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Microscopic calculation of the surface contribution to optical reflectivity: Application to Si

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A microscopic calculation of the surface optical properties of Si(111) and Si(110) within the random-phase approximation is presented. Surface effects on optical matrix elements are found important in order to explain the anisotropic reflectance observed at surfaces of cubic semiconductors. At frequencies above the bulk indirect gap, a large contribution to differential reflectivity turns out to be related to the structural changes occurring upon oxidation.

The optical properties of surfaces have recently attracted strong interest, in particular after the measurement of anisotropic reflectance in cubic semiconductors.[1-3] Since the bulk properties of cubic materials are isotropic, any observed anisotropy must be related to the lower symmetry of the surface. A large subgap anisotropy has been found in differential reflectivity measurements on the clean Si(111)2×1 surface,[1] arising from transitions between surface states. Anisotropic above-gap structures are also present.[2] In this case, it is not *a priori* obvious to what extent these structures are related to surface states, rather than to surface modulation of bulk transitions. Actually an intrinsic anisotropy has been measured for naturally oxidized Si(110) and Ge(110) surfaces[3] where no optically active surface state is expected in the frequency range of interest. This anisotropy has been interpreted as arising from surface many-body effects,[3,4] i.e., the surface is assumed to have the same isotropic polarizability as the bulk, but responds to different local fields for different light polarizations as a consequence of the low symmetry of the (110) surfaces. In the following we show that the anisotropy of the surface polarizability itself—as induced by the microscopic structure of the first (few) layer(s)—gives rise to effects of the same order of magnitude as that of those previously considered.[4]

The purpose of this Rapid Communication is to present a realistic calculation of the surface optical properties of semiconductors that fully accounts for the microscopic structure of the surface. For the sake of simplicity we shall neglect excitonic and local-field effects. Our calculation is therefore complementary to that of Mochan and Barrera.[4] Here we present results for the clean Si(111)2×1 surface—reconstructed according to Pandey's π-bonded chain model[5]—and for the H-covered Si(111) and Si(110) surfaces. We identify four mechanisms contributing to surface optical properties: (i) Transitions involving surface states, which completely determine the reflectivity below the indirect bulk gap; (ii) indirect bulklike transitions allowed by the breakdown of the $k_z'=k_z$ selection rule (z is the direction normal to the surface); (iii) surface effects on optical matrix elements (i.e., the oscillator strength of bulklike allowed transitions may change near the surface). These effects lead to an anisotropic reflectance at surfaces of low symmetry, such as Si(110), even in the absence of surface states and of local-field effects; (iv) the effect of reconstruction. The folding of bulk bands on the Brillouin zone of the 2×1-reconstructed surface allows transitions which are forbidden in the infinite crystal.

Each of these mechanisms is found to yield a contribution of the order of 1% to the reflectance. In particular, we show that mechanism (iii) gives a relevant contribution to the anisotropic reflectance of Si(110). It must be taken into account, together with the local-field effect,[4] in any quantitative description of the measured anisotropy. In the case of Si(111)2×1, we find an anisotropic reflectance in good agreement with experiment, which confirms the validity of the π-bonded chain model.[5] We also show that the measured differential reflectance above the indirect gap contains a substantial contribution (more than 50%) not directly related to surface states, but rather to reconstruction via mechanisms (iii) and (iv). This implies that above-gap differential reflectivity measurements do not directly yield the spectrum of surface states.

Calculations are performed within the random-phase approximation (RPA) with the neglect of local-field effects. For the electronic structure we use the semiempirical tight-binding scheme of Vogl, Hjalmarson, and Dow,[6] with a five-orbital-(sp^3s^*) per-atom basis set, which has been extensively tested in calculations of bulk and surface electronic states.[7] For the hydrogenated surfaces, the tight-binding parameters describing the H $1s$ orbital and its interactions with Si are those of Ref. 8. The matrix elements of the momentum operator between atomic orbitals—needed to evaluate optical properties—are computed according to $\mathbf{p}=i(m/\hbar)[H,\mathbf{r}]$ and expanding the commutator on the (approximately) complete sp^3s^* basis set. Only intra-atomic matrix elements of $\mathbf{r}$ are retained, with the values $\langle s|x|p_x\rangle=0.2$ Å and $\langle s^*|x|p_x\rangle=1$ Å, which allow quite a good description of bulk optical properties. Silicon slabs of both 12 and 18 atomic layers are considered. Optical properties are found to be basically indentical for the two cases. This *a posteriori* justifies the use of a slab to mimic a semi-infinite crystal.

The surface contribution to reflection of normally incident light polarized along the α direction by a semi-infinite crystal is[9]

$$(\Delta R_\alpha/R_0)=4(\omega/c)\mathrm{Im}\{\Delta\epsilon_{\alpha\alpha}(\omega)/[\epsilon_b(\omega)-1]\} \quad . \tag{1}$$

Here $\Delta R_\alpha=R_\alpha-R_0$ is the difference between the actual reflection coefficient R_α, including surface effects, and R_0 given by the Fresnel formula; $\epsilon_b(\omega)$ is the bulk dielectric constant; and

$$\Delta\epsilon_{\alpha\alpha}(\omega)=\int_{-\infty}^{\infty}dz\int_{-\infty}^{\infty}dz'[\epsilon_{\alpha\alpha}(z,z';\omega)-\delta(z-z')]$$
$$-\int_{-\infty}^{\infty}dz\int_{-\infty}^{\infty}dz'\int_{-\infty}^{\infty}dz''\int_{-\infty}^{\infty}dz'''\epsilon_{\alpha z}(z,z';\omega)\epsilon_{zz}^{-1}(z',z'';\omega)\epsilon_{z\alpha}(z'',z''';\omega)\ , \tag{2}$$

where $\epsilon_{\alpha\beta}(z,z';\omega)$ is the microscopic dielectric tensor of the vacuum-crystal interface at $\mathbf{q}_{\parallel}=0$. The first integral in (2) can be computed from slab wave functions in a straightforward way. The second fourfold integral—which vanishes by symmetry for all the cases considered, except for Si(111)2×1 with light polarized along $[\bar{2}11]$—is here estimated within the three-layer model,[10] assuming a surface-layer thickness $d_s=3.5$ Å and 5 Å for the clean and H-covered surfaces, respectively. The resulting values turn out to be very small, at most 10% of the first term. Transitions up to $\hbar\omega=8$ eV have been included in the calculation of the imaginary part of (2). As a consequence, the Kramers-Kronig transform, yielding the real part, becomes inaccurate for $\hbar\omega>4$ eV.

We now turn to the results of our calculations and consider first the case of the Si(111) surface. The simplest geometry we discuss is the ideal surface covered by one monolayer of hydrogen, each H atom being on top of the first-layer Si atoms. For this surface the contributions to reflectivity due to surface states, geometric anisotropy, and reconstruction, are not present. The percent deviation of reflectance from the classical Fresnel formula $\Delta R/R_0$ computed for an 18-layer slab, is plotted in Fig. 1(a). The main features of this curve can be understood in terms of mechanism (ii), i.e., the breakdown of the $k_z'=k_z$ selection rule. The onset of surface-induced indirect transitions is at 2.5 eV, corresponding to transitions from $\Gamma_{25'}$ to L_1, which are allowed since the Λ line is normal to the surface. The oscillator strength of transitions occurring along the Λ line is spread over a larger energy range than in the bulk, where they give rise to a steep increase of the absorption between 3 and 3.5 eV. The intensity of the E_1 peak, arising from $L_{3'}\rightarrow L_1$ transitions, is therefore reduced. This gives rise to the negative peak of $\Delta R/R_0$ at 3.5 eV. A similar spreading occurs also for the E_2 structure at 4.3 eV ($X_4\rightarrow X_1$ transitions).

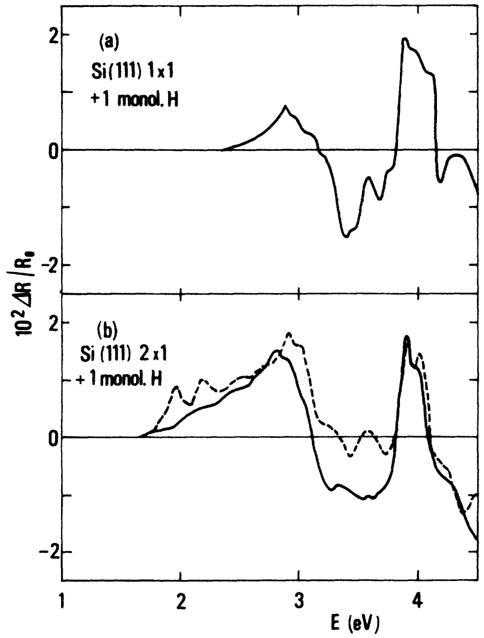

FIG. 1. (a) Calculated percent deviation from the Fresnel formula of the normal incidence reflectance of the ideal Si(111) surface, covered by one monolayer of atomic hydrogen. (b) Same as above for the H-covered Si(111)2×1 surface. Full line: light polarized along $[1\bar{1}0]$ (y); dashed line: light polarized along $[11\bar{2}]$ (x).

We next consider the clean (111) Si surface.[11] The contribution to reflectivity of dangling-bond (DB)-like surface states can be singled out by considering the difference between the clean-surface reflectivity and that of the hydrogenated surface, when hydrogen just saturates the DB's but the 2×1 structure is retained. This difference is shown in Fig. 2 for x (perpendicular to the chains, i.e., along $[11\bar{2}]$) and y (parallel to the chains, i.e., along $[1\bar{1}0]$) polarizations. A strong peak at 0.6 eV—arising from transitions along the $\bar{J}\bar{K}$ edge of the surface Brillouin zone (SBZ)— is present for y and not for x polarization, in agreement with the experiment[1] (where the peak occurs at 0.45 eV). In contrast, the smaller structure—more pronounced for x polarization—at about 1 eV is an artifact of our tight-binding approach. It is indeed related to the gap between DB-like surface states along $\bar{\Gamma}\bar{J}'$, which is known to actually have a value of about 2 eV.[12,13] The other features in Fig. 2 are quite small, and probably arise both from transitions between DB-like and band states, and from small changes in matrix elements, induced by the presence of hydrogen. [Some noise is also present, due to the limited number (64) of k points used in the calculations.]

$\Delta R/R_0$ for the H-covered Si(111)2×1 surface is shown in Fig. 1(b). Mechanisms (ii)-(iv) are all present in this case. As a consequence of the folding of the bulk Brillouin zone, the onset of indirect transitions moves down to 1.8 eV. It is clear that the anisotropy above the indirect bulk gap is not

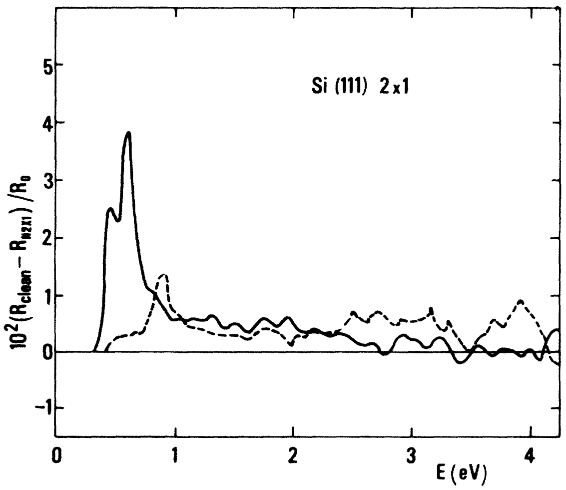

FIG. 2. Differential reflectivity of Si(111)2×1 calculated as the difference between the clean and H-covered 2×1 surface reflectivities. Full line: y polarization; dashed line: x polarization.

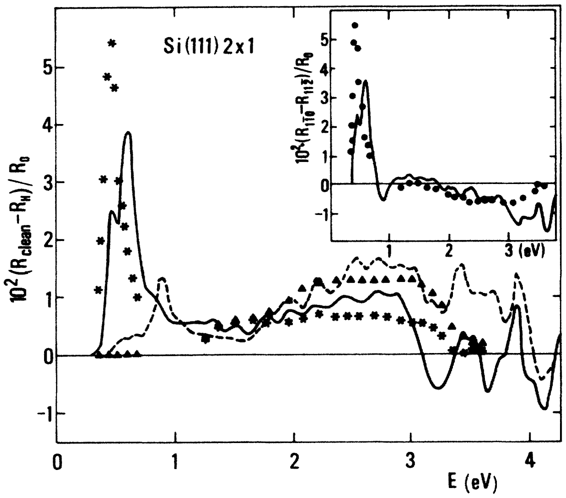

FIG. 3. Same as Fig. 2, but with a 1×1 ideal structure for the H-covered surface. Stars and triangles are experimental results (Ref. 2) for y and x polarizations, respectively. Inset: reflectance anisotropy $(\Delta R/R)_y-(\Delta R/R)_x$. Full line: calculation; dots: experimental results.

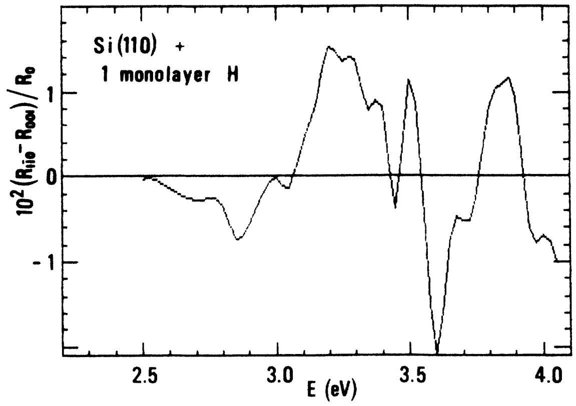

FIG. 4. Calculated normal incidence reflectance anisotropy, $(\Delta R/R)_{1\bar{1}0}-(\Delta R/R)_{001}$, for the H-covered Si(110) surface.

related to DB-like surface states, not present here, but to the anisotropic structure of the reconstructed surface.

Figure 2 is not very meaningful for the purpose of comparison with experiment, since the isotropic reflectivity of a 1×1 oxygen-covered surface was subtracted in that case.[1,2] A more realistic choice is to consider the difference between the reflectivities of the 2×1 clean surface and the H-covered Si(111)1×1 ideal surface. In particular, the reflectance anisotropy of the clean surface is not affected by subtraction of any isotropic background. The results of this calculation are shown in Fig. 3. The structures of Figs. 2 and 3 are very similar up to about 1.5 eV, confirming that they originate from DB-like surface states. Large differences occur instead in the range of 2–4 eV, where the structures in Fig. 3 are about a factor 3 stronger than in Fig. 2. A substantial contribution to the differential reflectivity of Fig. 3 in the range of 2–4 eV arises therefore from the difference between $\Delta R/R_0$ for the H-covered (111)1×1 and (111)2×1 surfaces. This difference is not related to surface states but is of structural origin [mechanisms (iii)–(iv)]. It is probably so large because of the strong surface rearrangement occurring in the π-bonded chain model.

The results of Fig. 3 are in overall qualitative agreement with experiment[1,2] and well account for the observed difference between x and y reflectivities (see inset). A more quantitative agreement would most probably require both a more accurate electronic structure calculation and the inclusion of excitonic and local-field effects. Such effects should be of minor importance for the 0.5-eV peak,[14] but may be relevant in the above-gap region.[4] The most important conclusion which can be inferred from the results of Fig. 3 is that differential reflectivity structures above the bulk indirect gap—usually attributed to transitions involving surface states—actually contain a large contribution of other transitions, yielding information not directly related to surface states, but rather to surface geometry.

In order to understand the origin of the anisotropic reflectance measured at the oxydized Si and Ge (110) surfaces,[3] we performed calculations for ideal (110) Si slabs, with dangling bonds saturated by H atoms. The use of such a simplified model should be justified, since experiments performed on naturally oxydized and Br^2-stripped surfaces give rather similar results. This implies that the reflectance should not depend significantly on the adsorbed species. In Fig. 4 we show the calculated anisotropy in the surface plane, i.e.,

$$(\Delta R/R_0)_{1\bar{1}0}-(\Delta R/R_0)_{001} \; .$$

It appears that the geometrical anisotropy of the surface alone [mechanism (iii)], even in the absence of surface states and reconstruction, can give rise to an anisotropy of the order 1%. This is not related to surface many-body effects,[4] but to the effect of the low symmetry of the (110) surface on wave functions and optical matrix elements. Our results are in fair agreement with experiment for order of magnitude and line shape, except for the negative reflectance difference between 3.5 and 3.8 eV, which is not present in the experiment.

In conclusion, we have performed a realistic calculation of the surface contribution to the reflectance of semiconductors, within RPA. We have identified, in addition to transitions involving surface states, a number of mechanisms giving rise to 1% changes of reflectivity. One of these, namely, the effect of the anisotropic geometry of the surface on optical matrix elements, should be taken into account, together with the local-field effect, to explain the anisotropic reflectance measured at low-symmetry surfaces of cubic semiconductors. We have found that such mechanisms also give a substantial contribution to the differential reflectivity of Si(111). At frequencies above the bulk gap the latter is not only related to surface states, but also to the structural changes of the surface upon oxidation.

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