H-Si distance is 1.54 Å, and the outward relaxation of the interlayer spacing between first- and second-layer Si atoms is around 3%. The electronic wave functions and eigenvalues are obtained from this self-consistent calculation using a plane-wave basis set with an energy cutoff of 15 Ry, and  $\vec{\chi}$  is calculated for a slab of up to  $N = 36$  atomic planes following Ref. 20. With the same DFT-LDA method we calculate the bulk dielectric function,  $\epsilon_b(\omega)$ , and the surface dielectric function,  $\epsilon_s(\omega)$ . As in the experiment, we take an angle of incidence  $\theta = 65^\circ$  and an azimuthal angle  $\phi = 30^\circ$ . For this azimuth the contribution of  $\chi_{\parallel\parallel\parallel}$  to  $r_{pP}$  and  $r_{sP}$  vanishes,  $r_{pS}$  is maximum, and  $r_{sP}$  is proportional to  $\chi_{\perp\perp\perp}$ .

### III. EXPERIMENTS

In our experiments we used samples from intrinsic Si(111) wafer material ( $n < 1.3 \times 10^{12} \text{ cm}^{-3}$ ) to ensure a flat-band condition. This excludes any electric-field-induced SHG,<sup>30</sup> possible in the space-charge region of doped material.<sup>31</sup> Monohydride termination of the surface was achieved by a standard procedure which involves stripping off a thin surface oxide in a buffered solution of  $\text{NH}_4\text{HF}$  as the last step.<sup>32</sup> The quality of the H-terminated surfaces was checked with sum-frequency generation (SFG) vibrational spectroscopy using a separate laser setup. Our SFG spectra revealed a single monohydride Si-H stretching vibrational band at  $2084 \text{ cm}^{-1}$  and absence of dihydrides and trihydrides modes,<sup>33</sup> indicating an atomically flat surface with large terraces. The monohydride termination was stable in ambient atmosphere for several hours. SHG spectra between a 2.5 and 5 eV two-photon energy range were measured with a picosecond optical parametric generator/amplifier laser system and a detection system with optical filters, a monochro-

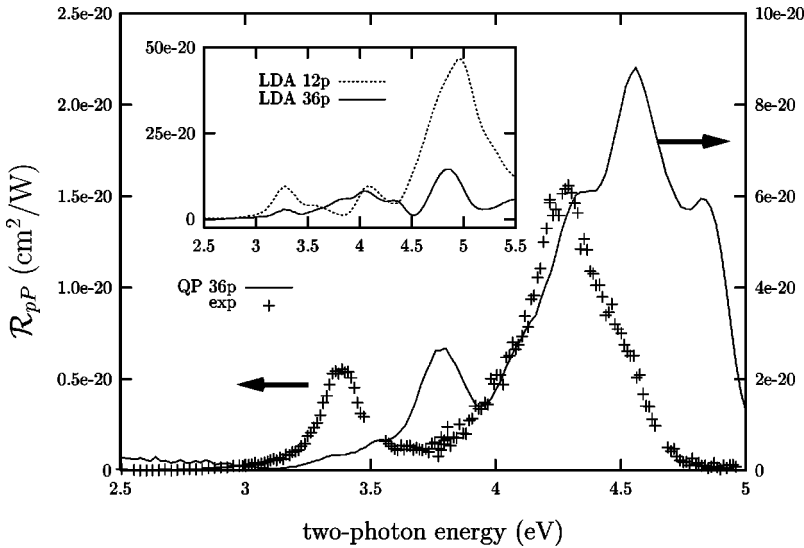


FIG. 1. QP-corrected ( $\Delta=0.5$  eV) spectra of  $\mathcal{R}_{pp}$  for 36 planes ( $\phi=30^\circ, \theta=65^\circ$ ), for the Fresnel model ( $\epsilon_s = \epsilon_b$ ) (right scale). Symbols: experimental data (left scale). The inset shows the LDA results for 36 (solid line) and 12 (dotted line) planes.

mator, and a photomultiplier.<sup>34</sup> The SHG signals from the Si surfaces were normalized against the SHG signal simultaneously generated in a crystalline quartz wedge as a reference sample. In addition, we have calibrated the SHG from the Si surface against that from crystalline quartz by replacing the Si sample with a quartz plate. This way, absolute values for the nonlinear reflection coefficients,  $\mathcal{R}_{if}$ , of the Si surface were deduced, making possible a quantitative comparison between experimental and theoretical spectra in a large spectral range.

#### IV. RESULTS

In Fig. 1 we compare  $\mathcal{R}_{pp}$  (taking  $\epsilon_s = \epsilon_b$ ) for  $N=12$  and 36 planes with the experimental spectrum that shows two-photon resonances at the energies corresponding to the  $E_1$  (3.4 eV) and  $E_2$  (4.3 eV) critical-point transitions of bulk Si. The result of LDA calculations (inset in Fig. 1) show peaks at about 3.3 eV and 4.1 eV that are redshifted by  $\sim 0.1 - 0.2$  eV from the experimental peaks. Below  $E_1$  the SHG yield is zero as there are no surface related states. Although a large number of planes (36 or more) is required in order for the spectra to reach convergence, the energy separation between  $E_1$  and  $E_2$  agrees well with the experiment and is independent of the number of planes. The calculated intensity is a factor-of-5 larger than the experimental one, a fact that could be related to the approximations involved in the method.

The observed resonances are related to  $2\omega$  transitions, rather than to  $\omega$  transitions, due to the fact that these resonant structures are the well-known  $E_1$  and  $E_2$  transitions from bulk Si, and for the laser frequencies applied in our experiments they have to be resonant with the second-harmonic frequency. Moreover, previous SFG experiments with oxidized Si revealed that the excitations are resonant with the same two-photon energies as in our SHG spectra.<sup>35</sup> This  $2\omega$  assignment could be further supported by a theoretical calculation similar to that of Ref. 17.

The lower energies of the peaks in the theoretical SHG spectra have their origin in the shortcoming of the DFT-LDA

approach which underestimates the gap. We therefore follow Ref. 20 and include quasiparticle (QP) corrections within the scissors approximation with a shifting parameter  $\Delta$ . The absence of surface states of the Si(111)( $1 \times 1$ )H surface produces an almost rigid shift of the spectra (Fig. 1), thus allowing a more straightforward interpretation of QP effects compared to systems with surface states where there is also a redistribution of the weights of the resonances due to the mixing of one- $\omega$  and two- $\omega$  transitions.<sup>20</sup> In Fig. 2 we show  $\mathcal{R}_{ps}$  (taking  $\epsilon_s = \epsilon_b$ ) that is governed by  $\chi_{\parallel\parallel\parallel}$ , with QP corrections for  $\Delta=0.5$  eV along with the experimental spectrum. As we see from Figs. 1 and 2, QP corrections within the simple scissors approximation do not give an adequate description of the experimental results, and show that in nonlinear optics these corrections affect differently the nonzero components of  $\tilde{\chi}$ . A possible solution would be to use full wave-vector- and band-index-dependent QP corrections as carried out in Ref. 36 for bulk SHG, however, this approach

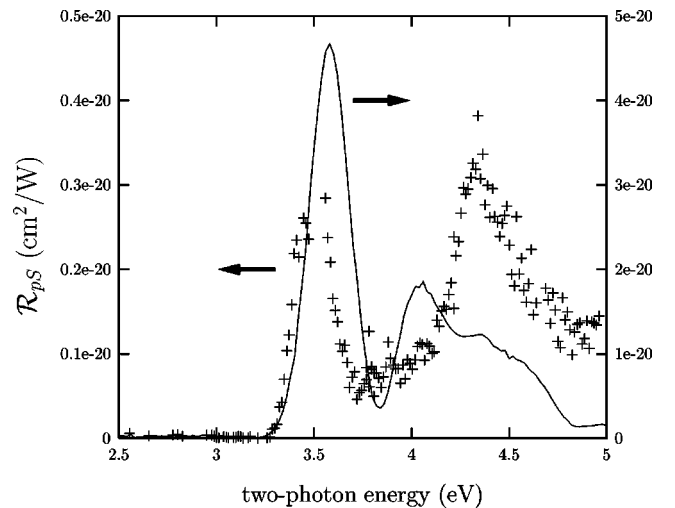


FIG. 2.  $\mathcal{R}_{ps}$  for 36 planes ( $\phi=30^\circ, \theta=65^\circ$ ), for the Fresnel model ( $\epsilon_s = \epsilon_b$ ) (right scale). The theoretical spectrum (solid line) is QP corrected with  $\Delta=0.5$  eV. Symbols: experimental data (left scale).

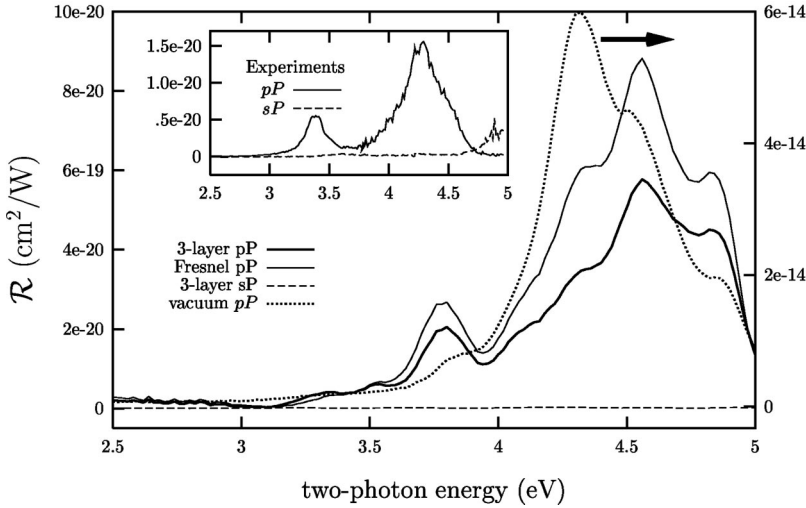


FIG. 3. QP-corrected ( $\Delta = 0.5$  eV) spectra of  $\mathcal{R}$  for 36 planes and for three different models of screening. Thick solid (dashed) line: three-layer model for  $pP$  ( $sP$ ) (left scale). Thin solid line: Fresnel model for  $pP$  (same as in Fig. 1) (left scale). Dotted line: vacuum model for  $pP$  (right scale). The inset shows the experimental spectra for  $pP$  and  $sP$ .

goes beyond the scope of the present paper.

An important issue in surface SHG is the screening of the electric field that induces the nonlinear response. For the evaluation of  $\vec{\chi}$  the screening of external fields at the fundamental and second-harmonic frequency [Fresnel factors  $T_f(2\omega)$  and  $t_i(\omega)$ ] in Eq. (2) has to be taken into account. In addition, for visible fundamental radiation it follows that  $(\omega/c)^2 \sin^2 \theta < k_{\perp}^2(\omega) < k_{\perp}(\omega)k_{\perp}(2\omega)$ , and although the different components of  $\vec{\chi}$  may be of the same order of magnitude,  $\chi_{\parallel\perp\perp}$  has the largest prefactor in  $r_{pP}$ . With the measurement of  $pP$ ,  $pS$ , and  $sP$  spectra of the Si(111)(1×1)H surface, we can conclusively determine the accuracy of the screening in the model for  $\mathcal{R}$  and  $\vec{\chi}$ . To this end, we compare  $\mathcal{R}$  calculated with  $\epsilon_s \neq \epsilon_b$  (three-layer model),  $\epsilon_s = \epsilon_b$  (Fresnel model), or  $\epsilon_s = 1$  (vacuum model). In terms of field screening the three-layer model represents a more detailed calculation, whereas the Fresnel model simply screens with the bulk dielectric function, and the vacuum model represents no screening at all and is equivalent to evaluate the fields above the surface. In Fig. 3 we show  $\mathcal{R}$  for the three-layer model, the Fresnel model, and the vacuum model. Notice that the Fresnel (same as in Fig. 1) and the three-layer models give similar spectra that agree reasonably well with experiment. Note that the three-layer model gives an intensity that is closer to the experimental result. Also, the intensity ratio between  $pP$  and  $sP$  spectra agrees well with the experimental one, for both the Fresnel and the three-layer models. On the other hand, for the vacuum model (unscreened fields),  $\chi_{\perp\perp\perp}$  dominates but the spectrum is in severe disagreement with the experiment. In this case,  $\mathcal{R}_{pP}$  is six orders-of-magnitude larger than the experimental results shown in the inset of Fig. 3. The three-layer model indicates that the proper screening of the fields in the subsurface SH active layer only lowers the SHG intensity, leaving the same peak positions as with the Fresnel screening. Therefore, the present calculation along with the experiments allow us to conclude that the screening is qualitatively accounted for by the Fresnel model. With the help of Eq. (7), we also conclude that  $\chi_{\parallel\perp\perp}$  dominates  $\mathcal{R}_{pP}$ , with a small contribution from  $\chi_{\perp\perp\perp}$  at high energies, and a negligible contribution from  $\chi_{\perp\perp\perp}$ .

Another important aspect is the dependence of the SHG spectra on the detailed atomic structure of the surface. For instance, changing the vertical position of the second-layer Si atoms induces significant changes in the spectra. Figure 4 shows  $\mathcal{R}_{pP}$  for a vertical displacement of the back-bonded Si towards the surface (bulk) by 30% of its interlayer length, and clearly shows a blueshifted (redshifted)  $E_1$  peak. This displacement is equivalent to a  $\sim 3\%$  decrease ( $\sim 4\%$  increase) in bond length of the Si-Si back bond for the 30% contraction (expansion). On the other hand, changing the Si-H bond distance by as much as 5% of its equilibrium value does not alter the SHG spectra appreciably (not shown). A similar result is obtained for  $\mathcal{R}_{pS}$ . Although the vertical displacements in Fig. 4 are arbitrary and do not represent equilibrium structures, the calculations clearly demon-

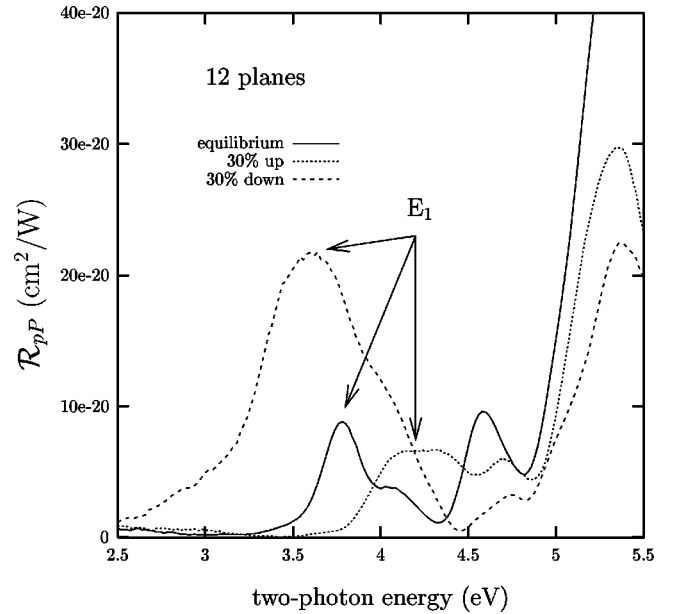


FIG. 4. QP-corrected ( $\Delta = 0.5$  eV) spectra of  $\mathcal{R}_{pP}$  for 12 planes, and for the Fresnel model ( $\epsilon_s = \epsilon_b$ ). The back-bonded Si atoms are moved vertically up by 30% (dotted line) and vertically down by 30% (dashed line), respectively, from their equilibrium positions (solid line).

strate the sensitivity of surface SHG to a variation of the positions of the second-layer Si atoms. It has been argued that besides the H atom it is the back-bonded Si atoms, and not the top-layer Si atoms, which are prone to interact with approaching molecules.<sup>29</sup> Thus, since such interactions induce relaxations of the back-bonded Si layer, SHG spectroscopy of the  $E_1$  band could be used to monitor interactions between molecules and the Si surface.<sup>11</sup>

## V. CONCLUSIONS

In conclusion, we have shown that experimental SHG spectra of the Si(111)(1×1)H surface are in semiquantitative agreement with state-of-the-art LDA-QP calculations. A simple physical interpretation of the spectra emerges: the main spectral structures arise from  $2\omega$  resonances across surface-modified bulk states. Their intensity and line shape are sensitive to relaxations of the second Si layer. A comparison of the calculated and measured intensities for different screening of the surface fields shows that the nonlinear con-

version occurs just below the surface, as expected, and not on the vacuum side. Also, we showed that the intensity discrepancy between theory and experiment is reduced for the three-layer model where the screening of the fields is calculated with more detail, thus a more careful calculation of the fields in the surface region would close this difference. Finally quasiparticle corrections beyond the scissors approximation and the inclusion of excitonic and local-field effects will render the theoretical calculation of SHG on firmer physical grounds.

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