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Surface-state contribution to the optical anisotropy of Ag(110) surfaces: A reflectance-anisotropy-spectroscopy and photoemission study

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The (110) surface of an Ag crystal was investigated by reflectance anisotropy spectroscopy and angle-resolved photoemission spectroscopy. A strong resonance in the optical spectra of the clean surface is assigned to a surface-state transition at the $\overline{Y}$ point of the surface Brillouin zone. This resonance is absent on the oxygen-covered surface. The accompanying photoemission spectra show the corresponding occupied surface state on the clean surface as well as its disappearance with oxygen coverage. [S0163-1829(98)52040-1]

Reflectance anisotropy spectroscopy (RAS) is an optical method which allows the sensitive investigation of surface optical properties of semiconductors[1–3] and metals.[4,5] RAS measures the difference of the complex reflectivity along two perpendicular axes in the surface. In the case of optically isotropic bulk materials, any RAS signal must be related to anisotropies induced by the surface.[6]

Several mechanisms may contribute to the surface-induced optical anisotropy. (i) Electronic transitions between localized surface states constitute one of the interesting cases allowing for direct surface state spectroscopy.[7,8] (ii) Transitions involving near surface bulk states whose symmetry is reduced by the presence of an anisotropically reconstructed surface (surface-induced bulk states) may be another origin for optical surface ansiotropies.[9,10] They give rise to features in the spectra close to the bulk critical points. Finally, apart from these single electron contributions (iii) collective free-carrier oscillations at the surface (surface plasmons) may also affect the optical spectra.[11]

The only example for surface-state contributions to the reflectance anisotropy on a metal surface so far is the Cu(110) surface. Here a sharp peak in the spectrum at an energy of 2.1 eV was assigned to electronic transitions involving surface states at the $\overline{Y}$ point of the surface Brillouin zone.[8,12] However, since in Cu the transition energies of bulk d electrons to the Fermi level are also located in this energy range, the observed feature in the Cu(110) spectra might as well also contain contributions arising from surface modified bulk states. Indeed, the RAS spectra indicate such a contribution from near surface bulk states because part of the anisotropy still remains after exposure of the surface to O or CO.[8] Thus the 2.1 eV structure in the Cu(110) spectra does not constitute a pure surface-state transition.

Silver, on the other hand, has a surface electronic structure similar to Cu. However, contributions from the d-band transitions to the optical spectra are expected at much higher energies [above 4 eV (Ref. 13)] than the surface-state transition energies [1.7 eV (Ref. 7)]. An anisotropic contribution from surface-state transitions to the RAS spectra of the Ag(110) surface thus would be expected in the near infrared region, energetically separated from the d bands.

Measurements of the optical anisotropy of Ag(110) under ambient[14] and UHV conditions[15] have been already reported. In these experiments no contributions from surface electronic states to the RAS spectra were detected. In our paper we report angle-resolved photoemission and RAS measurements on clean and oxygen-covered Ag(110) crystals. On the clean surface we find a peak in the RAS spectra whose appearance correlates with the occupied surface state observed simultaneously with photoemission spectroscopy. We consider the appearance of the surface state in the photoemission spectra as the most sensitive check of the surface preparation. The peak in RAS and photoemission is immediately quenched upon oxygen adsorption. We assign this peak therefore to a transition involving surface states at the $\overline{Y}$ point of the surface Brillouin zone.

Experiments were performed in an ultrahigh-vacuum (UHV) chamber (base pressure 5×10^{-11} Torr) at the SX700 beamline of the Århus electron storage ring ASTRID. The vacuum chamber was equipped with standard facilities for sample preparation and characterization. The Ag(110) sample of 10 mm diam was aligned with Laue x-ray backscattering to 0.1° and mechanically polished to a final roughness better than 0.03 μm. It was mounted in UHV by two tungsten wires. *In situ* cleaning of the surface was done using cycles of argon ion sputtering (8 μA/cm^2, 500 eV, 10 min at 300 K) and subsequent annealing to 670 K until no contaminations could be detected anymore by XPS. Thereafter the LEED pattern showed the typical (1×1) structure with sharp spots and a low background intensity. After surface preparation, oxygen was dosed. The Ag(110) face shows a series of oxygen-induced $(n\times1)$ reconstructions with $n=7,6,5,4,3,2$.[16] The Ag(110)-(3×1)-O and (4×1)-O reconstructions were prepared by backfilling the chamber with 5×10^{-6} Torr O_2 for 290 s and 5×10^{-7} Torr O_2 for 500 s at room temperature, respectively.

The RAS spectrometer is a custom built system which is based on the standard design by Aspnes.[6] A spectral range from 1.2 to 6 eV was accessible using a tungsten lamp for the low-energy region (1.2 to 3.2 eV) and a short arc xenon lamp for the higher photon energies (1.5 to 6 eV) together

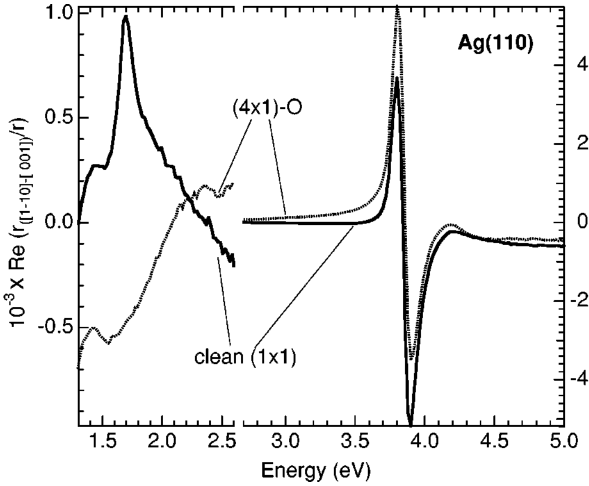

FIG. 1. Real part of the RAS spectrum for the clean Ag(110)-(1×1) and the oxygen-covered Ag(110)-(4×1) surface at $T=300$ K.

with a double grating monochromator. The RAS system was mounted in front of a strain-free quartz window[17] at the UHV chamber. The RAS signal consists of the real and the imaginary part of the reflectance anisotropy:

$$\frac{\Delta r}{r}=2\,\frac{r_{[1\bar{1}0]}-r_{[001]}}{r_{[1\bar{1}0]}+r_{[001]}}. \tag{1}$$

Real and imaginary parts of the RAS data were checked afterwards for consistency by using the Kramers-Kronig relations.[18]

The RAS spectra were further analyzed in terms of the surface dielectric anisotropy. For this purpose a three-phase model was considered. It assumes a homogeneous bulk with an isotropic dielectric function ϵ_b, an optically anisotropic surface layer (thickness $d \ll \lambda$) with $\Delta\epsilon=\epsilon_{[1\bar{1}0]}-\epsilon_{[001]}$, and the surrounding vacuum. Within this model the surface dielectric anisotropy is related to the measured reflection anisotropy[19] by

$$\Delta\epsilon d=\frac{\lambda}{4\pi i}(\epsilon_b-1)\,\frac{\Delta r}{r}. \tag{2}$$

The bulk dielectric function which is needed for this analysis was obtained from data taken *ex situ* with a standard rotating analyzer ellipsometer.[18]

Angle-resolved photoemission data were collected using a commercial VG BLADES electron analyzer with an angular resolution of 4°. All experiments were performed at a fixed energy of $h\nu=32$ eV which gives a high cross section for the surface state at $\overline{Y}$.[20] The angle of incidence of the photons with respect to the surface normal was fixed to 45°. The sample was orientated with the [001] azimuth parallel to the polarization of the incident light.

RAS spectra (real part) of the clean Ag(110)-(1×1) and the oxygen induced (4×1) reconstructed surface are shown in Fig. 1. The dominant feature in both spectra is a peak with a derivativelike line shape around 3.9 eV. Similar results have been already obtained in previous measurements.[14,15] These structures have been described by Tarriba and Mochan[21] using a phenomenological surface local field model. A more microscopic explanation could probably involve near surface bulk transitions since the derivativelike peak structure around 3.9 eV in our spectra is close to the onset of the bulk d band transitions at 4 eV.

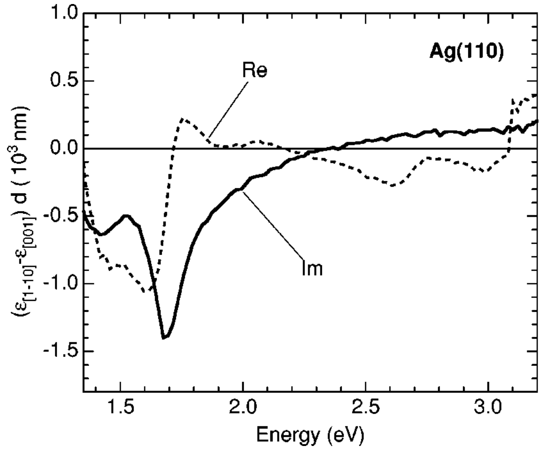

FIG. 2. Real and imaginary part of the surface dielectric anisotropy (SDA) of the clean surface. The SDA was calculated using RAS data measured at $T=300$ K.

The positive value of the anisotropy in the energy range between 2.5 and 3.8 eV occurring on the oxygen-covered surface [Ag(110)-(4×1)-O] probably has its origin in the excitation of surface plasmons. The formation of Ag-O chains[22] with an increased surface roughness was deemed responsible for the excitation of surface plasmons by light due to a relaxation of k conservation. This is consistent with the results of Rocca *et al.*,[23] who indeed found an anisotropy of the surface-plasmon dispersion on Ag(110) surfaces even for small wave vectors parallel to the surface.

The new feature besides these well known structures is a much smaller peak occurring at an energy of 1.7 eV. It is assigned to a transition between an occupied surface state 0.1 eV below (see Fig. 3) and an unoccupied surface state 1.6 eV above the Fermi level,[24] both located at the $\overline{Y}$ point of the surface Brillouin zone. As expected, this transition is absent on the oxygen-covered surface. The anisotropy in the optical reflection spectra of the clean Ag(110) and Cu(110) surfaces

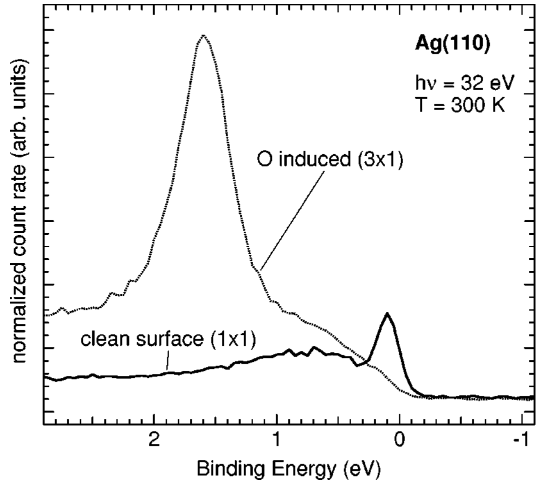

FIG. 3. Photoemission spectra for the clean and oxygen-induced (3×1) surface taken at $\Theta=16.5°$ off-normal emission. The spectrum for the clean surface shows the surface state at $\overline{Y}$.

was predicted by Jiang and co-workers.[7] Their dipole selection rules for the surface-state transition can be summarized as follows: The occupied surface state (σ_y) (y denotes the [001] direction) derived from a p_y-type bulk state has even symmetry in the $[1\bar{1}0]$ and odd symmetry in the [001] direction. The unoccupied state of $\bar{s}$-type character possesses even symmetry in both the $[1\bar{1}0]$ and [001] directions. Therefore the transition ($\sigma_y \rightarrow s$) is only allowed for light polarized along [001]. Since RAS probes the difference in reflectivity for light polarized along [001] and $[1\bar{1}0]$, one expects to observe this surface-state transition due to the absorption for light polarized along [001].[7]

The imaginary part of the surface dielectric anisotropy in Fig. 2 shows, as expected, a negative absorption structure in $\Delta\epsilon = \epsilon_{[1\bar{1}0]} - \epsilon_{[001]}$ in agreement with the dipole selection rules. The same transition was also found in an experiment using second-harmonic generation.[25] The fact that this transition has not been seen before in RAS data might be due to the poor surface quality.

We used photoemission spectroscopy to verify the presence of the occupied surface state and its disappearence upon oxygen adsorption. The results are plotted in Fig. 3 for the clean Ag(110) and the Ag(110)-(3×1)-O surface. The spectrum of the clean surface shows the surface state at $\bar{Y}$ just below the Fermi level. We estimate a binding energy of 0.10 ± 0.05 eV, a value consistent with the literature.[20] On the oxygen-covered surface, this peak is absent and a new prominent feature appears at ~1.6 eV below the Fermi level which has been assigned to an antibonding oxygen-induced p state.[26,27]

In summary we have investigated clean and oxygen covered Ag(110) surfaces with relectance anisotropy spectroscopy and photoemission spectroscopy. The clean surface shows a resonance in the reflectance anisotropy spectra due to transitions between surface states at 1.7 eV. Simultaneously a peak due to the occupied surface state is seen in the photoemission spectra. Oxygen adsorption leads to a quenching of this surface state which correlates to the disappearance of the peak in the optical spectra.

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