Identification of Metals in Scanning Tunneling Microscopy via Image States

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An oscillatory reversal of the contrast between Cu and Mo is observed with scanning tunneling microscopy (STM), using sample bias voltages of +5 V and higher. It is attributed to tunneling via a series of discrete states that are induced by a combination of the image potential and the applied field. They are offset in energy due to the different work functions of Cu and Mo. This effect provides a generally applicable mechanism for elemental contrast in STM.

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Achieving contrast between different chemical elements has always been one of the major objectives for microscopic studies. As one of the younger methods, scanning tunneling microscopy (STM) is still evolving towards new schemes for obtaining contrast that goes beyond the well-established topographic contrast. The principal source of elemental contrast has been based on the difference in local density of states associated with different surface atoms, which results in different apparent heights when imaging with certain bias voltages. While this chemical sensitivity has been obtained for a variety of semiconductor surfaces [1,2], it has been much more difficult to obtain elemental contrast between different metal atoms. The primary reason is that the tunneling current is dominated by the electronic states near the Fermi level, where most metals have a large density of states. On occasions where element-specific surface states exist in the neighborhood of the Fermi level, elemental contrast can be obtained [3]. Unidentified foreign atoms attached to the end of the tunneling tip have also produced contrast for certain metals [4].

Even for systems which possess strong variations in the density of states near the Fermi level, the success of obtaining elemental identification is far from guaranteed because not all surface states contribute equally to tunneling. On transition and noble metals, for example, localized d states contribute very little, while delocalized s, p states dominate tunneling. Thus, in addition to identifying element-specific surface states with other spectroscopies, such as photoemission and inverse photoemission, one has to determine the spatial extent of their wave functions. Therefore, it is very desirable to have a contrast mechanism that is based on a simple property of a surface species, and does not involve many details of the electronic structure.

Here we report a new method to obtain elemental contrast in STM, which is based on the local work function of different materials. By operating the STM with higher bias voltages in a transition region between tunneling and field emission, a series of sharp resonances are available for enhanced tunneling [5–7]. They can be viewed as image states distorted by the field of the tip. Since the lowest image state is bound by about $\frac{1}{16}$ Ry = 0.85 eV below the vacuum level, its energy position is tied to the local work function of a material [8–11]. The applied electric field of the tip shifts the energy of the image state back up, such that the lowest STM resonance occurs at a bias slightly above the work function. By switching the bias between the resonances of different materials we are able to identify elements, e.g., Cu stripes formed along the surface steps of vicinal Mo(110). From the general nature of image states and STM resonances we anticipate broad applicability of this method.

The experiments were carried out in an ultrahigh vacuum STM system (operating pressure 4×10^{-11} Torr). In parallel, both image and surface states were characterized with inverse photoemission on the same crystal. A vicinal Mo(110) crystal with about a 50 nm average terrace width was electropolished in 15% sulfuric acid in methanol and cleaned by sputtering at elevated temperature, heating in oxygen, and flashing off the surface oxide. Submonolayer amounts of Cu were deposited at room temperature and annealed for 2 s at 600 °C in order to allow Cu atoms to diffuse and attach themselves to the Mo(110) step edges (see Ref. [12]). A detailed account of the growth of Cu along steps on Mo(110) will be published elsewhere (compare also Refs. [3] and [12]).

The contrast induced by tunneling via image states is demonstrated by a series of STM pictures in Fig. 1. A few Mo(110) step edges are seen to cross the image from top to bottom, which are decorated by Cu stripes containing dark spots [13]. Without contrast between Cu and Mo the terraces would appear as a sawtooth pattern, since the average z position of each line scan has been set to zero by subtracting a linear background. Increasing the sample bias continuously towards positive voltages we find an oscillatory reversal of the contrast between Cu and Mo, starting at about +5 V bias. Cu stripes appear substantially brighter than Mo at sample bias voltages of 5.3, 7.1, and 8.2 V (right side of Fig. 1). They are slightly darker than Mo in between these maxima (left side of Fig. 1). The Cu intensity maxima are very pronounced, with only a few tenths of an eV width. Their positions are

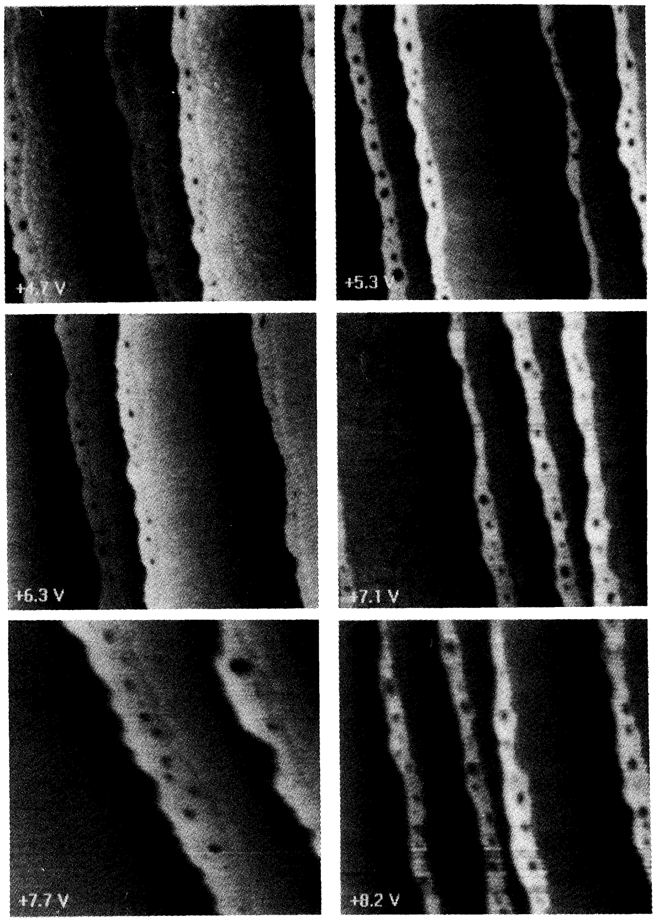

FIG. 1. STM pictures of Cu monolayer stripes attached to step edges of a Mo(110) surface ($200 \times 200\ \mathrm{nm}^2$). The contrast between Cu and Mo exhibits oscillatory reversals with sample bias voltage. They are explained by tunneling via a series of discrete states, which are plotted in Fig. 2.

plotted in Fig. 2 (full circles), including further maxima not shown in Fig. 1.

The clue for explaining the contrast reversal comes from comparing our series of Cu intensity maxima with oscillations in the dI/dV spectra obtained by Binnig *et al.* [6] for Ni(100) (open circles in Fig. 2). These oscillations have been assigned to tunneling via quantized states in the potential well that is induced by a combination of the image potential and the applied field [5–7]. The lowest of these resonances resembles the lowest, $n = 1$ image state, but is shifted upward by the applied field from the position found with inverse photoemission (Fig. 3). For example, our inverse photoemission measurements give energies of 3.99 and 4.51 eV for the $n = 1$ image state on Cu/Mo(110) and Ni(100), respectively, while the corresponding STM resonances appear at 5.2 and 5.3 eV, respectively. Because of their field dependence, the STM resonances depend on the tunnel current used for the tip position feedback (0.1 nA in our case). However, it is always possible to identify the surface patches with the lowest work function by approaching from low bias voltages and finding the position of the lowest resonance. The lowest resonance can then be used as a reference point to determine work function differences across the surface.

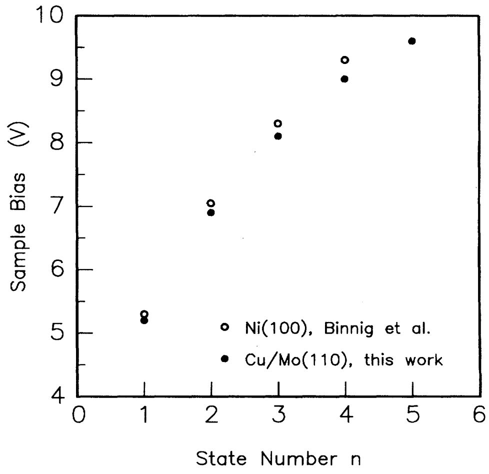

FIG. 2. Energies of the tunneling states that produce maximum brightness for Cu stripes on Mo(110). For comparison, similar maxima observed in dI/dV spectra of a Ni(100) surface by Binnig *et al.* [6] are given. They correspond to standing waves in the potential well produced by a combination of the image charge and the applied electric field.

The explanation for the contrast between Cu and Mo is based on their different image state positions, which can be seen directly from the inverse photoemission data of Fig. 3. Mo(110) has the $n = 1$ image state at 4.35 eV, 0.36 eV higher than the Cu monolayer on Mo(110). Therefore, the whole series of resonances will be offset towards higher bias for the Mo(110) patches, and we get an alternating series of Cu and Mo resonances. The Cu resonances are more pronounced, an effect that might be related to the lower work function barrier of Cu. It would be interesting to explore this point further by modeling the tunnel probability. The image state position is tied to the work function of the material, since the binding energy of the $n = 1$ state is given by $\frac{1}{16}\ \mathrm{Ry} = 0.85$ eV, scaled down by a factor that depends on the bulk band topology [8–11]. Comparing image state data with work functions, one finds typical binding energies around 0.6 eV [10,11]. Although an exact determination of image state energies from the work function requires substantial calculations, there are simple phase shift models [8,9] that allow estimates with an accuracy comparable to the intrinsic width [11]. For our inverse photoemission data on Mo(110), Cu/Mo(110), and Ni(100) we may use reported work functions of 4.95 [14], 4.40 [14,15], and 5.09 eV [11], resulting in binding energies of 0.60, 0.41, and

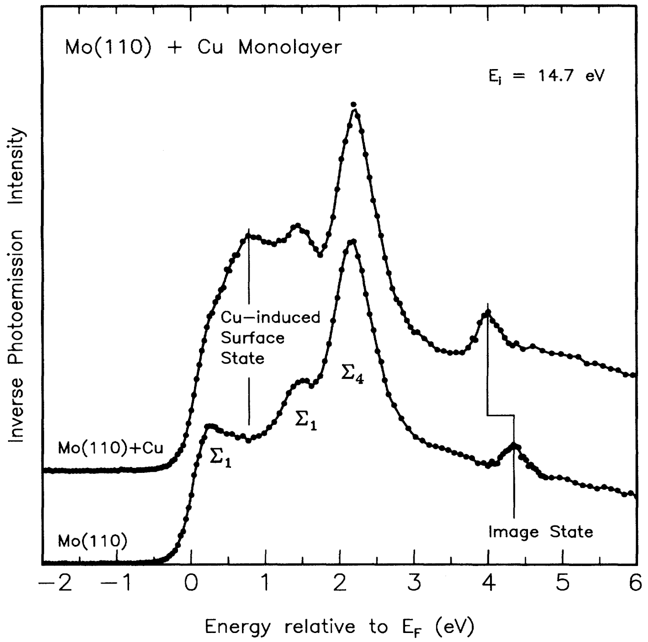

FIG. 3. Inverse photoemission spectra of clean Mo(110) and a monolayer of Cu on Mo(110), showing a 0.36 eV downshift of the $n = 1$ image state due to the lower work function of Cu. This shift produces different energies for the corresponding tunneling state of Cu and Mo and thus provides a contrast mechanism for STM imaging.

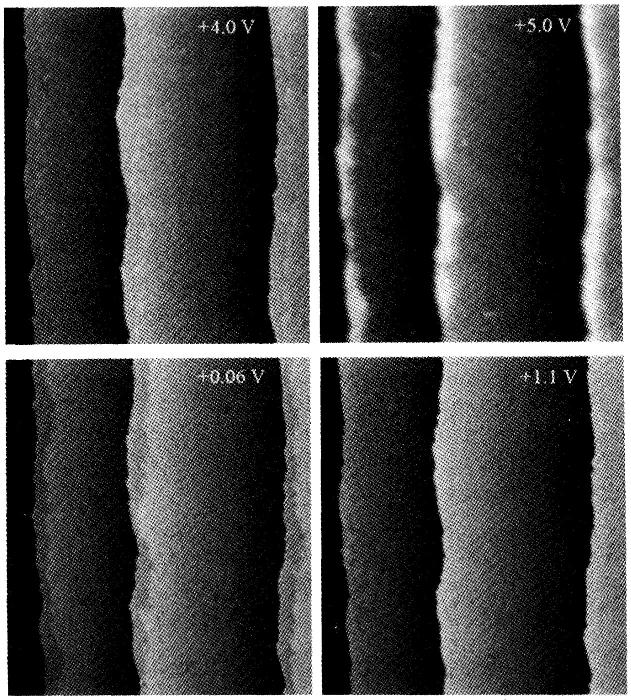

FIG. 4. Comparison of the image state contrast (top pair) to that induced by a surface state (bottom pair). The image state produces about twice the contrast, but degrades the spatial resolution somewhat. For spectra of the corresponding states, see Fig. 3 (90×110 nm^2).

0.58 eV, respectively. The variation in binding energies is comparable to the uncertainty in the absolute work function determined by different methods [14], and its dependence on surface preparation.

The contrast between Cu and Mo obtained from image states is found to be larger than that from ordinary surface states. We have tested this by using a Cu-induced surface state at 0.8 eV above the Fermi level (see Fig. 3) to enhance tunneling into Cu patches. This state is the analog to a p_z-like Σ_1 surface state reported previously [16] for Cu on W(110) and used for obtaining contrast between Cu and W in STM [3]. Quantitative analysis of individual line scans in Fig. 4 shows that the contrast induced by the image state (difference between the top two pictures in Fig. 4) is 60% of the step height, while that induced by the p_z-like surface state is only 30% of the step height (difference between the bottom pair of pictures in Fig. 4).

The ultimate resolution limit of our technique in resolving work function differences is determined by the intrinsic width of image states. Theoretical [9] and experimental [11] work indicates typical widths ranging from 0.02 for noble metals to 0.07 eV for transition metals. That would give a fair number of channels over a work function range [14] from 2.5 (for Eu and other rare earths) to 5.9 eV [for Pt(111)]. In a realistic application one would not attempt to identify the atomic number of an element from scratch, however. That can be done by traditional techniques, such as Auger spectroscopy. After identifying the constituents of a given surface by traditional methods, their spatial distribution can be determined by our method. In typical STM experiments one deals with 2–4 different elements on a given surface, and does not have to discriminate against the whole periodic table.

In summary, we have found a new way of obtaining spectral contrast in STM, using image states to differentiate patches with different work function. Compared to conventional spectroscopic imaging with surface states near the Fermi level, one can list advantages and drawbacks. A limitation is a decrease in spatial resolution to about 1 nm which is caused by retracting the tip at high bias voltages (Fig. 4). We have found that this is not critical in practice, since one can identify a patch at high bias with low resolution, and then zoom in at low bias. It may be difficult to identify single atoms that way, but the work function and image state of a single adatom are ill-defined quantities anyway.

The advantages of the method are its strong contrast, its general applicability and its straightforward interpretation. The contrast induced by the image state is twice as strong as that produced by a Cu surface state (compare Fig. 4), possibly because the image state is sharper (see Ref. [9]). Image states occur on practically all metal surfaces, while it may be difficult to always find surface states appropriate for spectral contrast. Tunneling via image resonances has even been seen on semiconductors [6]. The position of image states is closely tied to the work function, one of the basic characteristics of a material. Both the work function [14] and the image state energy [10,11] are being tabulated, and many individual papers have been published on the influence of crystallographic orientation, adsorbates, and overlayer thickness [e.g., Ref. [15] for Cu/Mo(110)]. Thus we expect widespread applicability of the method for obtaining elemental contrast and identification in STM.

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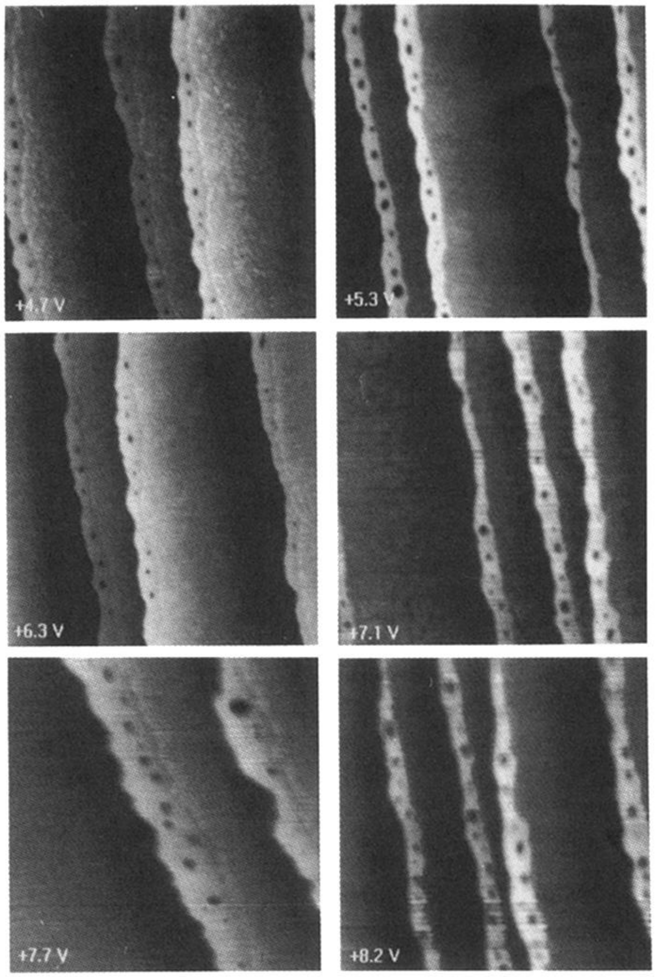

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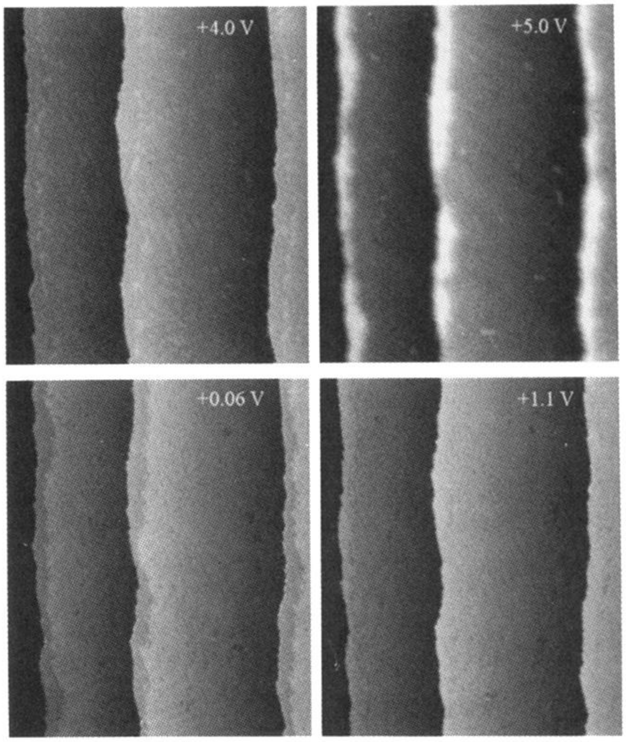

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