New Evidence for Localized Electronic States on Atomically Sharp Field Emitters

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We have studied field emission from atomically sharp tungsten-carbide-coated W⟨111⟩ tips, and from atomically sharp HfC⟨100⟩ and ZrC⟨100⟩ tips. We observed multiple-peaked total energy distributions from the apex atoms. These narrow and intense peaks have strong angular anisotropy, and their relative magnitudes depend on the extraction field. They suggest the presence of localized states on the atom at the apex of the tip. [S0031-9007(96)00929-5]

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In a 1992 Letter, Binh *et al.* [1] reported that the total energy distribution (TED) of field-emitted electrons from single-atom tungsten ⟨111⟩ tips consist solely of well-separated peaks. This first observation of multiple-peaked TED's implies the presence of localized electronic levels for the atom at the apex of a solid-state tip. They proposed that electron tunneling through these localized levels gives the multiple peaks in the TED's. This is distinctly different from the broad features commonly observed in TED's from resonant tunneling through broadened atomic energy levels of adsorbed atoms. These observations can change our understanding of the electronic states of tips in scanning tunneling microscopy and field-emission electron sources. Their results were, however, controversial. Three other groups attempted to reproduce the experiment but obtained negative results [2]. In this Letter, we report new evidence of multiple-peaked TED's from metal-carbide field emitters, confirming the presence of localized states at tip apexes under certain circumstances.

We have studied the TED's of field-emitted electrons from tungsten-carbide-coated W⟨111⟩ tips, and single-crystal Zr⟨100⟩ and HfC⟨100⟩ tips. All these carbides are metallic with very high melting points [3]. These carbide tips have much improved emission stability over conventional tungsten tips [4]. Our goal is to develop advanced electron emitters for electron-beam microcolumns [5]. The tungsten-carbide-coated W⟨111⟩ tips were formed by heating sharpened W⟨111⟩ tips in 4×10^{-6} Torr of acetylene at 1100 K for 5 min to form a thin tungsten carbide layer [4]. Sharp ZrC⟨100⟩ and HfC⟨100⟩ emitters were prepared first by the electrochemical etching of single crystal ZrC and HfC rods. The tips were cleaned by 2000 K thermal annealing and field evaporation in our VG FIM-100 ultrahigh vacuum (UHV) analysis chamber. They were then heated in 4×10^{-6} Torr of acetylene at 1100 K to replenish carbon lost in thermal annealing [4]. To obtain single-atom tips, we used the buildup process [6], following Binh *et al.* [1,7]. A strong electric field is applied at elevated temperature to the apex of a field emission tip. It generates a driving force $\nabla(F^2/8\pi)$, where F is the electric field, to move the tip atoms toward the local field maximum. The elevated temperature promotes atomic mobility. A nanostructure is formed at the tip apex that can end with a single atom. Since the driving force is independent of the direction of the electric field, we produced built-up tips with both positive and negative bias. Our typical procedure was to apply several kV positive bias at the tip at 1500 K for a few seconds, or apply a negative bias on the tip to give a large emission current (a few μA) at room temperature until buildup occurred. We preferred the second technique since we could watch the buildup process by field-emission microscopy (FEM). The field emission at the buildup site would increase suddenly, giving intense emission within a semicone angle of a few degrees. The crystalline direction of the buildup varied from one experiment to the other. Occasionally, more than one buildup site can occur on the same tip. We were not successful in preparing built-up tips on clean carbide tips without the acetylene treatment.

Tips prepared were examined *in situ* by field-emission and field-ion (FIM) microscopies in our VG FIM-100 system. FIM analysis of built-up sites showed a bright, round atomic image. It suggests a single atom at the apex. This was consistently observed on our built-up tips. Unfortunately, we were unable to control the field evaporation well enough to systematically analyze the structure of built-up nanostructures on carbide tips as we could with W⟨111⟩ tips [8]. We measured the energy distributions in a FEM chamber with a hemispherical energy analyzer. Tips were prepared *in situ* using the recipes developed above for single-atom apexes and examined by FEM. To measure the TED, the FEM image of the single atom tip was displayed on a phosphor screen which has a probe hole at the center. A VSW HR-50 hemispherical energy analyzer was placed directly behind the probe hole. Guided by the FEM image, the tip position was adjusted so that about 1 msr of the center portion of the electron emission from the single

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atom site was let through the probe hole into the energy analyzer. The analyzer had been modified to give an estimated energy resolution of about 55 meV. In our experiment, we biased the tips at -1 kV with respect to the ground of the spectrometer. An extractor electrode was placed within 1 mm of the tip. The extraction voltage is the voltage difference between the tip and the extractor. With this arrangement, no change in the tip voltage and spectrometer settings was necessary when we studied the shift of the TED's with the extraction field. All energy distribution measurements were performed with the tip holder at room temperature.

We did not observe multiple-peaked TED's from built-up W⟨111⟩ tips in accord with the results of Ernst *et al.* [2]. However, we observed them in all three kinds of built-up metal-carbide field emitters. Figure 1 depicts the various TED's obtained from tungsten-carbide-coated W⟨111⟩ tips. In this Letter, we have normalized and offset the TEDs along the *y*-axis for clarity. Curve 1a is the TED before the buildup process. It has a single peak with full width at half maximum (FWHM) of about 0.23 eV. We approximate the Fermi level E_F by the midpoint of the high-energy edge. Multiple-peaked TED's can have different amounts of emission at E_F. Curve 1b shows a TED with a peak at -0.25 eV, but with substantial emission at E_F. Curve 1c shows a TED with peaks at -0.6 and -1.2 eV with a small amount of emission at E_F. Curve 1d shows a TED with peaks at -0.8 and -1.8 eV, but with negligibly small emission at E_F. Curve 1d is qualitatively similar to the multiple-peaked TED's reported by Binh *et al.* [1]. The FWHM of the peaks was usually below 0.5 eV. At this moment, we do not have sufficient control to form the various types of built-up sites reproducibly.

While the built-up tip results from the application of a strong electric field, a large field can also change the structure of the built-up tip. Relative peak heights and peak positions can change. Figure 2 shows an interesting example from a ZrC⟨100⟩ tip. Curve 2a shows the TED from a ZrC⟨100⟩ tip before buildup. The FWHM is about 0.22 eV. Curve 2b shows a TED after buildup. There is a strong peak at -0.5 eV with substantial emission at E_F. Then the extraction voltage was increased and the emission became unstable. The extraction voltage was lowered immediately and raised slowly to return to stable emission. The FEM image was not changed. However, curve 2c taken after the instability shows that the emission at E_F is noticeably reduced, but the -0.5 eV peak is not appreciably affected. The observation suggests that the emission peak at E_F and the peak below E_F may have different origins.

The peaks below E_F shift to lower energy with increasing extraction field. Figure 3 depicts a set of TED's from a HfC⟨100⟩ tip taken at different extraction voltages. Curve 3a shows a TED of electrons emitted from a HfC⟨100⟩ tip before buildup. It has a FWHM of about 0.32 eV. Curves 3b to 3f show the TED's from a built-up tip with extraction voltage varying from 1 to 1.2 kV in 50 V steps. There is a small shift of the peak positions toward the low-energy side at a rate of approximately -0.5 mV/V. This phenomenon is commonly observed in field emission when field penetration causes the adsorbate level to shift with the extraction voltage [9]. This rate is smaller than the -1.65 mV/V reported by

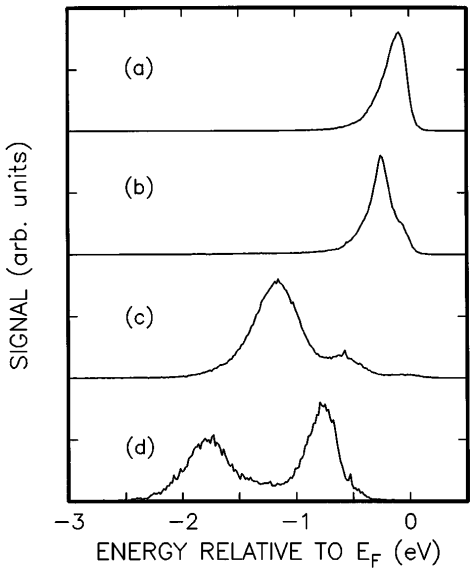

FIG. 1. Total energy distribution of field-emitted electrons from tungsten-carbide-coated W⟨111⟩ tips (a) before buildup, and (b)–(d) after different cases of buildup. The extraction voltages were -1.7, -1.7, -1.0, and -0.95 kV, respectively.

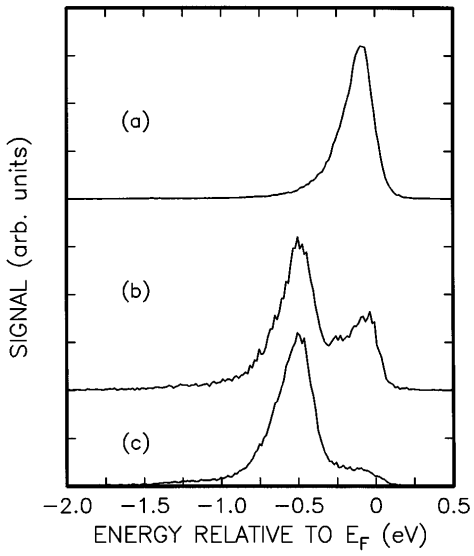

FIG. 2. Total energy distribution of field-emitted electrons from ZrC⟨100⟩ emitters (a) before buildup, (b) after buildup but before instability, and (c) after field-induced instability. The extraction voltages were -1.2, -1.3, and -1.35 kV, respectively.

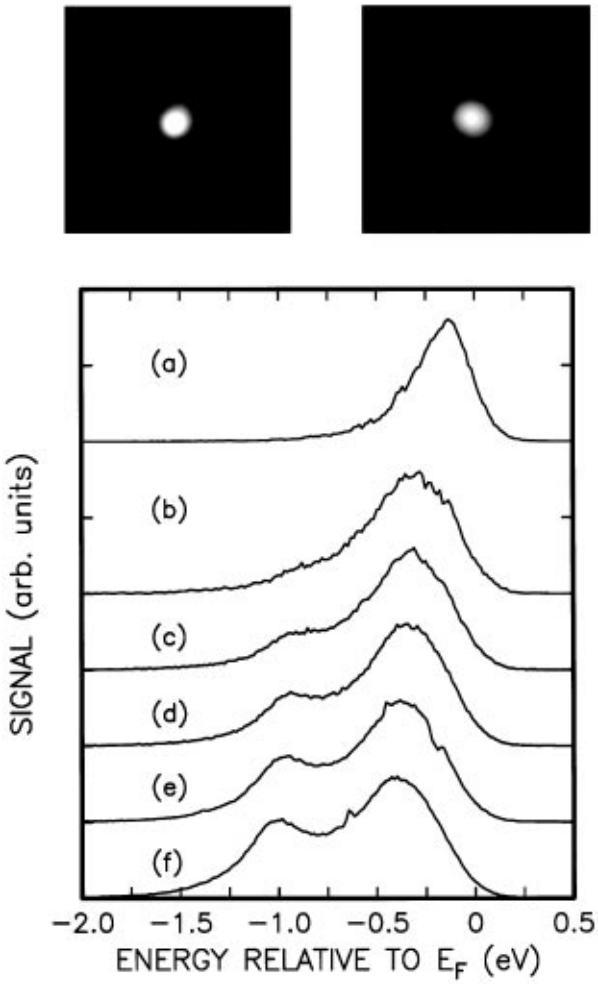

FIG. 3. Total energy distribution of field-emitted electrons from HfC⟨100⟩ emitters (a) before buildup, and (b)–(f) after buildup with extraction voltages of −1.0, −1.05, −1.1, −1.15, and −1.2 kV, respectively. The top left inset shows an FIM image of a built-up HfC⟨100⟩ tip taken with Ne at 12.8 kV. The top right inset shows the corresponding FEM image. The magnification of the FEM image is 0.38 times that of the FIM image.

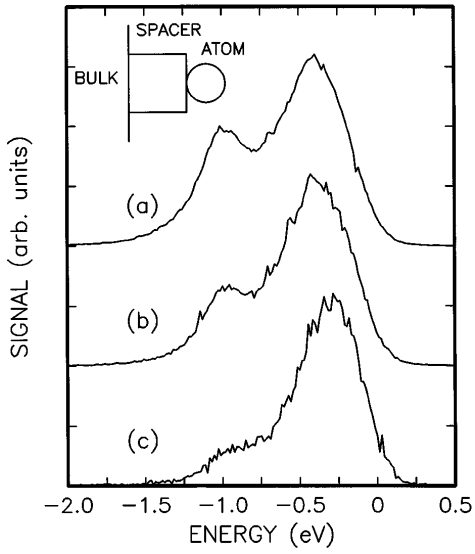

FIG. 4. Total energy distribution of field-emitted electrons from a built-up HfC⟨100⟩ emitter (a) along the axis, (b) 2° away from axis, and (c) 4° away from axis. Inset is a schematic diagram of the built-up tip. The extraction voltage was at −1.2 kV.

Binh *et al.* [1], and it is at the limit of our resolution. Higher extraction fields enhance the ratio of the low energy (−1.0 eV) peak to the high energy (−0.35 eV) peak. This is consistent with the Fowler-Nordheim theory where the width of the tunnel barrier decreases with increasing field [10]. The effect is that the tunneling probability increases more rapidly for states deeper in energy. Results from built-up ZrC⟨100⟩ tips were qualitatively similar.

Electron emission from the built-up site is highly anisotropic. The emission intensity is confined to a small cone with about 2° semi-cone angle. The TED also varies rapidly with angle. Figure 4 curve (a) shows the TED of a built-up HfC⟨100⟩ tip measured at the maximum of the angular emission. Curves 4b and 4c depict the TED's taken at 2° and 4° off of the maximum. The −0.35 eV peak signal falls from 10 608 counts to 3039 counts to 465 counts correspondingly, showing the strong forward peaking of the emission. In addition, the data clearly show a rapid decrease in the relative intensity of the −1 eV peak relative to the −0.35 eV peak. Again, according to the Fowler-Nordheim theory, these changes are consistent with a rapid decrease of the electric field away from the emission axis. A decrease in the electric field increases the width of the triangular tunneling barrier. It reduces the tunneling probability overall, and reduces it faster for electrons with lower energies. In field emission, such rapid field variation with angle occurs when there is a bump or protrusion on the tip surface [10,11]. It is known that the buildup process causes the growth of nanoprotrusions with the apex atom at the tip end [7]. The structure consists of the apex atom, a part that might be called the protrusion spacer, and the bulk as shown schematically in the inset of Fig. 4. We do not have a direct experimental determination of the structure and chemical composition of the protrusion. Therefore, we shall use available experimental data to guide our understanding.

The atom at the tip apex behaves like an adsorbed atom. The shifting of the peaks below E_F with extraction field, as shown in Fig. 3, is similar to those expected for peaks from adsorbates [9]. Therefore, in agreement with Binh *et al.* [1], we believe that the narrow peaks observed were associated with the apex atoms. Since the narrow TED peaks are close to the Fermi level, it is most likely that the apex atoms are metal atoms. Electron tunneling through the resonant level of an adsorbate gives

rise to enhancement of field emission at the energy of the broadened adsorbate level. The enhancement factor is usually less than three for adsorbates on surfaces [12]. By contrast, we have observed enhancement factors as large as 200 for the peaks below E_F. According to the model calculation of Duke and Fauchier [13], narrow peaks with enhancement factors of the order of 10^3 in the TED can result if the atom is placed over 3 Å from the surface where the interaction between the atom and the tip is weak. For a typical electric field of 0.2 V/Å, a peak shift rate of -0.5 mV/V observed at -1 kV extraction voltage would imply that the atom is at least about 2.5 Å from the surface, which is consistent with the results of Duke and Fauchier. This is a lower limit since we assume complete field penetration to the surface of the bulk of the tip.

We conclude from the above argument that the apex atom is only weakly interacting with the bulk of the tip. It is likely that it is the protrusion spacer that weakly couples the apex atom to the bulk. As mentioned above, we notice that carburization of the tip surface is essential to obtain our built-up tips. We consider the case that the spacer is a single carbon atom or an aggregate of carbon atoms. Carbon has low-lying valence states. For example, photoemission studies [14] have shown that the density of states of carbon adsorbed on W(110) peaks at -3.7 eV. This spacer would thus have a low density of states in the energy range of the localized levels of the tip atom so that it would effectively minimize the overlap of the valence electrons of the apex atom with the states in the bulk substrate. This would be consistent with the enhanced magnitude and narrowness of the field emission peaks. The electrons in the spacer at and near E_F can tunnel through the apex atom to give the emission peak at the Fermi level, while the localized level of the apex atom is the origin of the peak below E_F. This interpretation is consistent with our experimental observation shown in Fig. 2 that the emission peak at E_F and the peak below E_F have different origins.

In conclusion, we have presented strong evidence of localized electronic states for atoms at the apexes of certain atomically sharp tips. They are revealed by the multiple-peaked TED's, as a form of single-atom spectroscopy, from our built-up field-emitter tips. Their properties suggest that the apex atom is only weakly coupled to the bulk metal by a spacer which has low density of states around the Fermi level. The phenomenon was seen on tungsten-carbide-coated W⟨111⟩, and HfC⟨100⟩ and ZrC⟨100⟩ field emitters.

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