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Local-field effects on the reflectance anisotropy of Si(110):H

R. Del Sole
Dipartimento di Fisica, II Università di Roma "Tor Vergata," via E. Carnevale, I-00173 Roma, Italy

W. L. Mochan
Laboratorio de Cuernavaca, Instituto de Fisica, Universidad National Autónoma de México,
Apartado Postal 139-B, 62191 Cuernavaca, Morelos, Mexico

R. G. Barrera
Instituto de Fisica, Universidad National Autónoma de México,
Apartado Postal 20-364, 01000 México, Districto Federal, Mexico
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We present calculations of the optical properties of a hydrogenated (110) Si surface, including the surface-induced changes of the electron polarizability and the changes in the local-field effect. While the surface local-field effect alone yields results in good agreement with reflectance anisotropy experiments performed on natural surfaces, the polarizability changes give rise to substantial modifications of the anisotropy spectra. The origin of the difference between the optical properties of surfaces with dissimilar terminations is discussed.

I. INTRODUCTION

The measurement of the reflection anisotropy of cubic materials is an important tool for the investigation of surface structure.[1-6] Since the bulk optical properties of cubic crystals are isotropic, any observed anisotropy must be related to the lower symmetry of the surface. Some of these anisotropies are due to surface states and surface reconstruction.[2] However an intrinsic reflectance anisotropy (RA) has also been measured for the natural (110) surfaces of Si and Ge,[1] where no optically active surface state is expected in the frequency range of interest. It was proposed a few years ago that this anisotropy arises from the surface local-field effect.[7] More specifically, the surface is assumed to have the same isotropic polarizability as the bulk, but to respond to different local fields for different light polarizations. This yields a calculated RA in good agreement with experiment. It has been successively suggested, however, that a concurring reason for RA may be the anisotropy of the surface polarizability itself, arising from the reduced surface symmetry at Si and Ge (110). A tight-binding random-phase-approximation (RPA) calculation for Si(110):H shows indeed that the latter effect gives a RA of the same order of magnitude as that due to the local-field effect.[8] The resulting line shape is substantially different from that of the natural (110) Si surface.

In this paper we present calculations which take into account both effects, intrinsic anisotropy and local fields. We find that the surface local-field effect qualitatively modifies the RPA line shape and makes it more like that corresponding to the natural surfaces. The difference however is still considerable, showing the great sensitivity of reflectance anisotropy spectroscopy to the surface termination.

II. THEORY

We first recall the theory of the surface local-field effect. In the presence of a long-wave disturbance, the crystal response can be represented by the induced polarization $P(r)$, which is related to the perturbing field by the polarizability tensor.[9] This can be calculated from linear-response theory within various approximations, which basically differ for the different partitioning of the total Hamiltonian into zero-order Hamiltonian and perturbation.[10]

A convenient approach is to include only Coulomb (longitudinal unretarded) electron-electron interactions in the zero-order Hamiltonian,[11] letting the perturbing field account for the induced transverse electric field. In this case the excitations of the unperturbed system (called "Coulomb excitons" in Ref. 10) included longitudinal collective modes, i.e., plasmons, but not transverse polaritons. These are generated by the interaction with light, or, in mathematical terms, by the solution of Maxwell's equations for the perturbing field in the presence of the crystal polarization.

A simpler approach, however, consists in removing the long-range (small-k) Coulomb interaction responsible for plasmons from the zero-order Hamiltonian. The excitations of the unperturbed system (called "mechanical excitons" by Agranovich and Ginzburg[10]) do not include any collective excitations, which are recovered after solution of the complete set of Maxwell's equations for the perturbing field.

Once the small-k part of the Coulomb electron-electron interaction has been removed from the zero-order Hamiltonian, a long-range many-body effect still survives, namely the dipole-dipole interaction, which is responsible for the local-field effect. In the case of a cubic array of point dipoles, this is described by the Lorentz-Lorenz formula:

$$\epsilon_M(\omega)=1+[4\pi\alpha(\omega)/\Omega]/[1-(4\pi/3\Omega)\alpha(\omega)] \ , \quad (1)$$

where ϵ_M is the macroscopic dielectric constant, $\alpha(\omega)$ is the dipole polarizability, and Ω is the cell volume.[12] This equation can be interpreted as the response $\alpha(\omega)/\Omega$ of a system, whose zero-order Hamiltonian does not include the dipole-dipole interaction, to the local field $E/[1-(4\pi/3\Omega)\alpha(\omega)]$, which does include the field generated by the dipoles.

In the following, we generalize the latter picture (that we call the dipole picture) to real crystals. We start by dividing the crystal into suitable polarizable entities or cells. In the framework of the local-orbital formulation of the dielectric response,[9,11,13] we assume that each cell contains one relevant pair of filled and empty Wannier functions, in terms of which the induced polarization can be expressed. The integral of the induced polarization over the i cell yields the dipole p_i, at the site R_i. This can be expressed as

$$p_i=\sum_j \alpha_{ij}(\omega)E_j^{\mathrm{loc}} \ , \quad (2)$$

$$\alpha_{ij}(\omega)=-f_i S_{ji}^0(\omega) f_j \ , \quad (3)$$

where E_j^{loc} is the local field at the site R_j and f_i is the dipole matrix element between the local orbitals of the i cell. The polarizability $S_{ij}^0(\omega)$ can be obtained from the RPA polarizability N_{ij}^0 through the matrix equation[13]

$$S^0=N^0+N^0V^{\mathrm{sr}}S^0 \ , \quad (4)$$

where V^{sr} is the (short-range) Coulomb interaction between electrons in the zero-order Hamiltonian. This accounts both for central-cell exchange, and for any difference between the real intercell Coulomb interaction and the dipole-dipole interaction.[13] (The long-range tail of the exchange interaction, which is screened by the crystal dielectric constant, is here neglected.)

The field generated by the dipoles, not considered in S^0, is taken into account in the local field appearing in Eq. (2), which becomes

$$p_i=\sum_j \alpha_{ij}\left[E_j^{\mathrm{ex}}+\sum_{k\neq j} T_{jk}p_k\right] \ , \quad (5)$$

where E_j^{ex} is the external field at the site R_j and T_{jk} is the dipole-dipole interaction tensor.[7]

Solution of the linear system (5) yields the induced dipoles as functions of the field E_j^{ex}:

$$p_i/\Omega=\sum_j \alpha_{ij}^M E_j^{\mathrm{ex}} \quad (6)$$

which defines the macroscopic polarizability α_{ij}^M. It can be easily shown[13] that in an infinite cubic crystal the relation of the macroscopic dielectric constant $\epsilon_M=1+4\pi\sum_j \alpha_{ij}^M$ to the "atomic" polarizability $\alpha(\omega)=\sum_j \alpha_{ij}$ is given by the Lorentz-Lorenz formula (1), as it occurs for an assembly of independent atoms.

If both the short-range [V^{sr} in (2)] and dipolar long-range [T_{jk} in (5)] electron-electron interactions are neglected, the macroscopic polarizability becomes simply related to the RPA N_{ij}^0:

$$\alpha_{ij}^{M(\mathrm{RPA})}(\omega)=-f_i N_{ji}^0(\omega) f_j \ . \quad (7)$$

The short-range and dipolar interactions—although independently quite large—cancel each other to a large extent, so that the one-electron approximation actually works quite well in bulk semiconductors.

III. CALCULATIONS AND RESULTS

In the rest of this paper we follow the approach of Mochan and Barrera[7,14] to calculate the surface local-field effect on the optical properties of Si(110). We consider one dipole per cell and assume the polarizability to be local, i.e., we take $\alpha_{ij}=0$ for $i\neq j$. The polarizability of inner dipole layers is derived from the computed dielectric constant of bulk Si, but, at variance with Ref. 7, the first few layers are allowed to have a different polarizability.

We start from a tight-binding calculation of electronic states and RPA optical properties of bulk Si, as described in Ref. 8. The imaginary part of the resulting RPA dielectric constant $\epsilon_b(\omega)$ is shown in Fig. 1. A similar

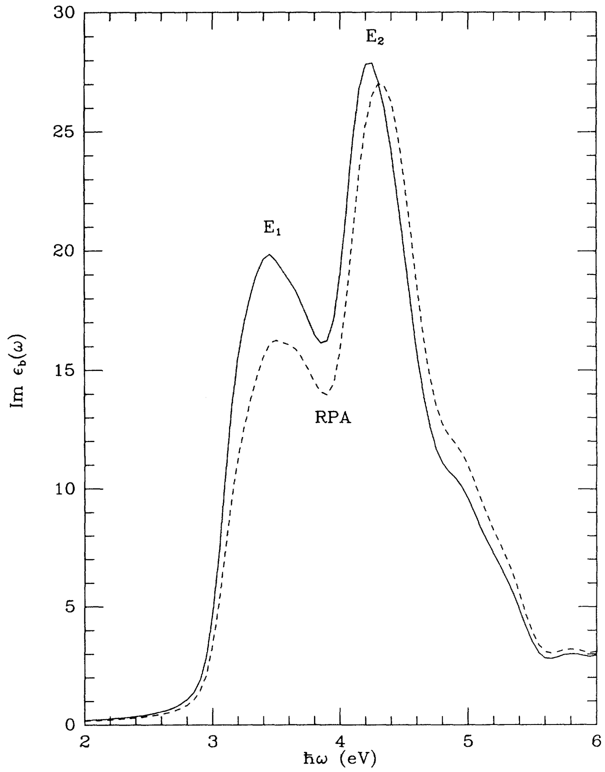

FIG. 1. Dashed line: imaginary part of the RPA dielectric constant of bulk silicon, computed using the tight-binding method of Ref. 9. Solid line: imaginary part of the macroscopic dielectric constant of bulk silicon, computed using Eq. (9).

calculation is performed also for a slab of $N=23$ Si(110) layers, with hydrogen-covered surfaces. The output of the calculation is in this case the integral $I(\omega)$ of the slab RPA dielectric susceptibility $\epsilon(\omega;z,z')$ over z and z'.[8] Neglecting nonlocality and assuming that the first N_s layers at each surface have dielectric constant ϵ_s, while the inner layers have the bulk dielectric constant, we get

$$2N_s d_l \epsilon_s(\omega)=I(\omega)-(N-2N_s)d_l\epsilon_b(\omega) \ , \qquad (8)$$

where d_l is the interlayer spacing. This assumption does not introduce errors in the calculation of the s-wave reflectivity, where only the integral $I(\omega)$ and the bulk dielectric constant are involved.[8] Its reliability in the case of local-field effects needs to be checked. However, it is the only reasonable way of avoiding the exceedingly time consuming calculation of the dielectric susceptibility $\epsilon(\omega;z,z')$ for many values of z and z'. Because of the symmetry of the (110) surface, ϵ_s will be different for light polarized along [001] (x) or [1$\bar{1}$0] (y). The choice of N_s is dictated by the physical requirement of a thin surface layer, which is however contrasted by the appearance of a negative imaginary part of ϵ_s for too small N_s. We choose $N_s=3$, which is the smallest value for which the imaginary part of ϵ_s is always positive in the frequency range between 0 and 13 eV. The final results do not change significantly for $N_s=4$.

The imaginary part of ϵ_s for x and y polarizations is shown in Fig. 2. The main surface effects are the splitting of the E_1 peak (occurring at 3.4 eV in our bulk calculation) into a doublet at 3 and 3.6 eV, with polarization-dependent oscillator strengths, and a reduction of the E_2 peak (occurring at 4.2 eV in our bulk calculation). This behavior may be understood as follows. In the bulk, the transitions contributing to E_1 occur along the four equivalent Λ lines, where the relevant bands are nearly parallel, and are allowed for light polarized perpendicular to the Λ lines. When bulk bands are projected on the (110) surface Brillouin zone (SBZ), one sees that two Λ lines lie in the surface plane, as the diagonals of the SBZ. Since the $k_z'=k_z$ selection rule is not broken along these lines, they should give rise to the less perturbed (upper) component of the surface E_1 doublet, with nearly isotropic oscillator strength. The other Λ lines, instead, which have components along z and x, give rise to the more perturbed (lower) component of the surface E_1 doublet, mainly allowed for light polarized along y. The E_2 peak originates from transitions at X in the bulk Brillouin zone. Since in this case the bands do not run parallel over extended regions, one may expect the surface effect, related to the breaking down of the k_z conservation, to be smaller, in agreement with Fig. 2.

The next step is to extract the dipole polarizability from the calculated RPA dielectric constant. The Lorentz-Lorenz formula (1) relates the former to the macroscopic dielectric constant, which is different from the RPA one. It is however known that many-body effects (i.e., the difference between the macroscopic and RPA dielectric constants) are not too large in semiconductors: peak energies of ϵ_b are weakly affected, while larger changes occur in line shape.[15] A simple approximation, used here, is to describe bulk many-body effects according to a simplified model developed in Ref. 13:

$$\epsilon_M-1=(\epsilon_{\mathrm{RPA}}-1)/\{1+[(V_0+V_1-V_x/2)\Omega/4\pi f^2]\times(\epsilon_{\mathrm{RPA}}-1)\} \ . \qquad (9)$$

Here V_0 and V_x are the Coulomb and exchange interaction in the same cell, respectively, while $V_1=-4\pi f^2/3\Omega$ is the dipole-dipole interaction energy, which can be estimated from the strength of the optical transitions. The term $(V_0+V_1-V_x/2)$ in Eq. (9) determines the strength of many-body effects: it is usually small in semiconductors. It is taken to be -0.1 eV in Si, which well reproduces the results of the many-body calculation of Ref. 15. The imaginary part of the macroscopic dielectric constant ϵ_M is compared in Fig. 1 with the RPA result. It is apparent that the differences are quite small. Nevertheless the macroscopic dielectric constant is in better agreement with experiment,[15] since it has a higher E_1 peak at 3.5 eV.

In the bulk we can extract the dipole polarizability from ϵ_M using the Lorentz-Lorenz formula (1).[7] Alternatively, we can substitute (9) into (1), and get a relation between the "atomic" or dipole polarizability $\alpha(\omega)$ and the RPA dielectric constant:

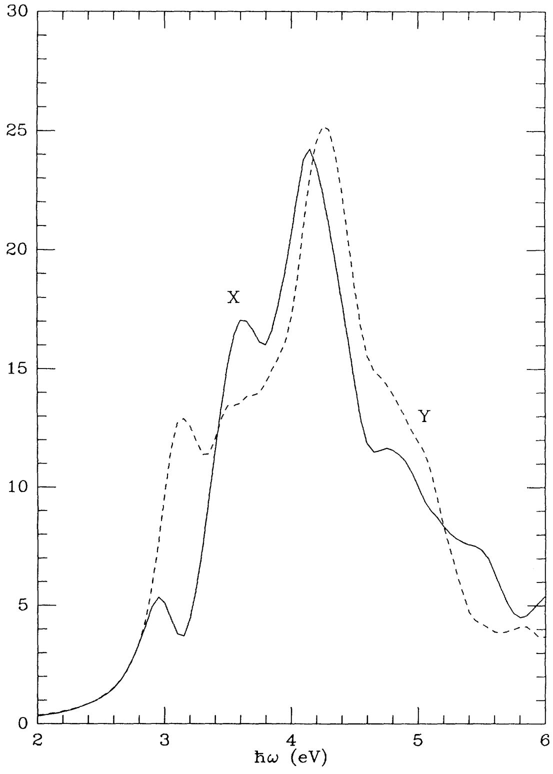

FIG. 2. Imaginary part of the surface (i.e., first three layers) RPA dielectric constant of Si(110):H, obtained from Eq. (8). X and Y indicate light polarized along [001] and [1$\bar{1}$0], respectively.

$$4\pi\alpha(\omega)/\Omega=(\epsilon_{\rm RPA}-1)/\{1+[(V_0-V_x/2)\Omega/4\pi f^2]\times(\epsilon_{\rm RPA}-1)\}\ . \qquad (10)$$

We assume that this relation—which does not involve the dipole-dipole interaction, but only short-range interactions—holds also near the surface, and from it we derive the polarizability of bulk (using $\epsilon_{\rm RPA}=\epsilon_b$) and surface (using $\epsilon_{\rm RPA}=\epsilon_s$) dipoles. By doing this, we simply assume that the short-range electron-electron interaction is not modified by the surface.

The method of Ref. 7 for computing the reflectance is easily generalized[14] to the case of local layer-dependent dipole polarizabilities in (5). From α_{ij}^M the surface contribution to the normal-incidence reflectivity R can be computed according to[7]

$$(R-R_0)/R_0=16\pi d_l(\omega/c)\,{\rm Im}\left[\sum_{ij}\frac{\alpha_{ij}^M}{(\epsilon_b-1)}\right]\ , \qquad (11)$$

where R_0 is given by Fresnel formula.

First we compute the reflectance anisotropies by assuming that surface dipoles have the same polarizability as in the bulk. In this case the RA originates from the surface local-field effect only. The result is shown in Fig. 3 together with the experimental RA of a natural surface.[1] A good agreement between theory and experiment is apparent, indicating that the polarizability near the oxidized surface is probably similar to that within the bulk. Note that in the calculation shown here we have extracted the dipole polarizability from the experimental dielectric constant.[16] However similar results and equally good agreement are obtained when the calculated ϵ_b is used.

Next we allow the dipoles in the first three layers to have different polarizabilities than bulk dipoles, as discussed above. The resulting RA of Si(110):H is shown in Fig. 4, together with the RPA result. It is clear that local-field effects substantially affect the RPA line shape: the main peak at 3.2 eV is reduced, while the negative valley between 4 and 5 eV is suppressed. [Similar local-field effects are induced in GaAs(100) and GaP(110).[17]] Although the calculation including local fields resembles more the spectrum of the natural surface (Fig. 3) than the RPA calculation, there is still a significant difference in the line shape. The main deviation is the low intensity of the peaks near 4 and 4.5 eV (Fig. 4), instead of a large peak at 4.3 eV. Such low intensity originates from the negative valley around 4.2 eV present in the RPA calculation. We have checked that this is not directly related to the polarizability of Si—H bonds, which is peaked at 7.2 eV. It is possibly due to the surface- and H-induced perturbation of bulklike states, which, by relaxing the $k_z'=k_z$ selection rule, spreads the transitions contributing to E_2 into a broader energy range, yielding a reflectance dip near E_2. Similar features appear in recent calculations of the optical properties of the hydrogenated GaAs and GaP (110) surfaces, while they are not present for clean surfaces.[18] It is not clear why they do not appear at oxidized surfaces. A possible—yet only speculative at this stage—explanation might be the occurrence of oxy-

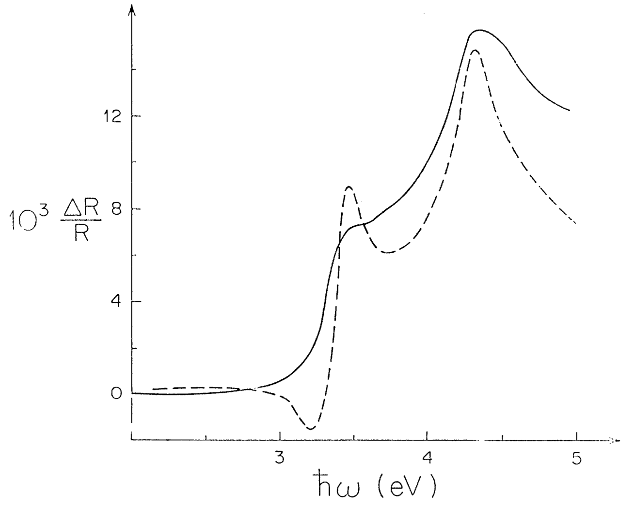

FIG. 3. Solid line: reflectance anisotropy calculated for Si(110) assuming an isotropic surface polarizability equal to the bulk polarizability. The dipole polarizability is extracted from the experimental bulk dielectric constant (Ref. 16). The dashed line is the experimental RA spectrum, after Ref. 1.

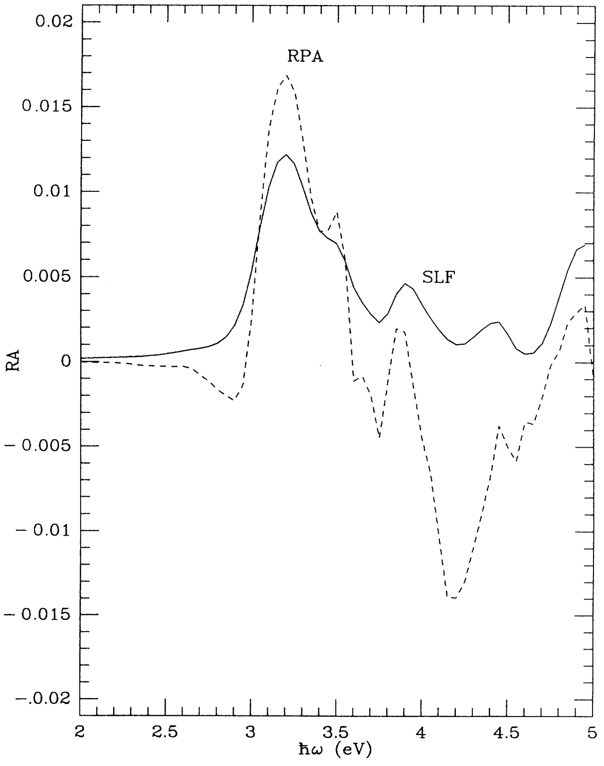

FIG. 4. Reflectance anisotropy $0.5(R_y-R_x)/(R_y+R_x)$ calculated for Si(110):H. The dashed line is computed within one-electron RPA. The solid line includes the surface local-field effect.

gen at bridging sites above the top Si layer, as it happens at the GaAs(110) surface.[19] Silicon-oxygen bonds in this situation might well mimic the missing silicon-silicon bonds, leaving essentially bulklike the "atomic" polarizability of the first layers. Further calculations, involving the real structures of oxidized surfaces, should clarify this point.

IV. CONCLUSION

We have performed a microscopic calculation of the optical anisotropy spectra of a Si(110) surface. A calculation involving the surface local-field effect yields results in very good agreement with an experimental spectrum obtained from a natural surface. On the other hand, a RPA calculation for a hydrogenated surface yields a reflectance anisotropy of the same order of magnitude but with a different line shape. Adding the local-field effect to the latter calculation substantially modifies the results, and diminishes the difference with the experiment on natural surfaces. However, there is still a large difference probably due to a H-induced perturbation. Our calculation implies that the reflectance anisotropy is very sensitive to the crystal termination, that surface-electronic and surface local-field effects are important, and that both should be taken into account together. The agreement between the theory ignoring electronic effects and experiment on natural surfaces is probably due to an emulation of the silicon-silicon bonds by the silicon-oxygen bonds. Further calculations involving oxidized surfaces are desirable.

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