

Lateral confinement of surface states on stepped Cu(111)

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By means of scanning tunneling microscopy we observe the lateral confinement of the two-dimensional electron gas of a s, p -like surface state by a regular distribution of steps on vicinal Cu(111). The surface state appears with a reduced binding energy as a result of scattering at steps and partial confinement within the terraces, as revealed by local scanning tunneling spectroscopy. The energy shift of the bottom of the surface state band is measured for several vicinal Cu surfaces with angle-resolved photoemission and found to be consistent with a simple one-dimensional Kronig-Penney model.

The behavior of a two-dimensional (2D) electron gas is receiving widespread attention for both fundamental and technological reasons. A 2D electron gas can be found at metal-semiconductor interfaces, in artificially layered semiconductors, or in some organic charge-transfer salts. The electrons occupying the s, p -like surface state band in the closed-packed noble metal surfaces (Cu, Ag, Au) are confined normal to the surface between the vacuum barrier and the crystal band gap. They effectively behave as free electrons in two dimensions, providing a useful ground for testing the properties of the 2D electron gas. In fact, electron scattering processes at point defects, steps, and isolated atoms result in the formation of standing waves, recently visualized by means of the scanning tunneling microscope (STM)^{1,2}. Further confinement of electrons to artificial structures at the nanometer scale has been demonstrated to yield the archetypal "particle-in-a-box" behavior.³ The quantum well states of electrons confined on a *single* terrace of Au(111) have also been observed recently.⁴ In this paper we address the confinement of surface state electrons by another sort of artificial structure, namely, 1D arrays of regularly spaced monoatomic steps on vicinal surfaces. The partial electron confinement leads to a shift of the energy of the bottom of the surface state band towards the Fermi level that can be observed at room temperature (RT). The shift depends on the terrace size as predicted by a simple 1D Kronig-Penney model and observed in angle-resolved photoemission experiments.

The STM experiments have been performed in an ultrahigh vacuum chamber equipped with a homemade STM, low-energy electron diffraction (LEED), and angle-integrated ultraviolet photoelectron spectroscopy. The angle resolved photoemission (ARPES) experiments were performed at the SU6 beamline in LURE with an energy resolution of 80 meV and an accuracy in determining binding energies of 15 meV. The STM tip was made with a polycrystalline tungsten wire electrochemically etched and cleaned *in situ* by field emission. A vicinal Cu sur-

face was obtained by mechanically eroding a flat Cu(111) crystal, at an angle of 8° away from the (111) direction. The resulting surface was electrochemically polished, sputter annealed (500 eV, 800 K) for 10 min, and cooled slowly to 300 K. After this treatment the LEED pattern displays sharp and bright spot splitting at low energy (50–200 eV).

The terrace width distribution obtained from several dozens of images is plotted on the upper panel of Fig. 1. It is a Gaussian sharply centered around terraces of 7 ± 1 atomic rows. This distribution results in a local 7.7° deviation of the surface normal from the (111) direction, which is close to the nominal miscut value. The central panel of Fig. 1 reproduces a representative $100 \times 100 \text{ \AA}^2$ topographic image from such a stepped Cu(111) surface. Monoatomic, close-packed steps run along the $[1\bar{1}0]$ direction, with the $[\bar{1}\bar{1}2]$ direction perpendicular to the step in the terrace plane. The step edges appear frizzy at RT.⁵

The lower panel of Fig. 1 shows a spectroscopic image, $(dI/dV)(x, y)$, of the region illustrated in the middle panel. Both images were recorded simultaneously at RT. A spatial map of $(dI/dV)_{V_s}$ gives the local density of states (LDOS) at the energy $eV_s = -0.3 \text{ eV}$, i.e., the amplitude of the surface state of Cu(111) at different locations on the surface. The decrease of dI/dV at steps reveals a reduction in the amplitude of the surface state, first observed by Everson *et al.*,⁶ indicating that isolated steps act as strong scattering centers for the electrons in the s, p -like surface state of Cu(111).

Figure 2 probes that the major part of the contrast at steps is due to the scattering of the surface state electrons by showing differential conductance $(dI/dV)_{V_s}$ line scans for two representative bias voltages (-0.3 V and -0.1 V) in the direction perpendicular to the steps. The corresponding topographic scan appears in the bottom of Fig. 2. The highest contrast between steps and terraces is obtained for $V_s = -0.3 \text{ V}$, i.e., close to the bottom of the surface state band. For $V_s = -0.1 \text{ V}$, above the bottom of the band, the overall intensity is lower, but the

reduction in the local conductance at the steps is still observed. Notice that the contrast depends on V_s such as at positive bias voltages, a maximum in the LDOS has been observed at steps.^{1,4}

If, in addition to the scattering into bulk states (absorption), there is a partial reflection, as demonstrated for *isolated* steps on Cu(111),¹ Au(111),² and Ag(111),⁷ it should be possible to confine partially these surface electrons on terraces bounded by a regular array of step barriers, thereby increasing their kinetic energy and reducing their binding energy. This is proven in Fig. 3, which shows a number of individual conductance (dI/dV) versus sample bias spectra (normalized by $I-V$) recorded with the tip positioned on the same terrace (20 Å wide) and the corresponding average. The figure also re-

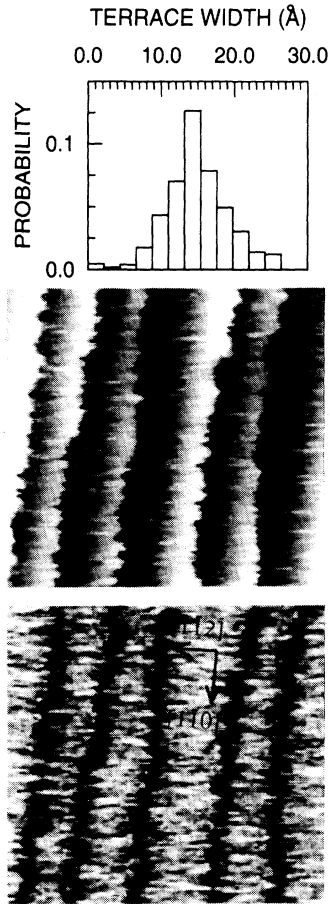


FIG. 1. Upper panel: Terrace width distribution of a vicinal Cu(111) surface cut 8° away from [111], as obtained from STM images. Middle panel: STM topographic image from the 8° stepped surface taken with a sample bias voltage of $V_s = -0.3$ V and a gap resistance of $7.5 \times 10^8 \Omega$. The indicated crystallographic vectors lie in the terrace planes. Lower panel: Spectroscopic image of $(dI/dV)_{V_s}$ recorded simultaneously with the topographic image of the middle panel by modulating the bias voltage (40 meV) with a frequency (8 kHz) higher than the feedback loop response and lock-in detection of the ac component of the current.

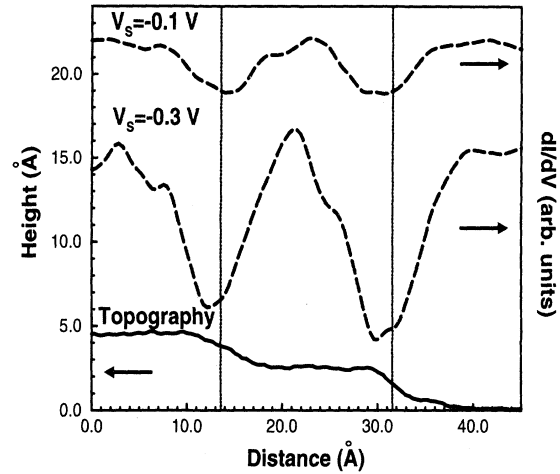


FIG. 2. $(dI/dV)_{V_s}$ line scans taken at two selected bias voltages ($V_s = -0.3$ and -0.1 V) within the dispersion range of the surface state of Cu(111). The corresponding topographic line scan is reproduced in the lower part of the image.

produces a (dI/dV) spectrum recorded on a 40-Å-wide terrace. The maximum of the LDOS appears for the larger terrace in the same position as in the flat Cu(111) surface,^{1,8} while it is shifted to lower binding energies (well above the noise level) for the smaller terrace. In agreement with this observation, the maximum of the STM conductance over a terrace in a 30-Å-periodic array of steps acting as repulsive barriers was calculated to shift towards zero bias relative to the flat surface.⁹

For the regular array of steps of a vicinal surface, the

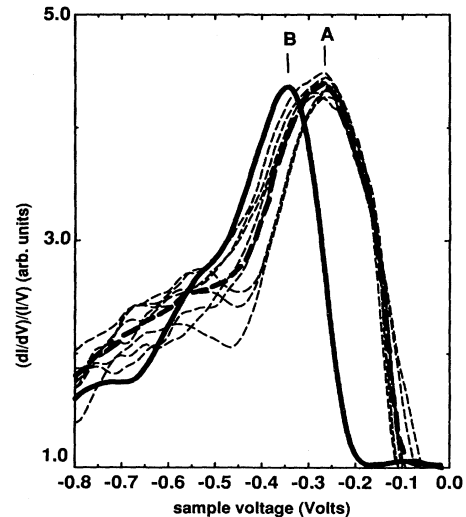


FIG. 3. Normalized conductance $(dI/dV)/(I/V)$ vs bias voltage V_s at room temperature. (a) Several spectra recorded at different places of a 20-Å-wide terrace in Cu(111) 8° as well as the average of the individual spectra (thick broken line). (b) Spectrum obtained on a 40-Å-wide terrace (solid line). The tip was kept stationary by opening the feedback loop during the voltage ramps.

kinetic energy increase of surface state electrons affects the whole surface. Therefore, it should be observable by nonlocal, averaging techniques. ARPES is the standard method to measure energies and dispersion relations for surface states. Figure 4 displays angle-resolved photoemission spectra that further confirm the energy shift associated to lateral confinement in stepped surfaces. The spectra show the surface state peaks for flat Cu(111) and vicinal surfaces cut at nominal angles of 5.5° and 8° obtained at the bottom of their respective surface bands. The position of the surface state peak for flat Cu(111) (-0.39 eV) agrees with the literature.¹⁰ This peak appears shifted towards the Fermi level by 45 meV and 80 meV, respectively for the 5.5° and 8° stepped surfaces. It is also significantly wider for the vicinal surfaces (FWHM of 0.15 eV for the flat surface and 0.27 eV for the stepped case), probably due to overlap with bulk states backfolded into the gap by wave vectors of the step superlattice. For the same reason the intensity of the peak at the stepped surfaces is much lower than in flat Cu(111).

The observed shift is consistent with a simple one-dimensional model. For a regular array of steps, like in a vicinal surface, the surface potential changes periodically in one direction. Electronic states, in particular the s, p -like surface state in such a superlattice, can be described in general by backfolding the surface bands via the reciprocal superlattice vectors. In a first approximation,

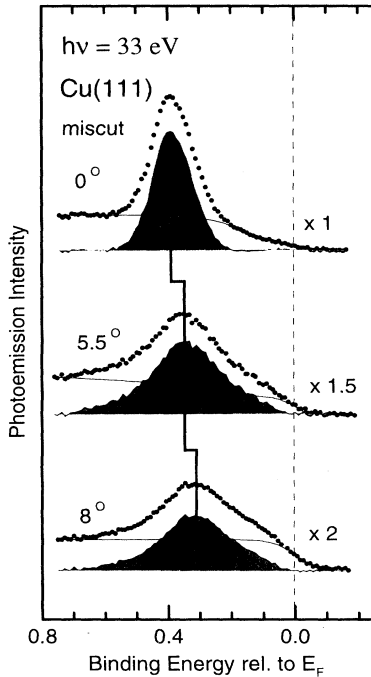


FIG. 4. Angle-resolved photoemission spectra from Cu(111) (top), 5.5° vicinal Cu(111) (middle), and 8° vicinal Cu(111) (bottom) showing the surface state at the bottom of the corresponding band. Emission from bulk states leads to a steplike background (thin line). The photon energy was 33 eV.

the motion of the electrons in the direction perpendicular to the steps can be described within a 1D Kronig-Penney model of δ -function potential barriers, $U_0 a \delta(x)$.⁹ The bottom of the two dimensional surface state band is shifted up in energy by

$$\Delta E = (\hbar^2/2m^*L^2)[\cos^{-1}(|T|) - \phi]^2, \quad (1)$$

where L is the step-step distance and $T = |T|e^{i\phi}$ is the energy-dependent transmission coefficient through the step barrier. For Cu(111) 8° , $L = 15.4$ Å, and $m^* = 0.45m_e$. In the case of total confinement, Eq. (1) predicts $\Delta E = 340$ meV, which is much higher than the observed shift. (Here we suppose that the Fermi level is pinned by the bulk bands.) In order to estimate $|T|$, we use the energy dependence of the transmission coefficient through a barrier $U_0 a \delta(x)$, which has the complex form

$$T = q/(q + iq_0), \quad (2)$$

where $E = (\hbar^2 q^2/2m^*)$ is the energy above the bottom of the flat surface band, and $q_0 = (m^* U_0 a/\hbar^2)$ is related to the barrier height at steps. This is the simplest approach, involving only one adjustable parameter, q_0 . From Eqs. (1) and (2) and the observed energy shift of 80 meV, we estimate $|T|^2 = 0.64$, $\phi = -0.20\pi$, and $U_0 a = 1.2$ eV Å for Cu(111) 8° . A similar analysis applied to the shift observed in the Cu(111) 5.5° sample gives $|T|^2 = 0.60$, $\phi = -0.22\pi$, and $U_0 a = 1.0$ eV Å. There is another set of ARPES data in the literature for Cu(332), a stepped Cu(111) surface with $L \simeq 12$ Å,¹¹ reporting an upward shift of 110 meV for the surface state binding energy. When analyzed within this framework, it yields $|T|^2 = 0.69$, $\phi = -0.18\pi$, and $U_0 a = 1.25$ eV Å.

In summary, we have demonstrated that monoatomic steps on vicinal Cu(111) surfaces act as repulsive barriers for free-electron-like, 2D surface states. The partial confinement of electrons by the ordered array of steps leads to an energy shift, confirmed by photoemission, which can be analyzed by a simple 1D Kronig-Penney model yielding small (1 eV Å) and rather permeable ($T \approx 0.6$) barriers for clean, monoatomic steps. The energy shifts could be related to the individual terraces or to the average potential for a larger region including several terraces nearby the measurement location. The first possibility would be expected for high step barriers that could effectively isolate neighboring terraces. The other extreme is more appropriate for relatively small step barriers, such as observed in this work for arrays of closely spaced monoatomic steps. The step barriers could be purposely modified by depositing a different kind of atom (e.g., Co or Fe) that absorbs preferentially at the steps,¹² a point that deserves further investigation. The existence of a periodic array of potential barriers has two consequences: the shift of the bottom of the surface state band by ΔE , as given by (1) and the opening of a minigap at $k_x = \pi/L$. We have reported evidence for the first effect at RT. In order to observe the second, it would be necessary to lower the operating temperature substantially since the expected effects are small.

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⁸ This can be understood since the coherence length of the Cu(111) *sp* surface state is 20–30 Å (Ref. 10).

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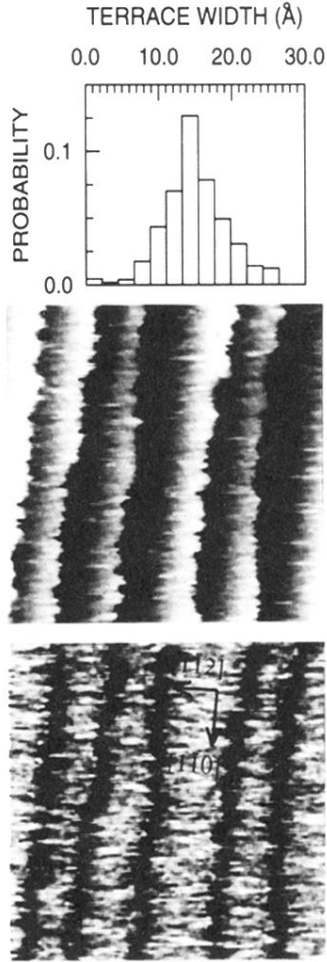


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