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One-dimensional image state on stepped Cu(100)

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A one-dimensional, step-induced image state is found at vicinal Cu(100) surfaces with inverse photoemission and two-photon photoemission. Its energy nearly coincides with the bottom of the two-dimensional image-state band of the flat surface. The one-dimensional nature of the step state manifests itself in a lack of dispersion perpendicular to the steps. Parallel to the steps it exhibits free-electron-like dispersion, making this type of state an ideal model for one-dimensional electron physics.

Interest in low-dimensional systems and their electronic structure is growing, as techniques are becoming available to produce artificial structures on an atomic scale. The appeal of lower dimensionality lies in a qualitative change of the electronic properties, such as the vanishing of a Fermi edge in one dimension,[1,2] which is caused by correlations between electrons that cannot avoid each other moving along the same line in space. Also, Van Hove singularities in the density of states at critical points increase in lower dimensions. Structural properties change together with electronic properties, e.g., due to Peierls distortion,[1,3] or via the loss of long-range order below a critical dimensionality.

Various electronic states have been found to exhibit one-dimensional character, i.e., significant overlap and band dispersion along a single direction only. Examples are bulk solids with a chainlike structure,[1,2] oriented polymer films,[4] surfaces with chainlike reconstructions,[5,6] and stepped surfaces.[7-9] Here we focus on a particularly simple variety of states, i.e., image states.[10-12] These are electrons bound outside a metal surface by their image charge, and kept away from the interior of the metal by Bragg reflection. They approach the free electron since they exhibit nearly free-electron-like, parabolic $E(k^{\parallel})$ band dispersion for k vectors parallel to the surface. We expect them to provide a model for low-dimensional states in general, and for extending the concepts found in the two-dimensional electron gas to lower dimension.[13] Our aim is to lower the dimensionality of image states from two to one by introducing a regular array of linear steps at a surface. Electronic states in such a lateral superlattice can be described in general by backfolding the bands via the reciprocal-superlattice vectors. Depending on their wave function, one may distinguish terrace states and step states. When the interaction between steps ceases in the limit of large step spacing, the step states become one dimensional.

The idea of our experiment is to start with two-dimensional image states and localize them at a step by a local lowering of the vacuum level, which is their reference energy. The origin of this effect is a smoothing of the charge density near a step, which creates a dipole that lowers the local work function.[14,15] For example, a work function decrease of 0.3–1.0 eV has been determined[15] from the level shifts of Xe atoms adsorbed at steps. The corresponding potential trough could confine image states to a step. Such a confinement has already been observed at islands of an adsorbate with lower work function.[16] Looking for one-dimensional phenomena at steps, we indeed find an additional state at the bottom of the image-state band in Cu(100). It is seen with inverse photoemission as well as with two-photon photoemission. Its band dispersion is characteristic of a one-dimensional state, i.e., dispersion parallel to the steps only, and not perpendicular.

We have found the one-dimensional step state at two vicinal Cu(100) surfaces, one with steps along the [010] direction, the other along [011]. Both were cut 10° from the (100) plane, giving an average step spacing of 10 Å. Here we will focus on results for the [011] step orientation. It exhibits close-packed steps, which are expected to be the most stable configuration.[17] Indeed, we observed low-energy electron-diffraction (LEED) patterns with sharp double spots (Fig. 1), indicating straight and equidistant steps. Surfaces which exhibited diffuse double spots did not produce the step state reported here. The miscut angle of 10° corresponds to 3–4 rows per terrace [between (711) and (911)], which we find to be an energetic optimum for the terrace width, in agreement with previous scanning tunneling microscopy results.[18] In order to obtain optimum surface quality the surfaces were electropolished and sputter annealed at an angle of ±30° from grazing.[12] The azimuthal direction of the sputter

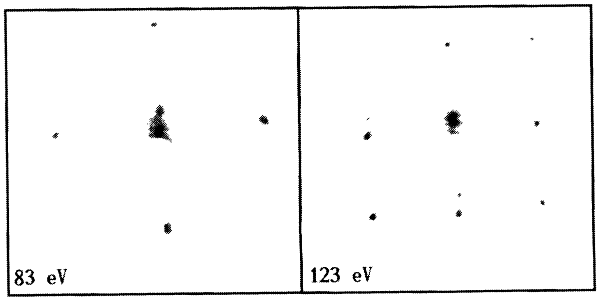

FIG. 1. Low-energy electron-diffraction (LEED) patterns from stepped Cu(100), exhibiting well-defined, split spots indicative of a regular step structure. The sample is tilted up to make the (0,0) beam visible.

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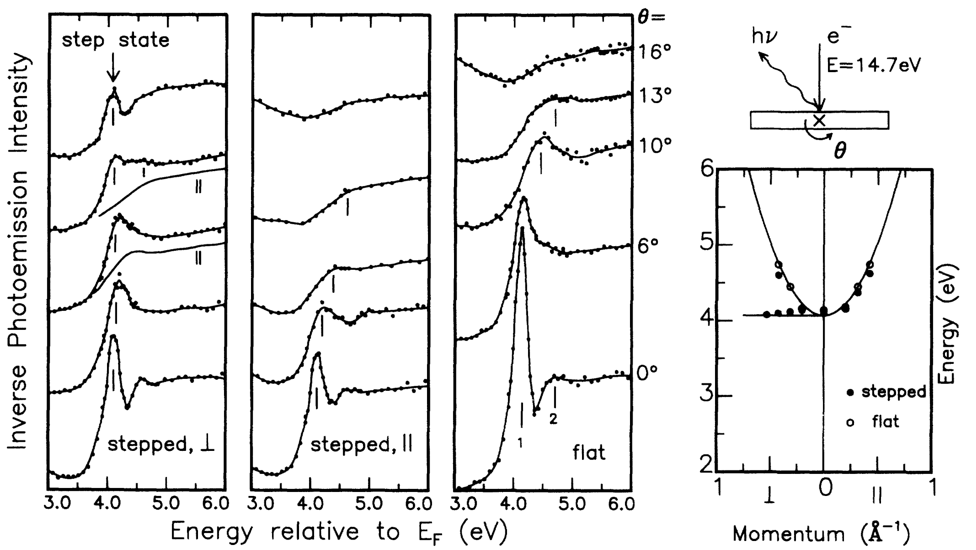

FIG. 2. Angle-dependent inverse-photoemission spectra for flat and stepped Cu(100) showing two- and one-dimensional image states. θ is the polar angle relative to the surface normal. The azimuth is parallel (||) and perpendicular (⊥) to the steps. For the stepped surface an extra state is seen along the perpendicular direction (left panel, arrow). The energy vs in-plane momentum dispersions obtained from these data are shown on the right. The step state does not disperse perpendicular to the steps (⊥), thus demonstrating its one-dimensional nature. Parallel to the steps (||) it follows a free-electron-like parabola with effective-mass unity, as the two-dimensional terrace state.

beam was along the steps, which produced straighter steps by preferentially exposing kink sites to the ion beam. An additional reason for choosing the (100) terrace orientation is a large bulk band gap centered at $k^{\parallel}=0$, which supports image states over a wide $k^{\parallel}$ range.

Figure 2 shows inverse photoemission spectra for flat and stepped Cu(100) in the region of the image potential states. Inverse photoemission probes unoccupied electronic states via the time-reversed photoemission process, i.e., incident electrons drop radiatively into unoccupied states, and outgoing photons are detected. On the flat Cu(100) surface we see the first two members of the hydrogenic image-state series ($n=1,2$) at $\theta=0$ (see Ref. 10 for a review on image states). The $n=1$ state exhibits a clear upwards dispersion away from normal incidence, following a free-electron-like, parabolic $E(k^{\parallel})$ band dispersion (see Fig. 2, right). The $n=2$ state becomes too weak away from normal to follow its dispersion. At the stepped surface the two azimuths parallel and perpendicular to the steps (|| and ⊥) become inequivalent. In addition, one has to distinguish "downhill" and "uphill" directions perpendicular to the steps (here we show only data for the "uphill" direction, i.e., tilting toward the [100] terrace normal). Parallel to the steps the periodicity is preserved, and we see an image-state feature with a dispersion identical to that of the flat surface. Perpendicular to the steps, however, we find in addition to the dispersing image state a nondispersing peak. The existence of this additional feature is particularly clear at large angles (arrow), where the dispersing feature lies at much higher energies. At smaller angles the two features are unresolved, but by subtracting the || spectrum from the ⊥ spectrum one obtains again a single peak with no significant band dispersion, as shown in Fig. 2 (right). This extra state is assigned to an image state based on its near-coincidence with the bottom of the image-state band and its narrow width (see also Fig. 3, inset). Its lack of dispersion perpendicular to the steps is taken as evidence for one-dimensional character.

In order to further characterize the one-dimensional image state we have performed two-photon photoemission experiments (Fig. 3), where a first photon pumps electrons into the image state and a second photon probes

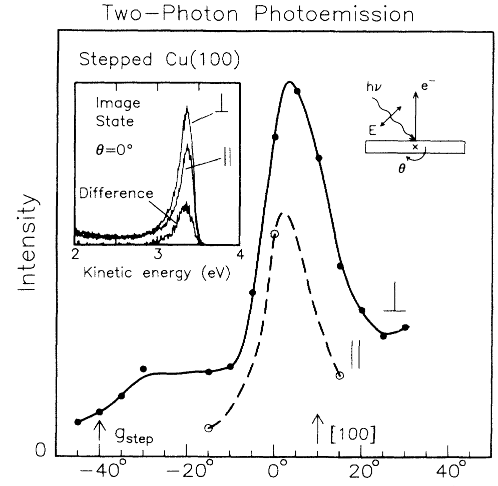

FIG. 3. Two-photon photoemission results from stepped Cu(100) for two geometries with the steps parallel (||) and perpendicular (⊥) to the plane of the drawing. In the normal emission spectra (inset) both the step state and the bottom of the two-dimensional image state band are excited. The step state can be selected either by polarization selection rules (difference curve in the inset) or by going to off-normal emission, where the two-dimensional state has dispersed beyond the pump energy of the laser. As the inverse-photoemission spectra, the step state is observed in the direction perpendicular to the steps.

them, similar to ordinary photoemission. The energy of the pump and probe photons was 4.07 eV, with a pulse length of 0.8 ps (50 μJ/pulse). The inset of Fig. 3 compares two-photon photoemission spectra in the energy range of the $n=1$ state, collected with the plane of the polarization vector of the light parallel and perpendicular to the steps. The pump energy is just enough to populate the bottom of the two-dimensional image-state band and the one-dimensional state, both at about 4.1 eV above the Fermi level, but it is insufficient to sample the upwards dispersion of the two-dimensional state away from normal. Consequently, we find enhanced intensity within ±15° around normal, where both states contribute. Outside this angular range only the one-dimensional state can be populated. Looking along azimuthal angles parallel and perpendicular to the steps, we find that it is primarily seen with the electron momentum $k^{\parallel}$ perpendicular to these steps (full circles in Fig. 3). Parallel to the steps the intensity vanishes almost completely outside the ±15° cone (open circles in Fig. 3), as it does for the flat Cu(100) surface (not shown). This confirms the inverse photoemission result in Fig. 2, where the extra step state was observed for an azimuthal angle perpendicular to the steps only.

An additional way to identify a step-induced state is via the breakdown of polarization selection rules in the lower symmetry at the step.[7,19] While two-dimensional image states are excited by the electric-field component perpendicular to the surface only,[20] there is an extra possible channel for step states with the electric field in the surface plane, but perpendicular to the steps. This effect is demonstrated in the inset of Fig. 3, where two normal emission spectra are shown for p-polarized light with the plane of incidence parallel and perpendicular to the steps, respectively. (A switch of 180° between the uphill and downhill directions did not make any difference.) The extra intensity observed in the perpendicular geometry is assigned to the step-induced state. Taking the difference between $\perp$ and $\parallel$, we can isolate a step spectrum (see Fig. 3, inset). Similar spectra are obtained off-normal, where the difference between the two polarizations becomes more pronounced, since the two-dimensional band has dispersed beyond the pump energy. Using s polarization instead of p polarization, we find the same effects, but with much less intensity.

Comparing the image-state intensities between flat and stepped Cu(100) in Fig. 2, one can see a weakening of the $n=1$ state at $k^{\parallel}=0$ at the stepped surface. This may be an indication that spectral weight is transferred toward the step state at large momentum perpendicular to the steps. In two-photon photoemission we find an even larger reduction of the intensity from flat to stepped surfaces. This probably reflects a smaller population of the intermediate state, due to a shorter lifetime of image states at the stepped surface.

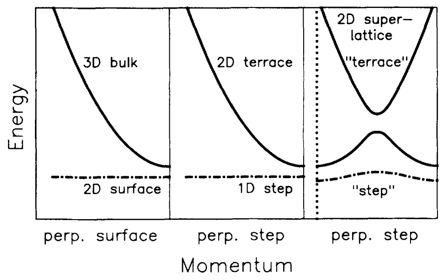

FIG. 4. Schematic of electronic states in various dimensions. Left: A two-dimensional surface state split off from a three-dimensional bulk band. Middle: A one-dimensional step state split off from a two-dimensional terrace state band, as in our data. Right: The effect of multiple steps in a lateral superlattice.

For the interpretation of the observed step state, we limit ourselves to a general outline of the possible low-dimensinal states at a stepped surface (Fig. 4). There exist some previous models[8-11] of states at stepped surfaces, but none of them applies directly to our situation. Starting with the familiar situation of a three-dimensional crystal with a two-dimensional surface, we can distinguish a three-dimensional bulk band that disperses perpendicular to the surface, and a two-dimensional, nondispersing surface state that is split off from the bulk band (Fig. 4, left). Reducing the dimensionality by one, we now consider a two-dimensional surface with a single, one-dimensional step. In this case we have a two-dimensional surface-state band on the terraces that disperses perpendicular to the step, and a one-dimensional, nondispersing step state that is split off from the terrace state band (Fig. 4, middle). With a regular array of steps, i.e., a lateral superlattice, this picture is modified in several respects (Fig. 4, right). The step periodicity induces a reciprocal-lattice vector (vertical dotted line) that folds the bands back. In addition, the step-step interaction causes minigaps at the band crossings and a finite, periodic dispersion of the step state. Our observations fit well into the framework of the isolated step, with a one-dimensional, nondispersing step state split off from a two-dimensional image-state band. We do not observe any superlattice effects. This is consistent with calculations on related, but not identical step states,[8] which predict very small minigaps (0.03 eV), since the lateral kinetic energy of the electrons is large compared to the step potential. The only place where the step potential might become significant is at the bottom of the image-state band, where the lateral velocity is zero. According to the calculations[8] this happens within 0.005–0.034 eV of the band edge. There we might expect a backfolding of the two-dimensional band minimum, or the formation of a split-off step state. We are not able to detect back folding (see the location of the reciprocal-lattice vector g_{step} in Fig. 3), but we do find a split-off step state.

For designing more detailed experiments it is useful to have some rough figures for the binding energy and lateral extent of the split-off state. Therefore we briefly consider a model potential with two components, similar to an approach used in Ref. 16. Perpendicular to the surface, the electron is assumed to be bound by the image potential. The lateral potential is approximated by a square well, which confines the electron to a step. Considering the lateral part separately, we anticipate a well depth V of about 0.3–1.0 eV, based on the local work-function lowering at steps,[15] and a well width L of atomic dimensions, due to the short metallic screening length.[14] Such a narrow well provides only a single bound state with a small binding energy $E_b \approx (2m/\hbar^2)(VL/2)^2$, e.g., 0.065 eV for a well 0.5 eV deep and 2 Å wide. Thus we expect our well state to be bound just slightly below the bottom of the terrace state band, which is consistent with the location of we find for the step-induced image state. The corresponding decay length of the wave function is $\hbar/\sqrt{2mE} \sim 7$ Å. It gives attenuation factor of $\exp(-10/7) \approx 0.2$ at our step separation of 10 Å. Although this estimate depends sensitively on the assumed well width and depth, it makes the observation of weak step-step interaction plausible, and suggests that the interaction can be turned on at somewhat smaller step spacings.

In summary, we have discovered one-dimensional behavior in the electronic structure of image states on a stepped surface, both from the band dispersion and the polarization dependence. This finding opens the way to the study of one-dimensional states with very basic, free-electron-like characteristics. A systematic variation of the depth and width of the confining one-dimensional potential trough should be achievable in the future if steps can be decorated with stripes of a low work function adsorbate.

Recently, we have become aware of a two-photon photoemission study[21] of alkanes adsorbed on Ag(111), where a nondispersing image state is observed at the bottom of the two-dimensional image-state band, similar to our step state. The lack of dispersion is attributed to localization, as it is in our case.

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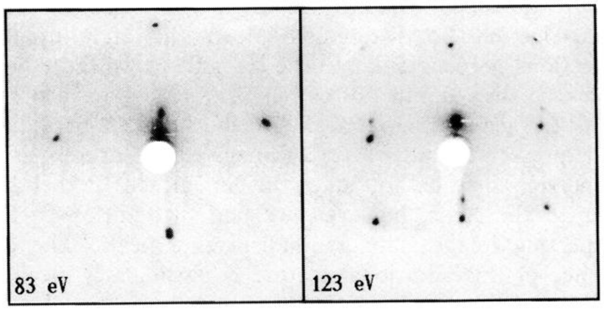

FIG. 1. Low-energy electron-diffraction (LEED) patterns from stepped Cu(100), exhibiting well-defined, split spots indicative of a regular step structure. The sample is tilted up to make the (0,0) beam visible.