

Reflection anisotropy spectroscopy of the Na/Cu(110)(1×2) surface reconstruction

D. S. Martin,^{*} A. M. Davarpanah, S. D. Barrett, and P. Weightman

Surface Science Research Centre and Department of Physics, University of Liverpool, Liverpool, L69 3BX, United Kingdom

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The optical technique of reflection anisotropy spectroscopy (RAS) has been used to study the Cu(110)-(1×2) surface reconstruction induced by Na adsorption. Room temperature deposition of submonolayer coverages of Na onto the Cu(110) surface results in the (1×2) reconstruction and is known to induce energy shifts in both the occupied and unoccupied surface states at the \bar{Y} point on Cu(110). Transitions between these surface states have been associated with a peak observed at 2.1 eV in the RA spectrum. We report RAS studies of the reconstruction and relate changes in the RA spectra at 2.1 eV to changes in the surface states induced by Na adsorption.

Surface reconstruction of fcc (110) metals induced by alkali-metal adsorption has been studied extensively both experimentally and theoretically.¹ Similar phases are observed for comparable coverages of the adsorbates Na, K, and Cs on the late 3*d* and 4*d* transition and noble metal (110) surfaces. Low-energy electron diffraction (LEED) has been used to chart the progression of the reconstruction as a function of adsorbate coverage²⁻⁴ and scanning tunneling microscopy has shown that the mechanism of reconstruction is initiated by local nucleation involving only a single alkali-metal adatom.^{5,6} The Na-induced (1×2) missing row reconstruction of the Cu(110) surface has received particular attention⁷⁻¹⁰ and it has been established that the reconstruction induces shifts in the energies of both the occupied and unoccupied surface states.^{7,10} The contributions from the adsorbate bonding and the reconstruction mechanism to the energy shifts of the surface states at the \bar{Y} point of the surface Brillouin zone (SBZ) have each been identified.⁷

Reflection anisotropy spectroscopy (RAS) probes as a function of energy the optical response of a surface with linearly polarized light by measuring the difference in reflection at normal incidence of two perpendicular directions (Δr) normalized to the mean reflection (r). The complex reflection anisotropy is defined in terms of Fresnel reflection amplitudes:

$$\frac{\Delta r}{r} = \frac{2(r_{[1\bar{1}0]} - r_{[001]})}{r_{[1\bar{1}0]} + r_{[001]}}. \quad (1)$$

Materials possessing cubic crystal structures have isotropic bulk optical properties and RAS, when applied to a cubic crystal, becomes a sensitive optical probe of anisotropy in the surface electronic structure.

The RAS spectrum of the Cu(110) surface has been studied by a number of groups¹¹⁻¹⁶ and significant progress has been made in the interpretation of the spectrum. A peak in the RA spectrum at 2.1 eV was first assigned to the surface local-field effect^{17,18} in detailed calculations for the Cu(110) surface by Hansen *et al.*¹³ It has since become clear that there is an additional strong contribution to the 2.1 eV peak arising from a transition between surface states at the \bar{Y} point.^{11,16} The contribution from surface states disappears as

expected upon oxygen adsorption,^{11,15,16} however, the surface retains anisotropy in this region following oxygen adsorption^{11,15,16} and also under ambient conditions.^{15,16} RAS work on metals has focused upon the study of clean and molecular-adsorbate-covered noble metal surfaces. We report here a RAS study of a metal surface reconstruction induced by alkali-metal adsorption.

The experiments were carried out in an ultrahigh vacuum (UHV) environment of base pressure in the 10^{-11} mbar region. The mechanically polished Cu(110) single crystal was aligned using Laue x-ray diffraction to $<0.25^\circ$ before introduction into the vacuum chamber. A clean Cu(110) surface was prepared by cycles of Ar ion sputtering and subsequent annealing to 850 K. Surface order was confirmed by a sharp (1×1) LEED pattern and cleanliness was monitored using x-ray photoelectron spectroscopy (XPS). Na was deposited from a fully outgassed commercial SAES dispenser with pressure rises during evaporations of less than 2×10^{-10} mbar. All depositions took place at room temperature. Coverage was determined from the relative intensities of the Na 1*s* and Cu 2*p* core-level photoelectron lines and supported by LEED analysis.²⁻⁴ We define Na coverage as the ratio of Na atoms to Cu atoms in the unreconstructed surface layer, i.e., $\theta=1$ ML (monolayer) corresponds to 1.1×10^{15} Na atoms/cm². The RA spectrometer of the design of Aspnes *et al.*¹⁹ projected and received light through a low-strain window on the UHV system. Experimental artifacts were removed from the spectra using a correction function obtained by measuring spectra with the sample in two orthogonal positions. Spectra of the real part of the complex RA were taken over a photon energy range of 1.5–5.0 eV.

The RA spectrum for the clean Cu(110) surface at room temperature is shown in Fig. 1(a). The spectral profile of the unreconstructed surface exhibits the main characteristics reported by a number of independent studies,¹¹⁻¹⁵ namely, an intense peak at energy 2.1 eV and a bimodal feature around 4 eV. The peak at 2.1 eV is thought to arise from a combination of two different contributions. The first is electronic transitions at the \bar{Y} point of the SBZ. At room temperature, transitions occur between an occupied surface state at energy 0.4 eV below the Fermi level (E_F) and an unoccupied surface state that has been variously located at energies above

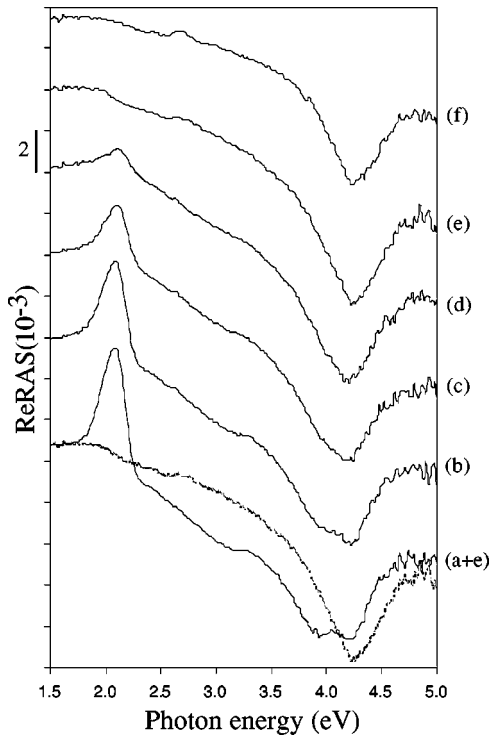


FIG. 1. RA spectra as a function of Na coverage (θ). (a) Clean Cu(110)(1×1). The spectrum observed at 0.25 ML (e) is shown superimposed by the dashed line. (b) $\theta\sim 0.05$ ML. (c) $0.05<\theta<0.11$ ML. (d) $\theta=0.16$ ML. (e) $\theta=0.25$ ML. (f) $\theta=0.25$ ML coverage following annealing to 350 K and cooling to room temperature.

E_F of 2.5 eV,²⁰ 2.0 eV,²¹ and 1.8 eV.²² The transition at \bar{Y} that generates the 2.1 eV feature is induced solely by light polarized along [001], leading to the observed reflectance anisotropy.^{11,23} The assignment of this transition to surface states is supported by the decay of the signal upon molecular adsorption. However, the surface retains anisotropy in this region under ambient conditions^{15,16} and upon the formation of the O/Cu(110)-(2×1) reconstruction.^{11,15,16} It has been suggested that there is also a contribution to the 2.1 eV RA feature originating from transitions from surface-terminated bulk d states to E_F ,^{13,16} and due to intrinsic anisotropy caused by the surface local-field effect.¹³

The peak at 3.8 eV is also suppressed upon molecular adsorption whereas the peak at 4.2 eV appears insensitive to both adsorption and reconstruction.¹¹ It has been suggested that anisotropy around 4 eV may arise as a result of the surface local-field effect.¹³ In a recent study, the observation of a sharp peak at energy 4.2 eV was attributed to transitions at the \bar{X} point between an occupied surface resonance and an unoccupied surface state.¹⁶ Bremer *et al.*¹⁴ and our own studies²⁴ indicate that anisotropy around 4 eV is sensitive to surface disorder and we suggest this is an important contribution to the signal in this region.

The effect of increasing Na coverage upon the Cu(110) RA line shape is shown in the sequence of spectra in Fig. 1. While the energy of the 2.1 eV peak remained constant its intensity was found to decrease with increasing Na coverage. The feature observed at 3.8 eV on the clean surface was also suppressed with increasing Na coverage. LEED results from

the surfaces corresponding to the spectra shown in Figs. 1(b)–1(c) showed sharp (1×1) spots with very-low-intensity streaks in the [001] direction localized in the positions where the (1×2) half-order spots of reconstruction would be expected. A comparison with published LEED data² indicates that the observed diffraction patterns from the surfaces corresponding to the RAS spectra of Figs. 1(b) and 1(c) are characteristic of Na coverages of $\theta\sim 0.05$ ML and $0.05<\theta<0.11$ ML, respectively. A Na coverage of 0.16 ML is indicated by the observed LEED pattern corresponding to the RA spectrum of Fig. 1(d). A (1×2) LEED pattern with well-defined streaks in the [001] direction at the positions ($\pm 1/2, 0$) was observed from the surface associated with the RAS spectrum of Fig. 1(e). This LEED pattern indicates Na coverage of 0.25 ML, a result that was confirmed by XPS and corresponds to a well-ordered (1×2) surface reconstruction that has been assigned to a (2×2)- $1D$ structure⁴ to reflect the nature of the Na overlayer. On the perfect reconstructed surface, the Na overlayer consists of rows of adatoms located in the missing row troughs along the [$1\bar{1}0$] direction.^{3,4} The streaks observed in the LEED pattern arise from diffraction from the Na overlayer, in which the Na atoms possess some long-range order within each row and suffer discrete random positional shifts between adatom rows.^{2–4} The main result of this work is the disappearance of the 2.1 eV RAS peak accompanying the formation of the Na-induced Cu(110)-(1×2) reconstruction.

We explain the reduction in intensity of the 2.1 eV feature with increasing Na coverage as follows. It is known that the Na-induced reconstruction influences both occupied and unoccupied surface states at \bar{Y} on Cu(110).^{7,10} With increasing Na coverage up to ~ 0.2 ML, both occupied and unoccupied surface states move to higher energy but maintain a constant energy separation.⁷ The fact that the two surface states maintain their relative separation in energy with increasing Na coverage and our observation that the 2.1 eV peak maintains its position support the identification of a major contribution to this feature with a transition between these surface states. The decrease in intensity of the peak with increasing Na coverage is consistent with a fall in occupation of the initial state as it approaches and overlaps E_F . At a coverage of 0.25 ML, the surface is reconstructed to (1×2), the occupied state has reached E_F , and the separation of surface states determined from the photoemission study predicts an increase in the transition energy to ~ 2.6 eV. However, at this coverage the initial state is at $\sim E_F$ and photoemission and inverse photoemission intensity arising from both states, particularly the unoccupied state, is considerably reduced.⁷ Defining the direction y along [001] and z as normal to the surface plane, the occupied and unoccupied Cu(110) surface states have predominantly p_y and ($s+p_z$) hybrid character, respectively, with respect to the Cu atoms in the surface layer.⁷ Upon interaction with Na, the character of the occupied state is known to change from p_y to p_z and, crucially, the amount of charge remaining in the p_y -derived surface state at 0.25 ML Na coverage is significantly reduced.⁷ These considerations explain the absence of structure in the 0.25 ML RA spectrum at 2.6 eV [Fig. 1(e)].

Following a procedure whereby a coverage of 0.3 ML was deposited and the sample first annealed to 350 K and then cooled to room temperature, we observed a weak feature in the RA spectrum at ~ 2.6 eV [Fig. 1(f)]. The annealing procedure resulted in a final coverage of 0.25 ML at room temperature and the appearance of the 2.6 eV feature indicates that for some of the Cu atoms the p_y character of the occupied surface state has returned. This is to be expected if the loss of Na adatoms on annealing reduces the number of Cu atoms that have direct interaction with Na adatoms. We note that the residual anisotropy in the region of the 2.1 eV peak that remains following the adsorption of oxygen, and that on the clean unreconstructed Cu(110) surface has been associated with the surface local-field effect, appears to be absent from the Na/Cu(110)(1×2) surface.

The RA spectrum of the Na-induced (1×2) surface [Fig.

1(e)] has a single minimum at 4.2 eV, the same energy as one of the two minima of the clean surface, but with an increased intensity. This observation is in agreement with other studies that find the energy of this feature to be insensitive to reconstruction,¹¹ and supports the view that the feature arises from intrinsic anisotropy caused by the surface local-field effect.¹³

The Cu(110)-(1×2) surface reconstruction upon Na adsorption has been observed by RAS. The behavior of the RA response around 2 eV upon Na adsorption and reconstruction is consistent with the known behavior of the surface states at \bar{Y} as determined by photoemission and inverse photoemission studies.

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*Corresponding author. FAX: +44 151 708 0662, Email address: davidm@liv.ac.uk

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