Surface electronic structure of a vicinal Cu crystal

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The surface of a 12° vicinal Cu(111) crystal is formed by a regular distribution of (111) terraces, giving rise to a well-ordered step superlattice. Angle-resolved photoemission experiments show that the modulation plane of the Cu(111) surface state is the optical mean surface. The surface state is observed at the edge of the surface Brillouin zone regularly repeated with the superlattice periodicity. The intensity distribution of the surface state in the reciprocal space has been probed using different photon energies. The results can be well understood on the basis of a simple diffraction-like model involving the bulk band properties. © *2003 American Vacuum Society.*
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I. INTRODUCTION

Vicinal surfaces have been investigated in the last years for several reasons. On the one hand, these surfaces can be used as templates for growing low dimensional nanostructures[1–3] or to model the surface sites active in heterogenous catalysis.[4,5] On the other hand, vicinal surfaces are a natural playground to investigate the electronic properties of a lateral nanostructure, because the lateral periodicity can be tuned to a large extent by changing the miscut angle.

Noble metal surfaces vicinal to the (111) direction have deserved ample attention in the research of the properties of a two dimensional electron gas, due to the prominent Schockley surface state that appears at the *L* point bulk band gap of noble metals.[6] This surface state exhibits strong two dimensional confinement in the (111) surface. The surface state electrons scatter in surface defects such as steps, and indeed it has been shown by scanning tunneling microscopy (STM) that this scattering gives rise to electron confinement within terraces.[7,8] This is in part modified in a vicinal surface, due to the sensitivity of the surface state wave function to any lateral nanostructure, such as a step superlattice.[9] A change in the miscut angle modifies the lateral periodicity, and this gives rise to different ranges in the properties of the two dimensional electron gas.[9,10] Previous photoemission experiments on Cu(111) have found that there is a critical miscut angle close to 7° below which the surface state propagates parallel to the (111) terraces.[10] Above this critical value, the surface state wave function is referred to the mean surface. The confinement within the terraces affects the binding energy (BE) at the bottom of the surface band, that diminishes as the miscut angle increases.[11–13] The effect has been explained modeling the steps as repulsive barriers that confine the surface states.[11] Several other interesting effects have been reported, as the observation of one dimensional states or the influence of the step superlattice in the Fermi surface.[14,15]

The crystal surface is vicinal to (111) with a 12° miscut. Previous STM results[16] have shown that the surface exhibits a regular distribution of monoatomic, (100)-like steps running along the [$\bar{1}$10] direction. Surfaces with (100)-like steps instead of (111)-like were chosen, since regular arrays are easier to prepare. The average terrace width measured with STM is 10 ± 1.5 Å, consistent with a 12° miscut.[16,17]

Photoemission spectroscopy is a powerful technique to probe the momentum dependence of electron energy bands, but it is an averaging technique and thus it requires a high degree of long range order. Nevertheless, real surfaces have a variety of defects and the terrace size distribution is broad, thus information from local techniques such as STM is also important for an adequate characterization of the vicinal surface. The use of a high-quality surface in this article allows the observation of the superlattice periodicity in the surface state propagation parallel to the surface. Most probably, the lack of an adequate step superlattice prevented the observation in previous studies. This analysis is combined with the use of different photon energies to provide a full map of its intensity distribution in reciprocal space.

II. EXPERIMENT

The photoemission experiments have been performed at two different ultrahigh vacuum chambers in order to cover a broader photon energy range. The first chamber is equipped

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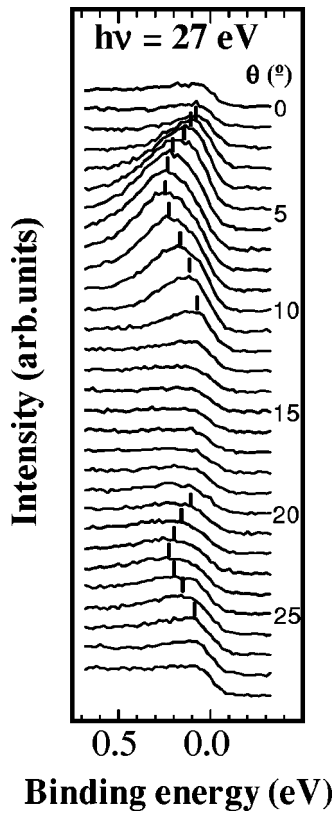[a]Electronic mail: enrique.garcia.michel@uam.es

FIG. 1. Angle-resolved, valence band photoemission spectra for 12° vicinal Cu(111) at 27 eV photon energy. Emission angles (θ) are measured with respect to the surface normal. The surface state dispersion is shown along. the [$11\bar{2}$] direction (perpendicular to the steps of the substrate).
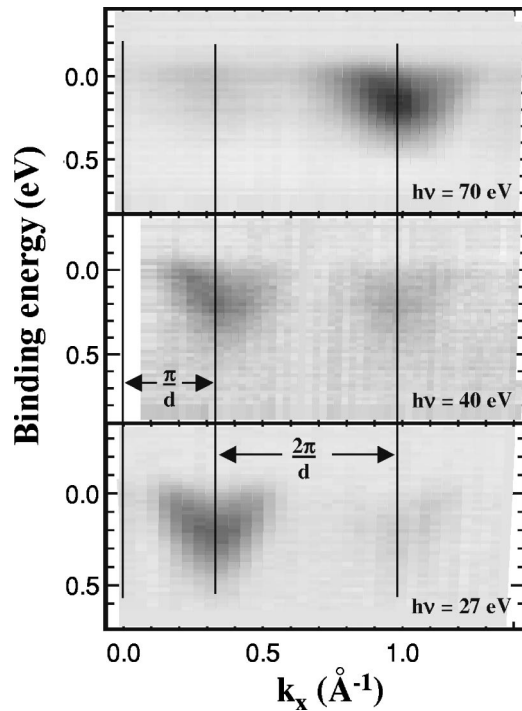

FIG. 2. Angle-resolved, valence band photoemission intensity for 12° vicinal Cu(111) at 27, 40, and 70 eV photon energy vs parallel momentum along the [$11\bar{2}$] direction (perpendicular to the steps of the substrate). Black color denotes a higher intensity.

with low energy electron diffraction (LEED), a quartz crystal microbalance, and an angle-resolving hemispherical analyzer that receives synchrotron light from the Seya–Namioka 1 m normal-incidence monochromator F2.2 at HASYLAB (Hamburg, Germany). It covers the photon energy range 9–27 eV. The second chamber is also equipped to perform angle-resolved photoemission and LEED measurements. It is mounted at the SU8 undulator beam line of SuperAco storage ring at LURE (Orsay, France). A plane grating monochromator was used in the range 22–110 eV. In both cases data were taken with 70° incidence angle of the light. The Cu crystal was electrochemically polished and cleaned *in situ* by cycles of Ar sputtering and annealing until a sharp spot splitting was observed in LEED patterns.[16]

III. RESULTS AND DISCUSSION

Figure 1 shows valence band spectra at 27 eV photon energy in the BE area closer to the Fermi energy. Angles are measured with respect to the mean optical surface. The Cu(111)-like surface state is observed close to normal emission and was always measured along the [$11\bar{2}$] direction (perpendicular to the steps). The bottom of the surface state band appears at an emission angle of $\theta_m = 7.7°$. The surface state peak is observed again at higher emission angles, with the band bottom at $\theta_m = 23.3°$. Figure 2 shows similar spectra with photoemission peak intensity represented in a gray scale, both for low (27 eV), intermediate (40 eV), and high (70 eV) photon energies. The angular scale is converted to $k_\parallel$ in Fig. 2, assuming momentum conservation parallel to the optical surface from $k_\parallel = [(2m_e/\hbar^2)E_{\text{kin}}]^{1/2}\sin\theta$, where E_{kin} is the electron kinetic energy and θ is the emission angle. Several interesting features can be observed in this figure. First, the minima of the two surface state parabolas are split by $\Delta k_\parallel = 0.63$ Å^{-1}, in agreement with the step lattice vector $2\pi/d = 0.63$ Å^{-1}. Second, the intensity shifts from the first to the second parabola as the photon energy increases. We consider the lateral periodicity first. The appearance of a second parabola at $k_\parallel = 3\pi/d$ is due to the interaction of the surface state electrons with the step superlattice, which produces a new periodicity along the surface plane. Obviously, the new periodicity can be observed only for a sufficiently coherent step array in the Cu surface, consistently in this case with STM images[16] and the observation of a sharp spot splitting in the LEED pattern, which describe a superlattice periodicity of outstanding quality. These findings remind us of similar effects observed in high-quality stepped Au surfaces.[9,18] The surface state band minimum is located at 0.26 eV. This value agrees well with previous findings for other vicinal Cu(111) surfaces with 15.8° miscut (0.17 eV)[14] and 9° miscut (0.3 eV).[10]

Photon energy dependent photoemission allows us to perform a three-dimensional wave vector analysis of the surface state wave function, which is essential to obtain a correct description of electron wave functions at lateral nanostructures.[9,18] The behavior shown in Fig. 2 can be ra-
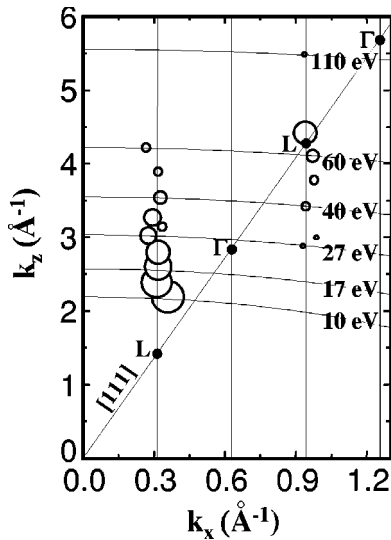
FIG. 3. Wave vector analysis for surface states at 12° vicinal Cu(111). The photoemission final state wave vector components (k_z) at the band minima from Fig. 2 (and additional photon energies) are represented vs parallel momentum. The experimental points are aligned at π/d (0.31 Å^{-1}) and $3\pi/d$ (0.94 Å^{-1}). The size of the points is proportional to the photoemission intensity (in logarithmic scale).
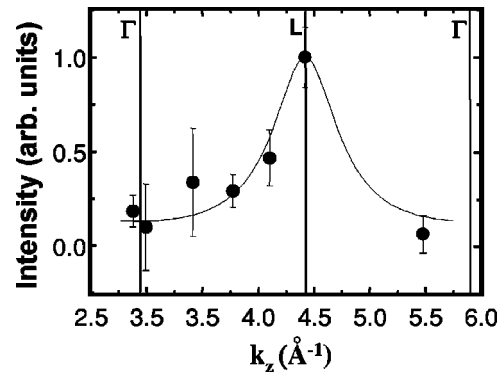

FIG. 4. Normalized intensity of the experimental points in Fig. 3 is represented vs k_z. Symmetry points correspond to the projection along surface normal direction (see Fig. 3). The intensity reflects the spectral composition of the surface state wave function. The maximum weight corresponds to the L points of the bulk band structure. The continuous line is a fit to Eq. (1).

tionalized in the wave vector plot of Fig. 3. Here the bottom of the surface band θ_m and the measured E_{kin} are converted into k_x and k_z values via[10,18] $k_x=[(2m_e/\hbar^2)E_{kin}]^{1/2}\sin\theta_m$ and $k_z=[(2m_e/\hbar^2)(E_{kin}+V_0)-k_x^2]^{1/2}$. k_z represents the wave vector perpendicular to the surface inside the crystal. It can be approximately obtained assuming a free-electron-like final state band in a constant inner potential $V_0=-13.5$ eV.[10] Figure 3 shows the k_x and k_z values for the data of Fig. 2, and also for several other photon energies in the range 10–110 eV. By covering a broad photon energy range, the distribution in k_z of the surface state intensity can be probed. Data points in Fig. 3 line up at π/d and $3\pi/d$, as expected for p_z-like surface states of Cu(111) vicinals[18] with a miscut angle larger than 7°, because in this case the surface state wave function propagates along the average surface.

The size of the data points in Fig. 3 is proportional (in logarithmic scale) to the photoemission intensity normalized to the photon flux. The photoemission intensity is maximum for transitions close to the L point of the bulk band structure. The spectral map in Fig. 3 qualitatively reflects the Fourier distribution of the surface state wave function in the vicinal surface. In the direction parallel to the surface and perpendicular to the steps, the surface state is a Bloch wave of the step lattice with $k_x=g/2=\pi/d$. In the direction perpendicular to the surface, the k_z broadening corresponds to an evanescent wave with the fundamental frequency $k_z=k_L$. The relative intensity of the surface state parabolas in Fig. 2 depends on the spectral weight of the component of the wave vector perpendicular to the surface. Thus, the intensity shift observed in Fig. 2 can be understood in view of Fig. 3. As in LEED,[19] the intensity peaks for in-phase interference (low and high photon energies in Fig. 2) and the band (spot) split-

ting is better observed near out-of-phase conditions (intermediate energy in Fig. 2). At variance with LEED, the maxima in photoemission appear at the projection of L bulk points, while in LEED the maxima correspond to the projection of Γ points.

While k_x is a good quantum number for the description of the surface state bands in a vicinal surface, k_z is strongly broadened due to the electron confinement at the surface region. The distribution of experimental points in Fig. 3 directly describes a surface state wave function delocalized along the mean Cu surface and modulated by the step superlattice periodicity.

The intensity distribution along k_z [$\alpha(k_z)$] has been modelled for Cu(111) using a semi-infinite linear chain model[20]

$$\left|\frac{\alpha(k_z)}{\alpha(\pi/a)}\right|^2=\frac{(\chi-1)^2}{1+\chi^2-2\chi\cos(k_za-\pi)}, \quad (1)$$

where a is the Cu lattice parameter, $\alpha(\pi/a)$ represents the intensity at the zone edge (L point), and χ is a parameter that depends on bulk band properties of Cu.[21] The experimental intensities for the surface state second parabola are represented in Fig. 4 together with the best fit to Eq. (1) (continuous line).[22] We obtain $\chi=2.1\pm0.2$, which compares well to the Cu(111) value of $\chi=1.8$.[20]

IV. CONCLUSIONS

The surface electronic states of a 12° vicinal Cu(111) crystal have been probed using photoemission. The L gap Cu surface state reproduces the step induced superlattice periodicity. When probed along the surface normal, the photoemission intensity is maximum for the vicinity of bulk L points. The periodicity and intensities observed are rationalized in a simple model involving the step superlattice properties and bulk band parameters.

ACKNOWLEDGMENTS

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[21] $\chi = 4|\Delta/W|$ where Δ is the shift in the self-energy of a surface orbital relative to the bulk and W is the bandwidth.
[22] This analysis assumes that the photoemission intensity is not affected by other factors different from the spectral contents of the initial state wave function, as for instance a photon energy dependent cross section. The energetic range of the second parabola fulfills reasonably well this condition. On the contrary, in the energetic range of the first surface state parabola there is a strong cross section change that hinders a simple analysis.