

Study of Surface States on Cu(110) Using Optical Reflectance Anisotropy

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We report spectroscopic measurements of the azimuthal anisotropy in the normal incidence reflectivity of a clean and adsorbate-covered single-crystal metal surface: Reflectance anisotropy spectra were taken between 1.5 and 6 eV from Cu(110). On the clean surface, a sharp resonance is found which is assigned to a transition between two surface states at the \bar{Y} point of the surface Brillouin zone. The resonance can be removed by adsorption, and its energetic position is in good agreement with photoemission and inverse photoemission work.

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The optical response of a solid is dictated by its complex dielectric tensor. In the case of a centrosymmetric material, such as a cubic crystal, the tensor is reduced to a complex scalar. Consequently, the normal-incidence reflectivity of a cubic crystal should not depend on the azimuthal orientation of the polarization vector. This is true, however, only for the dielectric response of the bulk crystal; at the surface, the inversion symmetry is broken. Any azimuthal anisotropy in the normal-incidence reflectivity of cubic crystals must therefore have its origin in the surface region. Reflectance anisotropy spectroscopy (RAS) probes the difference in the normal-incidence reflectivity along two mutually perpendicular orientations of the polarization vector as a function of photon energy [1,2]. Usually, one or both of these directions coincides with the principal crystallographic directions in the surface. The technique provides useful information about the electronic structure of the surface, although the interpretation of the features observed in the spectrum often requires elaborate model calculations. Recently, Borensztein *et al.* [3] have measured the reflectance anisotropy of an Ag(110) surface in air, and ascribed the structure in the spectrum to optical absorption enhanced by surface local-field effects.

In this Letter we report spectroscopic RAS measurements on a clean and adsorbate-covered single-crystal metal surface under ultrahigh vacuum conditions. We have chosen the clean Cu(110) surface and the adsorbate systems Cu(110)-(2 × 1)-CO, Cu(110)-(2 × 1)-O, and Cu(110)-(2 × 3)-N. The geometric structure of the first three systems is known precisely [4–9] so that calculations of the reflectance anisotropy should eventually be possible. A strong resonance is observed on the clean surface and is attributed to a transition between surface states. Surprisingly, this appears to be the first direct observation of surface states on a metal surface with a simple reflection technique [10].

The Cu(110) sample was prepared by the usual methods of x-ray Laue orientation, spark machining, pol-

ishing, and *in situ* cleaning with argon ion bombardment and annealing cycles. Surface order and cleanliness were monitored by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The CO (2 × 1) overlayer was produced by exposing the surface to 1.6×10^{-6} mbar·s CO at 120 K. The oxygen-induced (2 × 1) reconstruction was prepared by dosing 1.4×10^{-5} mbar·s O₂ at room temperature. The nitrogen structure was prepared by implanting nitrogen ions with a kinetic energy of 500 eV into the crystal for 20 min at room temperature. The ion current was 2.5 μA. Subsequently, the sample was annealed to 670 K for 2 min. The RAS spectra were taken at 120 K and room temperature, respectively. The RAS spectrometer [11] was mounted on the ultrahigh vacuum system in front of a low-strain quartz window. The spectrometer measures the normalized difference between the complex reflectivity r along the two main azimuthal directions of the sample $\Delta r/\bar{r} = 2(r_{[\bar{1}10]} - r_{[001]})/(r_{[\bar{1}10]} + r_{[001]})$. The coolable UHV manipulator unfortunately did not allow sufficient sample rotation to enable the measurement to be performed in two orthogonal sample azimuths. This is the standard approach to removing background effects which occur due to residual strain in the window as well as to the use of nonideal optical components. The imaginary part of $\Delta r/\bar{r}$ (see Fig. 2 below) thus has a pronounced negatively sloping background. Spectra were taken for clean Cu(110) as well as for the three adsorbate systems between 1.5 and 6 eV.

Figures 1 and 2 show the real and imaginary parts, respectively, of the RAS spectra for clean Cu(110), Cu(110)-(2 × 1)-O, and Cu(110)-(2 × 1)-CO. The spectrum for the Cu(110)-(2 × 3)-N structure was almost identical with that of oxygen and is, therefore, not displayed in the figures. The most prominent feature in both sets of spectra is found at ~2.1 eV for the clean surface; it is small for the (2 × 1)-O structure and completely absent for the CO structure. The 2.1 eV feature in $\text{Re}(\Delta r/\bar{r})$ is also sensi-

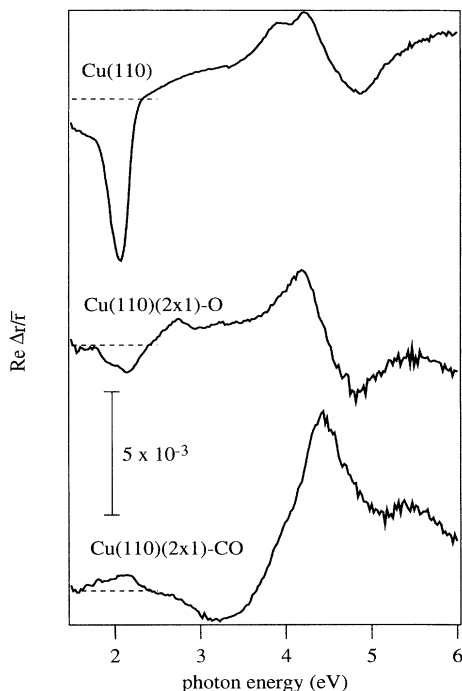


FIG. 1. Real part of the RAS spectrum for clean Cu(110), Cu(110)-(2 × 1)-O, and Cu(110)-(2 × 1)-CO. The dashed horizontal lines represent the zeros of the corresponding spectra.

tive to surface contamination in that its intensity decreases when the freshly cleaned sample is subject to contamination from the residual gas. For all three systems, a second feature in the RAS spectra is found at ~ 4 eV; in the case of the clean surface, this has peaks at 3.8 and 4.2 eV in $\text{Re}(\Delta r/\bar{r})$. The 3.8 eV feature is quenched by adsorption in the same way as the 2.1 eV feature.

We assign the feature at ~ 2.1 eV on the clean surface to an interband transition between two surface states following a prediction by Jiang, Pajer, and Burstein [12]: At the \bar{Y} point of the surface Brillouin zone, two surface states can be found in the gap of the projected bulk band structure. One is derived from an occupied p -type band and the other from an unoccupied s -type band (Fig. 3) [13]. The occupied state has been identified at 0.4 eV below E_F in photoemission [14,15] and the unoccupied state at ~ 2 eV above E_F in inverse photoemission [15–17]. Dipole selection rules indicate that a transition between these two surface states (p_y - s) can be induced only by light polarized in the [001] azimuth (or y direction), and hence a resonance in the RAS spectrum is to be expected [12]. The behavior upon adsorption supports this assignment: Contamination of the surface or the adsorption of oxygen, nitrogen, or carbon monoxide leads to a quenching of the surface states which causes the RAS structure to disappear.

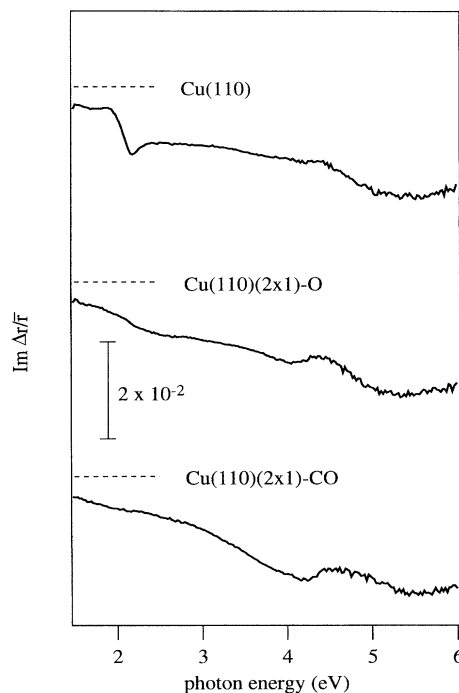


FIG. 2. Imaginary part of the RAS spectrum for clean Cu(110), Cu(110)-(2 × 1)-O, and Cu(110)-(2 × 1)-CO. The dashed horizontal lines represent the zeros of the corresponding spectra. The negative slope of the spectra might contain a contribution from the nonideal polarization.

Some indication of an azimuthal anisotropy in the optical response of clean Cu(110) has already been reported in a spectroscopic ellipsometry investigation by Hanekamp, Lisowski, and Bootsma [18]. The difference between the ellipsometric parameters, Δ and Ψ , determined with the plane of incidence perpendicular and parallel to the [001] direction shows a resonance around 2.1 eV. However, the surface contribution in conventional ellipsometry is very small, and the large error bars did not permit any definitive conclusions. Kötz and Kolb have measured the normal-incidence electroreflectance spectra of Cu(110) in 0.5 M H_2SO_4 for light polarized parallel and perpendicular to the [001] direction [19]. They observed a distinct difference between the two $\Delta R/R$ spectra and, interestingly, the difference spectrum appears to be very similar to the real part of the RAS spectrum reported here. In a more definitive experiment using second harmonic generation (SHG), Woll *et al.* [20] have very recently found the same resonance at ~ 2.1 eV but were reluctant to identify it with the p_y - s surface state transition at \bar{Y} .

In the RAS spectrum of Ag(110), a feature due to the same transition should be present at ~ 1.7 eV. Unfortunately, RAS experiments on this surface have so far been carried out only in air and in a restricted energy range [3]. However, as in the case of Cu(110), the transition has also

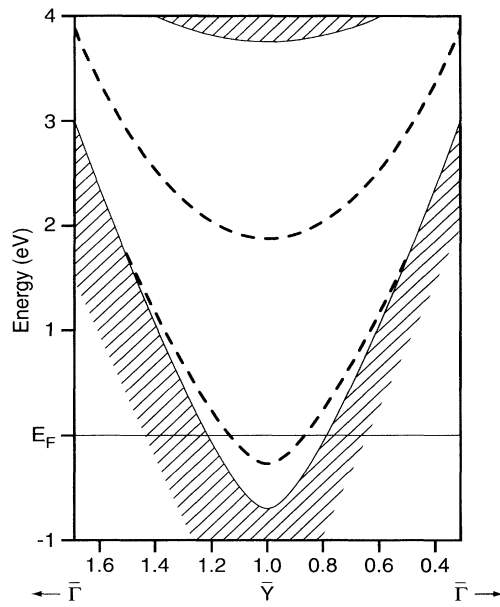


FIG. 3. Surface electronic structure of Cu(110) near the \bar{Y} point. The shaded regions are the projected bulk bands and the dashed lines are the two surface states. After Ref. [13].

been found with SHG: Urbach *et al.* have shown that it leads to a resonant enhancement at 1.7 eV for light polarized along the [001] azimuth of the sample [21].

The assignment of the two features around 4 eV is less straightforward. Since the feature at 3.8 eV is quenched by adsorption, it must be assigned—similar to the 2.1 eV feature—in terms of a transition involving electronic states which exist only on the clean surface. Inspection of the surface band structure near the \bar{X} point [12,13,20,22] reveals that there is an unoccupied surface state band in the gap of the projected bulk band structure at ~ 2 eV above E_F with p_x character. Further, there is an occupied surface band along $\bar{\Gamma}\bar{X}$ at ~ 2 eV below E_F with d_{xy} character. A transition between these two states would be dipole allowed and could account for the clean surface transition at 3.8 eV. However, if the symmetry assignments are correct, the selection rules show that the transition would be polarized in the y direction. From Fig. 1, it is clear that the orthogonal direction is involved, i.e., E_x is required. Another, and more likely, possibility is a transition between a high density of states at the surface Fermi surface and the well-known image potential state which is found ~ 4 eV above E_F in the vicinity of the $\bar{\Gamma}$ point [16].

The second higher-energy feature at 4.2 eV occurring on both the clean and adsorbate-covered surfaces requires a different explanation. It is due most likely to an intrinsic anisotropy caused by the surface local-field effect as recently investigated by Mochan and co-workers [23]. These authors have developed a simple model describing

the reflectance anisotropy of a cubic crystal which is caused just by truncation of the bulk, and does not require the introduction of new electronic states at the surface. The model takes into account the geometric structure of the surface as well as interband and intraband transitions. It has been applied successfully to structure in the RAS spectra of Ag(110) and Au(110) taken in air [3,24], suggesting that contamination or even oxidation of the surface is only of minor importance. Our 4.2 eV structure has a similar form to that on the Ag and Au surfaces and is only little affected by the presence of CO, oxygen, and nitrogen. Moreover, the adsorption of oxygen induces a major reconstruction of the surface in which half of the outermost layer metal atoms are displaced. We may therefore conclude that this intrinsic reflectance anisotropy does not necessarily give useful information on surface structure. Nevertheless, it is important to identify the effect in order to characterize the additional anisotropy introduced by surface states or adsorbates.

Optical techniques such as RAS allow time-resolved studies in a gaseous ambient. Combined with the possibility of restricting the origin of the signal to the surface region, this may allow some interesting applications in the investigation of adsorption or desorption processes or other surface chemical reactions. Figure 4 shows $\text{Re}(\Delta r/\bar{r})$ at 2.1 eV as a function of time when the clean surface is exposed to oxygen by backfilling the chamber with a partial pressure of 4×10^{-8} mbar O_2 .

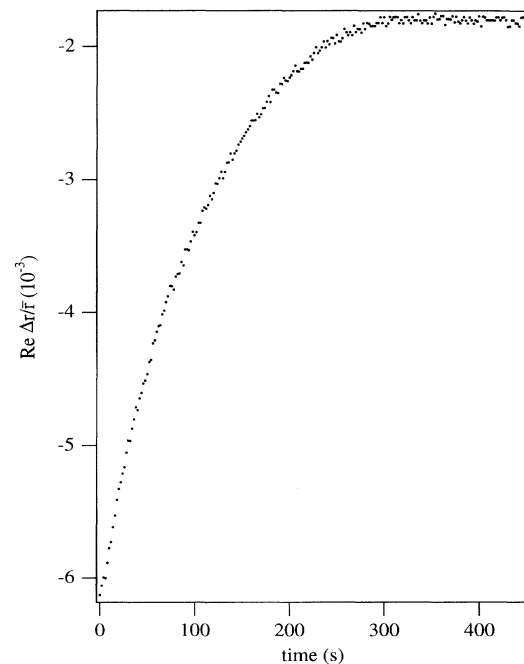


FIG. 4. Real part of the RAS complex reflectivity at 2.1 eV as a function of time during exposure of the clean surface to molecular oxygen at room temperature, beginning at $t = 0$ s.

The increase in the signal is due to the quenching of the surface states with oxygen coverage. Clearly, the saturation coverage is reached after 300 s corresponding to an exposure of 1.2×10^{-8} mbar·s O_2 . Indeed, the real-time investigation of the dynamics of surface processes is the most promising future application of RAS on metal surfaces and adsorbates. Note that the surface states involved could also be electronic energy levels of an adsorbed species. Pemble *et al.* [25] have recently shown that RAS can be used to monitor adsorption-induced changes on the Cu(110) surface using a HeNe laser. The photon energy of 1.96 eV matches approximately that of the p_y - s surface state transition at \bar{Y} , which has been investigated spectroscopically in the present work.

In summary, we have presented an RS investigation of a clean and adsorbate-covered metal surface. A transition between surface state bands leads to a distinct resonance in the spectrum of the clean surface at 2.1 eV, as predicted by Jiang, Pajer, and Burstein [12]. Another clean surface feature at 3.8 eV may be related to an image potential state. A further structure at ~ 4.2 eV, not quenched by adsorption, is due to an intrinsic anisotropy rather than a transition involving surface states. We note that the dynamics of adsorption or desorption phenomena or even of chemical reactions may be studied in real time using characteristic surface state transitions in RAS.

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