# Large Anisotropy in the Optical Reflectance of Ag(110) Single Crystals: Experiment and Theory

Y. Borensztein
*Laboratoire d'Optique des Solides, Université Pierre et Marie Curie, Boîte 80, 4 place Jussieu, 75252 Paris Cedex 05, France*

W. L. Mochan and J. Tarriba
*Instituto de Fisica, Universidad Nacional Autonoma de Mexico, Laboratorio de Cuernavaca, Apartado Postal 139-B,*
*62191 Cuernavaca, Morelos, Mexico*

R. G. Barrera
*Instituto de Fisica, Universidad Nacional Autonoma de Mexico, Apartado Postal 20-364, 01000 Mexico D.F., Mexico*

A. Tadjeddine
*Laboratoire d'Electrochimie des Interfaces, Centre National de la Recherche Scientifique, 1 place Aristide Briand,*
*92195 Meudon Cedex, France*
(Received 5 February 1993)

We report the first observation of a large (more than 10%) reflectance anisotropy on a Ag(110) single crystal. We reproduce the experimental data fairly well by use of a theoretical model, based on the quasistatic approximation, which takes into account both the actual geometry of the crystal surface and the interband and intraband transitions. This demonstrates that the main effect is the screened surface local-field effect on resonant dipolar oscillations localized near the surface.

PACS numbers: 78.66.Bz, 73.20.Mf, 78.20.Ci

The symmetry of crystal surfaces has been shown to have a great influence on the physical and chemical properties of materials [1-3]. It is therefore of crucial interest to reach the surface properties of crystals by means of nondestructive techniques which can be applied in environments other than vacuum, such as gas or liquids. Reflectance difference spectroscopy (RDS) is a powerful tool for studying semiconductor surfaces [4,5] and monitoring semiconductor crystal growth, even in a gas atmosphere [6]. However, up to now, metal surfaces have not been investigated by RDS, although anisotropy effects have been observed on (110) surfaces of single Ag crystals by electroreflectance [7,8] and by electron energy loss spectroscopy experiments [9], and the dispersion relation of surface plasmons has been shown to depend on the direction of propagation along the surface [8,9].

In this Letter we present an experimental and theoretical investigation of the optical reflectance of Ag(110). In particular, we report the first experimental observation by RDS of an anisotropy in the optical reflectance of the Ag(110) surface, the size of which is larger than that of semiconductor surfaces by 1 to 2 orders of magnitude [4,10,11]. We also reproduce fairly well the experimental reflectance anisotropy (RA) with a theoretical model which takes into account both *d* and *s-p* electron transitions, as well as the crystalline geometry of the (110) surface [12]. This large optical anisotropy originates from resonances in the surface conductivities, which are found to be different for the two principal symmetry directions of the (110) surface.

The Ag 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 mirrorlike finish using successively finer grades of diamond polishing suspension down to 0.25 $\mu$m. Then they were chemically polished using a well-established chromium trioxide/hydrochloric acid etching procedure described previously [13]. This chemical treatment results in the selective dissolution of the cold-rolling layer formed during the mechanical polishing and was shown to provide well-defined single crystal Ag surfaces by capacitance and scanning tunneling microscopy studies [13]. The real and imaginary parts of the $RA\Delta r/r = (r_{[1\bar{1}0]} - r_{[001]})/r_{[001]}$ were measured with a commercial RDS instrument, developed by ISA Jobin-Yvon Company (France). $r_{[1\bar{1}0]}$ and $r_{[001]}$ are the complex reflectances for the electric field aligned along the $[1\bar{1}0]$ and the [001] directions, respectively. A RDS setup is equivalent to a normal incidence ellipsometer, which directly delivers the real and imaginary parts of the ratio $r_{[1\bar{1}0]}/r_{[001]}$. Therefore, for a bulk isotropic crystal, it is sensitive to the anisotropy of the surface optical response only. A description of the instrument can be found in Ref. [14]. The light source is a 75 W xenon lamp and the angle of incidence is 2.75°. Both the polarizer and the analyzer are Glan-Taylor polarizers and the photoelastic modulator consists of a fused silica bar submitted to a periodical stress (50 kHz). The energy of the light is analyzed by a double grating monochromator. The analog amplified signal given by the photomultiplier is converted into a digital signal and then is Fourier analyzed through a digital signal processor, yielding directly the real and imaginary parts of $\Delta r/r$. In order to avoid any spurious anisotropy signal due to the apparatus, the measurements were performed for each sample at two angles rotated by 90° in the plane of the sam-

0031-9007/93/71(14)/2334(4)$06.00

ple, and the data were then combined in order to get a mean value of $\Delta r/r$.

RA measurements were performed for photon energies between 2.5 and 4.8 eV, but anisotropy was observed in the 3.7–4.1 eV range only. The real and imaginary parts of $\Delta r/r$ are shown in Figs. 1 and 2, respectively. Spectra were obtained (*I*) on an Ag sample chemically polished just before the optical measurements and (*II*) on a Ag sample chemically polished 48 h prior the measurements, thus with a slightly contaminated surface. The RA spectra for both samples display a very similar feature; they only differ by the intensities of the two characteristic peaks, which are significantly larger for the contaminated Ag. A remarkable characteristic is that the RA reaches very large values, of the order of 10%.

Tadjeddine, Kolb, and Kötz have proposed a simple explanation for the observed difference between the dispersion relations of surface plasmons (SP's) on different faces of Ag crystals, as well as along the two principal symmetry directions of Ag(110) [8]. They found, for all measured wave vectors $q$, that the energy $\hbar\omega_{\mathrm{SP}}(q)$ of the SP excitation increases as the packing of the Ag surface in the direction of the SP field. For the Ag(110) face, the highest $\hbar\omega_{\mathrm{SP}}(q)$ were observed in the $[1\bar{1}0]$ direction. This effect was explained by assuming that the free electrons have a smaller optical effective mass along the denser surfaces and, for the (110) surface, along the $[1\bar{1}0]$ direction which is parallel to the atom rows. To test the validity of this interpretation in our case, we present the results of a crude calculation where a surface region 0.2 nm thick is assumed anisotropic and has two different free-electron conductivities: the bulk Ag one along $[1\bar{1}0]$ and zero along [001]. This leads to a RA shown in Figs. 1 and 2 (dotted lines). One can see that the line shapes of the experimental spectra are not reproduced. Moreover, our calculation shows that the anisotropy of the scattering time of the conduction electron leads to very weak effects on $\Delta r/r$. A difference in the optical effective mass and in the scattering time of the conduction electrons along both directions is clearly not sufficient to explain our experimental results, and a more elaborate model should be used.

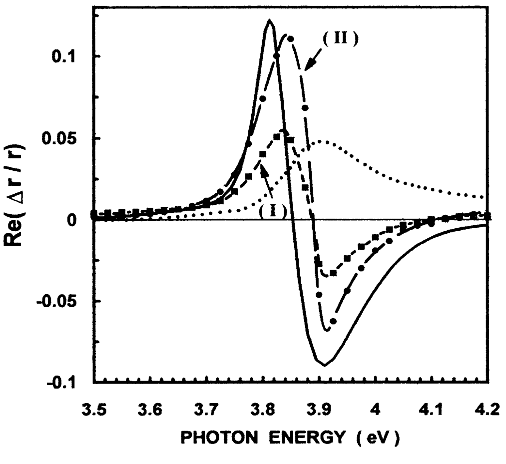

FIG. 1. Real part of the reflectance anisotropy. Short-dashed line (*I*): experimental data for the clean sample; long-dashed line (*II*): experimental data for the contaminated sample. Dotted line: simple calculation based on Tadjeddine's phenomenological result [8]. Solid line: local-field effect calculation.

Recently, Tarriba and Mochan [12] have developed a local electromagnetic model to attempt to reproduce the electron-energy loss dispersion curves observed on the Ag single crystal faces [9], accounting for both interband and intraband transitions. With this model, they also predicted large deviations of the reflectance, with respect to the Fresnel values, for the Ag(110) surface, which were different for electric field aligned along the $[1\bar{1}0]$ and the [001] directions [9], leading to a large RA. Here we use this model in order to interpret our RA results. First, one considers that the $d$ electrons are mostly localized around the ionic core positions, whereas the $s$-$p$ conduction electrons are delocalized. One then assumes that the $d$ electrons are confined within an imaginary sphere centered around each ion, while the interstitial region outside the spheres contains predominantly conduction electrons. The Ag crystal is then modeled by a uniform electron gas where spherical cavities centered at the fcc lattice sites are carved. The polarization of each cavity is described by a point dipole $p_1^i$ located at its center ($i$), whose polarizability $\alpha'$ accounts for interband transitions, conduction current within the spheres, core polarization, and all intracavity interactions. These induced dynamical dipoles, within the cavities, are sources of an electric field which is screened by the surrounding electron gas, located in the interstitial region, and characterized by a local Drude response: $\varepsilon_g = 1 - \omega_p^2/(\omega^2 + i\omega\tau^{-1})$, where $\omega_p$ is the free-electron plasma frequency and $\tau$ the relaxation time.

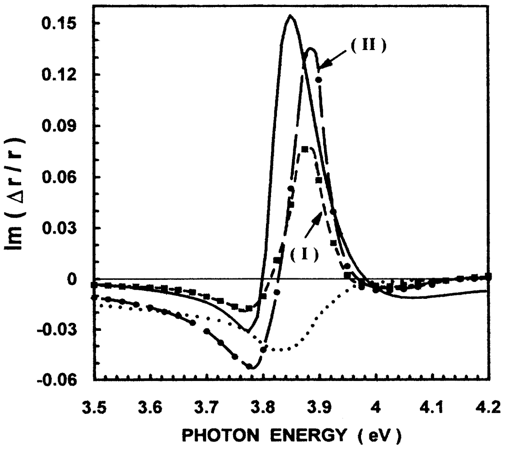

FIG. 2. Imaginary part of the reflectance anisotropy. Same as Fig. 1.

The second step is the calculation, within the quasistatic limit, of the induced apparent dipoles $p_i'$ at every site,

$$p_i' = \alpha' E_{\text{loc}\,i} \,, \tag{1}$$

where the local electric field $E_{\text{loc}\,i}$ is the sum of the external field screened by the semi-infinite electron gas, the fields created by all the other dipoles $p_j'$, and the fields created by the images of all the dipoles through the surface of the electron gas [9]. One is able to determine the effective polarizability $\alpha'$ of the dipoles by considering that in an infinite system with cubic symmetry it obeys the Clausius-Mossotti relation,

$$(\varepsilon - \varepsilon_g)/(\varepsilon + 2\varepsilon_g) = 4\pi n \alpha'/3 \,,$$

where $\varepsilon$ is the Ag bulk dielectric function and $n$ is the number density of ions. After Eq. (1) is solved numerically [15], the surface conductivity $\sigma$, defined through $j = \sigma E$, can be expressed as a function of $\varepsilon$, of $\varepsilon_g$, of the interplanar distance, and of a sum over the induced apparent dipoles $p_i'$ in the crystalline planes [12]. $j$ and $E$ are the surface current and the electric field (parallel to the surface) [16]. We obtain two different surface conductivities $\sigma_{[1\bar{1}0]}$ and $\sigma_{[001]}$ from which the RA can be calculated [16]. The comparison with the experimental data is a test for the validity of the model.

Our calculations have shown that the choice of different realistic values for the plasma frequency $\omega_p$ of the interstitial free-electron gas has little influence on RA spectra. On the other hand, the bulk dielectric function $\varepsilon$ has an important effect on the line shape of the spectra. In the present calculation, we have taken $\omega_p$ corresponding to the average free-electron density in bulk Ag, 9.2 eV, and the values of $\varepsilon$ determined by Johnson and Christy [17], which describe well the optical response of Ag. The final results are shown by continuous lines in Figs. 1 and 2. The agreement with the experimental data is very good, indicating that our model provides a good description of a Ag crystal. The magnitude of the anisotropy increases with the surface contamination. This can be attributed to the growth of a sulphur overlayer which reduces $r$, hence the denominator in $\Delta r/r$. Our theoretical model assumes an abrupt interface and very localized $d$ electrons, so it most probably overestimates the surface local-field effect and therefore agrees better with experiments on the most contaminated sample. The remaining disagreement between experiment and theory, especially in the position of the change of sign in $\mathrm{Re}(\Delta r/r)$, could be due to the values chosen in the model for the bulk dielectric function. Several experimental sets of data for the dielectric function can be found in the literature. In Ref. [12], where another choice had been made, the line shape of RA was different from the present experimental data. However, we performed preliminary standard spectroscopic ellipsometry experiments in order to determine the bulk dielectric function of our samples, which led to values close to the Johnson and Christy ones used here. Other theoretical approaches that account for similar effects may also be useful [18].

The origin of the observed optical anisotropy is, according to our model, the very large deviations of the reflectances of the Ag(110) surface for both symmetry directions from the Fresnel reflectance. These deviations are due to large resonant surface optical absorptions, corresponding to self-sustained dipolar oscillations localized close to the surface [12]. Their energies, near the interband transition threshold (3.87 eV [19]), depend on the orientation of the electric field on the Ag(110) face. This is illustrated by Fig. 3, which shows the real part of the surface optical conductivities $\sigma$ along the $[1\bar{1}0]$ and [001] directions. The surface optical absorption, proportional to $\mathrm{Re}(\sigma)$, has a resonance at 3.82 eV along the [001] direction and at 4.06 eV along the $[1\bar{1}0]$ one, shifted from that of the effective polarizability $\alpha'$, located at 3.96 eV, due to the coupling between dipoles through direct and image Coulomb fields. The observed anisotropy on Ag(110) therefore originates from the orientation dependence of $\sigma$, due to the dependence of the dipolar sums on the surface geometry [15]. The surprisingly large size of the RA has two different origins. On the one hand, the surface local-field effect shifts the resonance to the plasma frequency region (3.78 eV) where dissipation is small, so that the conductivities $\sigma$ display values about 1 order of magnitude larger than in other systems. On the other hand, the small values of the reflectance $r$, around 3.9 eV, enhance the size of $\Delta r/r$ by another order of magnitude.

In conclusion, we have observed a very large RA on a Ag(110) crystal, whose spectra were reproduced successfully using a theoretical model. The origin of the anisotropy is the existence of localized dipolar resonances located at the Ag atom sites. The electrostatic interactions between the corresponding dipoles, screened by the Ag free electrons, depend on the direction of the applied electric field with respect to the surface, leading to different shifts

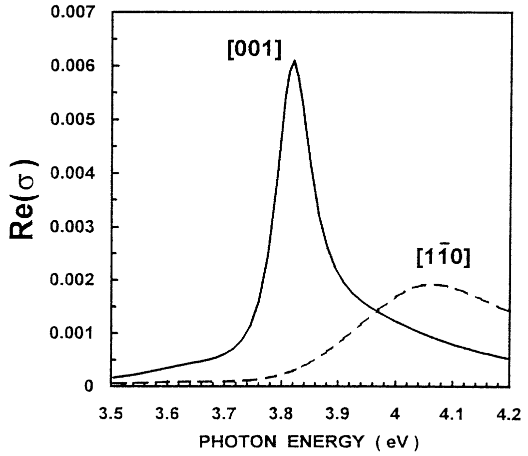

FIG 3. Real parts of the surface conductivities $\sigma_{[001]}$ and $\sigma_{[1\bar{1}0]}$.

of the resonance for the [001] and [1$\bar{1}$0] directions. There are other contributions to the surface induced anisotropy. Some are extrinsic such as directional surface roughness, and others are intrinsic such as transitions involving surface states and surface modified bulk states. Their relative importance depends on the surface preparation. However, the close agreement between our essentially parameter-free model and our experiment demonstrates the importance of the screened surface local-field effect at noble metal surfaces. Our results also confirm that RDS is a linear optical technique that is inherently sensitive to the surface of isotropic materials. It can then be used to investigate the surface electronic profiles of metal single crystals in dense media, where most surface techniques are ineffective. A promising perspective is the study of metal surfaces in an electrochemical environment, where the surface electronic properties and the surface reconstruction can be easily monitored by the electrode potential and the electrolyte composition [3,20].

We are grateful to ISA Jobin-Yvon Company and R. Benferhat for having allowed us to perform the RDS measurements on their instrument. We thank M. Stchakovsky for his technical assistance, B. Drevillon for his help in managing the experiments, and M. L. Thèye for her critical reading of the manuscript. Two of us (W.L.M. and R.G.B.) acknowledge the partial support of DGAPA-UNAM through Grants No. IN-102592 and No. IN-102493.

Laboratoire d'Optique des Solides is UA CNRS 781.

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[1] D. E. Aspnes, J. P. Harbison, A. A. Studna, and L. T. Florez, Phys. Rev. Lett. **59**, 1687 (1987); V. L. Berkovits *et al.*, J. Appl. Phys. **70**, 3707 (1991); I. Kamiya *et al.*, Phys. Rev. Lett. **68**, 627 (1992).

[2] A. Tadjeddine, D. Guay, M. Ladouceur, and G. Tourillon, Phys. Rev. Lett. **66**, 2235 (1991).

[3] B. M. Ocko, G. Helgesen, Bruce Schardt, Jia Wang, and A. Hamelin, Phys. Rev. Lett. **69**, 3350 (1992).

[4] D. E. Aspnes and A. A. Studna, Phys. Rev. Lett. **54**, 1956 (1985).

[5] P. Chiaradia, A. Cricenti, S. Selci, and G. Chiarotti, Phys. Rev. Lett. **52**, 1145 (1984).

[6] D. E. Aspnes *et al.*, Phys. Rev. Lett. **61**, 2782 (1988); E. Colas *et al.*, J. Cryst. Growth **94**, 613 (1989); S. M. Koch *et al.*, J. Appl. Phys. **69**, 1389 (1991).

[7] T. E. Furtak and D. W. Lynch, Phys. Rev. Lett. **35**, 960 (1975).

[8] A. Tadjeddine, D. M. Kolb, and R. Kötz, Surf. Sci. **101**, 277 (1980).

[9] S. Suto, K.D. Tsuei, E. W. Plummer, and E. Burstein, Phys. Rev. Lett. **63**, 2590 (1989); M. Rocca, M. Lazzarino, and U. Valbusa, Phys. Rev. Lett. **67**, 3197 (1991); G. Lee, P. T. Sprunger, E. W. Plummer, and S. Suto, Phys. Rev. Lett. **67**, 3198 (1991); M. Rocca, M. Lazzarino, and U. Valbusa, Phys. Rev. Lett. **69**, 2122 (1992).

[10] W. L. Mochan and R. G. Barrera, Phys. Rev. Lett. **55**, 1192 (1985); A. Selloni, P. Marsella, and R. Del Sole, Phys. Rev. B **33**, 8885 (1986); F. Manghi, R. Del Sole, A. Selloni, and E. Molinari, Phys. Rev. B **41**, 9935 (1990).

[11] R. Del Sole, W. L. Mochan, and R. G. Barrera, Phys. Rev. B **43**, 2136 (1991).

[12] J. Tarriba and W. L. Mochan, Phys. Rev. B **46**, 12902 (1992).

[13] A. Hamelin, T. Vitanov, E. Sevastyanov, and A. Popov, J. Electron. Chem. **145**, 225 (1983); A. Hamelin, L. Stoicoviciu, L. Dubova, and S. Trasatti, Surf. Sci. **201**, L496 (1988); W. J. Lorenz *et al.*, Electrochem. Acta **37**, 2173 (1992).

[14] O. Acher and B. Drevillon, Rev. Sci. Instrum. **63**, 5332 (1992).

[15] B. R. A. Nijboer and F. W. de Wette, Physica (Utrecht) **23**, 309 (1957); **24**, 422 (1958); F. de Wette and G. E. Schacher, Phys. Rev. **137**, A78 (1965); N. Kar and A. Bagchi, Solid State Commun. **33**, 645 (1980).

[16] W. L. Mochan, R. Fuchs, and R. G. Barrera, Phys. Rev. B **27**, 771 (1983).

[17] P. B. Johnson and R. W. Christy, Phys. Rev. B **6**, 4370 (1972).

[18] K. M. Ho, B. N. Harmon, and S. H. Liu, Phys. Rev. Lett. **44**, 1531 (1980); M. Y. Jiang, G. Pajer, and E. Burstein, Surf. Sci. **242**, 306 (1991); A. Liebsch, Phys. Rev. Lett. **71**, 145 (1993); W. L. Schaich (unpublished).

[19] M. M. Dujardin and M. L. Thèye, J. Phys. Chem. Solids **32**, 2033 (1971).

[20] P. Guyot-Sionnest, A. Tadjeddine, and A. Liebsch, Phys. Rev. Lett. **64**, 1678 (1990).