

Local-Field Effect on the Surface Conductivity of Adsorbed Overlayers

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We show, using a simple local-field-effect theory, that the ratio of the surface conductivity of an overlayer physisorbed on a crystalline surface to its surface conductivity in the absence of the local-field effect is proportional to the square of the local field produced by the substrate, and is therefore very sensitive to the position of the adsorbate. The application of this result to the optical determination of adsorption sites is analyzed.

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Despite the rather long wavelength of light as compared to atomic distances, some very surface-sensitive optical spectroscopies have been developed lately.¹ In particular, optical-anisotropy spectroscopies^{2,3} are a valuable new tool for the investigation of clean and adsorbate-covered cubic-crystal surfaces. In these spectroscopies the crystal is rotated around its surface normal while the consequent change of its optical properties is measured. From the optical point of view only the surface region rotates since the bulk of a cubic crystal is isotropic. Therefore, a great surface sensitivity is achieved and the anisotropy of the surface conductivity can be determined.

In a recent Letter² Aspnes and Studna reported measurements of the normal-incidence reflectance-anisotropy spectra of brominated and H₂O-stripped Ge(110) surfaces. From the difference between the two spectra they determined the anisotropy of the surface dielectric response of the overlayer. This was compared to the anisotropy of a monolayer of Br₂ oriented along the $\langle 1\bar{1}0 \rangle$ direction, which they calculated employing the molecular polarizability extracted from extinction data in the gas phase.⁴ The size and line shape of their calculation differed from their experimental result, although approximate agreement was obtained when the former was multiplied by 2 and phase shifted by -45° . In this Letter we focus our attention on the origin of this disagreement.

We show below that the difference between the macroscopic electric field at the surface of the crystal and the local field that actually polarizes the adsorbate produces a substantial modification of the adsorbate's surface conductivity. This modification depends on the orientation of the adsorbate, and it can even lead to an anisotropic conductivity for an intrinsically isotropic adsorbate. Moreover, it is an extremely sensitive function of the position of the adsorbate so that an optical determination of the adsorption site becomes possible.

The difference ΔR between the normal-incidence reflectance anisotropy ($R^x - R^y$) of an adsorbate-covered and that of a clean crystal ($R^x - R^y$)⁰ is given

by [see Eq. (40) of Mochán, Fuchs, and Barrera⁵]

$$\frac{\Delta R}{R} = \frac{16\pi}{c} \operatorname{Re} \left\{ \frac{\langle \langle \Delta \sigma^x \rangle \rangle - \langle \langle \Delta \sigma^y \rangle \rangle}{\epsilon - 1} \right\}, \quad (1)$$

where R is the average reflectance, ϵ is the bulk dielectric function of the crystal, and x and y are the principal axes of the surface conductivity of the adsorbate $\langle \langle \Delta \sigma \rangle \rangle$. The latter is defined through

$$\Delta \mathbf{i} = \langle \langle \Delta \sigma \rangle \rangle \cdot \mathbf{E}_M, \quad (2)$$

where \mathbf{E}_M is the macroscopic field at the surface and

$$\Delta \mathbf{i} \equiv \int d^3r [\mathbf{j}(\mathbf{r}) - \mathbf{j}^0(\mathbf{r})]/A \quad (3)$$

is the surface current associated with the adsorbate. Here $\mathbf{j}(\mathbf{r})$ and $\mathbf{j}^0(\mathbf{r})$ are the current densities at position \mathbf{r} in the presence and in the absence of the adsorbate, respectively, and A is the area of the crystal surface.

In order to calculate $\langle \langle \Delta \sigma \rangle \rangle$ we use a model of polarizable entities which has proved useful in understanding the reflectance anisotropy of clean semiconductor surfaces.⁶ Our model consists of an overlayer of point polarizable adsorbates with polarizability tensor α_0 and positions \mathbf{R}_κ over a semi-infinite cubic lattice of polarizable entities with isotropic polarizability α and positions \mathbf{R}_i . We will use the convention that the indices κ and λ denote adsorbate positions while i and j denote substrate positions. We choose α in such a way that the bulk macroscopic dielectric function of the substrate, given by the Clausius-Mossotti relation, matches the experimental bulk measurements, that is,

$$\alpha \equiv (3/4\pi n) (\epsilon - 1)/(\epsilon + 2), \quad (4)$$

where n is the number density of polarizable entities.

The induced dipole moments of the adsorbates \mathbf{p}_κ and of the substrate \mathbf{p}_i obey the coupled equations

$$\mathbf{p}_\kappa = \alpha_0 \cdot (\mathbf{E}_{\text{ex}} + \sum_\lambda \mathbf{T}_{\kappa\lambda} \cdot \mathbf{p}_\lambda + \sum_j \mathbf{T}_{\kappa j} \cdot \mathbf{p}_j), \quad (5a)$$

$$\mathbf{p}_i = \alpha (\mathbf{E}_{\text{ex}} + \sum_\lambda \mathbf{T}_{i\lambda} \cdot \mathbf{p}_\lambda + \sum_j \mathbf{T}_{ij} \cdot \mathbf{p}_j), \quad (5b)$$

where \mathbf{T}_{ab} is the dipole-dipole interaction tensor

between the positions \mathbf{R}_a and \mathbf{R}_b of either the adsorbate or the substrate. Since we are concerned with the polarization only at small distances away from the surface and since we are dealing with normal incidence, we ignore retardation; we take the external field $\mathbf{E}_{ex} = \mathbf{E}_M$ to be independent of position, and

$$\mathbf{T}_{ab} = (1 - \delta_{ab}) \nabla_a \nabla_b |\mathbf{R}_a - \mathbf{R}_b|^{-1}, \quad (6)$$

where δ_{ab} is the Kronecker delta.

From Eq. (3), the surface current is

$$\Delta \mathbf{i} = -i\omega [\sum_{\kappa} \mathbf{p}_{\kappa} + \sum_j (\mathbf{p}_j - \mathbf{p}_j^0)] / A, \quad (7)$$

where ω is the frequency of light and \mathbf{p}_j^0 are the dipole moments of the substrate before adsorption takes place; they obey an equation similar to Eq. (5b) but with $\mathbf{p}_{\lambda} = 0$. The first term on the right-hand side of Eq. (7) is the direct contribution of the adsorbates to the surface current. The second term is an indirect contribution through the change $\mathbf{p}_j - \mathbf{p}_j^0$ in the dipole moments of the substrate induced by the presence of the adsorbates. Solving Eqs. (5) for \mathbf{p}_{κ} , \mathbf{p}_j , and \mathbf{p}_j^0 , and assuming that the \mathbf{R}_{κ} 's are equivalent modulo to the 2D unit cell of the clean surface, we obtain

$$\Delta \mathbf{i} = -i\omega n_s \boldsymbol{\gamma}^T \cdot (\mathbf{I} - \alpha_0 \mathbf{T}^*)^{-1} \cdot \alpha_0 \cdot \boldsymbol{\gamma} \cdot \mathbf{E}_{ex}, \quad (8)$$

where $n_s \equiv N_s/A$ is the number of adsorbates per unit area, $\boldsymbol{\gamma}$ is the enhancement tensor defined by $\mathbf{E}_{loc}^0 \equiv \boldsymbol{\gamma} \cdot \mathbf{E}_{ex}$, $\boldsymbol{\gamma}^T$ is its transpose, and \mathbf{T}^* is the self-interaction of the adsorbed overlayer, defined through

$$(\mathbf{I} - \alpha_0 \cdot \mathbf{T}^*)^{-1} = \sum_{\kappa\lambda} (\delta_{\kappa\lambda} \mathbf{I} - \alpha_0 \cdot \mathbf{T}_{\kappa\lambda}^*)^{-1} / N_s. \quad (9)$$

Here we introduced the local field at the adsorption site in the absence of the adsorbates,

$$\mathbf{E}_{loc}^0 = \mathbf{E}_{ex} + \sum_j \mathbf{T}_{\lambda j} \cdot \mathbf{p}_j^0, \quad (10)$$

and the full (direct plus substrate-mediated) interaction between the adsorbed molecules at positions κ and λ ,

$$\mathbf{T}_{\kappa\lambda}^* = \mathbf{T}_{\kappa\lambda} + \sum_{ij} \mathbf{T}_{\kappa i} \cdot (\delta_{ij} \mathbf{I} - \alpha \mathbf{T}_{ij})^{-1} \cdot \alpha \mathbf{T}_{j\lambda} \quad (11)$$

From Eq. (8) the surface conductivity is

$$\langle \langle \Delta \boldsymbol{\sigma} \rangle \rangle = \boldsymbol{\gamma}^T \cdot (\mathbf{I} - \alpha_0 \mathbf{T}^*)^{-1} \cdot \langle \langle \Delta \boldsymbol{\sigma}_0 \rangle \rangle \cdot \boldsymbol{\gamma}, \quad (12a)$$

where $\langle \langle \Delta \boldsymbol{\sigma}_0 \rangle \rangle = -i\omega n_s \alpha_0$ is the surface conductivity in the absence of the local-field effect. If the principal axes of all the tensors involved in Eq. (12a) coincide, it can be rewritten as

$$\begin{aligned} \frac{\langle \langle \Delta \sigma^{\mu} \rangle \rangle}{\langle \langle \Delta \sigma_0^{\mu} \rangle \rangle} &= \frac{1}{1 - \alpha_0^{\mu} (T^*)^{\mu}} (\gamma^{\mu})^2 \\ &= \frac{1}{1 - \alpha_0^{\mu} (T^*)^{\mu}} \left[\frac{(E_{loc}^0)^{\mu}}{E_M^{\mu}} \right]^2, \end{aligned} \quad (12b)$$

where $\mu = x$ or y is a principal direction. This could happen if the adsorbates occupy high-symmetry posi-

tions over the crystals's surface.

Equations (12a) and (12b) are the main results of this paper. They show that there are two local-field corrections to the conductivity of adsorbed overlayers: One is the square of the local-field-enhancement tensor in the absence of the adsorbate, which depends only on the properties of the substrate and on the position of the adsorbates over the 2D surface unit cell. The other is the self-interaction of the adsorbed overlayer, which depends also on its coverage and spatial arrangement.

Some effects of the self-interaction on the surface conductivity of noble-gas overlayers adsorbed on metal surfaces⁷ and on second-harmonic generation by adsorbates⁸ have already been discussed in the literature. However, in these studies the atomic structure of the substrate has been neglected. This corresponds in our theory to an enhancement tensor $\gamma^{\mu\nu} = \delta^{\mu\nu}$, and a substrate-mediated self-interaction given by image theory. While this might be appropriate for a metallic substrate, it is not so for insulators or semiconductors. Hence, in the following we focus our attention on the enhancement tensor and on its dependence on position. We choose the (110) face of Ge where our model of polarizable entities has already proved to give an adequate explanation of the intrinsic reflectance anisotropy.⁶ As discussed in Ref. 6, we modeled the substrate as an fcc lattice of polarizable tetrahedra, each consisting of a Ge atom at its center and four shared Ge atoms at its vertices. The required dipolar sums were performed by a planewise-sum technique.⁹

In Fig. 1 we show the absolute value and the argument of $(\gamma^x)^2$ as a function of frequency at four positions above the (110) face: (A) directly above a lattice point, (B) halfway between two lattice points along the x , $\langle 1\bar{1}0 \rangle$, direction, (C) halfway along the y , $\langle 001 \rangle$, direction, and (D) above the middle of the 2D unit cell, and at two distances from the surface: $z_0 = 1.0d$ and $1.5d$, where $d = 5.658/2\sqrt{2} \text{ \AA}$ is the interplanar distance. Notice that from the symmetry of these positions, the x and y are principal directions of all the tensors appearing in Eq. (12) provided that they are principal directions of α_0 . As can be seen, the magnitude and the line shape of the enhancement tensor are extremely sensitive to the position of the adsorbate. Similar results hold for $(\gamma^y)^2$. Moreover, the results for the x and y directions differ markedly as shown in Fig. 2 where we plotted the absolute value and the argument of $(\gamma^x)^2 - (\gamma^y)^2$. This means that the local field of the substrate can be quite effective in inducing an anisotropic response on an otherwise isotropic adsorbate.

The strong dependence of the enhancement tensor on the position of the adsorbate suggests that reflectance anisotropy could be used as an optical probe of the adsorption site. This could be determined by

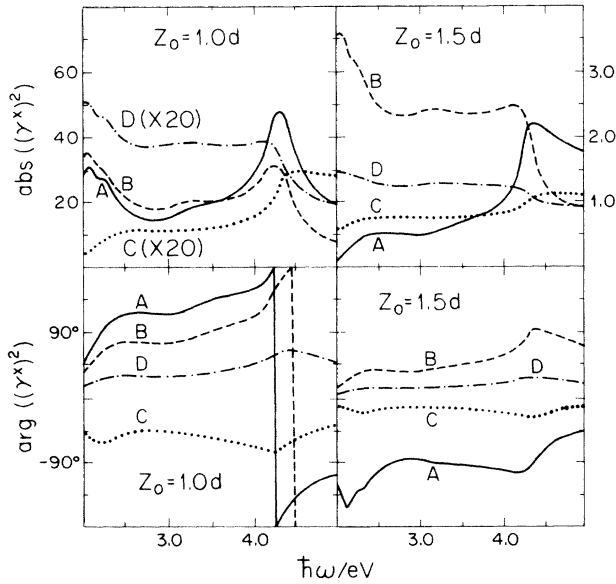


FIG. 1. Absolute value and argument of the square of the enhancement factor along the $\langle 110 \rangle$ direction, $(\gamma^x)^2$, vs frequency at positions *A* (solid), *B* (dashed), *C* (dotted), and *D* (dash-dotted), and at distances of $1.0d$ and $1.5d$ from a (110) Ge surface.

matching the experimentally found values of the anisotropy of the surface conductivity to the calculated ones. One of the few experimental results reported so far is the surface dielectric response of a Br_2 overlayer physisorbed on (110) Ge.² We have calculated $\langle\langle\Delta\sigma^x\rangle\rangle - \langle\langle\Delta\sigma^y\rangle\rangle$ for a Br_2 monolayer occupying

the positions *A*, *B*, *C*, and *D* discussed above, at various distances from the surface. We assumed Br_2 polarizes only along its molecular axis with a polarizability that was obtained from measurements in the gas phase.⁴ We have performed calculations with the molecular axis along the *x* and *y* directions as well as for a random orientation. The best agreement with our calculations corresponds to Br_2 oriented along the $\langle 001 \rangle$ direction; the best positions are *A* and *B* at a distance from the surface $z_0 = 1.17d = 2.34 \text{ \AA}$ and $z_0 = 0.89d = 1.78 \text{ \AA}$, respectively. In Fig. 3 we show the real and imaginary parts of the calculated and the experimental values of $\xi \equiv \langle\langle\Delta\sigma^x\rangle\rangle - \langle\langle\Delta\sigma^y\rangle\rangle / \langle\langle\Delta\sigma^{\xi}\rangle\rangle$. The theoretical spectra for the two positions chosen above are almost identical and so we only show the one at *B*. The calculated line shape resembles the experiment quite well; the agreement of the imaginary part below 3.2 eV is striking.

The comparison of our calculation to the bromine experiments might be criticized for several reasons. First, our fcc calculation artificially distinguishes the Ge atoms at the center from those at the vertices of the tetrahedra that form the basis of the diamond lattice, and we expect our model to overestimate the surface local-field effect.⁶ An fcc calculation might be better suited for ionic semiconductors, whose polarization process is dominated by the electron cloud near one kind of ion. We are presently working on more elaborate models better suited for Ge and Si. Second, α_0 is not really the molecular polarizability in the gas phase since the wave functions and energies of the ad-

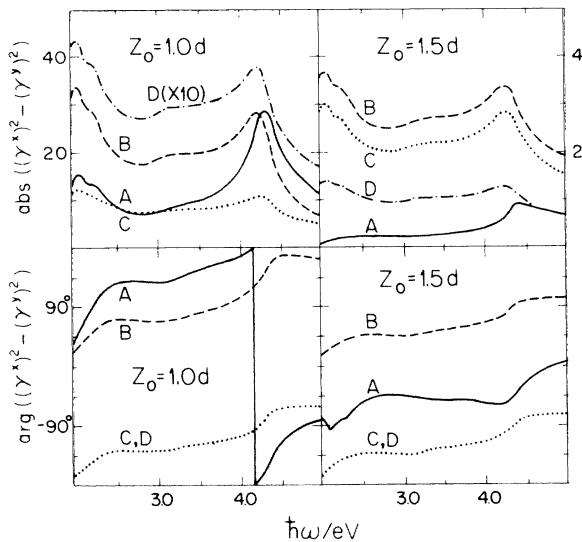


FIG. 2. Absolute value and argument of $(\gamma^x)^2 - (\gamma^y)^2$ vs frequency at positions *A* (solid), *B* (dashed), *C* (dotted), and *D* (dash-dotted), and at distances of d and $1.5d$.

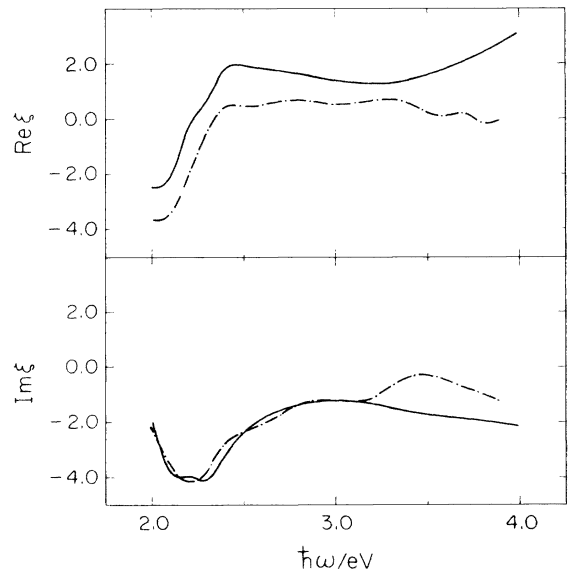


FIG. 3. Real and imaginary part of the correction factor ξ vs frequency; solid line, calculated for a monolayer of physisorbed Br_2 oriented along $\langle 001 \rangle$ at position *B* and at a distance $0.89d$ from a (110) Ge surface; dash-dotted line, experimental.

sorbate are modified by the substrate, and its transition matrix elements are further modified by the inhomogeneities of the polarizing field.^{8,10} Thus the line shape of $\alpha_0(\omega)$ is modified.

The interpretation procedure would be simplified in experiments using adsorbates with resonance frequencies above those of the substrate, since then α_0 would be a real, slowly varying function of ω . This procedure would be further simplified if the self-interaction is negligible ($|\alpha_0 \cdot \mathbf{T}^*| \ll 1$). According to Lehnen and Bruch,¹¹ the order of magnitude of $|\mathbf{T}^*|$ can be estimated for distances down to one interplanar distance by using classical image theory¹² but locating the image plane as discussed by Zaremba and Kohn.¹³

In conclusion, we have shown that the surface conductivity of a physisorbed overlayer on a crystalline surface is modified by the self-interaction of the overlayer and by the local-field enhancement of the substrate. The latter depends very strongly on the position of the adsorbate, making feasible the optical determination of adsorption sites. We have illustrated this possibility by analyzing recent optical-anisotropy spectra of a brominated (110) Ge surface, obtaining very good agreement with experiment at two positions only. Further experiments are desirable, as well as more elaborate calculations of the local field near the surface of real cubic crystals.

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