Spectroscopic signature of Cu on W(110) from scanning tunneling microscopy and inverse photoemission

Y. W. Mo and F. J. Himpsel
IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598
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Monolayer Cu stripes attached to the steps of W(110) are distinguished from W terraces by scanning tunneling microscopy using a Cu-induced empty state, which is characterized by inverse photoemission spectroscopy. While the contrast between Cu and W atoms is dominated by the difference of the atomic sizes at most biases, it can be reversed with a bias such that tunneling into the Cu state overwhelms the size difference. This effect provides an unambiguous and well-understood mechanism for identifying different metal atoms.

Controlling the growth kinetics to create nanoscale structures on solid surfaces has attracted much interest recently. One particular method is to grow quantum wires or dots using substrate step arrays as a template. The interaction of the adatoms with surface steps plays an important role in determining surface growth and much progress has been achieved to understand this interaction both for metal[1] and semiconductor[2] surfaces. Recently, scanning tunneling microscopy (STM) has been widely used to study the atomistic mechanism of film growth kinetics. To obtain a direct view of nanoscale structures formed by adsorbates on substrates of a different material, STM needs to be able to distinguish different chemical elements.

Progress has been made to make STM chemical sensitive, especially on semiconductor surfaces because of the presence of the energy gap at the Fermi level and the directional nature of the bonds for semiconductors.[3] It is more difficult, on the other hand, to obtain contrast between different metallic elements because metals all have electronic states at the Fermi level and valence electrons are typically delocalized. For metal atoms with very different atomic sizes, a contrast could be obtained by the different apparent heights ("geometric" contrast).[4] Several studies have also reported distinction between different metals when the STM tip undergoes certain changes which are not understood but believed to be the adsorption of foreign atoms at the end of the STM tip.[5] In particular it has been found that the introduction of oxygen into the chamber sometimes induces a change in the STM tip resulting in a reversal of the STM sensitivity to O and Cu atoms.[6] To our knowledge, however, there have not been STM observations of contrast between different metal species based on a well-characterized electronic state.

We report the observation of a spectroscopic signature of Cu deposited on W(110) that allows for unambiguous identification of Cu stripes attached to the W substrate steps. By combined STM and inverse photoemission spectroscopy studies of Cu growth on W(110), we have identified a Cu-induced empty state. At adequate tunneling biases, this electronic state provides a contrast opposite to the "geometric" contrast observed using most other biases. Based on this mechanism, we are able to obtain a direct view of nanoscale Cu "wires" grown at the edge of W(110) terraces.

The experiments were carried out in two separate ultrahigh vacuum (UHV) chambers, one with a STM, the other with an inverse photoemission spectrometer. The base pressures of both systems are in the 10^{-11}-Torr range. The same W(110) sample is used in both systems. It is initially cleaned by repeated sputtering and oxygen treatment, to segregate and subsequently remove carbon impurities from the sample bulk. Before exposing to air for transferring from one to the other chamber, the sample is covered with a thick protection layer of either Cu or W oxide. The protection layer is then removed under UHV conditions by flashing to 2500 °C. All STM images and inverse photoemission spectra are obtained at room temperature (RT). The W substrate used is nominally (110), with a residual miscut angle of $\sim 1.5°$. Cu sources are thoroughly outgassed so that the chamber pressure during deposition is lower than 4×10^{-10} Torr. Cu coverage is controlled by a shutter and calibrated by a quartz crystal monitor.

After sample cleaning, STM shows arrays of flat terraces separated by rather straight, monatomic steps. Figure 1 shows an STM image of the surface after the deposition of ~ 0.1 ML of Cu with the sample held at RT. It can be seen that Cu grows in the step-flow mode, indicating sufficient mobility for the Cu atoms to reach and attach to the W terrace edges at RT.[7] Boundaries between Cu stripes and W terraces are visible and the mechanism of the contrast is discussed below. This boundary is rather straight and sharp, suggesting a lack of intermixing between W and Cu atoms, at least for room-temperature growth. On the other hand, the outer edge of the Cu stripes attached to the W steps is significantly rougher than the W terrace edges. This roughness appears not to be due to the kinetic limitation because it persists even after thermal anneals at temperatures as high as 400 °C. Along certain particular azimuthal orientations, however, the Cu outer edges can be made nearly atomically smooth.[8]

Another feature is the presence of some dark spots only in the W terraces, not in the Cu stripes. They appear dark when imaged with both positive and negative biases. We believe that they are likely to be caused by oxygen contamination.[9] Cu, as a noble metal, is much less sensitive to O and other types of contaminations than W. The concentration of the dark spots varies in different preparations. Their presence, however, does not affect the contrast between Cu stripes and the areas of W terraces not covered by the dark spots.

Also, from many STM images taken after submonolayer Cu depositions at RT, we observe that the width of Cu stripes is approximately proportional to the width of the W terrace on which the Cu stripe resides. This suggests that Cu atoms are confined to the terraces on which they initially land, indicating the presence of an energy barrier that prevents Cu atoms from crossing the W steps. Many studies of metal surfaces have observed an energy barrier at the terrace edges which prevents adatoms from crossing downward at low temperatures.[1] The existence of this barrier at terrace edges is one of the important factors determining the roughness of the growth front of thin films.[10] The ability to observe the spatial distribution of different metal atoms provides a direct way to study it.

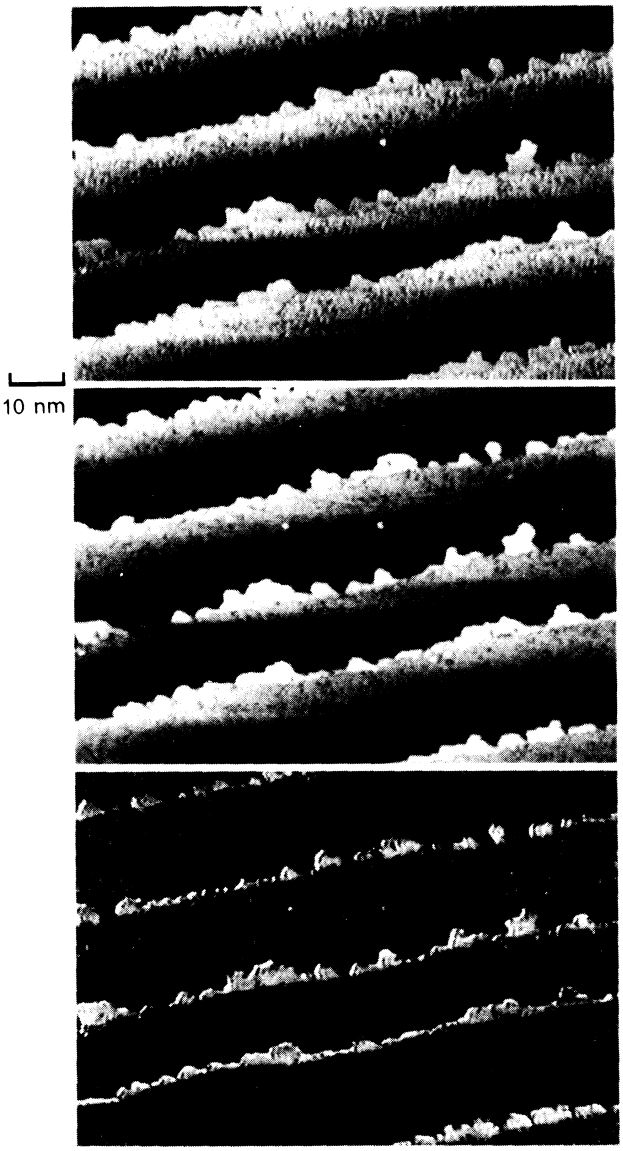

FIG. 1. STM images of Cu stripes formed along W steps after the deposition ~0.1 ML of Cu on W(110). Top: sample bias of −0.6 V, tunneling from the occupied states in the sample to the tip. Middle: sample biased at +0.6 V, tunneling into the empty states in the sample. Bottom: subtraction of the top image from the middle image, to enhance the spectroscopic contrast between Cu and W. Image area: 100×70 nm^2.

The central point of this paper is the STM contrast between Cu and W. Figure 2 shows close views of the boundaries between Cu stripes and W terraces, taken again with two different tip biases, as well as the line scans of the height distribution across two W steps decorated with Cu ledges. It can be seen that the apparent height of the Cu layer relative to the W layer depends on the tunneling bias voltage. For filled state imaging, taken with a negative sample bias, the Cu layer appears lower than the W layer. The opposite is seen for a positive sample bias. This contrast reversal is perfectly repeatable and is qualitatively independent of the tip condition. We believe that the lower apparent height of the Cu step at negative bias is mainly due to the smaller size of Cu atoms compared to W (about 10% smaller in the covalent radii). The increase in the height of the Cu layers at positive bias will be assigned to spectroscopic contrast as explained in the following.

In order to identify the origin of this contrast reversal, we need to determine the bias voltage around which the reversal occurs. This can be obtained by quantitative measurements of the relative step heights as a function of the bias voltage. STM images of the same area are taken with a series of different sample biases. To reduce the statistical error of a simple line profile as shown in Fig. 2, selected areas on both W and Cu are fit to parallel planes. The vertical separation between these planes is taken as a quantitative measurement of the apparent step height. Plotted in Fig. 3 is the apparent height of the W-to-Cu step as a function of the sample bias, normalized to the W-to-W step height which exhibits no dependence on the bias. A pronounced rise of the W-to-Cu step height can be seen at about +0.6 V sample bias, i.e., the reversal occurs when electrons tunnel from the Fermi level of the tip into unoccupied surface state 0.6 eV above the Fermi level.

Using inverse photoemission spectroscopy, we find indeed a strong unoccupied state at 0.6 eV above the Fermi level for a Cu monolayer on W(110), as shown in Fig. 4.[11] The W(110) substrate, on the other hand, exhibits a gap of states at this energy (see Ref. 11 for a detailed analysis of the inverse photoemission spectrum). Just from tunneling into this empty Cu state we expect a step-function behavior of the apparent step height with bias voltage (compare Fig. 3). For a bias above 0.6 eV electrons can tunnel from the tip into the Cu state, thereby increasing the apparent height of Cu patches. With a bias below 0.6 eV this process is not possible. Instead of

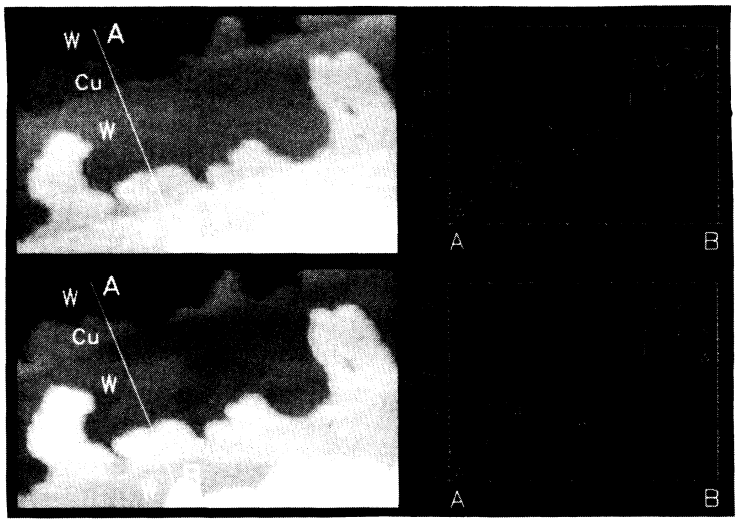

FIG. 2. STM images of Cu stripes along W steps and cross-sectional line cuts, showing the reversal of the apparent Cu step height by changing the sample bias. Top left: image taken with the sample biased at −1.0 V. Top right: height profile along the line shown in the STM image, showing that Cu layers appear lower than the equivalent W terrace. Bottom: image at +0.6 V and corresponding height profile, showing that CU layers appear higher than W at this bias. STM image area: 75×48 nm^2. About 0.3 ML of Cu is deposited.

the expected step function we observe a sawtooth. It appears that the spectroscopic contrast disappears at high positive and negative bias voltages. At least for positive bias such an effect can be rationalized. In this case one requires tip states far below the Fermi level to tunnel into the Cu state. Their density is low as one approaches the bottom of the valence band, and of course disappears when going below it.

Further supporting the proposed origin of the contrast reversal, detailed mapping of the Cu-induced state in energy and momentum space indicates that it is *s,p*-like, i.e., it has a large spatial extension of the wave function, and is centered at zero parallel momentum, ideal for STM imaging.[11] Obviously, this state density is so high that it overwhelms the geometric difference as soon as the Fermi level of the tip is biased high enough to allow tunneling into the Cu state. As a result the Cu layer appears higher than the W layer, despite the smaller atomic size of Cu.

In summary, we show that elemental contrast can be achieved in STM from metal surfaces by using spectroscopic characteristics. To our knowledge, this is the first

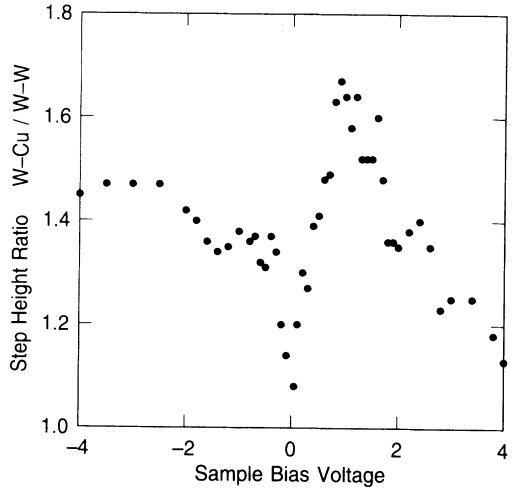

FIG. 3. Quantitative determination of the switchover point where the contrast between Cu and W layers reverses. Near 0.6 V bias, the apparent height of W-to-Cu increases sharply (see also Ref. 12). The point of sharp rise of the Cu apparent height corresponds to the onset of tunneling into an empty Cu state at 0.6 V above the Fermi level (see Fig. 4), which produces higher tunneling current for Cu than for W.

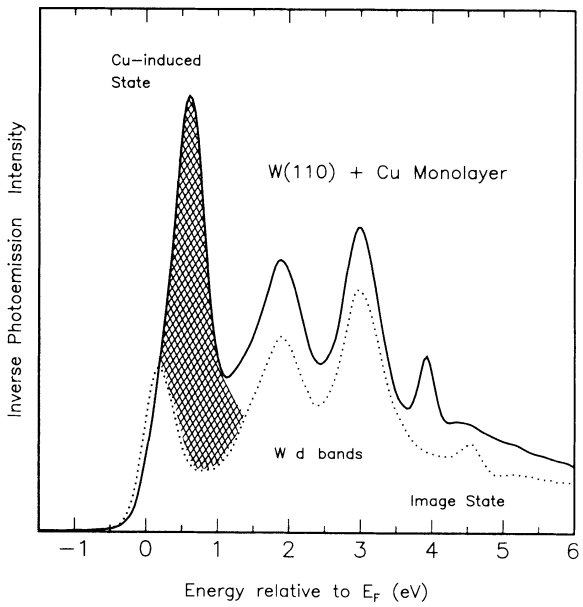

FIG. 4. Inverse photoemission spectra of clean (dotted line) and Cu-covered (solid line) W(110), showing a Cu-induced state at 0.6 eV above the Fermi level (hatched area). This intense state is responsible for the spectroscopic contrast between Cu and W.

example of distinguishing different metal species on a metal surface based on a well-characterized spectroscopic state by combining STM with an independent spectroscopic technique. With this ability to distinguish Cu from W, we are able to determine many details of the growth kinetics important for achieving controlled formation of nanoscale structures.

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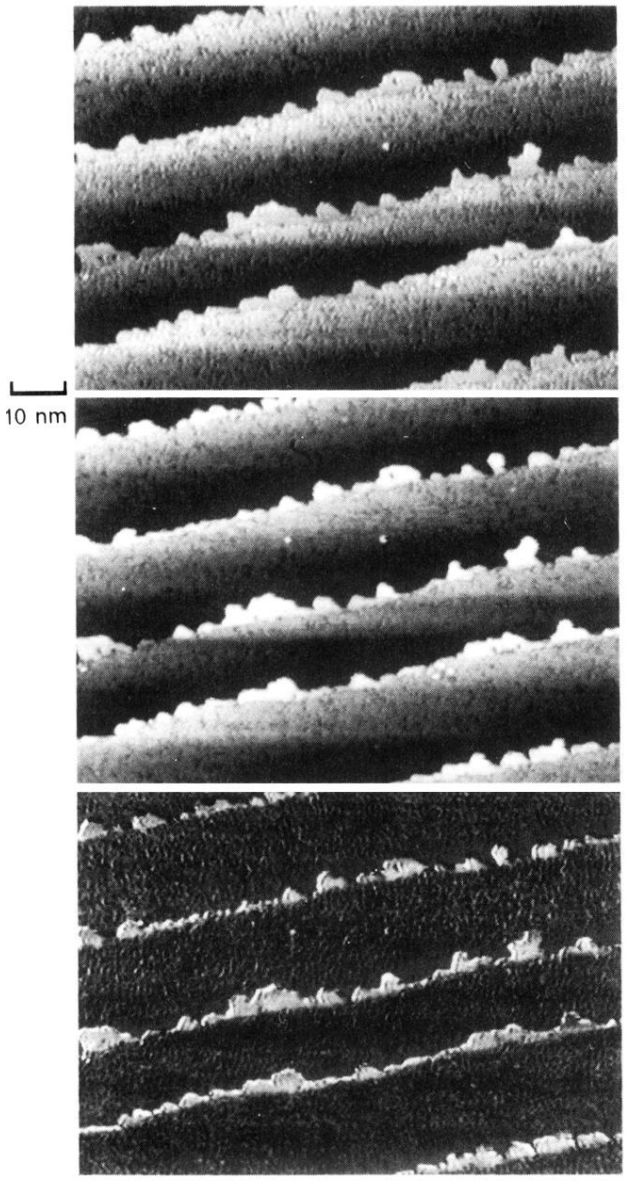
[1]See, e.g., G. Ehrlich, Appl. Phys. A **55**, 403 (1992).
[2]Y. W. Mo and M. G. Lagally, Surf. Sci. **246**, 13 (1991).
[3]R. M. Tromp, E. J. van Loenen, J. E. Demuth, and N. D. Lang, Phys. Rev. B **37**, 9042 (1988).
[4]H. Roder, R. Schuster, H. Brune, and K. Kern, Phys. Rev. Lett. **71**, 2086 (1993).
[5]M. Schmid, H. Stadler, and P. Varga, Phys. Rev. Lett. **70**, 1441 (1993); K. E. Johnson, D. D. Chambliss, R. J. Wilson, and S. Chiang, J. Vac. Sci. Technol. A **11**, 1654 (1993).
[6]L. Ruan, F. Besenbacher, I. Stensgaard, and E. Laegsgaard, Phys. Rev. Lett. **70**, 4079 (1993).
[7]Low-energy electron microscopy has observed step-flow growth of Cu on W(110) at 700 K, see, H. Poppa, H. Pinkvos, K. Wurm, and E. Bauer, in *Magnetic Ultrathin Films: Multilayers and Surfaces/Interfaces and Characterization,* edited by B. T. Jonker, S. A. Chambers, R. F. C. Farrow, C. Chappert, R. Clarke, W. J. M. Devonge, T. Egami, P. Grunberg, K. M. Krishman, E. E. Marinero, C. Rau, and S. Tsundshima, MRS Symposia Proceedings No. 313 (Materials Research Society, Pittsburgh, 1988), p. 219.
[8]Y. W. Mo and F. J. Himpsel (unpublished).
[9]K. E. Johnson, R. J. Wilson, and S. Chiang, Phys. Rev. Lett. **71**, 1055 (1993).
[10]G. Rosenfeld, R. Servaty, C. Teichert, B. Poelsema, and G. Comsa, Phys. Rev. Lett. **71**, 895 (1993).
[11]F. J. Himpsel and J. E. Ortega, Phys. Rev. B **50**, 4992 (1994).
[12]The W-to-Cu step height normalized to the W-to-W step height does not go below 1.0 at negative bias in this data set because of a systematic offset in the measurement due to dark defect spots appearing only in W terraces. While their presence does not affect the measurement of W-to-W step height, it artificially enhances the average height of W-to-Cu steps.



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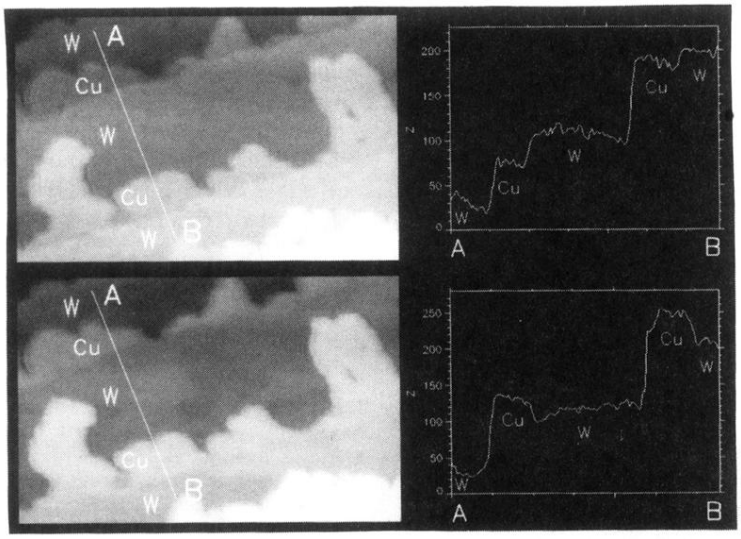

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