Field-Emission Electron Spectroscopy of Single-Atom Tips

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We show here that the experimental field-emission electron spectra from W nanoprotrusion tips ending in a single atom consist solely of well-separated peaks. Each spectrum shifts linearly with the applied field-emission voltage. The peaks in the spectra strongly suggest that the tunneling occurs only through a localized band structure at the topmost atom. A charge confinement and a field penetration over the top atom is introduced to explain the linear shifts.

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Well-defined field-emission tips ending with a single atom are of current interest for producing self-collimated, coherent electron beams [1,2]. A knowledge of the total-energy distributions (TED) of the field-emitted electrons is needed for an understanding of the physics of field emission from one atom and for the use of the beams in applications such as electron microscopy [3,4]. It may help to explain, for example, the high value of the tunneling barrier found in our former work [5]. It is also important for the detailed analysis of scanning tunneling spectroscopy (STS) because tunneling characteristics then vary with the electronic structure of both the tip apex and the sample surface [6].

The measure of TED's is termed field-emission electron spectroscopy (FEES). FEES has been used previously to study the electronic states of individual surface atoms and molecules chemisorbed on the metallic surfaces of tips [7]. For macroscopic tips, with radius greater than 100 nm, the area sampled by FEES has a diameter of more than 20 Å [8]. Recently, the controlled formation of nanoscale protrusions on the tops of macroscopic tips has been obtained by the field-surface-melting mechanism [5]. These protrusions are fabricated by the application of field and temperature under ultrahigh vacuum (UHV) conditions. They have been shown by field-ion microscopy to have a conical shape with 2–3 nm height ending in one atom. The sharply pointed geometry of the protrusions strongly enhances the applied field over the topmost atom [9] which then permits all of the field emission (FE) to come from only one atom. The emitted electrons are then self-collimated to form a beam of ~4° and the field-emission microscopy (FEM) pattern of such a single-atom tip consists only of a single spot [5]. FEES measurements from such a spot then allow the determination of the TED of the electrons coming from one atom. In this Letter we describe FEES studies of both macroscopic and single-atom tips formed on a W⟨111⟩ single crystal.

FEES is derived from FEM in which the field-emitted electrons from the tip project enlarged images of the tip apex on a screen. A selected portion of the emission pattern passes through a probe hole in the screen to enter an electron energy analyzer, which is inserted behind the probe hole. For this study, the FE screen is at ~3 cm from the tip and the probe hole has a diameter of 0.8 nm. The energy analyzer is a hemispherical analyzer with a resolution of ~10 meV (VG-Clam 2), of which we have modified the entrance lenses for FEES. The tip is held on a mechanical movement that allows the choice of the analyzed region. The whole system is in a vacuum of about 5×10^{-11} Torr. Details on other parts of the installation are given in Ref. [5]. The tip used in this study is a W⟨111⟩ single crystal, sharpened and cleaned in the UHV chamber at ~3200 K. The protrusion was formed on the ⟨111⟩ axis of the macroscopic substrate tip by using the field-surface-melting mechanism with field and temperature. The cleanness of the tips was controlled by FEM. After formation of the protrusion, the FEM pattern was a single spot (diameter < 2 mm) along the ⟨111⟩ direction coming from the topmost atom. No other pattern outside of this spot was detected on the screen or by the analyzer channeltron over a large range of FE applied voltages ($V_{\rm app}$). This agrees with the field enhancement behavior for a protruding geometry [9].

The experimental procedure was as follows: (i) *in situ* fabrication of a clean macroscopic tip of less than 100 nm radius; (ii) FEES measurements of this tip centered on the (111) region; (iii) fabrication of a single-atom protrusion on top of this tip; (iv) FEES study from this protrusion; (v) destruction of this protrusion by a controlled heating of the tip, and FEES measurements of the resulting macroscopic tip at the (111) region. During this experimental sequence the vacuum was $\sim5\times10^{-11}$ Torr. All measurements were performed at room temperature.

The TED spectra recorded for macroscopic tips during steps (ii) and (v) had the same shape, were located at the same Fermi level (E_F), and showed the well-known behaviors for clean W⟨111⟩ tips [10]. Two example spectra, measured after the destruction of the protrusion, for different values of the applied voltage are presented in Fig. 1(a). Basically, one strong peak was observed with a sharp edge at E_F for any $V_{\rm app}$. An increase of $V_{\rm app}$ did not change the position of the Fermi edge, only causing a broadening of the peak on the low-energy side. We fitted the spectra with the classic equation for the tunneling current from a free-electron metal through a triangular barrier [11]. Excellent agreement between the experimental data and theory was found, as is shown in Fig. 1(a). The fits are represented by the solid curves over the experimental points. The value of E_F from the fits was taken as the reference level for all the spectra. The measured full width at half maximum (FWHM) for the spectra in Fig. 1(a) were 0.23 and 0.30 eV for 2050 and 2550 V, respectively, a variation which is a consequence of the increase of the slope of the tunnel barrier.

The TED spectra were recorded for different V_{app} after formation of a protrusion on top of the macroscopic tip. Characteristic examples of the observed spectra are shown in Figs. 1(b)-1(d). Four salient features, that are not present for macroscopic tips, can be discerned in the experimental observations.

(1) The spectra are composed solely of well-separated peaks. At the lowest V_{app} there are two peaks, labeled *a* and *b*. Peak *a* is near E_F and peak *b* ~1.1 eV lower in energy. The number of peaks depends on V_{app}. For example, another peak, labeled *c* in Fig. 1(d), becomes detectable at ~1200 V with energy ~0.26 eV above peak *b*.

(2) A linear shift of the whole spectrum is observed as a function of V_{app}. This is illustrated in Fig. 2 where we plot the positions of the peak maxima as a function of V_{app}. All the data fall on parallel lines with slope of 1.65 ± 0.02 meV/V, showing that the separation between the peaks remains constant. The total shift of the peaks for the range of V_{app} in this experiment was ~0.7 eV. Note that no shift was detectable for macroscopic tips and for similar changes of V_{app}.

(3) None of these peaks could be fitted satisfactorily by Eq. (1), as was possible for the macroscopic tip. For the same FWHM, the spectra from the macroscopic tip have wider tails on the low-energy sides and much sharper maxima than the peaks from the protrusion.

(4) The shapes of the peaks do not vary with V_{app}. The FWHM's remain ~0.24 eV for all values of V_{app} except where there is an obvious overlap of peaks, as for example, peaks *b* and *c* in Fig. 1(d).

The shifts and the intensity variations of the peaks were reversible; they could be varied reproducibly by changing V_{app}. For clean single-atom protrusion tips, stable FEM patterns and FEES spectra, with constant FE intensities, were observed over a period of many hours. The presence of adsorption from the background gases on top of the protrusion was easily characterized by large instabilities of the emission current and strong modifications of the TED's. The adsorption could be removed by application of field and temperature after which the emission properties were again stable. The

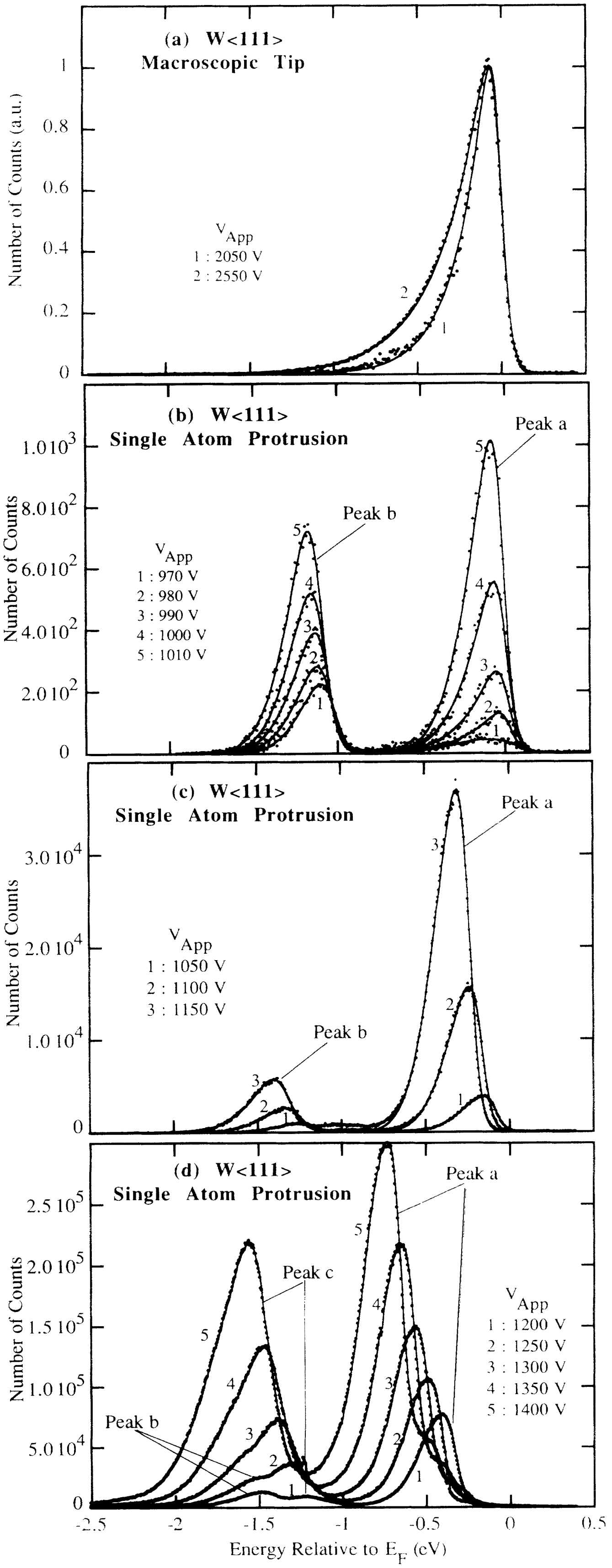

FIG. 1. (a) Experimental TED spectra measured at room temperature from a macroscopic tip. (b)-(d) Experimental TED spectra measured from a protrusion ending in a single atom for various values of applied voltage (V_{app}).

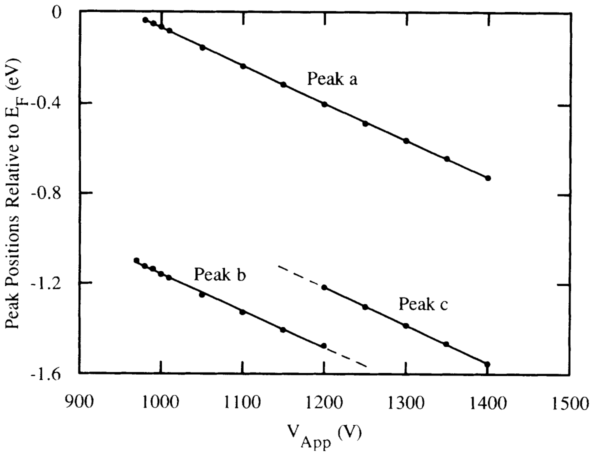

FIG. 2. Position of the peaks of Figs. 1(b)-1(d) vs $V_{\rm app}$. The slope of the straight lines is 1.65 ± 0.2 meV/V.

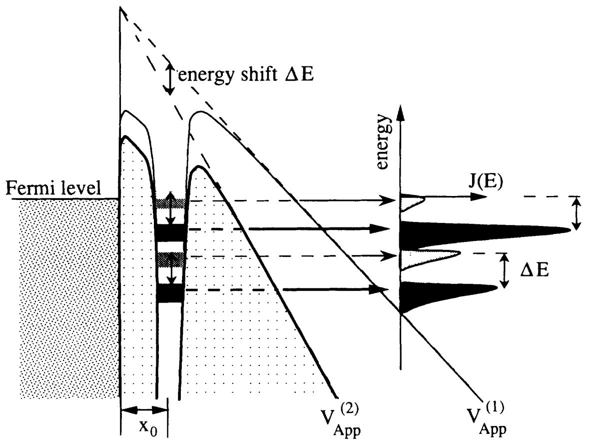

FIG. 3. Simplified model of field emission from single-atom tips for two values of $V_{\rm app}$. The lightly shaded bands signify the positions of two bands for $V^{(1)}_{\rm app}$ and the two darkly shaded bands are the same bands after they were shifted by increasing the applied voltage to $V^{(2)}_{\rm app}$.

FEES spectra could be the same as before the cleaning or show changes in the positions and relative intensities for the same $V_{\rm app}$, probably reflecting a slightly different structure in the geometry of the protrusion.

The fact that the single-atom TED spectra could not be fitted with the free-electron-metal theory means that the electrons do not tunnel directly from the Fermi sea to the vacuum. The well-separated peaks in the TED spectra suggest the presence of a localized band structure at the tip apex. This could have its physical origin in the W apex atom itself which has a reduced coordination number. The peaks in the TED spectra are then explained by FE resonant tunneling only through these bands. To take into account the band structure, we multiplied the equation for free-electron metal by a Lorentzian distribution. We then found very good agreement between the experimental TED spectra and the fits. This is illustrated in Figs. 1(b) and 1(c) where the fits are shown as the solid curves over the experimental points. The spectra in Fig. 1(d) are not fitted because of the overlap of several peaks. This result supports the hypothesis of a local band structure on the topmost atom of the protrusion which in turn explains the peaks in the TED spectra and the constant band gap observed experimentally.

Resonant tunneling through atomic energy levels of adsorbed atoms, which have been broadened due to interaction with the underneath surface, was first introduced by Gadzuk [12]. This was used to explain the small bumps added to the energy distributions of the clean macroscopic tips observed in earlier FEES experiments [13] with chemisorbed atoms on metallic surfaces. It must be emphasized that the presence of chemisorbed atoms in these experiments only slightly modified the standard peak of a clean macroscopic tip, in contrast to the spectra from the protrusions which consist solely of well-separated peaks.

The shifts of the peaks also run counter to a metallic behavior of the topmost atom. The linearity of the shifts versus $V_{\rm app}$ (Fig. 2) means linear shifts versus applied field F at the cathode surface because $F=\beta V_{\rm app}$. β is a geometrical factor that depends on the tip shape [9]. We propose to explain this shift and its linearity versus the applied voltage by a charge confinement in the region of the topmost atom, which implies a field penetration into the tip.

To illustrate the above hypothesis, a model for tunneling from the single-atom protrusion tip is presented in Fig. 3, which shows the one-dimensional potential energy diagram in the presence of an applied field. The band structure, the field penetration, the band shifting, and the TED for field emission are all depicted. Many of these features are similar to a semiconductor, except they pertain only to the topmost atom of the protrusion.

Two further points deserve comment. The first one, illustrated by peak a in Fig. 1(b), was the evolution of the peak when the related band crossed the Fermi level for increasing $V_{\rm app}$. The intensity variation versus $V_{\rm app}$ did not follow the expected behavior for a triangular barrier, as can be noticed by following the intensity ratio between peaks a and b in Fig. 1(a). We impute this difference to the variation of the density of filled states inside the band related to peak a when it crossed the Fermi level. This phenomenon can then be used as a probe of the density of states in the band. The second one is the strong increase of peak c for high applied fields, as seen in Fig. 1(d). This could be due to a modification of the density distribution inside the band, which implies that the fine band structure is field dependent. This needs further investigation.

In conclusion, the enhancement of the applied field over the topmost atom of a nanoprotrusion allows FEES of a single atom. The main experimental results showed TED spectra with multiple peaks separated by gaps and undergoing a linear shift with the applied FE voltages.

We interpreted the presence of these peaks as due to localized bands at the topmost atom of the protrusion. Moreover, a field penetration into the region of the apex was revealed by the linear shift in energy as a function of the applied field, implying a charge confinement at the top of the tip.

These properties are important for the use of the self-collimated *e* beam produced by such a protrusion. Also, they have to be taken into account for quantitative interpretations of scanning tunneling spectroscopy at the atomic level. The hypothesis that the electronic structure of the scanning tip is the same as a macroscopic tip is no longer valid in general. Much experimental and theoretical work needs to be done to understand the band structure revealed here and its relation to the atomic levels of the apex atom. Moreover, this study shows that single-atom properties can be measured by using nanoprotrusions.

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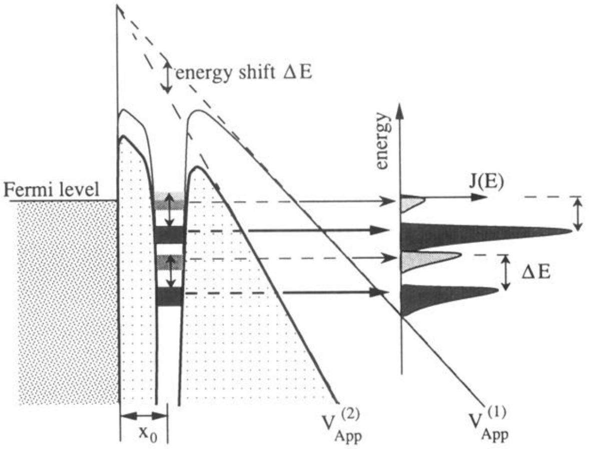

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