Optical anisotropies of Ag single crystals

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Abstract

We present a model for the electromagnetic response of Ag single-crystal surfaces that accounts for both interband and intraband transitions, taking advantage of the localized nature of the dipole moments associated with the transitions from the d levels. The response functions display structure near the plasma frequency which are related to the resonant dipolar oscillations localized near the first crystalline plane. The surface response is incorporated in a calculation of the optical reflectance which yields large corrections to Fresnel's formulae, of the order of 10%. Furthermore, these corrections depend on the surface orientation and on the angle between the polarization vector and the surface principal directions. We have confirmed this result experimentally for the (110) face of Ag. We have performed reflectance difference spectroscopy (*i.e.* normal incidence ellipsometry) on this face, and measured the real and imaginary parts of the anisotropy in the reflection amplitude for incident polarization along the [1$\bar{1}$0] and [001] directions. Measurements have been carried out on freshly polished and clean samples as well as on oxidized samples. We compare these results with the calculated anisotropies derived from the model.

1. Introduction

The investigation of the optical properties of Ag crystals has known a renewed interest in recent years [1–7]. After the pioneering study by Furtak and Lynch [1], who demonstrated anisotropic effects in electroreflectance on the (110) face of Ag, Tadjeddine *et al.* [2] observed that the surface plasmon on an Ag crystal displays a dispersion curve which depends on the face of the crystal and, for the Ag(110) face, on the orientation of the electric field. Recently, high resolution electron energy loss measurements [5–7] have revealed several loss peaks at or above the classical surface plasmon position $\hbar\omega_{sp}(0) = 3.67$ eV, for which $\varepsilon = -1$. However, the positions of these peaks as a function of the face of Ag or of the orientation, as well as their type of dispersion (quadratic or linear), are still debated [5]. Moreover, the origin of these losses is also controversial. They first were considered as due to the excitation by the electrons of surface plasmons with various wavevectors [5–7]. However, recently Tarriba and Mochan assigned the peaks to collective surface modes which originate from self-sustained dipolar oscillations localized close to the surface [8]. They developed a model of the optical response of an Ag(110) surface for explaining these experimental results which leads to important anisotropies in the electron energy losses. Moreover, this model predicts a very large anisotropy of the optical reflectivity of Ag(110) [8]. In order to check this model, we performed reflectance difference spectroscopy (RDS) on the Ag(110) face, which measures the anisotropy of the reflectance of the sample. RDS provides the real and imaginary part of the relative reflectance $(r_{[1\bar{1}0]} - r_{[001]})/r$, where $r_{[1\bar{1}0]}$ and $r_{[001]}$ are the complex reflection coefficients for light, with the electric field E polarized along the [1$\bar{1}$0] and [001] axes respectively.

2. Experimental details

The optical measurements have been performed by use of a commercial RDS apparatus which has been developed by ISA Jobin-Yvon Company (France). The RDS instrument can be considered as a normal-incidence ellipsometer which, when working with a sample with a bulk isotropic response, is only sensitive to the anisotropy of the surface. The sensitivity can reach

the order of 10^{-3}. The RDS apparatus measures the ellipsometric parameters Ψ and Δ, defined by $r_x/r_y = \tan \Psi \exp(i\Delta)$, where x and y denote two optical eigenaxes of the sample. A simple treatment of the data directly provides the real and imaginary parts of the differential reflectance. A complete description of the apparatus can be found in ref. 9. The light source is a 75 W Xe lamp. The incidence angle of the light is 2.75°. The polarizer and the analyser are Glan–Taylor polarizers. The photoelastic modulator consists of a fused silica bar submitted to a periodic stress (50 kHz). The angle between the modulator and the analyser is fixed at 45°. The energy of the light is analysed by a double-grating monochromator. The detector is a photomultiplier with an available wavelength range of 230–830 nm.

The Ag(110) single crystals were disks of 8 mm diameter and 2 mm thickness, cut from the same crystal rod by electroerosion. They were oriented by Laue X-ray back diffraction and mechanically polished to a mirror-like finish using successively finer grades of diamond polishing suspension down to 0.25 μm. They were chemically polished immediately (sample I) or 48 h (sample II) before the optical measurements, using the chromium trioxide–hydrochloric acid etch procedure described previously [10].

3. Theory

The theoretical model has been described and discussed in ref. 8. The main outlines are recalled here. In Ag, the d electrons are mostly localized around the ionic core positions. They contribute to the induced polarization only in region of space where their wavefunctions overlap those of the s–p bands. We model then the Ag crystal as a uniform electron gas with spherical cavities at the f.c.c. lattice sites, large enough for the contribution of the d electrons to be confined in them. The cavities are therefore occupied by polarizable entities, described by point dipoles at their centres. These dipoles are characterized by polarizabilities which account for the interband transitions, the conduction currents within the spheres and the core polarization. The dynamical dipoles induced in the cavities are sources of an electric field which is screened by the external electron gas. The electron gas in the interstitial region is described by a local Drude response $\varepsilon_g = 1 - \omega_p^2/(\omega^2 + i\omega\tau^{-1})$, for which we chose $\hbar\omega_p = 7.5$ eV and $\tau = 400/\omega_p$. The second step is the calculation in the quasi-static limit of the induced dipoles p'_i in every site. They are related to the local electric field E_{loc} by

$$p'_i = \alpha' E_{loc} \qquad (1)$$

where E_{loc} is the sum of an external field screened at the surface of the semi-infinite electron gas, of the fields

created by the other dipoles p'_j and of the fields created by the images through the surface of the electron gas of all the dipoles [8]. The polarizability α' of the dipoles in the cavities is obtained from the Clausius–Mosotti relation [11, 12], using the optically determined bulk dielectric function ε [13]. Equation (1) is then solved numerically [14, 15] and the surface conductivity σ is calculated [11]. The surface conductivity σ, which is defined through $i = \sigma E$, where i and E are the surface current and the electric field parallel to the surface [16], is thus expressed as a function of ε, of ε_g, of the interplanar distance a and of a sum over the induced apparent dipoles p'_i in the different crystalline planes. Two different values $\sigma_{[1\bar{1}0]}$ and $\sigma_{[001]}$ are obtained accordingly as the orientation of E is parallel to [1$\bar{1}$0] or [001].

The differential reflectance $\Delta r/r = (r_{[1\bar{1}0]} - r_{[001]})/r_0$, where r_0 is the Fresnel expression for reflectance, can then be obtained using $\sigma_{[1\bar{1}0]}$ and $\sigma_{[001]}$ from eqn. (38) of ref. 16. The real and imaginary parts of the calculated differential reflectance are drawn in Fig. 1. Both curves display very large structures (as large as 10%), either negative or positive. The peaks are related to strong resonances in the conductivities $\sigma_{[1\bar{1}0]}$ and $\sigma_{[001]}$. The first positive peak corresponds to a resonance in $\sigma_{[1\bar{1}0]}$, while the negative peak is due to a resonance in $\sigma_{[001]}$. These resonances correspond to self-sustained dipolar oscillations localized close to the surface. Their frequencies are shifted from the peak of the apparent polarizability α' owing to the coupling between dipoles through the direct and image Coulomb fields. The orientation dependence originates from the corresponding dependence of the dipolar sums [14]. Let us notice that, with a good approximation, $\Delta R/R = 2\,\mathrm{Re}\,(\Delta r/r)$, where $R = |r|^2$ is the reflectivity of the sample. This indicates that a resonance in $\sigma_{[1\bar{1}0]}(\sigma_{[001]})$ leads to a decrease in the reflectivity $R_{[1\bar{1}0]}(R_{[001]})$.
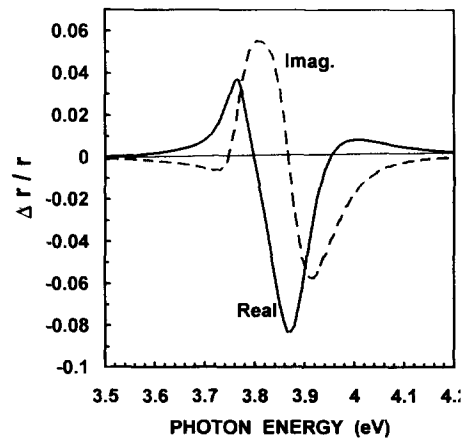

Fig. 1. Calculated differential optical reflectance $\Delta r/r = (r_{[1\bar{1}0]} - r_{[001]})/r$ vs. the photon energy $\hbar\omega$ of a (110) Ag surface.

4. Experimental results and discussion

The measurements have been performed on two Ag(110) crystals. In order to avoid any parasitic signal in the anisotropy due to the apparatus itself, the measurements were performed for each sample at two angles rotated by 90° in the plane of the sample. The two data files were then compounded to get the differential reflectance $\Delta r/r = (r_{[1\bar{1}0]} - r_{[001]})/r_{[001]}$.

The real and imaginary parts of $\Delta r/r$ are drawn in Figs. 2 and 3 respectively. Spectra I were obtained on the freshly prepared sample, which is considered to have a clean surface. Spectra II were measured on sample II of which the surface is lightly polluted, probably by sulphur atoms. The spectra for both samples display the same features, the intensity of which is larger for the oxidized sample. The important point

which has to be emphasized is the size of the anisotropy. The theoretical prediction of a very large anisotropy for Ag(110) is thus fully confirmed. Optical anisotropies have been previously observed [17] and theoretically explained [18] on semiconductor surfaces, but they were two orders of magnitude smaller. The difference in intensity between the clean and the oxidized surfaces can be tentatively explained. In the former case, the conduction electrons have the ability to spill over the surface, leading to a decrease in the screening effect. On the contrary, the presence of sulphur atoms on the surface prevents such a spilling. The theoretical model is therefore expected to reproduce the oxidized sample data better than the clean sample data.

Finally, the agreement in shape is not as good as that for the size. The low energy change of sign in $\mathrm{Re}(\Delta r/r)$ is reproduced but is shifted by a few tenths of an electronvolt. The corresponding intensities of the positive and negative peaks are not well reproduced. The same kind of observation can be made for $\mathrm{Im}(\Delta r/r)$: although the predicted peaks are present, they are shifted and display different intensities to those in the calculation. However, the shapes of the theoretical curves are strongly dependent on the strengths and positions of the resonances in $\sigma_{[1\bar{1}0]}$ and $\sigma_{[001]}$, and therefore on the values chosen for ω_g, τ and z_0, the distance from the first crystalline plane to the electron gas edge, and also on the bulk dielectric function ε. One would expect that a different choice of these various parameters could lead to a better agreement with the experimental data.
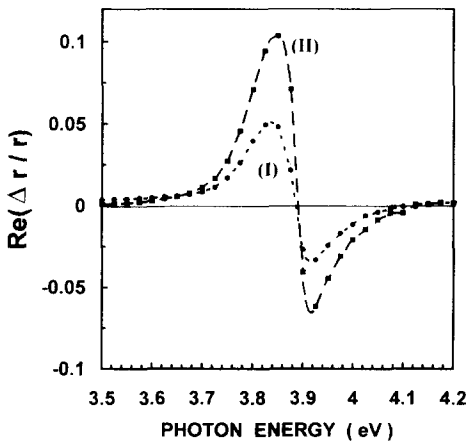

Fig. 2. Experimental real part of the differential optical reflectance $\Delta r/r$: curve I, clean (110) Ag single crystal; curve II, oxidized (110) Ag single crystal.
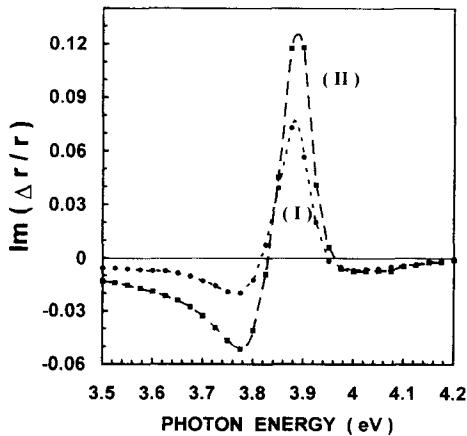

Fig. 3. Experimental imaginary part of the differential optical reflectance $\Delta r/r$: curve I, clean (110) Ag single crystal; curve II, oxidized (110) Ag single crystal

5. Conclusion

We have observed experimentally a very large optical anisotropy by RDS on the (110) face of a single Ag crystal. Such an anisotropy was predicted indeed by a model we developed that accounts for the surface crystalline geometry and for both interband and intraband transitions. The origin of these anisotropies is the screened local field effect on resonant atomic-like polarization processes. Further theoretical developments are required in order to incorporate also the effects of the spatial dispersion and of the surface density profile.

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