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Ab initio study of linear and nonlinear optical responses of Si(111) surfaces

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The linear and nonlinear optical susceptibilities of unreconstructed and reconstructed (2×1) Si(111) clean and hydrogen covered surfaces were studied by application of an *ab initio* approach, namely the self-consistent full potential linearized augmented plane-wave method within the local-density approximation. The components of the susceptibility tensor for the clean surfaces calculated as a function of the incident photon energy reveal prominent features in the energy range below 2 eV which are attributed to optical resonances associated with surface states. The calculated data are consistent with previous experimental and theoretical works. An *ab initio* technique was used to derive the second harmonic response as a function of the polarization angle of the incident light. The polarization angle dependence of the calculated second harmonic intensity of (2×1) Si(111) agrees well with experimental data which could now be interpreted.

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I. INTRODUCTION

Optical spectroscopies such as surface differential reflectance, reflectance anisotropy spectroscopy, and optical second harmonic generation (SHG) are of importance as sensitive probes for the electronic structure of a surface.[1] Among these techniques, SHG has particularly attractive features: it is highly sensitive to the symmetry of surface structures, and it results in spectra of surface electronic levels which depend on the transition energy. Experimental studies on surface SHG spectra were so performed for metals[2–4] and semiconductors.[5–7] Furthermore, Mizutani and Sano measured SHG responses of TiO_2 surfaces,[8,9] gold thin-film surfaces and interfaces,[10,11] and Ge/oxide interfaces.[12] The interpretation, however, of the observed SHG resonant peaks is—without any further knowledge—rather difficult. Therefore reliable *ab initio* data are needed in order to understand the results of measured SHG.

The intensity of the SHG response of matter is described by the second order nonlinear optical susceptibility tensor $\chi^{(2)}$. Calculations of components of $\chi^{(2)}$ were performed for bulk systems[13–15] as well as for surfaces,[16–20] in particular for various surfaces of Si.

Calculations of polarization angle dependence of surface sensitive SHG response are the main task of our study. As indicated by experiments of T. F. Heinz *et al.*, the polarization angle dependence shows symmetry properties of the surface atomic and electronic structure,[21] and it is also sensitive to the phases of the nonlinear optical susceptibility components. For a comprehensive interpretation of all these aspects of the measured polarization angle dependence of the SHG intensity, a phenomenological approach is not sufficient, and therefore an accurate calculation based on microscopic theory of the SHG response is required.

In the present study, we show calculated data of nonlinear susceptibilities of a (2×1) reconstructed Si(111) surface by using the self-consistent full potential linearized augmented plane-wave (FLAPW) method,[22,23] which is considered to be one of the most precise all-electron *ab initio* approaches available. For this surface we also derived the polarization angle dependence of the SHG response. Linear and nonlinear susceptibility components of other Si(111) surfaces, i.e., the unreconstructed case as well as a hydrogen covered surface were also derived. Our calculated results are consistent with former theoretical studies[18,19,24–26] as well as experimental data.[21,27–29] In particular our calculated SHG response of the (2×1) Si(111) surface agrees well with the experimental result of the SHG light intensity as a function of the polarization angle of the incident light.[21]

II. COMPUTATIONAL ASPECTS

A. Electronic structure

For modeling the surfaces we applied a repeated slab construction. The slabs contained 14 Si atomic layers for the unreconstructed and reconstructed (2×1) Si(111) surfaces, and 14 Si atomic layers plus 1 atomic layer of H on each slab boundary for (1×1) H/Si(111). For the reconstructed (2×1) surface, we adopted the geometrical structure of the π-bonded chain model, which has a buckling of 0.38 Å in the outer chain.[30] For H/Si(111) the atomic relaxations were determined by minimization of atomic forces.

The calculations of the ground state and the optical properties were made by application of the FLAPW method within the local-density approximation (LDA) of Hedin and Lundqvist.[31,32] The number of basis functions was restricted by momentum cutoffs of 4.0 a.u.$^{-1}$ for the (1×1) surfaces, and 3.85 a.u.$^{-1}$ for the (2×1) surface. Density, potential, and basis functions inside the atomic spheres were expanded into spherical harmonics up to $l_{max}=8$. For the (1×1) and the (2×1) surfaces regular meshes of 60 and 66 special **k** points in the irreducible part of the two-dimensional surface Brillouin zone excluding z reflection (SBZ) were chosen, generated by $17\times17\times1$ and $11\times11\times1$ Monkhorst-Pack parameters,[33] respectively. Reciprocal-space integration was performed with the Gaussian smearing technique applying a width of 0.1 eV.

B. Optical susceptibility

The polarization **P** induced by the incident electric field **E** is given as a power series in the field by

$$\mathbf{P}=\chi^{(1)}\mathbf{E}+\chi^{(2)}\mathbf{E}\mathbf{E}, \tag{1}$$

where $\chi^{(1)}$ and $\chi^{(2)}$ are linear and second-order nonlinear optical susceptibilities, respectively. In the present study, $\chi^{(2)}$ was calculated referring to the formalism of Refs. 16 and 17. The imaginary part of the surface nonlinear susceptibility is defined by

$$\begin{aligned}
\mathrm{Im}[\chi^{(2)}_{s,ijk}(\omega)]
&=\frac{2\pi}{\Omega}\left(\frac{e}{m\omega}\right)^3\sum_{\mathbf{k}\in SBZ}\Bigg(\sum_{s\in V}\sum_{r\in C}\sum_{n\in C}\big([\tilde{p}^i_{sn}\{p^j_{nr},p^k_{rs}\}/(E_{ns}\\
&\quad-2E_{rs})][\delta(E_{rs}-\hbar\omega)-2\delta(E_{ns}-2\hbar\omega)]\\
&\quad+[\tilde{p}^i_{nr}\{p^k_{rs},p^j_{sn}\}/(E_{ns}+E_{rs})]\delta(E_{rs}-\hbar\omega)\big)\\
&\quad-\sum_{s\in V}\sum_{l\in V}\sum_{n\in C}\big([\tilde{p}^i_{ln}\{p^j_{sl},p^k_{ns}\}/(E_{nl}-2E_{ns})]\\
&\quad\times[\delta(E_{ns}-\hbar\omega)-2\delta(E_{nl}-2\hbar\omega)]\\
&\quad+[\tilde{p}^i_{sl}\{p^k_{ns},p^j_{ln}\}/(E_{ns}+E_{nl})]\delta(E_{ns}-\hbar\omega)\big)\Bigg),
\end{aligned}\tag{2}$$

where the braces indicate a symmetrization of the components j and k, Ω is the volume of the slab in the unit cell, e and m are the electronic charge and mass, and ω denotes the frequency of the incident photon. The notations s, r, n, and l indicate electronic states of the valence (V) or conduction (C) bands. E_{ns} denotes the direct energy gap between the one electron energy levels n and s. The symbol $p^j_{nr}(k)$ denotes the matrix element of the momentum operator **p** defined by $p^j_{nr}=-i\hbar\langle\Psi_n(k)|\nabla_j|\Psi_r(k)\rangle$. The symbol $\tilde{p}^i_{nr}$ marks the matrix element of the modified momentum operator for the emission of SHG radiation defined by $\tilde{\mathbf{p}}=1/2[S(z)\mathbf{p}+\mathbf{p}S(z)]$, where S(z) is a function which decays inside the slab: it is unity at the top layer of the slab and zero at the bottom layer. By introducing the modified momentum operator into the calculation one can avoid destructive interference of the SHG polarizations possibly induced by the two surfaces of the finite slab, and thus the SHG response of just one surface is obtained selectively.[16,17] We applied the continuous function $S(z)$,

$$S(z)=\begin{cases}\cos^2\left(\dfrac{\pi(z-d)}{2(L-d)}\right) & \text{for } d<z\leq L \text{ (vacuum region)}\\[2ex] \sin^2\left(\dfrac{\pi z}{2d}\right) & \text{for } 0\leq z\leq d \text{ (inside slab)},\end{cases}\tag{3}$$

where d and L are the thickness of the slab and length of the unit cell, respectively. Therefore $z=d$ and 0 indicate the z positions of the top and bottom layers of the slab, respectively. In order to simplify the calculation, we assume that the value of $S(z)$ inside each atomic sphere is a constant value $S(z_i)$, where z_i is the z position of the center of the ith sphere. The function $S(z)$ not only picks up the surface contribution but also breaks a possible inversion symmetry of the bulk response, so that some bulk originated contribution to the SHG intensity might also occur. Since this side effect becomes weaker as the thickness of the slab increases, a sufficiently thick slab has to be used in the calculation requiring demanding calculations. For slab thicknesses practicable for the *ab initio* approach we cannot fully exclude such an effect.

The imaginary part of the linear optical susceptibility was derived from the expression

$$\begin{aligned}
\mathrm{Im}[\chi^{(1)}_{ij}(\omega)]=-i\frac{2\pi}{\Omega}\left(\frac{e\hbar}{m}\right)^2\sum_{\mathbf{k}\in SBZ}\sum_{g\in V}\sum_{n}\\
\times\frac{1}{E^2_{ng}}[p^j_{gn}p^i_{ng}\delta(\hbar\omega+E_{ng})\\
-p^i_{gn}p^j_{ng}\delta(\hbar\omega-E_{ng})].
\end{aligned}\tag{4}$$

In order to obtain the real part of the linear optical susceptibility, the Kramers-Kronig transformation was used. The optical response was calculated within the electric dipole approximation, and excitonic and local-field effects are not considered in the present calculation.

Since the unreconstructed Si(111) surface has a metallic character, intraband transitions within the surface states must also contribute to its optical properties. However, these intraband transitions are not taken into account in our calculation, because the resulting Drude tail appearing in the very low-energy region in the optical spectrum is not important for our present concern.

III. RESULTS AND DISCUSSION

A. Linear optical properties

Figure 1 shows the calculated linear optical susceptibility for all the three studied surfaces, for unreconstructed Si(111), (1×1) H/Si(111), and reconstructed (2×1) Si(111) as a function of the photon energy. The curves represent the averages of the three susceptibility components $\chi^{(1)}_{xx}$, $\chi^{(1)}_{yy}$, and $\chi^{(1)}_{zz}$, and they contain both bulk and surface contributions. The coordinate axes x, y, and z represent the $[2\bar{1}\bar{1}]$, $[01\bar{1}]$, and $[111]$ directions, respectively. The measured $\chi^{(1)}$ of Si

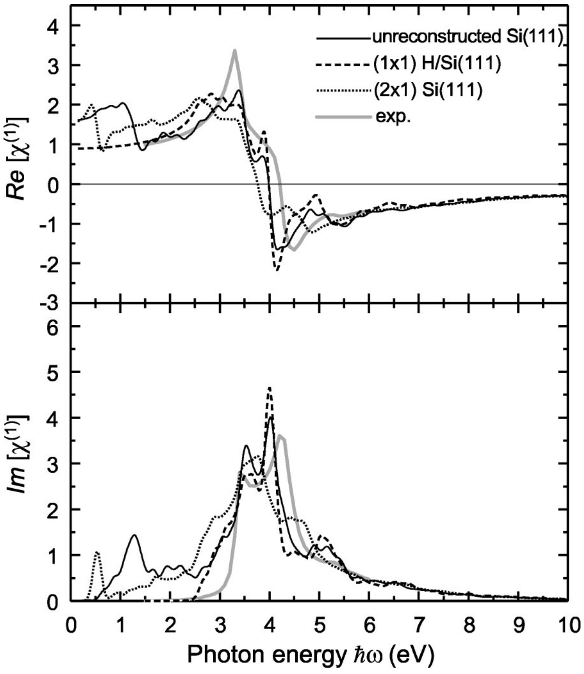

FIG. 1. Calculated linear optical susceptibility $\chi^{(1)}$ as a function of the photon energy: unreconstructed Si(111) (solid lines), (1×1) H/ Si(111) (dashed lines), and reconstructed (2×1) Si(111) (dotted lines). Gray lines: experimental bulk data of Ref. 27.

bulk[27] is also shown as gray curves, in order to confirm the validity of our calculation through the bulk contribution of the calculated $\chi^{(1)}$. The prominent structures in the energy range from 3 to 5 eV are due to the bulk optical transitions of the gaps E_1 (3.4 eV) and E_2 (4.3 eV). As can be seen the calculated susceptibilities roughly reproduce these structures, though there are some small discrepancies. Despite the limitation of Kohn-Sham theory to ground-state properties, the band topology of valence and conduction bands are for most cases rather well represented by standard density-functional theory (DFT) calculations. Band gaps, however, are typically smaller than experimental data. As is well known, DFT—as usually applied—describes the ground state only, but band gaps are derived from excitational properties. The DFT band-gap problem is the main reason for the discrepancies between measured and calculated optical properties in Fig. 1.

A small but sharp optical-absorption peak is seen at $\hbar\omega=0.5$ eV in Im($\chi^{(1)}$) for the (2×1) reconstructed surface. According to the analysis of our calculated data this optical absorption has a strong anisotropy in the surface plane because Im($\chi^{(1)}_{yy}$) is much larger than Im($\chi^{(1)}_{xx}$) at this energy. Our calculated data agree well with the experimental and calculated results reported in Refs. 24–26, 28, and 29.

Data of a tight-binding calculation[25,26] indicate that the optical absorption at $\hbar\omega=0.5$ eV for (2×1) Si(111) is due to optical transitions between occupied and unoccupied surface states. Our *ab initio* results support this interpretation, because we have also found surface states with an energy gap of ≈0.5 eV formed along direction $\overline{JK}$ of the electronic band structure in Fig. 2(c). In Fig. 2 for the unreconstructed surface, small structures are seen in the range of $\hbar\omega$ from 0.5 to 2 eV. It is suggested to ascribe these structures to optical transitions of surface states due to the dangling bonds, because these states arise close to the Fermi level as shown in Fig. 2(a). Furthermore, transitions between this occupied (unoccupied) surface state and the corresponding unoccupied (occupied) bulk state are allowed. In the case of H/Si(111), no surface state in the band gap is created according to Fig. 2(b) and no distinct structure is seen in $\chi^{(1)}$ below 2 eV.

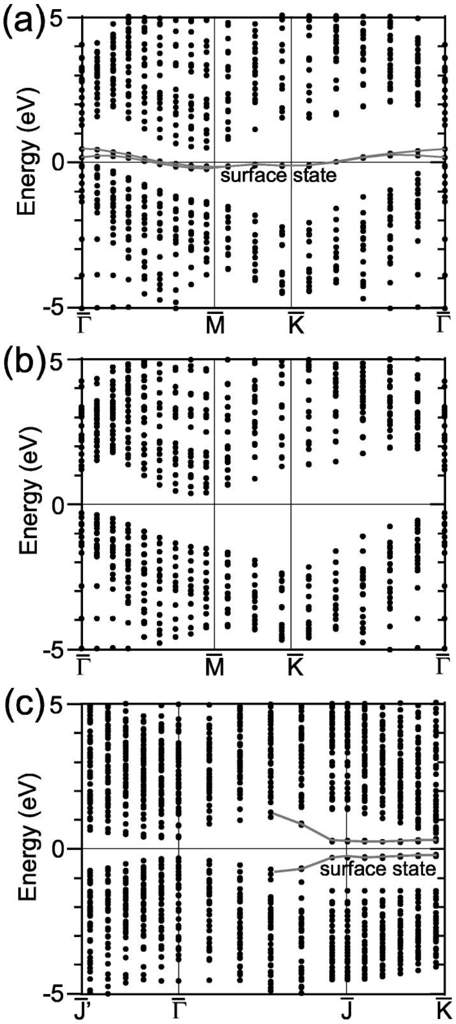

FIG. 2. Surface electronic band structures of (a) unreconstructed Si(111), (b) (1×1) H/Si(111), and (c) reconstructed (2×1) Si(111).

Summarizing the results for the linear optical properties, we conclude that correct surface states and reasonable linear optical properties of the studied Si(111) surfaces were obtained by the applied *ab initio* method. This check of reliability is important for the calculation of nonlinear optical properties.

B. Nonlinear optical properties

Calculated nonlinear optical susceptibility tensor components for the (1×1) Si(111) and H/Si(111) surfaces as a function of incident photon energy are presented by Fig. 3.[34] Components not shown are zero due to the selection rules of

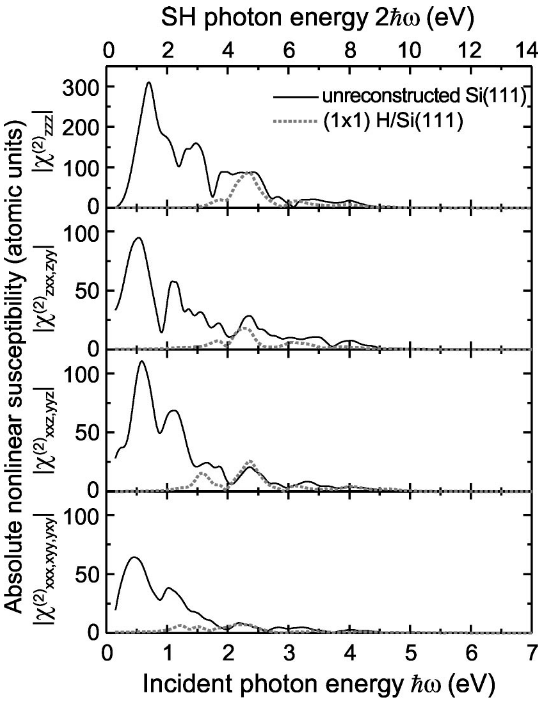

FIG. 3. Calculated nonlinear optical susceptibility tensor components $\chi^{(2)}_{ijk}$, $(ijk=xxx,xyy,yxy,xxz,yyz,zxx,zyy,zzz)$ as a function of the incident photon energy: unreconstructed Si(111)(solid lines) and (1×1) H/Si(111) surface (dashed lines). The unit of the vertical axis is Rydberg atomic units (Ref. 34).

the C_{3v} symmetry of the (1×1) surfaces.[35] The most remarkable feature of the calculated $\chi^{(2)}$ for the unreconstructed surface is the occurrence of large peaks in the range of $0.5<\hbar\omega<1.5$ eV which are not seen for H/Si(111). Referring to the calculated band structures shown in Fig. 2, we can say that the peaks below 2.0 eV in Fig. 3 result from resonant optical transitions associated with the surface states of the unreconstructed surface.

In Fig. 3, peaks near $2\hbar\omega=4.5$ eV are observed for both (1×1) surfaces. Since the intensity of these peaks is insensitive to the surface condition (i.e., clean or covered by H), these peaks are presumably due to the optical transition between bulk electronic states, namely a two photon transition in resonance with the bulk E_2 gap of 4.3 eV. However, within the dipole approximation SHG is forbidden in bulk Si because of its centrosymmetric crystal structure. The most likely explanation of this bulk resonance effect is the symmetry breaking of bulk states due to the presence of a surface. Another possible explanation could be a side effect of the $S(z)$ function described in the previous section. Since $S(z)$ breaks the inversion symmetry of the slab, the SHG signal from the central part of the slab (bulk region) may also be generated. At present, these two symmetry breaking effects are difficult to separate.

Gavrilenko *et al.* calculated the nonlinear susceptibility component $\chi^{(2)}_{zzz}$ of the unreconstructed Si(111) and H/Si(111) surfaces by applying a semiempirical tight-binding method.[18,19] According to their data a surface SHG peak at $2\hbar\omega\approx1.5$ eV arises for the clean surface, and the bulklike SHG peaks at $2\hbar\omega\approx4$ eV occur for both (1×1) cases. Our *ab initio* results agree qualitatively with these findings.

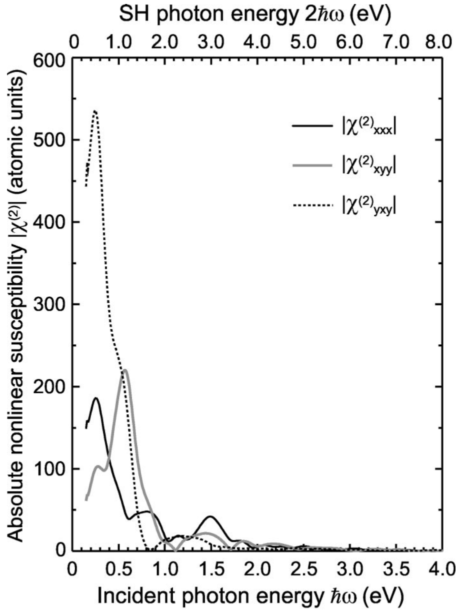

FIG. 4. Calculated nonlinear optical susceptibility tensor components $\chi^{(2)}_{ijk}$, $(ijk=xxx,\ xyy,\ yxy)$ as a function of the incident photon energy for (2×1) Si(111). The unit of the vertical axis is Rydberg atomic units (Ref. 34).

Figure 4 shows the incident photon energy dependence of $\chi^{(2)}_{xxx}$, $\chi^{(2)}_{xyy}$, and $\chi^{(2)}_{yxy}$ of the (2×1) Si(111) surface.[34] These components describe the nonlinear optical response with the incident and output electric field parallel to the surface. Peaks and shoulders of $|\chi^{(2)}|$ are seen at $\hbar\omega\approx0.25$ and 0.5 eV. These structures result from two-photon and one-photon resonances with surface states forming the energy gap shown in Fig. 2(c).

C. Polarization angle dependence of surface SHG

Heinz *et al.*[21] measured the SHG light intensity for (2×1) Si(111) as a function of the polarization angle of the normally incident pump beam having a photon energy of 1.17 eV. Their results are shown in Fig. 5(a), namely I_x and I_y corresponding to the SHG signal polarized along the $[2\bar{1}\bar{1}]$ and $[01\bar{1}]$ directions, respectively, and I_{total} being the total SHG signal. Under their experimental conditions, only the three components $\chi^{(2)}_{xxx}$, $\chi^{(2)}_{xyy}$, and $\chi^{(2)}_{yxy}$ are different from zero. The measured signals are defined by

$$I_{total}=I_x+I_y, \tag{5}$$

$$I_x=A\left\{|\chi^{(2)}_{xxx}|^2\cos^4\Theta+|\chi^{(2)}_{xyy}|^2\sin^4\Theta\right.$$
$$\left.+\frac{1}{2}\mathrm{Re}[\chi^{(2)*}_{xxx}\chi^{(2)}_{xyy}]\sin^2 2\Theta\right\}, \tag{6}$$

$$I_y=A|\chi^{(2)}_{yxy}|^2\sin^2 2\Theta, \tag{7}$$

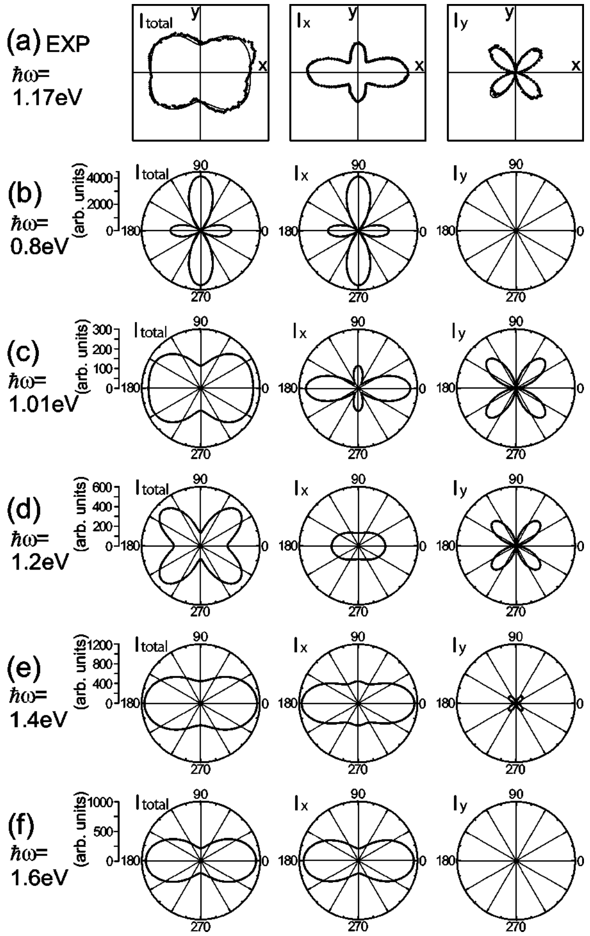

FIG. 5. SHG light intensity of reconstructed (2×1) Si(111) as a function of the polarization angle of the incident light: (a) experimental data of Ref. 21, (b)–(f) calculated patterns for several incident photon energies. I_x, I_y: SHG signal polarized along $[2\bar{1}\bar{1}]$, $[01\bar{1}]$, respectively. Total experimental intensity $I_{total}=I_x+I_y$. Note the agreement of the calculated patterns for $\hbar\omega=1.01$ eV with the experimental data.

where Θ is the polarization angle of the incident light with respect to the x direction, and A is a coefficient including Fresnel factors for incident and output fields. Heinz *et al.* carried out a least-square fit of the calculated values of Eq. (5) to the measured patterns in Fig. 5(a), and obtained the ratio of the three susceptibility components, $|\chi^{(2)}_{xxx}|:|\chi^{(2)}_{xyy}|:|\chi^{(2)}_{yxy}|=1:0.75:0.73$. By substituting our calculated complex susceptibility components into Eqs. (5)–(7), we obtained the SHG light intensity as a function of the polarization angle as shown in Figs. 5(b)–(f). These curves indicate that the calculated patterns, i.e., the anisotropy of the SHG response in the surface plane, depend drastically on the incident photon energy. In the energy range from 0.15 to 4.0 eV the calculated pattern agrees well with the measured one only at $\hbar\omega=1.01$ eV according to Fig. 5(c). At this energy the ratio of the calculated susceptibility components is 1 : 0.66 : 0.87 which is in reasonable agreement to the measured ratio. Since the incident photon energy of 1.01 eV in our Fig. 5(c) is close to the experimental value of 1.17 eV, we argue that our calculation reproduces the measured SHG response of (2×1) Si(111) very well. The difference of 0.16 eV of the two photon energies is probably due to the fundamental error of applying ground-state DFT as already discussed.

According to Eqs. (5)–(7) the phase of the complex nonlinear susceptibility components could affect the shapes of the polarization angle pattern considerably. Thus the agreement between the calculated and measured polarization angle patterns indicates the correctness of the phase of our calculated complex susceptibility tensor components.

IV. CONCLUSION

By the *ab initio* FLAPW method we calculated linear and nonlinear optical susceptibilities of unreconstructed Si(111), reconstructed (2×1)Si(111), and (1×1) hydrogen covered Si(111) surfaces. Our results for the linear optical response reproduce the measured bulk optical properties[27] and the surface optical absorption of the reconstructed surface.[24–26,28,29] The calculated nonlinear optical susceptibility of the unreconstructed Si(111) and H/Si(111) surfaces are consistent with previously reported semiempirical theoretical studies.[18,19] A polarization angle dependence of the SHG intensity was calculated by an *ab initio* approach, namely for the reconstructed (2×1) Si(111) surface, the results being in good agreement with experiment.[21] From the quality of our calculated data we conclude that both amplitude and phase of the complex nonlinear optical susceptibility for the Si(111) surface can be correctly described by an *ab initio* approach.

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