ELSEVIER

Surface Science 482–485 (2001) 764–769

SURFACE SCIENCE

www.elsevier.nl/locate/susc

Transition from terrace to step modulation in the surface state wave function at vicinal Cu(1 1 1)

J.E. Ortega [a,*], A. Mugarza [a], A. Närmann [a], A. Rubio [a,1], S. Speller [b], A.R. Bachmann [b], J. Lobo [c], E.G. Michel [c], F.J. Himpsel [d]

[a] *Donostia International Physics Center and Centro Mixto, CSIC-UPV, Departamento de Física Aplicada I, Universidad del País Vasco, Plaza Oñati 2, 20018 San Sebastián, Spain*

[b] *Fachbereich Physik, Universität Osnabrück, 49069 Osnabrück, Germany*

[c] *Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain*

[d] *Department of Physics, University of Wisconsin Madison, 1150 University Avenue Madison, WI 53706-1390, USA*

Abstract

The electron wave function at Cu(1 1 1) vicinal surfaces switches between two qualitatively different regimes, i.e. from terrace modulation at small miscut angles to step modulation for large miscuts. This is deduced in angle resolved photoemission experiments from the photon energy dependent shift of the surface band. In this work we examine the critical miscut of 7° (17 Å terrace width) at which the transition is observed. The analysis of the data within a diffraction-like framework is consistent with a mixed terrace–step modulation. The mechanism that triggers the switchover from terrace to step modulation of the surface state is discussed.

Keywords: Angle resolved photoemission; Surface electronic phenomena (work function, surface potential, surface states, etc.); Stepped single crystal surfaces; Metallic surfaces; Copper

1. Introduction

Vicinal surfaces are currently used as templates for growing low-dimensional structures with tailored electronic properties [1–4]. They can also serve themselves as model low-dimensional structures to understand the fundamental properties of these systems. For example, the basic issue of the nature of the wave function in lateral superlattices can be readily investigated using vicinal Cu(1 1 1) surfaces [5]. Here we have both the simplest electronic structure (free-electron-like surface state) and a superlattice of straight, monoatomic steps that scatter these surface electrons [6]. Such scattering indicates that the wave function of the vicinal surface should be modulated by two periodicities, that of the superlattice and that of the atomic corrugation of the terraces. This defines two types of Fourier components in the wave function, i.e. those defined along the average-surface plane (step modulation) and those defined with respect to the terrace (atomic corrugation). Based on a low energy electron diffraction (LEED)-like description of the photoemission experiment it is possible to show that the surface state is mainly

* Corresponding author. Tel.: +34-943-018-403; fax: +34-943-219-727.

E-mail address: ortega@sq.ehu.es (J.E. Ortega).

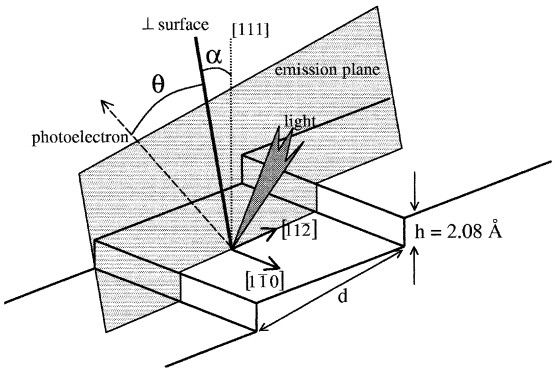
[1] On leave from Departamento de Física Teórica, Universidad de Valladolid, E-47011, Valladolid, Spain.

0039-6028/01/$ - see front matter
PII: S0039-6028(00)01065-7

modulated by the step lattice for high (9°) miscut angles and by the terrace plane for low (5°) miscuts, thus a switch-over should occur at an intermediate angle [5]. In this paper we examine such transition angle. Our photoemission results for a 7.3° miscut are consistent with a surface state that displays a mixed terrace–step modulation. Finally, we discuss the possible mechanisms that trigger the switchover between these two regimes.

2. Results

The vicinal Cu(1 1 1) surface was prepared with a 7.3° miscut about the $[\bar{1}\,1\,2]$ azimuthal direction. The crystal was electrochemichally polished, sputter annealed (500 eV Ar^+ ions, 800 K), and cooled slowly to 300 K. After this treatment, the quality of the surface was checked with LEED and scanning tunneling microscopy (STM). The LEED is characterized by a well defined spot-split pattern with low background. In Fig. 1 we show a close view of the surface in the STM topography. It shows a regular distribution of monoatomic, {1 0 0}-like steps running along the $[1\,\bar{1}\,0]$ direction. Compared with {1 1 1}-like steps, {1 0 0}-like steps display lower frizziness at step edges but similar terrace width distribution around the average value (17 Å) [7]. Photoemission experiments were performed using p-polarized synchrotron radiation using a vacuum generators analyzer at HASYLAB (Germany) and a Scienta analyzer at the SRC (Wisconsin). The measurement geometry is described in the top panel of Fig. 1. The step–step distance d is defined in the average surface plane and the step height is given by $h = a/\sqrt{3} = 2.08$ Å, where $a = 3.61$ Å is the lattice constant of bulk Cu.



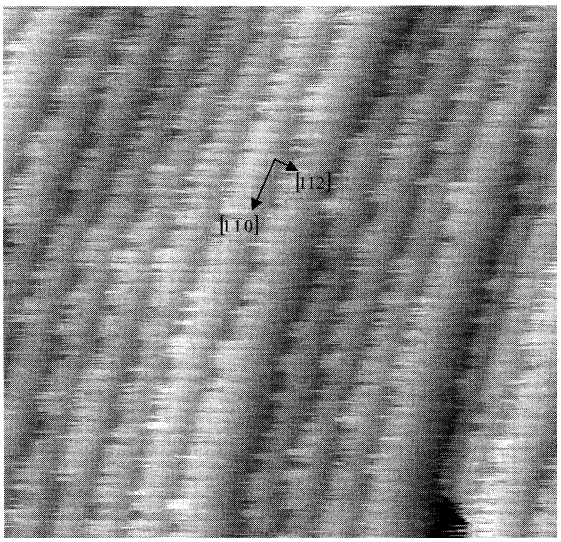


Fig. 1. Top: measurement geometry for angle resolved photoemission experiments from a vicinal surface. Bottom: STM topograph for a 7.3° miscut Cu(1 1 1) surface (160 Å^2, 0.9 V, 1 nA). Monoatomic steps display {1 0 0}-like packing at the edge.

In Fig. 2 it is shown the dispersion of the p_z-like surface state band as a function of θ in the direction perpendicular to the steps, measured at three different photon energies. High photoemission intensity is shown in dark. The parabolas fit the maximum intensity and they only serve as guide lines to better follow the dispersion. The bottom of the band shifts up to −0.29 eV from the value of the flat (1 1 1) surface (−0.4 eV [8]). This indicates the presence of a small repulsive energy barrier at the step [6]. As found in other vicinal Cu(1 1 1) substrates [5], there is a photon energy dependent shift of the band away from normal emission. The band minimum (θ^{min}) lies at 12.9°, 9.1° and 7.1° for 10, 14, and 22 eV. In contrast, for flat Cu(1 1 1) the surface band is centered around 0° at all photon energies.

These results can be conveniently analyzed and understood using the diffraction-like plot shown in Fig. 3 [5]. The data points represent the two wave vector components of the photoemission final state for electrons excited from the bottom of the band

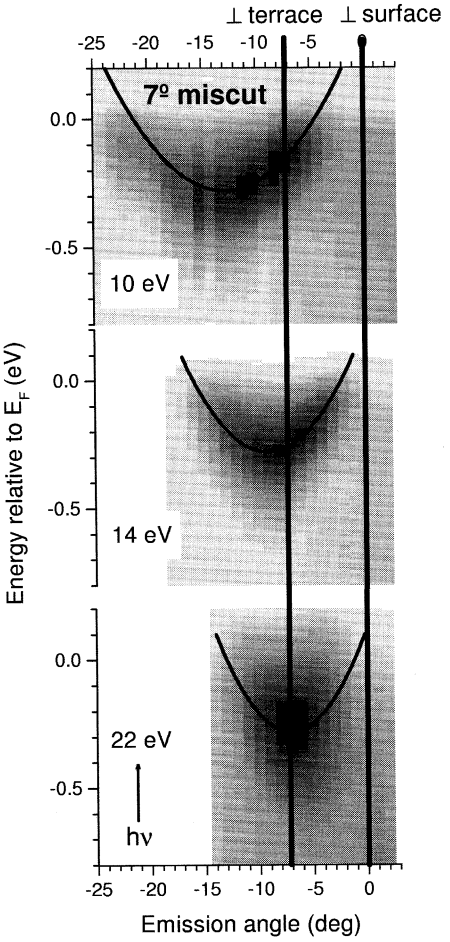


Fig. 2. Photoemission intensity (dark) versus energy and emission angle taken with different photon energies showing the p_z-like surface band for a stepped Cu(1 1 1) surface with a 7.3° miscut.

at $\theta^{\min}$. In order to better follow the discussion we focus only on these electrons. We include the data for higher (9°) and lower (5°) miscut surfaces from Ref. [5]. The parallel component of the photoelectron ($k_{||}$) is obtained assuming parallel wave vector conservation along the average surface. The perpendicular component ($k_{\perp}$) is deduced from the energy conservation rule and from $k_{||}$, using a free electron final state band in an inner potential V_0. Thus:

$$k_{||} = \sqrt{(2m/\hbar^2)E_{\mathrm{kin}}}\,\sin\theta \qquad (1)$$

$$k_{\perp} = \sqrt{(2m/\hbar^2)(E_{\mathrm{kin}} + V_0) - k_{||}^2} \qquad (2)$$

where E_{kin} is the measured kinetic energy at $\theta^{\min}$, and $V_0 = 8.8 - E_{\mathrm{F}}$ eV the crystal inner potential [9]. By increasing the miscut angle we can observe a qualitative evolution of the data points in Fig. 3. They line up along the average surface normal at $k_{||}^{\min} = \pi/d$ for 9° miscut but they rather follow the [1 1 1] direction for 5° miscut. For 7° the data points lie in between these two directions.

3. Discussion

Assuming wave vector conservation in the reduced Brillouin zone, Eq. (2) also defines the perpendicular component of the wave vector in the initial state. Therefore Fig. 3 reflects the total wave vector for the surface state at a fixed energy (the band bottom). This will allow us to draw conclusions about the nature of the wave function on these surfaces. On the top panel of Fig. 3 we show the different possibilities. We include the wave function perpendicular to the surface which is the key to understand transitions in three-dimensional **k**-space. The p_z-like, two-dimensional surface state in Cu originates at the L-neck gap of the bulk band structure. Its wave function in the vertical direction is defined by a Bloch state (with $k = \mathbf{k}_{\mathrm{L}} = (1/2, 1/2, 1/2)(2\pi/a)$) that decays perpendicular to the surface, thus giving rise to a broadened k-distribution around L [10]. That is indicated by the cigar-shaped hatched areas in Fig. 3. If the surface wave function is modulated by the step lattice along the average surface, its bulk part decays perpendicular to the average surface plane, i.e. the wave vector broadens from L along the average surface normal. For every photon energy we select a different Fourier component and data points line up at $k_{||}^{\min} = \pi/d$. This is observed for 9° miscut. For 5° miscut the data points are only compatible with a surface state that decays perpendicular to the terraces, i.e. a surface state that rather propagates parallel to the (1 1 1) terraces, ignoring the step modulation. Surface states with such terrace modulation can take all values of $k_{||}$ at a fixed binding energy, as can be deduced from

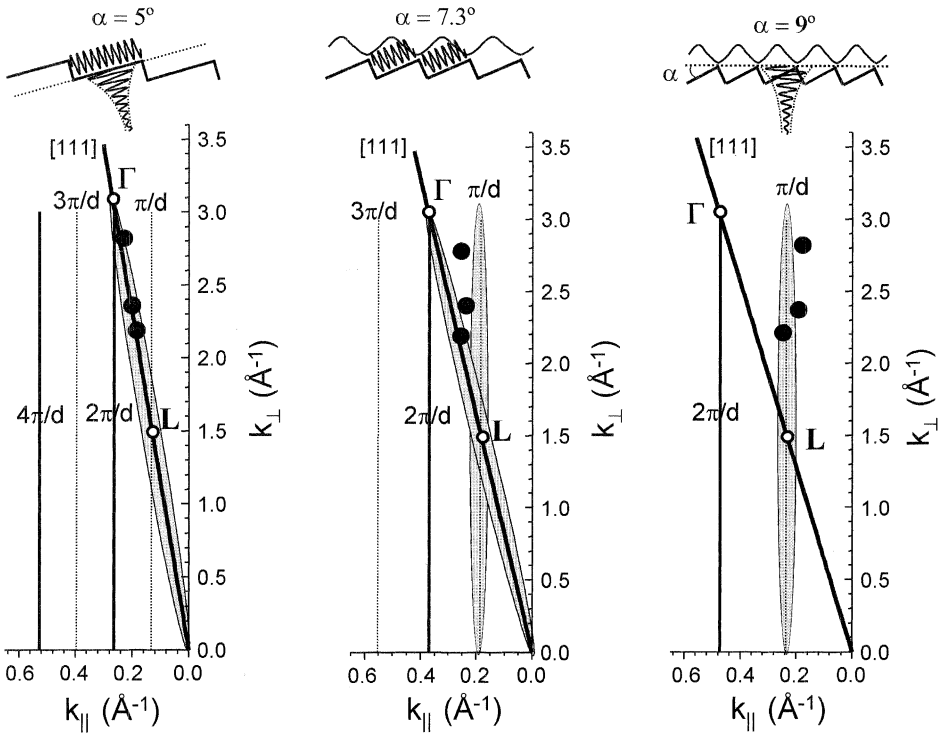


Fig. 3. Description of the photoemission experiment from a vicinal surface using an electron diffraction model. The dots are three-dimensional **k**-values obtained from the data in Fig. 2 using Eqs. (1) and (2) and from Ref. [5]. The cigar-shaped, hatched regions represent the spread of the surface state wave function in **k**-space. The corresponding wave function in real space is indicated on top. A characteristic switch of the type of surface state modulation occurs at a critical miscut angle of 7.3°. The data in this case are compatible with a mixed terrace–step modulation of the surface state. For the sake of the clarity, we omit the decaying part of the wave function in the top panel in the 7.3° case.

Fig. 3. Thus in this case $k_{||}$ is completely broadened and it is not a good quantum number. For 7.3° miscut we clearly observe the transition between terrace and average-surface-like surface states. This is consistent with a surface state wave function significantly modulated by both the step lattice and the terrace atoms. [2]

It appears rather intuitive that the wave function at a vicinal surface should be modulated along both the terrace and the average surface. It is less evident the switch from terrace to step modulation at ~7° miscut. In order to explain this switchover a number of arguments can be given.

The lateral coherence length of the electrons is the simplest quantitative argument for a switchover from terrace to step modulation at a given miscut. If the terrace width becomes large compared to the coherence length, the electron wave function of an electron placed at the center of a terrace does not see the step edges. The problem with this explanation is that it requires a lateral coherence length that is much smaller than expected from transport measurements at 300 K (about 300 Å). Previous photoemission experiments [8,11] gave a significantly smaller coherence length of 30 Å but still larger than the 17 Å terrace width for a 7° miscut where the switch occurs.

A smooth transition is expected from the continuous change in the relative spectral weight of

[2] Note that the intensity in the 22 eV parabola in Fig. 2 peeks sharply at 7.1°. This is not consistent with a mere superposition of signals from terrace and step modulated states, that should lead to two different parabolas shifted by ±3° in the θ scale.

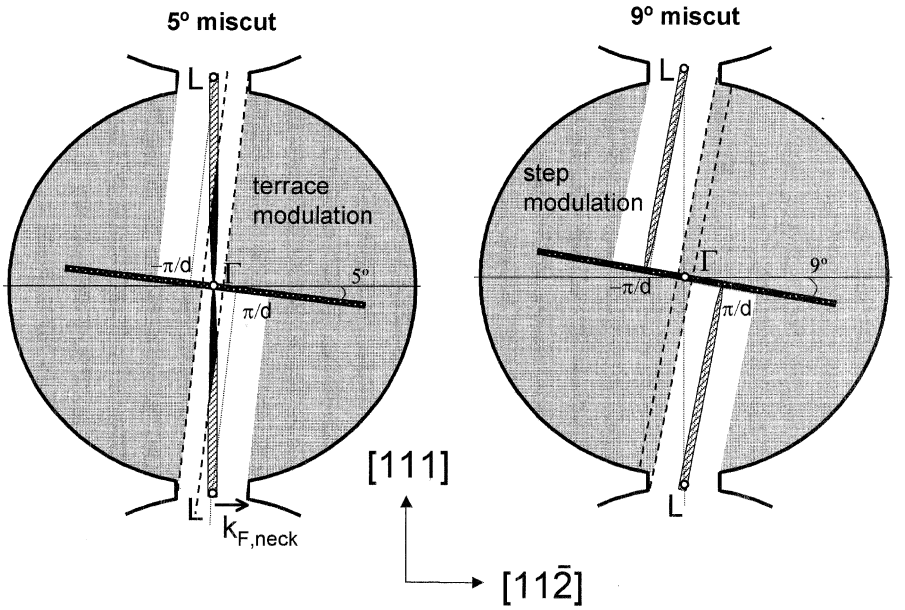


Fig. 4. Projection of the bulk band structure on a vicinal surface with 5° miscut (left) and 9° miscut (right). The projection of the L-neck leaves a gap around $\bar{\Gamma}$ for 5° miscut allowing terrace modulated states (cigars in the left panel) to have Fourier components with $k_{||}$ inside the gap (dark). At 9° miscut these terrace states overlap with the high density of bulk states at $\bar{\Gamma}$, thereby losing spectral weight. In contrast, the step modulated states that dominate at 9° (cigars in the right panel) lie at a region with lower density of projected states, i.e. around π/d.

the two different types of Fourier components as a function of miscut angle. In order to obtain the Fourier components originating from the atomic rows on terraces and from the step lattice we need to weigh the density of scatterers with their individual scattering strength. We observe that the step density is always lower than the row density on a terrace. However, the higher corrugation at a step edge produces a large scattering amplitude at the step that compensates the low step density. It is not obvious which of the opposite trends wins. [3]

[3] Additionally we could expect the effective atomic corrugation of the terrace to be reduced for small terrace size, since in this case the electron is expected to move out of the surface. In fact the energy increases as the terrace width decreases, but due to the contribution of the image potential to the vacuum barrier, the higher the energy is the further the electron is placed in front of the surface. However, the small upwards energy shift observed for the surface band (from −0.35 eV at 5° miscut to −0.30 eV at 9° miscut, [5]) does not justify a significant electron movement away from the surface.

The relative spectral weight of step and terrace Fourier components in the photoemission spectra can be altered due to overlap with bulk states. We can examine the resonant character of terrace and step modulated surface states as a function of the miscut angle by looking to their location in the projected bulk band structure, as done in Fig. 4. The circles represent the constant energy line for bulk states near E_F showing its characteristic neck of width $2k_{F;neck}$. Shaded regions inside the sphere describe the projection of bulk states in the first Brillouin zone on a vicinal Cu(1 1 1) surface with 5° miscut (left) and 9° miscut (right). The width of the neck at $E_F - 0.3$ eV has been assumed to be that given in Ref. [8], i.e. $k_{F;neck} = 0.2$ Å^{-1}. Note that necks are not projected at the same place in both cases, and this leads to three different types of $k_{||}$ regions, i.e. those with bulk states projected from the two halves of the Brillouin zone, regions where bulk states from only one half of the Brillouin zone are projected, and, in the case of the 5° miscut, the small gap around $\bar{\Gamma}$.

The cigars represent the Fourier spectrum of terrace and step modulated surface states described in Fig. 3.

The resonant character of the two types of surface states is quite different. At 5°, Fourier components of the terrace modulated states mostly lie on the projected gap, i.e. they are pure surface states with a high spectral contribution. [4] Therefore in this case we expect a wave function modulation by terrace rows, as proved in Fig. 3. At 7.3° miscut, the gap shrinks to almost zero. The critical angle for gap closing is directly deduced from Fig. 4, i.e. $\alpha_c = \mathrm{arctg}(k_{F;neck}/k_L) = 7.5°$ for $E_F - 0.3$ eV ($k_{F;neck} = 0.2$ Å^{-1}). [5] At this angle the surface Brillouin zone is filled with bulk states projected from one half of the first bulk Brillouin zone. Both terrace and step modulated surface states occupy a region with approximately the same bulk density of states, and that agrees with the mixed character of the wave function found for 7.3°. For 9° miscut bulk states from the two halves of the Brillouin zone are projected around $\bar{\Gamma}$, as we see in the right panel of Fig. 4. Consequently Fourier components of the terrace modulated surface states around the Γ point fully resonate with bulk bands, and hence the terrace state will lose significant spectral weight. In contrast, the step modulated states lie always at the lower bulk state density region around π/d, and therefore they are expected to dominate.

In summary, we have examined the angle at which surface states at vicinal Cu(1 1 1) surfaces switch from terrace to step modulated wave functions. The data analyzed within an electron diffraction framework indicate a mixed terrace-average surface wave function character. The switching mechanism has been reexamined. The results are compatible with the increasing overlap of the terrace state with bulk bands as a function of miscut angle. Considering the projection of bulk bands within the first Brillouin zone we observe that at 5° miscut most of the terrace state Fourier components lie on a projected band gap, whereas at 9° miscut these terrace states overlap with a high density of bulk states around the center of the Brillouin zone. Meanwhile, step modulated states are always located at a region with a low density of bulk states projected.

[4] States projected from the second Brillouin zone fill up the gap. Nevertheless, when other Brillouin zones are considered, the projected density of states still shows a minimum around $\bar{\Gamma}$ for 5° miscut.

[5] The gap closes at 9.1° at E_F ($k_{F;neck} = 0.26$ Å^{-1}, [8]).

Acknowledgements

J.E.O. and A.M. are supported by the Universidad del País Vasco (UPV057.240-EA197/97 and 026/98) and the Max-Planck Research Award Program. E.G.M. and J.L. are funded by the Spanish DGES (PB-970031) and the Comunidad de Madrid (07N/0031/1998). Experiments were performed at HASYLAB within the TMR-contract ERBFMGECTP950059 and at the SRC, which is supported by the NSF under Award no. DMR-9531009. F.J.H. is funded by NSF DMR-9815416. Helpful discussions with P.M. Echenique and E. Chulkov are acknowledged.

References

[1] R. Nötzel, K.H. Ploog, Adv. Mater. 5 (1993) 22.
[2] R. Nötzel, Z. Niu, M. Ramsteimer, H.P. Schönherr, A. Trampert, L. Däweritz, K.H. Ploog, Nature 392 (1998) 56.
[3] F.J. Himpsel, J.E. Ortega, G.J. Mankey, R.F. Willis, Adv. Phys. 47 (1998) 511.
[4] P. Segovia, D. Purdie, M. Hegsberger, Y. Baer, Nature 402 (1999) 504.
[5] J.E. Ortega, S. Speller, A. Bachmann, A. Mascaraque, E.G. Michel, A. Mugarza, A. Nrmann, A. Rubio, F.J. Himpsel, Phys. Rev. Lett. 84 (2000) 6110.
[6] O. Sánchez, J.M. García, P. Segovia, J. Alvarez, A.L. Vázquez de Parga, J.E. Ortega, M. Prietsch, R. Miranda, Phys. Rev. B 52 (1995) 7894.
[7] S. Speller, et al., in press.
[8] J. Tersoff, S.D. Kevan, Phys. Rev. B 28 (1983) 4267.
[9] P. Thiry, D. Chandesris, J. Lecante, C. Guillot, R. Pinchaux, Y. Petroff, Phys. Rev. Lett. 43 (1979) 82.
[10] S.G. Louie, P. Thiry, R. Pinchaux, Y. Petroff, D. Chandesris, J. Lecante, Phys. Rev. Lett. 44 (1980) 549.
[11] F. Theilmann, R. Matzdorf, G. Meister, A. Goldmann, Phys. Rev. B 56 (1997) 3632.