RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 43, NUMBER 14 15 MAY 1991-I

Surface-induced optical anisotropy of the Si(110) surface

G. P. M. Poppe, H. Wormeester, A. Molenbroek, C. M. J. Wijers, and A. Van Silfhout
University of Twente, Faculty of Applied Physics, P.O. Box 217, 7500 AE Enschede, The Netherlands

(Received 6 December 1990; revised manuscript received 25 January 1991)

The reflectance-anisotropy spectrum of a hydrogen-covered Si(110) surface is calculated taking into account anisotropic surface polarizabilities and exactly solved local-field effects. Including in the calculation the most important features of the (2×1) and (5×1) reconstructions, i.e., the missing chains along the [001] direction, it is clearly demonstrated that the shape of anisotropic reflectance spectra is extremely sensitive to local-field effects. The agreement between the measured spectrum of the oxidized surface and the calculated spectrum of the (5×1) reconstruction is striking as far as the order of magnitude, peak positions, and relative peak intensities are concerned.

Surface-induced optical anisotropy (SIOA), the anisotropic optical reflection at particular surfaces [especially (110)] of cubic crystals has become an important tool in the study of semiconductor surfaces.[1-4] Since the bulk optical response of such crystals is mainly isotropic, the effect originates from structural and electronic differences between bulk and surface region due to the lowering of the symmetry at the surface. As such SIOA is a valuable expedient in the characterization of the geometric and electronic structure of surfaces, which was shown clearly by Del Sole and Selloni,[5] in clarifying the actual reconstruction of the Si(111) 2×1 surface. However, the theoretical interpretation of the measured reflectance-anisotropy (RA) spectra is still far from completed. This is demonstrated by the unresolved discussion about the origin of the RA spectrum of the naturally oxidized and hydrogen fluoride etched Si(110) surface as measured by Aspnes and Studna.[1] Their experimental data exhibit an extensive anisotropy in the above-band-gap region despite the presence of a native oxide layer. This implies that one has to be careful with the usual assumption that the oxidized Si surface does not show any anisotropy.[6] They conclude from their measurements that about $\frac{2}{3}$ of the intrinsic contribution to the RA is due to surface many-body screening effects, while $\frac{1}{3}$ is due to bulk spatial dispersion. However, this conclusion is based on a fitting procedure, which assumes mutual independence of all contributions considered and which overestimates the bulk contribution to the anisotropy as we will show. A different interpretation of this oxidized RA spectrum has been given by Mochán, Tarriba, and Barrera,[7] who performed a calculation of the RA spectrum of Si(110) using a model of bulk-like point polarizable entities. They obtained an anisotropy spectrum giving the right order of magnitude and conclude from this that the surface local-field effect is the most important source of optical anisotropy in Si(110). Using tight binding Selloni, Marsella, and Del Sole[8] showed that in the random-phase approximation the optical matrix elements for a hydrogen covered Si(110) surface give rise to an anisotropy in the surface dielectric constant, yielding an effect on the RA signal of the same order of magnitude as that due to the surface local-field effect. In this Rapid Communication, we will show the result on the RA spectrum combining this latter effect with the local-field effect.

All above-mentioned theoretical attempts to describe the experimentally measured RA signal of the oxidized Si(110) surface, implicitly assume that the SIOA can be reproduced by taking the geometry of the unreconstructed Si(110) surface. We will show explicitly that taking into account the effect on the local field of a change in surface reconstruction, does influence the line shape. This is done by using the discrete dipole approach along the lines developed in Refs. 9-11. The effect of the reconstruction of the Si(110) surface is calculated by applying the reconstruction model proposed by Wormeester and Keim (WK).[12,13] We will hereby concentrate on the effect of the missing chains, whose existence was first reported in the scanning-tunnel microscope (STM) measurements of Becker, Swartzentruber, and Vickers[14] on the (5×1) reconstructed surface, and are also observed in the STM measurements of the (4×5) reconstructed surface.[15] The distribution of missing chains in the [001] direction is, in view of the WK model, the main reason for the observation of various periodicities at the surface in this direction reported by Olshanetsky and Shklyaev.[16] In our modeling of the WK reconstruction, we will not take into account the ad atoms and rest atoms present at the surface.

In order to perform the calculations with our model,[11] we have to specify the geometry of the semi-infinite Si crystal and the polarizability of its constituents. The crystal will be represented by dipoles, each corresponding to two neighboring Si atoms. The dipoles are represented by a polarizability $\hat{\alpha}_S(\omega)$ for the three outermost layers, whereas the others are characterized by a polarizability $\hat{\alpha}_B(\omega)$. The polarizabilities of the Si-Si dipoles in the case of reconstruction are taken the same as in the unreconstructed case. These polarizabilities are calculated by means of the Lorentz-Lorenz relation from the bulk and surface dielectric constants.[17] The dielectric constants in the bulk and surface region are derived from a tight binding RPA calculation of the electronic states of a silicon slab consisting of 18 atomic layers along the [110] direction.[8] This silicon slab is covered with H atoms in order to saturate the dangling bonds and to mimic an oxidized surface as in Ref. 8. Apart from their effect on the polarizability of the Si atoms in the surface region, the H atoms themselves are not taken into account in our modeling of the silicon surface.

In Fig. 1 the three geometries which will be used are depicted schematically. It is clear that the only difference between the three surfaces can be found in the top layer. The fact that the reconstructed surfaces have missing chains is described in our model by the size of the two-dimensional surface unit cell and the number of characteristic dipoles in this cell. Through the parallel translational symmetry[11] this builds a surface lattice with missing chains. The two-dimensional lattice of the top layer of the Si(110) surface is spanned by the vectors:

$$\mathbf{s}_1 = a\hat{\mathbf{x}}, \quad \mathbf{s}_2 = a\sqrt{2}\beta\hat{\mathbf{y}} ,$$

with $a\sqrt{2}$ being the Si bulk lattice constant and β will be 1, 2, or 5, for the unreconstructed, (2×1), or (5×1) reconstructed surface, respectively. All unit cells contain one characteristic dipole at their origin, but the (5×1) reconstructed surface cell has two more characteristic dipoles situated at a distance of $a\sqrt{2}$ and $3a\sqrt{2}$ in the $\hat{\mathbf{y}}$ direction relative to the origin. The geometry of the bulk layers is the one given in Ref. 10.

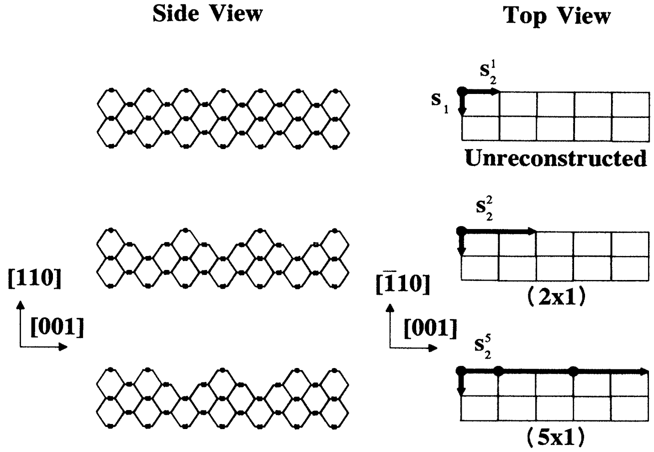

FIG. 1. Side and top view of the geometry of the Si surfaces considered. Vectors $\mathbf{s}_1$ and $\mathbf{s}_2$ span the two-dimensional lattice of the top layer. Upper index of $\mathbf{s}_2$ denotes specific reconstruction. 1, unreconstructed; 2, (2×1) and 5, (5×1) reconstructed; Si(110).

The model we use[11] is based on the discrete-dipole approach. It establishes a link between surface and bulk optical response using a projection technique. Through this, it matches the real-space approach of the surface (as established by Wijers and co-workers[9,10]) to the reciprocal space approach of the bulk (as established, in principle, by Litzman and Rózsa[18]). This approach has the advantage that we can deal with the three effects which we focus upon: anisotropic polarizabilities, local field effects, and the influence of the actual reconstruction in an integrated way. From Ref. 11 it follows that the expression for the reflection coefficient r in this model is given by

$$r = \left(\frac{ik^2}{2\epsilon_0 \beta k_z a^2} \right) \left(\frac{\mathbf{E}_0 \cdot \mathbf{P}^R}{|\mathbf{E}_0|} \right) , \tag{1}$$

$$\mathbf{P}^R = \sum_{j=1}^{N_S} e^{-i\underline{\mathbf{k}}\cdot\mathbf{r}_j}\mathbf{p}_j + e^{ik_z d_S} \sum_{m=1}^{2} \left(\sum_{w=1}^{N_B} \frac{\exp[i(k_z+q_m)z_w^B]}{1-\exp[i(k_z+q_m)d_B]} \right) v_m \mathbf{u}_m , \tag{2}$$

where $\mathbf{r}_j$ is the position vector of the jth surface dipole $\mathbf{p}_j$, z_w^B the z coordinate of the wth bulk dipole with respect to the origin of the first bulk cell, d_S the thickness of the first surface cell, d_B the thickness of the bulk cell, and βa^2 the area of the two-dimensional surface unit cell; q_m is the normal-mode wave number, $\mathbf{u}_m$ the normal-mode vectors, and v_m the normal-mode coefficients. $\mathbf{k} = (\mathbf{k}_\parallel, k_z)$ is the wave vector of the incident light of field strength $\mathbf{E}_0$ and $\underline{\mathbf{k}} = (\mathbf{k}_\parallel, -k_z)$. With this definition we can calculate $\Delta R/R$ both for the unreconstructed and reconstructed Si(110) surface. ΔR is defined as $\Delta R = R_{90} - R_0$, with R_0 (R_{90}) the reflectance for light polarized along the [001] ([$\bar{1}$10]) axis; R is the average value of R_{90} and R_0. The result is depicted in Fig. 2 and the influence of the local field as a result of the different reconstructions is obvious. The RA spectrum has changed entirely as to the absolute and relative intensities of the features present. The peak positions have changed partly. The most profound difference is the domination of the unreconstructed RA spectrum by a strong peak at about 3.2 eV, in contrast to the two reconstructed surfaces which exhibit their major peak at about 4.4 eV. The agreement between the experimental curve of Aspnes and Studna[1] and the calculated RA spectrum of the (5×1) reconstructed surface is striking as far as peak positions and relative peak intensities is concerned. This is illustrated in Table I. It is however difficult to draw conclusions from this agreement as the experimental spectra were obtained from oxidized or HF etched Si(110) surfaces whose reconstruction was not established. Furthermore, the question remains to what extent the hydrogen terminated surface can mimic the surfaces in Refs. 1 and 8. The fact that the experiments do not show a large difference in RA signal between the oxidized, the buffered hydrogen fluoride (BHF) stripped and the BHF stripped Br_2 covered surface, suggests however that the specific terminating species has no large influence.

We also investigated the contribution of bulk spatial dispersion to the RA. This was done by repeating the calculation for unreconstructed Si and extending the normal-mode decomposition up to the very surface, thus suppressing surface local-field effects. Throughout this whole region the bulk polarizability was used. This calculation indeed proves that the bulk anisotropy, yielding an RA signal of 10^{-4}, accounts for only about 1% of the measured RA (Fig. 3). On top of that we have added an

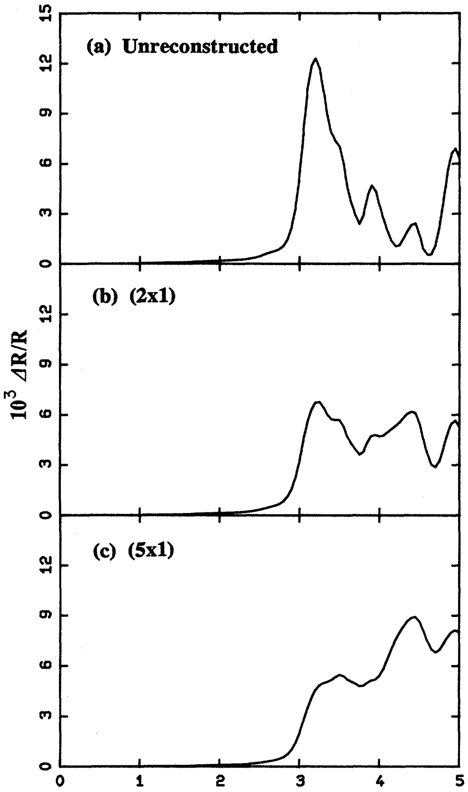

FIG. 2. Anisotropic reflectance vs photon energy for the 3 reconstructions of Fig. 1.

artificial anisotropy in the bulk polarizability of the order of magnitude given in Ref. 19:

$$\alpha^B_{xx}=\alpha^B+\delta,\ \ \alpha^B_{yy}=\alpha^B-\delta\,,$$
$$\delta=\left(\frac{\gamma-\alpha^B}{6\gamma}\right)^2 1.1393492k^2,\ \ \gamma=\frac{3\sqrt{2}}{4\pi N_B}\,, \tag{3}$$

(with α^B_{xx}, α^B_{yy} the xx and yy components of the bulk polarizability, α^B the zz component of the bulk polarizability, k the wave number of the incoming electromagnetic field, and N_B the number of characteristic dipoles in the bulk unit cell, in this case 2), but this appears to be a negligible correction to the bulk anisotropy. Therefore, the claim of Aspnes and Studna[1] that bulk spatial dispersion is responsible for $\frac{1}{3}$ of the anisotropy signal, cannot be sustained.

TABLE I. Comparison between the experimental reflectance anisotropy spectrum of Ref. 1 and the theoretical one calculated in this work.

	Ref. 1	This work
Peak positions first	3.39 eV	3.55 eV
Peak positions second	4.25 eV	4.45 eV
Relative peak intensity	0.654	0.640

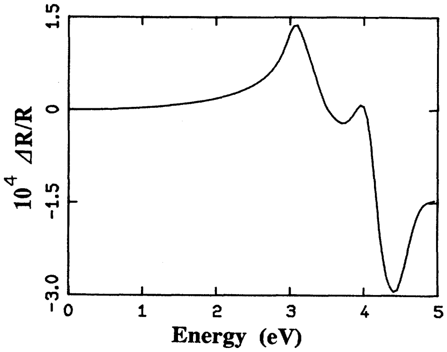

FIG. 3. Bulk contribution to the anisotropic reflectance vs photon energy.

From the fact that the bulk hardly contributes to the RA we can deduce what the origins are of the anisotropy signal. We calculate $\delta(\Delta R)$, the difference in ΔR between the unreconstructed (u) and the (5×1) reconstructed (r) case. Here we consider only the first three layers as the surface region of the semi-infinite crystal, since they have a polarizability different from the bulk. We can then define $\mathbf{P}_S$ ($\mathbf{P}_B$) as an effective surface (bulk) dipole moment such that the total dipole strength of the semi-infinite crystal can be written as: $\mathbf{P}=\mathbf{P}_S+\mathbf{P}_B$. Since the bulk hardly contributes to the anisotropy signal (see Fig.3) we put both the x and y components of $\mathbf{P}_B$ equal to P_B. The surface dipole moment can be written as $\mathbf{P}_S=\overleftrightarrow{\alpha}_S\cdot\mathbf{E}_{\mathrm{loc},S}$ where $\mathbf{E}_{\mathrm{loc},S}$, is defined as the average surface local field. Finally we put

$$\Delta E_{\mathrm{loc},y}=\Delta E-\delta E,\ \ \Delta E_{\mathrm{loc},x}=\Delta E+\delta E\,,$$

where $\Delta E_{\mathrm{loc},y(x)}$ is the difference in the average surface local field between the unreconstructed and reconstructed surface, for the 0° (90°) case; for the square of the local-field components an analogous relation holds. Through the expression of the reflection coefficient given in Ref. 11 we can then write:

$$\begin{aligned}\delta(\Delta R)&=\Delta R^{(u)}-\Delta R^{(r)}\\&=\mu\{(\alpha^2_{yy}-\alpha^2_{xx})\Delta E^2+2\,\mathrm{Re}[(\alpha_{yy}-\alpha_{xx})\Delta E P^*_B]\\&\quad+(\alpha^2_{yy}+\alpha^2_{xx})\delta E^2+2\,\mathrm{Re}[(\alpha_{yy}+\alpha_{xx})\delta E P^*_B]\}\,,\end{aligned} \tag{4}$$

where $\alpha_{yy(xx)}$ is the yy (xx) component of the surface polarizability, μ is a scalar, $*$ denotes the "complex conjugate of," and Re means "the real part of." The quantities ΔE, δE and ΔE^2, δE^2 are smooth functions of the photon energy $\hbar\omega$ and do not have any nodes. Numerical calculations show that the modulation of the peaks in the RA spectra of the different reconstructions is determined by the first term in (4), so by the sign of $(\alpha^2_{yy}-\alpha^2_{xx})$. This can clearly be seen in Fig. 4 where we compare this quantity to $\delta(\Delta R)$. The two curves show a striking analogy and certainly at the photon energies where the peaks in the $\Delta R/R$ curve occur (see Fig. 1) the signs are equal. The amount by which this change will occur is determined by the value of the difference in polarizability as well as

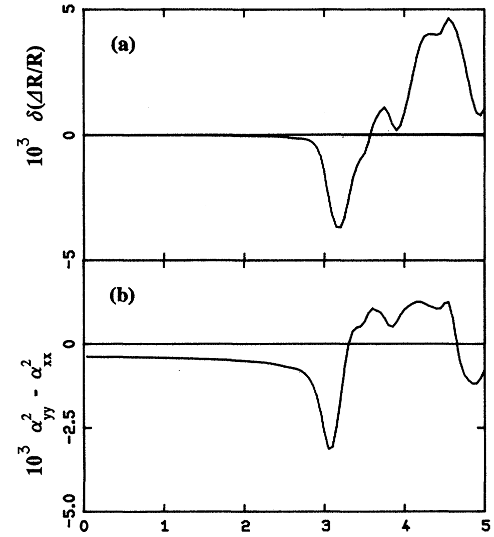

FIG. 4. Comparison between $\delta(\Delta R)$, the difference in ΔR between unreconstructed and (5×1) reconstructed case (upper figure) and $\alpha_{yy}^2 - \alpha_{xx}^2$ (lower figure, see text).

by the strength of the surface local field. Because of this and because of the small contribution the other terms in (4) give, the energy at which there is no change in ΔR is higher than the energy where $\alpha_{yy}^2 - \alpha_{xx}^2$ equals zero.

So, we have calculated the reflectance anisotropy spectrum of some H covered Si(110) surfaces, taking into account all local-field effects in an exact way as well as the anisotropic polarizability of the surface atoms. We found that by including into the calculation the most important feature of various possible reconstructions of this surface, i.e., the distribution of missing chains, the calculated line shapes are influenced drastically as well as the positions and intensities of the dominating peaks. The best reproduction of the experimentally measured spectrum[1] as far as photon energy and relative intensities are concerned is obtained by assuming a (5×1) reconstructed surface.

We believe that in order to be able to make a good comparison between the theoretical and experimental spectra, RA spectra of a well-defined surface, as the clean (5×1) reconstructed Si(110) surfaces should be measured. On the other hand the calculated RA spectra in this paper have the following shortcomings. First of all, we have used the same polarizabilities for the reconstructed and unreconstructed surfaces. One can expect that the polarizabilities will be influenced by the specific reconstruction. A critical discussion of the intrinsic shortcomings of the calculation of the polarizabilities as such can be found in Ref. 17. Finally we did not include the effect of surface screening[20] on the RA spectrum. In future calculations, these issues will be further investigated. The difference in RA between the possible configurations at the interface makes this type of optical probe an excellent diagnostic instrument of interface properties. Due to the general outline of the model and its sensitivity to structural changes it is not limited to the optical behavior of the very surface, but it is also able to include the effect of buried interfaces up to a depth comparable to the wavelength of light.

We would like to thank Professor Rodolfo Del Sole of the Rome II University for letting us use his surface dielectric constant data for Si(110):H.

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