Abstract
We present new results in the measured electron energy spectrum from diamond field emitters. The energy spectrum from a clean diamond surface has been measured and is comparable in shape and width to that of metal emitters. The results suggest that the emitted spectrum is sensitive to the presence of adsorbed species on the emitter surface. Electrons significantly below the cathode’s Fermi level are emitted by resonant tunneling. Furthermore, these resonant surface states can increase the total emitted current by more than an order of magnitude while maintaining a narrow spectral width (~0.5 eV). Experiments are also being performed with individual multiwall carbon nanotubes (MWCNTs). We have observed beams emitted from individual residual gas molecules that approach the quantum-degenerate limit of electron-beam brightness. This limit has profound consequences for the behavior of an electron. Tightly bound designer adsorbates may greatly enhance the emission properties and improve performance in electron injector systems.

BACKGROUND
The development of high-brightness electron sources is of significant importance to fields such as electron microscopy [1, 2], point-projection microscopy [3], Gabor holography [4, 5], and beam-driven radiation sources [6]. Brightness is a fundamental property of the electron beam and is determined by the nature of the emission source [7–9]. Quantum degeneracy in the electron ensemble limits the maximum phase-space density, or six-dimensional brightness, to a single spin pair per $h^3$ [10]. For most electron sources the degeneracy is too low to be of any practical consequence. However, the generation of electron beams with high degeneracy may be possible with certain types of field-emission cathodes. Recently, chemical-vapor deposited (CVD) diamond field-emitter arrays (DFEAs) have demonstrated promise as high-brightness electron sources [11]. DFEAs are produced using an inverse-mold transfer technique [12, 13]. These emitters consist of a combination of $s^2u^2$ and $s^4u^3$ carbon, and various levels of boron and nitrogen doping. In this report we present measurements of the electron energy spectra from these diamond emitters. These data provide insight into the fundamental physics which governs field emission from DFEAs, and suggest a path to the development of a quantum-degenerate electron beam source.
mesh is swept at a maximum rate of ~4 V/s. The instrumental broadening of the energy-analyzer system was determined using a LaB₆ thermionic cathode. The resolution function, which has a full-width half-maximum of 0.15 eV, was deconvolved from the measured energy spectrum using the well-known theoretical distribution for thermionic emission [15].

Measurements of field emitted beams from individual MWCNTs were performed in a UHV field-emission microscope. Figure 2 shows a schematic representation of the system.

![Figure 2: Schematic representation of the FEM used to examine MWCNTs.](image)

**RESULTS**

When the entire beam is allowed to pass the retarding mesh, the measured collector current exhibits stepwise fluctuations between discrete emission levels as seen in Fig. 3. These changes in current are coincident with spatial intensity fluctuations in the phosphor-screen image. A variety of field emitters including carbon nanotubes (CNTs) and Spindt-type molybdenum cathodes are known to exhibit this same type of emission behavior, and field-emission microscopy has shown that such fluctuations arise from the adsorption, desorption, and diffusion of atoms and molecules on the emitter surface [16–21]. While little is known about the specific emission processes of these diamond tips, in the present experiments the explanation of molecular adsorption and diffusion seems to best fit our data, and we analyze them in this context.

All electron-energy spectra presented in this letter were taken during periods of stable emission. For a retarding-mesh energy analyzer, the Fermi energy of the measured spectrum is shifted by the work function of the retarding-mesh material. Therefore the abscissa on each spectral plot has been shifted by the work function of nickel, ~ 5.15 eV, so the Fermi level is located at zero. Figure 4 provides examples of energy spectra that were taken under identical experimental conditions. Each distinct spectrum corresponds to a period of stability in the total current, similar to those seen in Fig. 3. Transitions between various stable spectra are concurrent with the aforementioned current fluctuations.

![Figure 3: The emission current from an individual CVD diamond field emitter fluctuates between discrete, stable levels. Periods of stability can range from fractions of a second to many minutes depending on the ambient pressure.](image)

A simple reduction of the work function by an adsorbate would result in more intense emission, however this emission would still be peaked at the Fermi energy. We have observed spectral features at energies several volts below, and in some cases at fractions of a volt above, the Fermi energy. This modification of the emitted electron-energy spectrum is interpreted as the result of resonant tunneling through adsorbed species. Modification of the potential barrier by an adsorbate can result in resonant surface states with significantly increased tunneling probabilities at the allowed energy levels of those states [22, 23]. This effect has been observed in a variety of field-emission systems including single atom tungsten emitters [24], gold nanoclusters on tungsten needles [25], single-crystal P-doped diamond [26], and adsorbed contaminants on CNTs [20, 27]. For given experimental conditions, we expect that emission from a clean surface should occur at a low intensity near

![Figure 4: For identical experimental conditions, the emitted energy spectrum fluctuates between a variety of stable configurations. These fluctuations are coincident with those of the emitted current. On occasion, dramatic results were recorded during individual adsorbate events.](image)
Figure 5: This spectrum is believed to have originated from the clean surface of the CVD-diamond emitter. It is located near the estimated Fermi energy and has a spectral width of ~0.3 eV.

Figure 6: In some cases, single adsorbate events increased the emission current by more than an order of magnitude without affecting the spectral width or shape.

The Fermi energy. Approximately 5-10 percent of the recorded spectra resemble the suspected clean distribution pictured in Fig. 5. The FWHM of this distribution is ~0.3 eV, comparable to that of metallic field emitters and similar to what has been measured for various diamond field emitters [28–31]. Figure 6 shows the measured emission spectrum before and after the arrival of a single adsorbate. The emitted current increased by more than an order of magnitude while the spectral width and shape remained unchanged. Some fraction of the ~2-eV shifts of the spectrum to lower energy is due to an ohmic drop across the emitter nanotip. However, we estimate that this ohmic shift is only on the order of ~0.1 eV.

For periods of highly stable emission, we are able to explore the effect of the applied electric field on the emitted spectrum. Preliminary data suggest a ~2 meV/V linear shift of the central energy of the spectrum to lower energies with increasing electric field. Such shifts have been observed in other field-emission systems with atomic-scale features and semiconductor surfaces, including diamond [24, 29, 32, 33], and can typically be interpreted as the result of field penetration. We observe changes in the number, shape, and position of the spectral peaks as the applied field is changed by small amounts, as seen in Fig. 7. The observed spectral changes were completely reversible by returning the field to previous levels. At this point it is not clear if this effect arises due to the resonant surface states of adsorbed species or from some inherent material property of the diamond nanotip.

CONCLUSIONS

In conclusion, we have performed spectral analysis of the electron beams emitted from individual CVD diamond field emitters. Step-wise fluctuations in the emitted current are matched by transitions between stable, distinct emission spectra. Observed properties of these spectra include strong features several volts below the estimated Fermi level of the cathode, order-of-magnitude increases in the emission current without spectral broadening, and sensitivity of the spectrum shape to the applied electric field. These data suggest that resonant tunneling through adsorbed atoms and molecules is an important, and for some conditions dominant, effect in field emission from CVD-diamond emitters. Because the emission enhancement by an adsorbate is extremely spatially localized, and the energy spread is narrow, field-emitted beams of several microamps may approach the quantum-degenerate limit of electron-beam brightness. Such beams have already been observed for short times (~1 sec) from residual gases on CNTs [34]. Figure 8 shows an FEM micrograph and current vs. time data for a 6 μA beam from a single adsorbate. The beam from the adsorbate is clearly visible as a bright spot against the dim background of the nanotube emission. Emission directly from the clean surface of the nanotube appears as pentagonal rings on the phosphor screen. By calculating the transverse momentum spread for this beamlet and assuming an energy spread of ~0.3 eV, we estimate that this beam is nearly quantum degenerate. More tightly bound adsorbates such as various metal atoms should stabilize the effect and provide a reliable quantum-degenerate...
electron beam source. Such a source would represent the ultimate limit of achievable brightness.

Figure 8: FEM micrograph and I vs. time trace of a nearly quantum degenerate beam from a single adsorbate.

REFERENCES


FEL Technology I : Accelerator