Edge state and terrace state for Cu on W(331) and W(110)

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The surface electronic structure of Cu on stepped and flat W(110) is determined with inverse photoemission. An intense, Cu-induced surface state is found at 0.6 eV above the Fermi level on W(110). It is located in the Σ_1 band gap. On the stepped W(331) surface there is a similar state at 0.7 eV. This terrace state shifts down to 0.3 eV when the coverage of Cu is reduced such that only a single row of Cu atoms remains at a step edge.

The capabilities of creating low-dimensional structures at surfaces have increased considerably in recent years.[1-3] Our interest lies in fine wires that are obtained by decorating steps. On a relatively coarse level (hundreds of Å) this is a well-known phenomenon. Steps at alkali halide surfaces have served as nucleation centers for growing metal clusters.[1] Low-energy electron microscopy and photoemission microscopy have shown[2] that metal-on-metal growth may proceed in the step flow mode, such that ribbons are formed along steps. For example, Cu grows on Mo(110) in this mode at 700 K. On a finer level (tens of Å), it has been demonstrated[3] that semiconductor quantum wires can be grown by molecular-beam epitaxy on off-cut surfaces. Our work makes an effort to push the idea to the atomic limit, i.e., to determine the electronic structure of atoms adsorbed at steps. The ultimate goal is to prepare and analyze a string of single atoms, or more precisely, 10^6 of these strings simultaneously.

We determine the electronic structure of Cu on stepped W(110) by inverse photoemission, all the way from a complete Cu monolayer down to an array of single Cu rows at step edges. For the Cu monolayer we find an intense new surface state, which is located in the Σ_1 band gap of W(110). A similar state is seen on the stepped W(331) surface at monolayer coverage. After reducing the coverage to a single row of Cu atoms per step, the Cu-induced state shifts down by 0.4 eV, thereby revealing a distinct electronic structure for Cu atoms at the step edge.

The experiments were carried out with a well-oriented W(110) surface and a 13° off-cut, which corresponds to the W(331) orientation. At this surface the steps run along the [1$\bar{1}$0] direction, with six atomic rows per terrace (Fig. 1). After electropolishing in NaOH and going through standard cleaning steps (sputtering at 1200–1500 °C to remove segregated C, oxygen treatment, and flashing[4]) we observed sharp low-energy electron diffraction (LEED) patterns with high contrast, and well-defined spot splittings for the (331) surface. Cu was evaporated in the low 10^{-10}-Torr range with the W substrates held at about 300 °C to facilitate Cu migration to steps. LEED showed Cu growing in registry with the W substrate up to a monolayer, with a misfit spot splitting developing above monolayer coverage along the [1$\bar{1}$0] direction. These results are in line with previous LEED

observations[4] on Cu/W(110). The Cu-induced state exhibited maximum intensity at monolayer coverage.

Figure 2 shows inverse photoemission results for the well-oriented W(110) surface. The unoccupied electronic states are measured along the [110] surface normal for two energies E_i of the incident electrons. At the clean W(110) surface we observe transitions into three bulk bands ($\Sigma_1, \Sigma_1, \Sigma_4$), and into an image potential surface state. These assignments are obtained from an earlier band-structure study,[5] which also shows that there is a bulk band gap of Σ_1 symmetry between the two Σ_1 transitions. It can support two-dimensional surface states. After adsorbing a Cu monolayer we indeed find an intense surface state in this Σ_1 gap, i.e., at 0.61 eV above the Fermi level. Its two-dimensional nature is confirmed by varying the energy of the incoming electrons, and thereby their perpendicular momentum (Fig. 2 top versus bottom). No perpendicular dispersion is observed for the Cu-induced state, while the bulk transitions change their energy, particularly the upper Σ_1 peak. The cross section also changes with electron energy, with s,p states becoming dominant at low energy over d states. The Cu-induced state and the lower
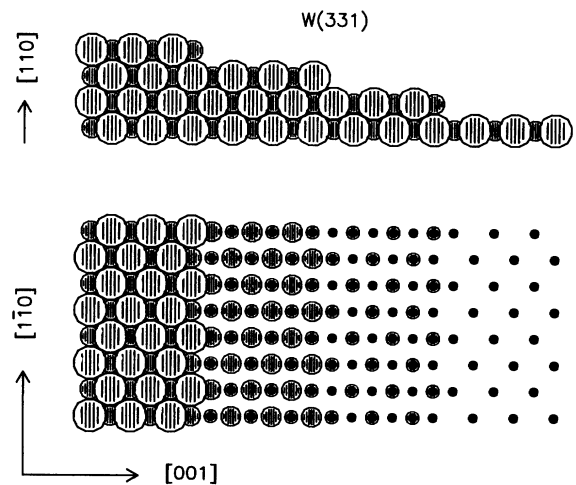

FIG. 1. Top view and side view of the W(331) surface. It exhibits (110) terraces, which are six atomic rows wide.
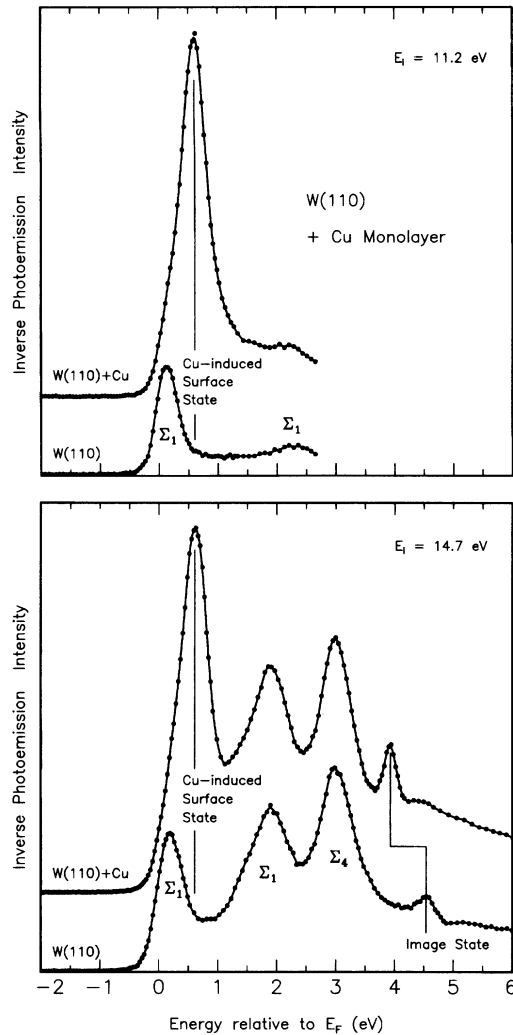
FIG. 2. Inverse photoemission spectra showing the empty electronic states for clean and Cu-covered W(110). An intense, Cu-induced surface state is seen at 0.61 eV in the gap between two Σ_1 bulk bands. Electrons are incident normal to the surface with energies of 11.2 and 14.7 eV above the Fermi level.

Σ_1 peak show such behavior, revealing their s,p character. In fact, the lower Σ_1 band converges towards the p_z-like N_1' point at low energies.[5] This suggests an interpretation of the Cu-induced state analogous to the well-known[6] Λ_1 surface state on Cu(111) surfaces, which splits off from the p_z-like L_2' point. This Cu(111) surface state has recently been used to image lateral charge fluctuations near steps with a scanning tunneling microscope.[7] The Cu monolayer on the close-packed bcc W(110) surface may be viewed as a uniaxially distorted, fcc Cu(111) surface layer (compare Fig. 1). The main difference is that we have W subsurface atoms instead of Cu. It would be interesting to see if there are connections with occupied surface states and their Fermi surface, which have been mapped[8] for clean and H-covered W(110), Ni(111) on W(110), as well as for Cu on W(110).[4] Preliminary results on the parallel dispersion of the Cu-induced state point towards a rather flat band.

An additional change upon Cu adsorption is a large down-shift of the image state from 4.54 to 3.93 eV. It mainly reflects the lower work function of Cu relative to W, plus a possible change in the binding energy of the image state. The difference of 0.61 eV is close to the observed work-function lowering[4] of 0.7 eV.

Cu adsorption on the stepped W(331) surface is characterized in Figs. 3 and 4. As on the flat W(110) surface, we find a Cu-induced surface state at monolayer coverage, which is labeled terrace state.[9] Unlike W(110), however, the stepped W(331) surface causes the Cu-induced state to shift down when reducing the Cu coverage to the single-row limit of $\frac{1}{6}$ layer. As the direct comparison in Fig. 4 shows, there is no such shifted state on the flat W(110) surface. This different behavior of the stepped and flat surfaces demonstrates that the shifted state is associated with Cu atoms adsorbed at step edges. The energy shift could be due to either the additional Cu-W bonds at the W step edge, or the lack of Cu-Cu bonds at the Cu step edge. The magnitude of the shift (0.49 eV in Fig. 3 and 0.40 eV in Fig. 4) is comparable to shifts of ≥ 0.4 and 0.3 eV observed for intrinsic step states versus terrace states on stepped Ir(111) and Ni(111), respectively.[10]

The observation of a shifted Cu state in the single-row limit is insensitive to experimental details. For example, Fig.
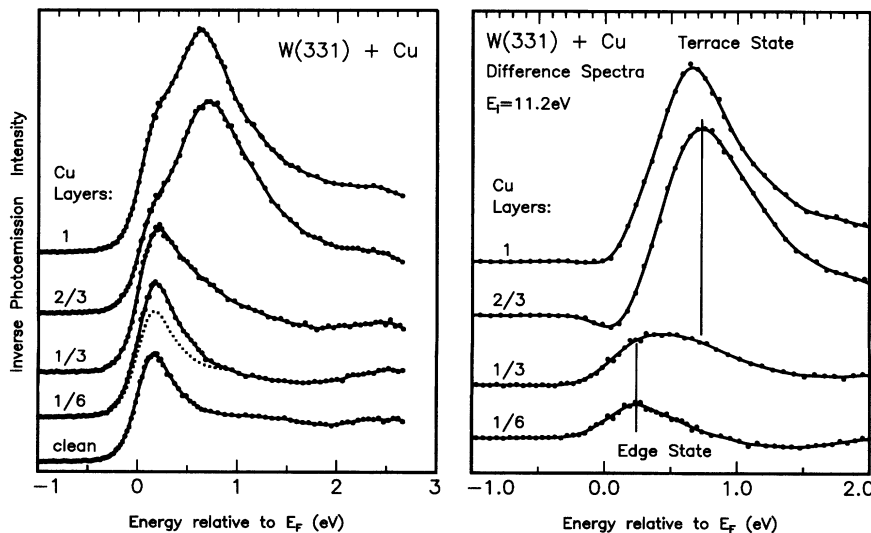

FIG. 3. Inverse photoemission spectra for the stepped W(331) surface at various Cu coverages. The Cu-induced feature is separated out in the right panel by subtracting the spectrum of the clean substrate (see dotted line in the left panel). A Cu-induced terrace state is seen at 0.73 eV similar to that in Fig. 2 for flat W(110). This states shifts down to 0.24 eV when the Cu coverage is reduced to $\frac{1}{6}$ layer, which corresponds to a single row of Cu atoms per step. Electrons are incident along the [331] average normal with an energy of 11.2 eV.
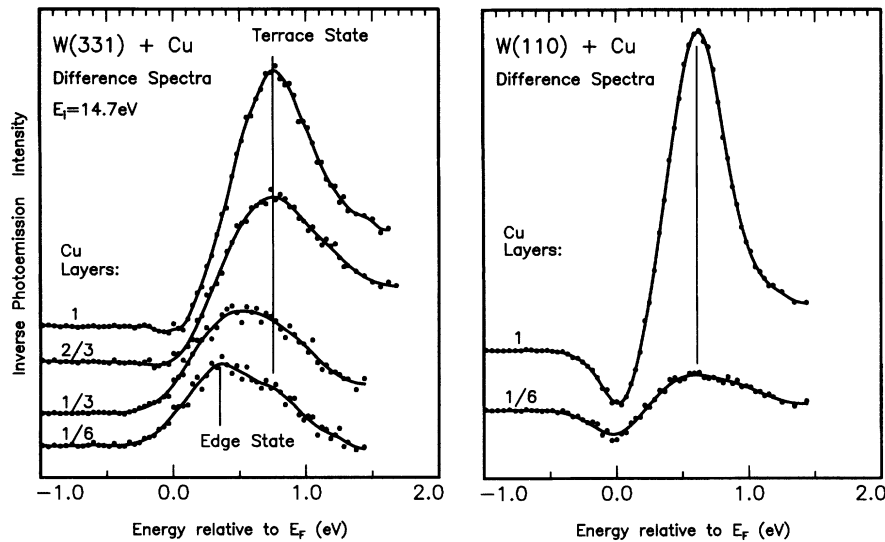
FIG. 4. Difference spectra showing Cu-induced features on stepped W(331) (left) and flat W(110) (right). The Cu-induced state shifts down at low coverage for the stepped W(331) surface, but remains unchanged for flat W(110), indicating a distinct edge state for Cu atoms adsorbed at steps. Electrons are incident along the [110] terrace normal with an energy of 14.7 eV.

3 (right) and Fig. 4 (left) exhibit the same effect, despite changing several parameters, i.e., the initial energy from 11.2 to 14.7 eV, the electron incidence from the [331] average normal to the [110] terrace normal, and the substrate from an electropolished to a mechanically polished surface.

At coverages larger than the single-row limit the interpretation of the data is uncertain, due to the complex growth morphology of Cu on W(110). While there is little doubt that the first row of Cu atoms would migrate to a W step edge to lower the step energy, there is a complex balance between misfit strain energy and Cu step energy determining the subsequent growth behavior. In fact, low-energy electron microscopy[2] and scanning tunneling microscopy[11] (STM) indicate that Cu atoms indeed migrate to steps, but exhibit a dendritic step-flow growth with increasing coverage. On W(110) the Cu atoms are found to form large islands along the few residual steps, being swept off the large terraces. This explains that the Cu state is always found at the monolayer position on W(110), even for small coverage.

Our results suggest some interesting experiments on decorated steps. For observing the decoration directly with an STM the large increase in the density of states induced by the Cu state at 0.3–0.8 eV above the Fermi level should make it possible to identify Cu atoms. The issue of identifying metal atoms has proven difficult in previous STM work, and a spectroscopic understanding of the electronic states associated with various metal surfaces should alleviate the problem. On-going STM work[11] indicates that spectroscopic contrast can indeed be used to identify Cu islands on W. For producing Cu ribbons attached to steps it may be better to try a Mo(110) surface, which does not exhibit dendritic growth.[2] Such ribbons could be used to trap image states into one-dimensional configurations, due to the lower vacuum level of Cu. Similar one-dimensional image states have been found at stepped Cu(100) surfaces,[12] where the local lowering of the vacuum level at a step has a similar effect.

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