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Step-induced one-dimensional surface state on Cu(332)

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The Shockley (L gap) surface state on Cu(332) has been studied by angle scanned ultraviolet photoelectron spectroscopy. The Fermi surface indicates a two-dimensional (2D) and a one-dimensional (1D) state, both propagating freely parallel to the steps. Normal to the steps, the 2D state is slightly confined while the 1D state is localized. The 1D state can be rationalized either by disorder in the one-dimensional step lattice or by surface-bulk coupling at the individual steps. In both scenarios this 1D state represents an important link between scanning tunneling microscopy/spectroscopy and photoemission data.

Shockley surface states behave like two-dimensional low electron density metals.[1] They are sensitive spectators of the surface but can as well be actors. The actor role is limited by the low density—on Cu(111) one surface state electron is shared by about 20 unit cells—but they are outermost, are first met by impinging objects, and can thus influence the first stage of a gas surface reaction. Furthermore these electrons act in a quantum ensemble where coherent operation may affect the macroscopic organization: They are scattered by nanostructures such as atomic steps and it can be expected that they themselves produce a feedback on the atomic arrangement.

Scanning tunneling microscopy (STM) and spectroscopy (STS) appear to be particularly sensitive to these surface states because they dominate in the zone between the tip and the surface.[2] These techniques map the local electronic density of states in real space. On an atomically flat surface, free-electron-like Bloch states exhibit a uniform charge density. In order to probe their momentum distribution, the surface states need to be perturbed, e.g., by island edges, surface steps, or single point defects. Under such circumstances standing wave patterns form that are accessible to observation by STM and STS.[3–5] Exciting applications arise from such experiments like, e.g., the tailoring of wave functions in fabricated nanostructures.[6]

Atomic steps are among the simplest of such nanostructures. STS images of the local differential tip-surface conductance have recently produced a wealth of information on how the surface state interacts with a single atomic step[7,8] or with a pair of adjacent steps.[3,9] From the measurement of Friedel-type oscillation periods it was possible to extract Fermi wave vectors[10] and complete energy dispersion curves.[11] Although these long-range oscillations appear to be well understood, it is important to study the effects of atomic steps on the surface states by a more conventional technique. From photoemission spectra the energy-momentum dispersion can be obtained directly. The problem is that the photoemission experiment is not sensitive enough for the resolution of a single-quantum object, it is restricted to objects that are present in relatively large numbers. Vicinal surfaces provide a convenient way to study a macroscopic array of more or less regular steps on a surface.

Photoemission experiments on vicinal Cu(111) showed a zero-point energy of the surface state proportional to $1/l$, where l is the step separation with a propagation parallel to the macroscopic surface and not to the (111) terraces.[12–14] The experiments of Sánchez *et al.*, found the steps to act as repulsive potentials and to confine the surface states.[14] Recent experiments of Ortega *et al.*, indicate a critical step separation $l_c = 17$ Å above which the surface state propagates parallel to the (111) terraces.[15] In the present paper we report the observation of a spectral feature appearing in the photoemission spectrum of Cu(332), which is vicinal to close packed Cu(111). Ideally this surface consists of monoatomic steps with $(11\overline{1})$ step facets and (111) terraces spanning $5\frac{1}{3}$ atomic rows ($l = 12$ Å). The feature appears near the bottom of the surface-state band, and its energy dispersion identifies a one-dimensional (1D) electronic state that is propagating parallel to the steps while it is localized in the direction perpendicular to the steps. We discuss possible origins and how this species may relate to earlier observations in photoemission[16,17] or STM/STS images.[18]

The experiments were performed in a modified VG ESCALAB 220 photoelectron spectrometer[19] with He Iα ($h\nu = 21.2$ eV) radiation. The k space was mapped for $k_\parallel < 1$ Å^{-1} and energies from 150 meV above the Fermi level to 700 meV binding energy. The overall energy/momentum resolution was better than 50 meV/0.02 Å^{-1} full width at half maximum and all presented data were taken at room temperature. $k_\parallel$ is determined from the electron kinetic energy in the vacuum and the polar emission angle θ with respect to the optical surface: $k_\parallel = \sin(\theta)\sqrt{2m_eE_{kin}}/\hbar$.

The Cu(332) crystal was polished mechanically to within $< 0.5°$ accuracy (Mateck, Jülich). It was cleaned by several cycles of Ar-ion sputtering at low energies (~ 200 eV), followed by mild annealing to 670 K and slow cool down to room temperature. The crystallographic directions were checked *in situ* by x-ray photoelectron diffraction and agree with the nominal orientation of the crystal. Surface crystallography was checked by low-energy electron diffraction. The observed spot splitting is consistent with a regular step structure over large areas. Sample cleanness was verified by x-ray photoelectron spectroscopy. Contaminations during the experiments were always below 0.04 monolayers (ML) carbon and 0.02 ML oxygen.

In Fig. 1 the Fermi surface map of Cu(332) is shown for $\theta < 30°$ or $k_\parallel < 1.05$ Å^{-1}. The k-space coordinates are cho-

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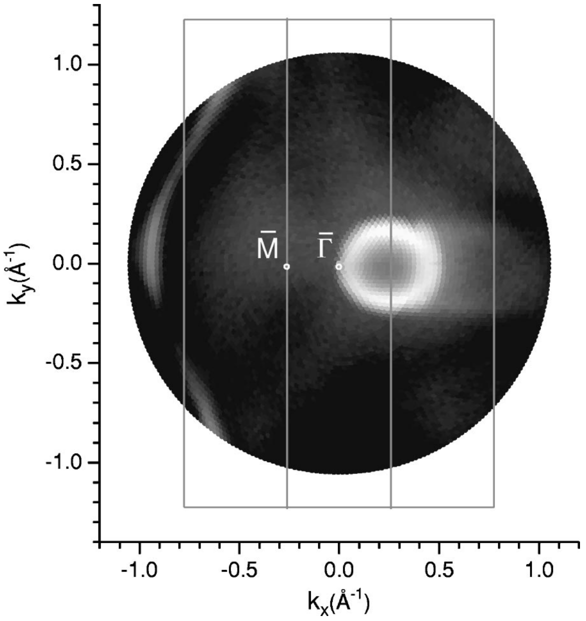

FIG. 1. Fermi surface map of vicinal Cu(332). The surface Brillouin zones and the high-symmetry points $\bar{\Gamma}_{00}$ and $\bar{M}_{0\bar{1}/2}$ are underlayed. The photoemission intensity is displayed on a logarithmic gray scale as a function of k_x (normal to the atomic steps) and k_y. The elliptical feature is the confined two-dimensional Shockley surface state while the faint lines to the right of the ellipse reflect a one-dimensional state.

sen as k_x normal to the steps (running upstairs from left to right) and k_y parallel to the steps. The photoemission intensity on a gray scale is bright for direct transitions. The feature on the left-hand side is a section across the three-dimensional sp-derived bulk Fermi surface of copper.[20] It shows that for the photon energy of 21.2 eV no bulk transitions with $k_{\parallel} < 0.8$ Å^{-1} are expected and all direct transitions within this range are surface-state related. The elliptical feature close to the center of the map is the 2D Shockley surface state. The dashed lines mimic the surface Brillouin zones that are given by the step separation. $\bar{\Gamma}_{00}$ is the projection of Γ_{000} along [332] and $\bar{M}_{01/2}$ that of $L_{1/21/21/2}$. It is seen that the surface state is centered within 0.02 Å^{-1} at the surface Brillouin zone boundary on $\bar{M}_{01/2}$ ($k_x = 0.26$ Å^{-1}), the projection of L and not on the projection of the [111] direction that is located at $k_x = 0.36$ Å^{-1} at this electron kinetic energy. This confirms the finding of earlier work[12–14] that these electrons propagate parallel to the macroscopic surface, which is modulated by the regular step lattice. The 2D Shockley surface state has an ellipsoidal Fermi surface with half-axes of $k_x^F = 0.21(2)$ Å^{-1} and $k_y^F = 0.17(3)$ Å^{-1}. From this a mean occupancy of 0.17 e^- in the surface Brillouin zone is derived. The two faint horizontal lines that start from the elliptical feature to the right give us a first glimpse on the new species: a 1D Fermi surface consisting of Fermi wave vectors $k_y = \pm k_F$ in the direction along the steps, independent of k_x. The species is only visible in a limited k_x range, which lies mostly in the second surface Brillouin zone in the up-step direction.

In Fig. 2 the dispersions of the two surface state features are shown. A cut along the $\overline{\Gamma M}$ direction is displayed in Fig. 2(a). The parabolic dispersion of the 2D surface state is centered at $\bar{M}_{01/2}$. From the maximum binding energy, $E_0^{2d} = 293(10)$ meV, and the Fermi wave vectors, as determined from the Fermi surface in Fig. 1 effective masses $m_x^* = 0.53(5) m_e$ and $m_y^* = 0.38(8) m_e$, are found. The value of m_y^* favorably agrees with the effective mass of the step free (111) surface [$m^* = 0.42(2) m_e$].[21] The small but significant relative increase of m_x^* with respect to m^* indicates the confinement of the electrons by the steps. Together with the smaller E_0^{2d} compared to the value of Cu(111) ($E_0^{(111)} = 390$ meV) it can be concluded that the step potentials are repulsive for the surface-state electrons as it was found experimentally[14] and theoretically.[22]

The state in the second surface Brillouin zone does not disperse along $\overline{\Gamma M}$ (Fig. 4). The maximum binding energy E_0^{1d} is 240 meV, decreases with respect to E_0^{2d}, and indicates the energy cost for the localization of the electrons. If we

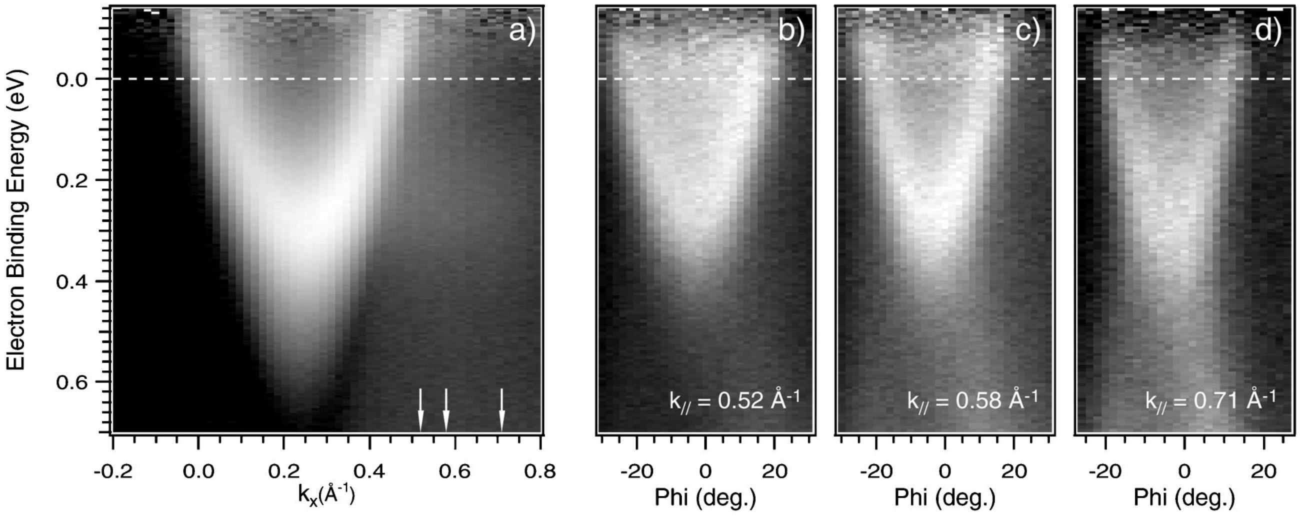

FIG. 2. Dispersion plots of the surface state related features in Fig. 1. (a) Polar cut along $\overline{\Gamma M}$ (logarithmic gray scale). The arrows indicate the $k_{\parallel}$ values in (b)–(d). (b)–(d) Azimuthal cuts for three different $k_{\parallel}$ values (linear-gray scale).

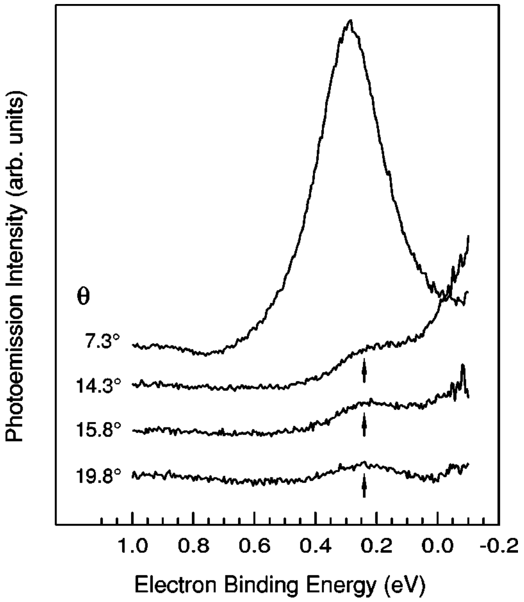

FIG. 3. Photoemisson spectra along $\overline{\Gamma M}$ for different polar emission angles θ. The intensities are normalized with a Fermi function as measured from polycrystalline silver. The arrows indicate the energy of the nondispersing surface-state resonance.

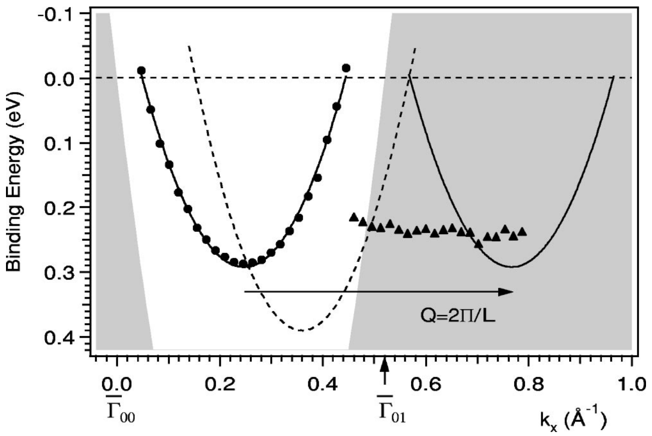

FIG. 4. Dispersion of the surface-state related features along $\overline{\Gamma M}$ (circles and triangles). The shaded area represents the surface projected bulk band structure at the upper L point of the first Brillouin zone. The faint lines indicate the position of an umklapp band and the dispersion as expected for a large (111) terrace (dashed line).

assume a particle in a box we get from the zero-point energy $E_{zero}=E_0^{(111)}-E_0^{1d}=150$ meV a box size of 24 Å or about 2 step separations.

In Figs. 2(b)–2(d) the dispersion of the 1D surface state is shown on *azimuthal* cuts for three different values of $k_{\|}$. Clearly a free-electron-like behavior parallel to the steps can be seen. The effective masses in the y direction are determined after projection $[k_y=\sin(\phi)k_{\|}]$. Again, the effective mass $[m_y^*=0.44(6)m_e]$ corresponds to that of the surface state on Cu(111). From the value of k_F along the steps an occupancy of $0.26e^-$ is found, which is larger than that of the 2D state.

The intensity ratio of the 2D and 1D states can be seen in Fig. 3 where energy distribution curves along $\overline{\Gamma M}$ are shown. Clearly, the 1D state is a minority species and has about 0.08 of spectral weight relative to the 2D state.

In the following we try to rationalize the occurrence of this 1D state or resonance, and to relate it to observations made in STM/STS images. There are two possible starting points: (i) Its energetic position and dispersion suggests that its origin is due to a perturbation of the 2D Shockley state by the 1D step sequence (2D-1D). (ii) It is well known that steps represent locations where the surface states and bulk states are no longer orthogonal and can thus couple. We therefore cannot *a priori* rule out the importance of all three dimensions (3D-1D) and the formation of step edge states.[16–18]

2D-1D scenarios: One-dimensional models have been rather successful for the description of the surface states on stepped surfaces.[14,22] This is further justified since the effective masses of the electrons parallel to the steps are all found to be equal to that of the Shockley surface state on the flat Cu(111), i.e., motion along the steps is completely unaffected by the presence of the steps. On a flat surface with just a pair of steps, the resulting trapped states observed in STS images on Au(111) (Ref. 3) and Ag(111) (Ref. 9) should have just the spectral signature that we observe, with a confinement energy that tells us roughly the separation of the steps. Now Cu(332) presents a regular array of steps, and we expect these trapped states to interact coherently to form Bloch states: the Shockley surface state propagating perpendicular to the steps is the consequence of this process. A likely explanation for the remaining 1D feature is localization due to disorder: on a real vicinal surface the terrace lengths fluctuate about the nominal value,[23] leading to a strongly peaked distribution function. Trapped states on adjacent terraces may then have different energies and can no longer couple to form propagating states. We have performed 1D model calculations for perturbed step sequences that were, unfortunately, not fully conclusive: tight-binding calculations using trapped states as basis functions were carried out for fully periodic step sequences and for randomly varying terrace lengths modeling realistic distribution functions.[24] The Kronig-Penney-type dispersion for the periodic sequence could be well reproduced, but disordered step lattices did not produce the type of localized states found in our experiment. On the other hand, enhanced wave amplitudes at perturbed sites within an otherwise periodic step array could be found using a transmission matrix approach.[25] Here, the boundary condition was chosen to be a propagating plane wave arriving from one side upon the finite step array. The physical picture is that of a plane wave of finite coherence length that is partially transmitted and partially reflected by the individual steps. Our results indicate partial trapping at perturbed sites for energies consistent with our experimental observation, and could thus provide a natural explanation for the 1D feature that would more appropriately be termed a resonance.

A further indication that limited coherence and disorder may play a role is the absence of umklapp bands related to the periodicity of the step lattice. In Fig. 4 the dispersions of the 2D and 1D features along the direction perpendicular to the steps are reproduced, and the position of the umklapp band is indicated. The range of $\vec{k}_{\|}$ where the 1D feature is observed may suggest a relation to step scattering but with a highly reduced coherence length. A rigorous treatment of this 2D-1D scenario, in which disorder must play a determinant role, seems quite involved. It should also include the effect of disorder along the steps, which is quite obviously present as observed in STM images from vicinal Cu(111) surfaces.[24]

3D-1D scenario: Early photoemission experiments on Ir(332) (Ref. 16) and Ni (79 11) (Ref. 17) indicated step edge states, i.e., electronic states that were induced by the charge redistribution at the steps. Using STM/STS images, Avouris *et al.*,[18] have reported such to be localized at isolated steps on Ag(111) and Au(111). These step-edge states result from the coupling of the surface states to the underlying bulk states at the steps, and they were rationalized in terms of the electronic charge redistribution associated with the Smoluchowski effect.[26] Such states are thus a further serious candidate for explaining our 1D spectral feature. In STM/STS the spectral signature of an isolated step-edge state extends over all energies throughout the surface-state band and has not been clearly resolved.[18] The reduction of the work function on vicinal surfaces related to the Smoluchowski effect can indeed be observed and we must therefore take the presence of such step-edge states as a reality. Do these states, in the presence of a periodic step lattice, exhibit the spectral signature that we observe? This question is definitely far beyond the scope of the present paper. The position of the 1D feature relative to the surface-projected bulk band structure (see Fig. 4) on the Cu(332) surface may indeed suggest such a connection, and in fact it ties this feature as a surface resonance. It should be noted that the rigorous projection of the bulk band structure on a vicinal surface, extending over all values of $\vec{k}_\perp$ in reciprocal space, would completely fill the surface Brillouin zone, and we have therefore projected only the bulk states in the k-space region near the upper *L* point of the first bulk Brillouin zone.

In conclusion, a 1D surface resonance related to the step lattice on a vicinal Cu(111) surface has been observed by photoemission. It may be explained either with disorder-induced dephasing of 2D Shockley states, or with step-edge states resulting from surface-bulk coupling. Discriminating between the two scenarios remains an experimental and a theoretical challenge, but will be an important step in comparing STM/STS and photoemission data from surface states.

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[1] W. Shockley, Phys. Rev. **56**, 317 (1939).

[2] J. Tersoff and D.R. Hamann, Phys. Rev. B **31**, 805 (1985).

[3] Ph. Avouris and I.-W. Lyo, Science **264**, 942 (1994).

[4] J. Li, W.D. Schneider, and R. Berndt, Phys. Rev. B **56**, 7656 (1997).

[5] J. Li, W.D. Schneider, R. Berndt, and S. Crampin, Phys. Rev. Lett. **80**, 3332 (1998).

[6] M.F. Crommie, C.P. Lutz, and D.M. Eigler, Science **262**, 218 (1993).

[7] O. Jeandupeux, L. Bürgi, A. Hirstein, H. Brune, and K. Kern, Phys. Rev. B **59**, 15 926 (1999).

[8] L. Bürgi, O. Jeandupeux, H. Brune, and K. Kern, Phys. Rev. Lett. **82**, 4516 (1999).

[9] L. Bürgi, O. Jeandupeux, A. Hirstein, H. Brune, and K. Kern, Phys. Rev. Lett. **81**, 5370 (1998).

[10] P.T. Sprunger, L. Petersen, E.W. Plummer, E. Laegsgaard, and F. Besenbacher, Science **275**, 1764 (1997).

[11] L. Bürgi, L. Petersen, H. Brune, and K. Kern, Surf. Sci. **447**, L157 (2000).

[12] R.S. Williams, P.S. Wehner, S.D. Kevan, R.F. Davis, and D.A. Shirley, Phys. Rev. Lett. **41**, 323 (1978).

[13] A.P. Shapiro, T. Miller, and T.-C. Chiang, Phys. Rev. B **38**, 1779 (1988).

[14] O. Sánchez, J.M. García, P. Segovia, J. Alvarez, A.L. Vázquez de Parga, J.E. Ortega, M. Prietsch, and R. Miranda, Phys. Rev. B **52**, 7894 (1995).

[15] J.E. Ortega, S. Speller, A. R. Bachmann, A. Maxcaraque, E. G. Michel, A. Närmann, A. Mugarta, A. Rubio, and F. J. Himpsel, Phys. Rev. Lett. **84**, 6110 (2000).

[16] J. F. van der Veen, D. E. Eastman, A. M. Bradshaw, and S. Holloway, Sol. State Commun. **39**, 1301 (1981).

[17] H. Namba, N. Nakaishi, T. Yamaguchi, and H. Kuroda, Phys. Rev. Lett. **11**, 4027 (1993).

[18] Ph. Avouris, I.-W. Lyo, and P. Molinas-Mata, Chem. Phys. Lett. **240**, 423 (1995).

[19] T. Greber, O. Raetzo, T.J. Kreutz, P. Schwaller, W. Deichmann, E. Wetli, and J. Osterwalder, Rev. Sci. Instrum. **68**, 4549 (1997).

[20] P. Aebi, J. Osterwalder, R. Fasel, D. Naumović, and L. Schlapbach, Surf. Sci. **307-309**, 917 (1994).

[21] R. Matzdorf, G. Meister, and A. Goldmann, Phys. Rev. B **54**, 14 807 (1996).

[22] G. Hörmandinger and J.B. Pendry, Phys. Rev. B **50**, 18 607 (1994).

[23] J.W.M. Frenken and P. Stoltze, Phys. Rev. Lett. **82**, 3500 (1999).

[24] A. Bachmann, A. Mugarza, J.E. Ortega, A. Närmann, and S. Speller, Phys. Rev. B (to be published).

[25] J. H. Davies, *The Physics of Low-Dimensional Semiconductors* (Cambridge University Press, Cambridge, 1998).

[26] K. Smoluchowski, Phys. Rev. **60**, 61 (1941).