

Electron Resonances in Sharp Tips and Their Role in Tunneling Spectroscopy

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The influence of the shape and electronic structure of the tip in scanning tunneling spectroscopy is studied by a combined theoretical and experimental approach. Tunneling conductance spectra of a Cu(111) surface are used to detect and characterize the electronic states of W tips. The characteristic tunneling conductance of the Cu(111) surface state is the only feature present in spectra recorded with a blunt tip, while spectra obtained with sharp tips display also tip resonances. By means of a self-consistent tight-binding model of realistic tip structures we show that a sharp W tip exhibits, in contrast with blunt tips, narrow resonant states around the Fermi level. [S0031-9007(97)05005-9]

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Ever since it was introduced [1] scanning tunneling spectroscopy (STS) was expected to offer a novel view of the electronic structure of surfaces because it could probe the energy dependence of the sample electron states (convoluted with those of the tip) with unprecedented spatial resolution. In spite of its initial success, mostly for dangling-bond states of semiconductors [2], the progress in STS, especially in the field of metals, has been slower than expected. Only recently, and in selected systems (e.g., surface alloying in Cr/Fe(100) [3]) it has been possible the atomic-scale chemical identification based on STS. An important part of the encountered difficulties comes from the fact that the electronic states of the tip, which were quickly recognized to be crucial [4], often influence, and even dominate, the measured tunneling spectra. The lack of complete experimental control over the tip structure is reflected in widely experienced difficulties of reproducibility.

On the theoretical side, the analysis of the influence of tip shape and electronic structure in STS has been mostly based on the assumption that either isolated W clusters [5] or few atoms (even a single one [6]) on an otherwise flat surface [7], provide a good starting point for the description of the tip electronic structure. In what follows we shall demonstrate that this is not always the case.

In this Letter we report on STS experiments and calculations carried out on a surface with well-defined electronic structure, Cu(111), with the aim to characterize the electronic states of W tips. We demonstrate that depending on the crystalline structure and morphology of the tip, the differential conductance spectra, dI/dV , either show only the surface state of the bare Cu surface or are dominated by intense peaks due to electronic tip resonances. By calculating the electronic states of tips with realistic geometries we shall show that sufficiently sharp tips exhibit narrow electron resonances around E_F . These states originate in

the specific geometric environment of the apex atom in a fcc-stacked sharp protrusion of the tip, which, as discussed below, can be stabilized by high-current field emission cleaning even in materials such as W with a bulk bcc structure. These results are relevant to interpret tunneling spectra in many systems, to clarify the origin of electronic states observed in sharp field ion microscope tips [8,9], and to unravel the origin of quantized conductance jumps in atomic-size contacts [10,11].

The experiments have been carried out in an ultra-high vacuum chamber containing a homemade scanning tunneling microscope (STM), a rear-view low energy electron diffraction optics (LEED) and facilities for ion sputtering, cooling the sample and depositing metals. The Cu(111) single crystal was electrochemically polished, sputter annealed (600 eV, 800 K) for 5 min and cooled to 300 K. After this treatment the LEED pattern displays an hexagonal array of sharp and bright spots with three-fold symmetry. The STM images show equally spaced, straight monoatomic steps and no traces of contaminants. The STM tips were made of polycrystalline W wire electrochemically etched. The tips were cleaned *in situ* by applying 1 kV to the tip and approaching a clean tantalum foil until a field emission current of 10 μ A was established. This current is kept constant for several minutes by readjusting the tip-foil distance until the current is stable. Tips cleaned with this method produced reproducible I - V spectra. This high-current, field-emission cleaning process [12], is believed to lead to local melting and recrystallization of the tip end, whereby the facets with the highest density of atoms, e.g., W(110) and W(111) are most likely to be present.

Several hundreds of differential conductance spectra (dI/dV) vs V of clean Cu(111) recorded at room temperature with W tips prepared in the standard fashion are systematically found to belong to two different types,

whose representative examples are shown in Fig. 1. Spectrum (a) exhibits only a peak with the onset at -0.4 eV superimposed on a decreasing background. It is essentially identical to the one obtained by Crommie *et al.* on Cu(111) at 4 K [13]. It originates from I - V curves with a metallic behavior close to the Fermi level. The spectrum (a) corresponds to the well-known, Shockley-type surface state of Cu(111), whose two dimensional nearly free electron gas has been used to visualize standing waves [13] and confinements effects [14,15] in various structures. Thus, there are no features associated with the tip local density of states (LDOS) in the spectrum (a).

The second type of reproducible tunneling spectrum is shown in Fig. 1(b). It is dominated by two extremely strong peaks separated ~ 1 eV placed at either side of the Fermi level. Their precise energy location (and accordingly, their separation) has been found to vary $\sim \pm 0.3$ eV, although the general shape of the spectrum does not change. Since the sample LDOS exhibits only the surface state contribution in this energy range, the

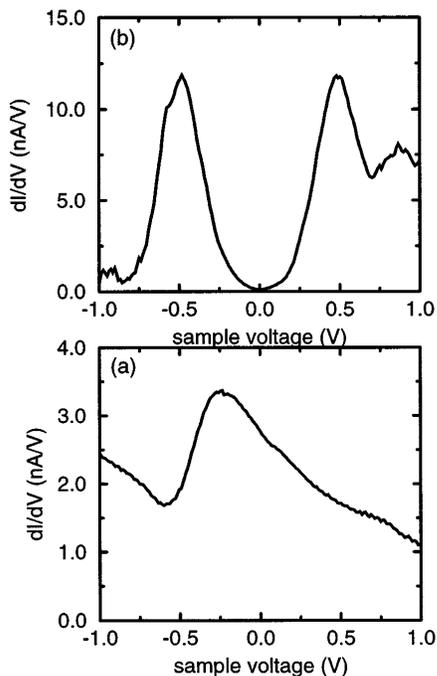


FIG. 1. Experimental differential conductivity for Cu(111). (a) and (b) represent the two kinds of spectra that are reproducibly obtained after cleaning the W tip by field emission. The tunnel junction was stabilized at -0.3 V and 0.4 nA. The current-voltage curves were measured with a constant separation between tip and sample as follows: The feedback was interrupted during 24 ms, the voltage between tip and sample ramped and the tunneling current was measured; at the end of the ramp the feedback was connected again during 66 ms and the current was stabilized. This procedure is repeated several times to improve the signal to noise ratio. From the measured I - V curves at fixed tunneling gap, dI/dV spectra are numerically obtained by calculating the local slope of the I - V curve within a window of 65 mV. No filters are applied to the I - V data.

states that dominate the tunneling spectrum (b) must originate in the tip.

The electronic structure of different tips with well-defined geometries has been calculated by using an atomic orbital basis leading to a tight-binding Hamiltonian

$$\hat{H} = \sum_{i\alpha,\sigma} \epsilon_{i\alpha} c_{i\alpha,\sigma}^\dagger c_{i\alpha,\sigma} + \sum_{i\alpha \neq j\beta,\sigma} t_{i\alpha,j\beta} c_{i\alpha,\sigma}^\dagger c_{j\beta,\sigma}, \quad (1)$$

where indexes i, j refer to the atomic sites and α, β denote the different (s , p , and d) atomic orbitals. The nearest neighbors hopping elements, $t_{i\alpha,j\beta}$, have been taken from fittings to *ab initio* band structure calculations [16]. The diagonal elements, $\epsilon_{i\alpha}$, are adjusted self-consistently to achieve local charge neutrality; we also allow for charge transfer between different orbitals in each atom introducing intrasite Coulomb interactions.

An efficient method to calculate the LDOS at a given orbital, i, α , is provided by the recursion method [17] that yields the local Green functions as a continued fraction

$$G_{i\alpha,i\alpha}(\omega) = \frac{1}{\omega - a_0 - b_0^2 g_1(\omega)}, \quad (2)$$

$$g_n(\omega) = \frac{1}{\omega - a_n - b_n^2 g_{n+1}(\omega)},$$

where the coefficients a_n, b_n are the diagonal and off diagonal elements of H in a new orthogonal basis generated by successively applying H to the initial state $|i\alpha\rangle$ [17]. These coefficients define an effective potential for the propagation along the tip axis and converge towards asymptotic values (a_∞, b_∞) for typically $n \geq 30$. We consider semi-infinite pyramidal tips built from perfect (100) and (111) planes stacked both in the bcc and the fcc structures. The LDOS on the apex atom s orbital, which is the one giving the main contribution to the tunneling current, is shown in Fig. 2 for bcc and fcc stacked, (111)-type of tips. While the (111) bcc tip yields a smooth, bulklike DOS, the (111) fcc tip exhibits two narrow resonances within the upper energy range of the bulk spectrum at both sides of E_F and separated by ~ 1.2 eV. The narrow resonances in the s -type LDOS of the apex atom *are not found* for tips with a larger opening angle such as fcc (100), bcc (111), or (100) stacked pyramids.

As discussed in Ref. [10], for a single s orbital per site model, tip resonances arise as a consequence of the large difference in the local environment between the apex region and that of the bulk. On the other hand, in the case of W, the d bands exhibit intrinsic peaks around E_F [7] which, however, are not reflected in the s density of states for blunt tips or flat surfaces. Nevertheless, for specific sharp tip geometries, they induce resonances in the s -type LDOS, whose precise energy location depends on the s - d hybridization. Thus, the resonances in the s -band LDOS at the apex atom, as a combined effect of spatial localization and intrinsic features of W electronic

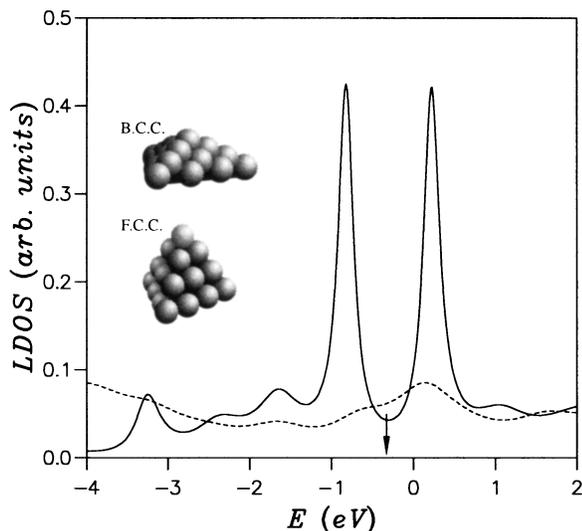


FIG. 2. Calculated local density of states (s states) at the apex atom for bcc (dashed line) and fcc (solid line) (111)-oriented W pyramids. The arrow indicates the position of the Fermi level. The inset shows the two tip geometries considered.

structure, are strongly dependent on the stacking of the last few planes of the tip and very different from those of small isolated clusters [5].

For a direct comparison with the experiments, we have calculated the tunneling spectra of the Cu(111) surface for the different tips by using the method presented in Ref. [18]. For tip-sample distances of 5–7 Å, such as used here, the tunneling current J can be written as a function of the Green functions $\hat{g}_{TT}(\omega)$ and $\hat{g}_{SS}(\omega)$ of the uncoupled tip and sample, respectively,

$$J \approx \frac{4\pi e}{h} \int_{-\infty}^{\infty} d\omega \text{Tr}[\hat{T}_{TS}\hat{\rho}_{SS}(\omega)\hat{T}_{ST}\hat{\rho}_{TT}(\omega)] \times [f_T(\omega) - f_S(\omega)], \quad (3)$$

where \hat{T}_{TS} defines the hopping elements coupling the tip and the sample atomic orbitals and Tr stands for the trace of the corresponding matrix. In Eq. (3) $\hat{\rho}_{TT}$ and $\hat{\rho}_{SS}$ are the LDOS at the tip and sample orbitals for $T_{TS} = 0$ and $f_{T,S}$ are the corresponding Fermi distribution functions. This expression has been evaluated using the atomic wave functions for the orbitals describing the valence bands of Cu and W. We have assumed that the main contribution to J comes from the s and p orbitals of both metals. Considering the different tip structures amounts to modifying the LDOS $\hat{\rho}_{TT}$ on the tip side.

The calculated differential conductance spectra for a Cu(111) surface and a bcc (111)-oriented tip is shown in Fig. 3(a). The onset of the surface state is clearly visible as a steep rise at -0.45 eV. It is in excellent agreement with the experiment [Fig. 1(a)] and previous calculations by Hörmandinger [19]. Similar results are obtained for tips with LDOS resembling free electron metals, such as W(110). Therefore, the standard spectrum (a) corresponds to tips with geometries expected

for the field-emission cleaning procedure employed. The spectrum calculated for a fcc (111) tip is reproduced in Fig. 3(b). The agreement with the experiment [Fig. 1(b)] is remarkable considering that there is no fitting involved. The theoretical spectrum displays two sharp peaks appearing below and above the Fermi level. These features in the differential conductance are associated with the resonances in the tip LDOS shown in Fig. 2(b). It must be noted that no attempt has been made to adjust the Fermi level or the peak positions in the calculations. The good agreement between theoretical and experimental STS results suggests that for the second kind of spectrum, in addition to the expected tip geometries, metastable fcc structures could also develop at the very end of the tip under these field-emission cleaning conditions.

In order to substantiate the argument, the stability of different fcc and bcc pyramidal tip protrusions on top of flat bcc (111) W surface has been analyzed by molecular dynamics with the interatomic potentials described by a Finnis-Sinclair potential [20]. Molecular dynamics simulations show that the fcc structure represents a metastable minimum even at temperatures close to the surface melting temperature. The electrical field present during the cleaning procedure additionally favors the formation of compact metastable structures.

In conclusion, we have used the well-defined surface state of Cu(111) to characterize experimentally the electronic states of W tips. We have found that, while bcc

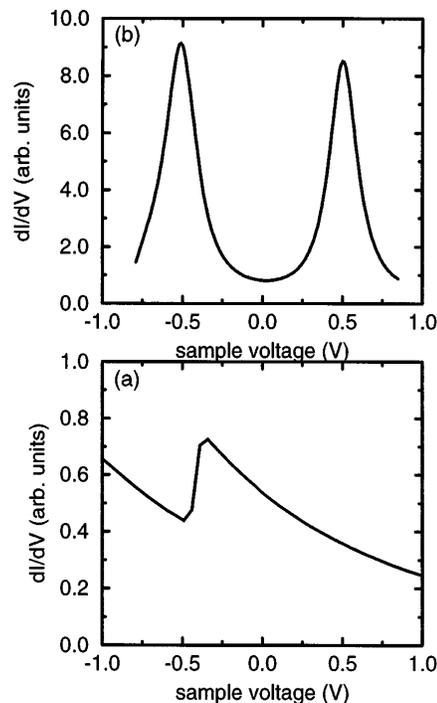


FIG. 3. Calculated tunneling spectra for Cu(111) and a W tip with geometries given by (a) bcc (111) pyramid and (b) fcc (111) pyramid. The conductance was calculated by numerical differentiation of the tunneling current.

(111) W tips show tunneling spectra representative of the sample, metastable tips ending with a fcc (111) pyramid exhibit resonant electronic states that strongly modify the spectra. These findings could explain a number of previous results in related fields: The localized states that exist on narrow tips have been shown to persist for atomic-size contacts [10] giving a mechanism for explaining the tendency to conductance quantization [11]. On the other hand, there were reports of field-emission electron spectra from sharp, single-atom-ended tips [8] where two peaks separated by 1.2 eV were observed. They were assigned to resonant tunneling through a single tungsten atom tip [8], a claim later refuted experimentally [9]. We suggest that the peaks experimentally observed are probably associated not with a single-atom tip, but with the localized electronic states reported here for fcc tips with the sharp geometry.

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