Reflectance anisotropy of the (110) reconstructed surface of gold

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The reflectance anisotropy of a Au(110) reconstructed surface has been calculated using a perturbative theory for the electromagnetic fields near the microrough interface. Since the induced fields have atomic-scale fluctuations, spatial dispersion was accounted for by applying a recently developed extension of the Rayleigh method to nonlocal rough systems. Significant differences are obtained between local and nonlocal calculations.

The study and measurement of anisotropies in the electromagnetic properties of different faces of cubic crystals[1-3] is a new tool for the investigation of surface structure. From the optical point of view, only the surface region contributes to the anisotropy signal because the bulk of a cubic crystal is isotropic in the long-wavelength limit.

Anisotropies on the dispersion relation of surface plasmons were first observed on the Ag(110) surface[4] and subsequently have been found on the Au(110) (Ref. 5) and Cu(110) surfaces,[6] also. Anisotropies on the above-band-gap reflectance of different faces of some semiconductor crystals have been successfully explained in terms of the induced local fields,[7] although the surface effects on the bulk wave functions are also important.[8] The below-band-gap anisotropies are attributed to transitions to or from surface states.[9] Recently, anisotropies in the far-ir spectrum due to the surface-induced coupling among photons and phonons have been predicted.[10]

In this paper we investigate the effects of the surface profile on the normal-incidence reflectance anisotropy of reconstructed faces of gold. As we know, gold stands out among the noble metals for its remarkable surface properties. The low-index surfaces reconstruct in such a way as to give rise to close-packed layers.[11] This behavior has been particularly well studied in Au(110). This reconstruction is characterized by the periodic alternation of missing rows of atoms. We simulate these reconstructed faces by a periodic grating of microscopic length scales whose valleys portray the missing rows of atoms. The conduction electrons are taken as an electron gas bounded by the surface of the microscopic grating. In our calculation, the reflectance anisotropy arises simply from the geometric anisotropy of the bounding surface. Since in this case the period of the grating is of atomic dimensions, the surface-dispersed waves include very large wave vectors; therefore, nonlocal effects are expected to be considerable. We present results of calculations with and without spatial dispersion using the hydrodynamic model for the dielectric response of the electron gas and the results of a previously developed theory.[12] Although the use of a hydrodynamic model might be questionable, since it ignores several surface related effects,[13] it does incorporate the coupling to bulk plasmons, and it has been possible to apply it to other systems besides the semi-infinite jellium.[14] The main physical effect incorporated in our model is the finite width of the surface-induced charge density, which is comparable to the characteristic grating dimensions in the present system.

We present results for gratings in which one, two, or three rows of atoms are periodically missing. We find that the effects of spatial dispersion are indeed large; the anisotropy spectrum of a nonlocal reconstructed crystal is appreciably smaller than in the local case, and the line shape differs in the high-energy region. The effects of spatial dispersion can be discerned, and one might discriminate between different microscopic models for the reconstruction by analyzing the experimental anisotropy reflectance spectra.

In Sec. II we describe the calculation and the results and Sec. III is devoted to conclusions.

II. CALCULATION AND RESULTS

In a previous paper[12] (referred to as I in what follows) we developed a perturbative procedure for obtaining the electric field near the rough surface of a metal with a nonlocal dielectric response function when plane-polarized light is incident upon it. In the case of a grating, the perturbation parameter is the height h divided by the spatial period of the grating.

In I we obtained formulas for the reflectance up to second order in the perturbation parameter in terms of amplitude functions which obey a set of recursive rela-

tions [see Eqs. (6), (15), and (22) of I]. The surface profile is given by the equation $z=h\xi(x,y)$, where $\xi(x,y)$ is a periodic function. The region $z>h\xi(x,y)$ is filled by a metallic medium with a nonlocal dielectric function, while the region $z<h\xi(x,y)$ is vacuum. Here we choose $\xi(x,y)=\cos(gx)$, where g is 2π over the spatial period of the grating. The anisotropy spectra is calculated as

$$\Delta R/R=\Delta R_{\parallel}/R-\Delta R_{\perp}/R\ , \tag{1}$$

where $\Delta R_{\perp}/R$ and $\Delta R_{\parallel}/R$ are the differential reflectances for normal incidence when the fields are polarized perpendicular and parallel to the grooves, respectively. We perform the calculation to second order in the perturbative parameter using the closed formulas for the amplitude functions given by Eqs. (17)–(19) of I. These formulas are given in terms of matrices (see Appendix B of I) whose elements depend on the nonlocal dielectric response of the electrons, written as

$$\epsilon(\mathbf{k},\omega)=\epsilon_b(\omega)-\frac{\omega_p^2}{\omega^2+i\omega/\tau-\beta^2k^2}\ , \tag{2}$$

where $\epsilon_b(\omega)$ is the bound-electron contribution, ω_p is the plasma frequency of the conduction electrons, τ is their lifetime, and $\beta^2=\frac{3}{5}v_F^2$, with v_F the Fermi velocity.

The response $\epsilon_b(\omega)$ was obtained from the experimental bulk dielectric function[15]

$$\epsilon_{\text{expt}}(\omega)=\epsilon_b(\omega)-\frac{\omega_p^2}{\omega^2+i\omega/\tau}=\epsilon(0,\omega)\ . \tag{3}$$

Then we calculate the amplitude functions using[16] $\omega_p\tau=420$, $\hbar\omega_p=9.2$ eV, and $\beta=0.0361c$. We simulate the Au(110) surface by a periodic grating with a spatial period of $2a$, where $a=4.01$ Å is the lattice constant of gold. For $\hbar\omega_p=9.2$ eV, we have $g=2\pi/2a\approx 165\omega_p/c$ and $h=a/2\sqrt{2}=0.006\,67c/\omega_p$. However, in order to display the dependence of the anisotropy spectra on the spatial period of the grating, in Fig. 1 we show $\Delta R/R$ as a function of energy for a grating with a long period $g=2\pi/32a\approx 10\omega_p/c$. We observe that, for this large-scale period, there is no noticeable line-shape difference between the local and nonlocal calculations. The most remarkable peaks in both cases are those coming from the surface plasmon corresponding to $\text{Re}[\epsilon_{\text{expt}}(\omega)]=-1$, and they approach each other for small g.

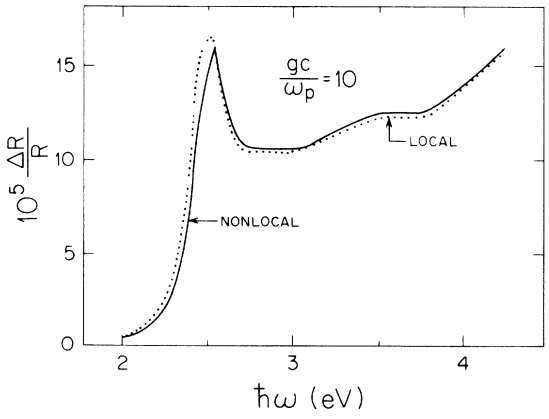

FIG. 1. Normal-incidence reflectance anisotropy of a local (dotted-dashed line) and a nonlocal (solid line) Au(110) surface as a function of frequency. The grating wave vector $g=10\omega_p/c$ and the grating height $h=0.006\,67c/\omega_p$.

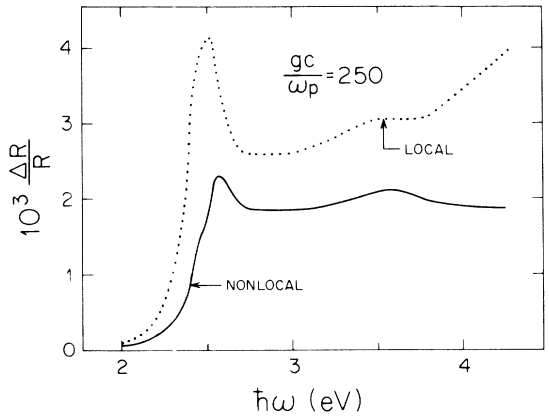

FIG. 2. Normal-incidence reflectance anisotropy of a local (dotted-dashed line) and a nonlocal (solid line) Au(110) surface as a function of frequency. The grating wave vector $g=250\omega_p/c$ and the grating height $h=0.006\,67c/\omega_p$.

As g increases, nonlocal effects become more important. In Fig. 2 we chose an exaggerated grating wave vector $g=250\omega_p/c$ in order to understand the structure of our results. Figure 2 shows that the normal-incidence reflectance anisotropy $\Delta R/R$ of this surface is very different in the local and nonlocal cases. A comparison with Fig. 1 shows that the line shape of the local calculation is independent of the corrugation. On the other hand, the nonlocal anisotropy spectrum depends on the spatial period of the grating, and is appreciably smaller than in the local case because of the depletion of conduction electrons near the surface. In particular, the peak of the surface plasmon is shifted with respect to the local results, and the line shape is similar to the local one except above 3.5 eV. This means that the anisotropy depends strongly on the surface microstructure when we take account of spatial dispersion.

In Fig. 3 we show the nonlocal reflectance anisotropy

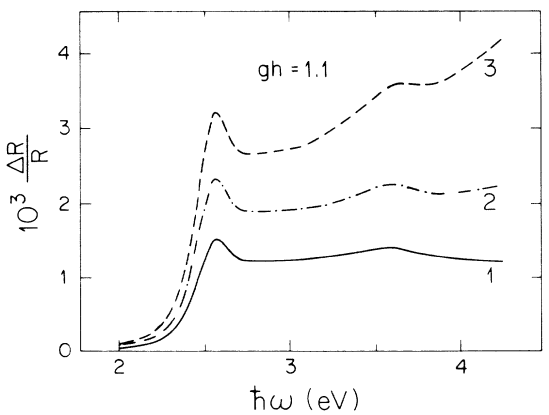

FIG. 3. Nonlocal reflectance anisotropy of a Au(110) surface as a function of frequency for grating wave vectors $gc/\omega_p=165$ (solid line), 110 (dotted-dashed line), and 82 (dashed line) with $gh=1.1$.

spectra of a Au(110) surface for different reconstructions consisting of one, two, and three consecutive missing rows, corresponding to $gc/\omega_p = 165$, 110, and 82, with $h = \pi/(2\sqrt{2}g) \simeq 1.1/g$. The line shapes of these three cases are different and approach the local line shape for small g. Conversely, the local line shape (not shown) is independent of g, and its magnitude scales with g and h as $h^2 g\omega/c$. For the present calculation, the local results are about twice as large as the corresponding nonlocal ones.

III. CONCLUSIONS

In summary, we have used a simple theory to calculate the normal-incidence reflectance anisotropy spectra of reconstructed Au(110), using a hydrodynamical model to describe the nonlocal contribution of the conduction electrons to the longitudinal dielectric function. The reconstruction is characterized by the absence of alternate rows of atoms, giving rise to a microscopic grating. Thus, we apply a previously developed theory[12] to the calculation of fields diffracted by this surface. Our calculation was carried out to second order in the grating amplitude and was performed for normally incident light with polarizations both parallel and perpendicular to the grooves. We present numerical results for the reflectance anisotropy as a function of frequency for different reconstruction periods.

The results show that the normal-incidence reflectance anisotropy $\Delta R/R$ of a Au(110) surface is different in the local and nonlocal cases. The nonlocal calculation yields a peak due to the roughness-induced coupling to the surface-plasmon polariton. The position of this peak depends on the microgeometry of the surface due to the surface-plasmon dispersion. Since this dispersion is positive in the hydrodynamic model, we obtained a blue shift away from the local resonance condition $\mathrm{Re}[\epsilon(0,\omega)] = -1$, and it increases with g. We would expect more elaborate jellium models[13] to yield a red shift, although the dispersion of the surface plasmon on noble-metal surfaces is still the object of active research.[3] On the other hand, the local results are about twice as large as the nonlocal ones, their line shape is independent of g, and the anisotropy increases linearly with frequency above 3.5 eV, in contrast to the nonlocal case. The origin of these differences is the finite width (roughly the Thomas-Fermi distance) of the charge density induced in the electron gas by the normal component of the electric field at the surface, whereas the induced charges occupy an infinitesimal region in the local case. Experimental measurements of the optical anisotropy spectra of metals with different surface preparations are desirable.

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