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Cutting of multiwalled carbon nanotubes by a negative voltage tip of an atomic force microscope: A possible mechanism

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Multiwalled carbon nanotubes (MWNT's) on Si(5 5 12) surfaces are demonstrated to be cut only by a negatively biased conducting tip of an atomic force microscope (AFM). By scanning with the AFM tip across a 30-nm-diam MWNT in contact mode, we could cut the MWNT only at a negative tip voltage below a threshold. As the tip-moving speed increased, the magnitude of the threshold voltage was increased. A graphite surface was etched in comparison by the same method. It was also etched only at a negative tip voltage below a threshold. As the magnitude of the bias voltage increased, the etch depth of the graphite surface increased exponentially to reach 7.9 nm, a thickness of 23 atomic layers of graphite, at a bias voltage of -10 V. The etching current from the graphite surface to the negatively biased tip was found to follow the Fowler-Nordheim equation and attributed to field-emission electrons from the negatively biased tip. The etch depth of the graphite surface was also found to follow the bias voltage dependence of the Fowler-Nordheim equation. The graphite etching is thus found to be controlled by the field-emission current so that we may propose a cutting mechanism based on the field-emission current density of the Fowler-Nordheim equation: both the MWNT cutting and graphite etching encounter the same reaction where the activation energy is supplied by electrons that are field emitted from the negatively biased AFM tip.

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Carbon nanotubes have attracted intensive attention due to their remarkable electronic and mechanical properties since their discovery in 1991.[1] Nanotubes could be bent, straightened, moved, rolled, and slid by the tip of an atomic force microscope (AFM).[2,3] Single-walled carbon nanotubes (SWNT's) could be worked by an AFM tip to make circuits of nanotubes,[4] to show single-electron charging,[5] and to fabricate a room-temperature single-electron transistor.[6] Also SWNT's were reported to be cut by the biased tip of a scanning tunneling microscope (STM) on a gold surface in ultrahigh vacuum.[7] The two small areas of the multiwalled carbon nanotube (MWNT) connected to electrodes were etched in oxygen plasma to form an island of MWNT's and the Coulomb blockade effect was observed at 4.5 K.[8] Carbon nanotubes were also incorporated between two layers of *e*-beam resist to be used as a shadow mask, blocking metal deposition at one point along a thin wire.[9] If a MWNT of a given diameter can be cut in precise length by an AFM tip at a specific position of quantum dots or nanowires, it can function as a conducting component of nanodevices such as a single-electron transistor and a resonant tunneling diode.

In this experimental work, we want to report our quantitative results in which MWNT's on Si(5 5 12) surfaces were cut by only a negatively biased conducting tip of an AFM in contrast to a previous report[7] where a positively biased tip was also cutting the nanotubes in ultrahigh vacuum. Recently Park *et al.*[10] reported that nanotubes of 3 nm diameter could be cut by applying only a negative voltage, larger than a threshold, in a pulse mode to a metal-coated AFM tip in air. However, no discussion was made of the microscopic mechanism of cutting. The graphite surface was taken as a reference of etching chemistry for carbon surfaces. The current through a tip and the graphite surface was measured *in situ* to verify the microscopic mechanism of etching.

MWNT's were grown on an *n*-type Si wafer by thermal chemical vapor deposition, and the average diameter and length were around 30 nm and 3 μm, respectively.[11] The MWNT's were collected by a razor blade and sonicated in dichloroethane for 8 h and spin coated on the Si(5 5 12) surfaces. The AFM (Digital Instruments Dimension 3100) was operated at a relative humidity of 40%–70% in air. A MWNT was cut by a W_2C-coated conducting AFM tip moving across the MWNT on the silicon substrate at a fixed angle, at a constant speed, and under a constant contact force in the contact mode.

Figure 1 shows the contact-mode AFM images of the MWNT's cut by the AFM tip at various bias voltages. When the conducting AFM tip was moved across MWNT's in contact mode, the MWNT's could be cut only at negative bias voltages larger than a threshold. The threshold voltage was varying in the range of -6 to -8 V, depending on the scanning speed of the AFM tip. The threshold voltage of -6 V was observed at a moving speed of 0.1 μm/s but at a higher speed of 1 μm/s the threshold voltage was increased to -7 to -8 V. Since the MWNT diameter is around 30 nm, the interaction time between the tip and MWNT is estimated to be about 30 ms at a tip speed of 1 μm/s and about 300 ms at 0.1 μm/s, respectively. In a recent work of Park *et al.*[10] the operating pulse width was between 10 and 100 ms, conforming with our estimations.

For a shorter interaction time, a larger bias voltage is required to cut the MWNT's. The threshold voltage is thus determined by the total energy supplied. The bright lines

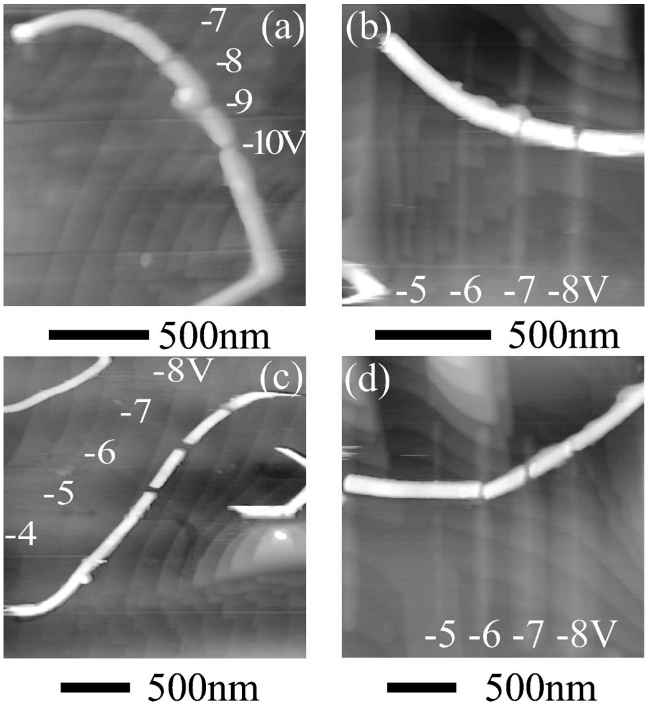

FIG. 1. Contact-mode AFM images of the MWNT's on a Si(5 5 12) substrate cut by a negatively biased AFM tip. The tip scanning was made at the speed of 1 μm/s (a), (b) and at the speed of 0.1 μm/s (c), (d). A close examination shows white lines inside the cutting grooves [most clearly in (d)] which represent the SiO_2 lines anodized by the negatively biased tip. The numbers representing the negative bias voltages also place each respective starting spot at different scanning cycles.

formed on the Si(5 5 12) surface after the scan cycles of the negatively biased tip represent the SiO_2 lines resulting from anodization of the Si surface.[12,13] The width and depth of the SiO_2 lines increase in linear proportion to the bias voltage applied to the tip, and these oxide lines indicate where the tip was scanning and how large bias voltages were applied to the tip.

In a previous report of Venema *et al.*,[7] a positively biased tip was also cutting single-walled carbon nanotubes in ultrahigh vacuum, where a high-voltage threshold was required to break the carbon-carbon bonds in nanotubes. But in our present work, nanotubes are cut only at a negative tip voltage larger than a threshold which depends on the interaction time. Therefore, the MWNT cutting in air may not have the same mechanism that the high-energy electrons break up directly the carbon-carbon bonds in the nanotube. A graphite surface, similar to MWNT's in the bonding structure, was tested for etching characteristics by the same method to verify the microscopic mechanism for the cutting of MWNT's.

A linear scan by a biased conducting AFM tip was made on a cleaved highly oriented pyrolytic graphite (HOPG) surface at a constant speed and under a constant contact force in contact mode to compare the respective etching data with the MWNT's. A graphite surface was etched in previous works by a STM tip in both positive and negative bias voltages applied between the STM tip and the graphite substrate in air, where the measured threshold voltage was in the range of 3–4 V.[14] Since the presence of residual water molecules was found to be a necessary condition for the etching process,[15] the graphite surface etching was attributed to an electron-transfer-enhanced chemical reaction where carbon atoms reacting with residual water molecules are removed from the graphite surface to produce H_2, CO, CO_2, or CH molecules.[16] Figure 2 shows a tapping-mode AFM image and average cross-sectional profiles over the parallel etch lines of the cleaved HOPG surface after scanning by the biased AFM tip at six different bias voltages in contact mode. Only negative bias voltages larger than a specific threshold could leave etch lines on the graphite surface. As can be seen from Fig. 2(b) the etch line depth was found to increase exponentially with increasing magnitude of bias voltage. The etch depth did not reach even 4 graphite atomic layers at bias voltages less than -8 V, but exceeded 20 graphite layers at a larger bias voltage of -10 V. The etching threshold voltage was increased with increasing scan speed.

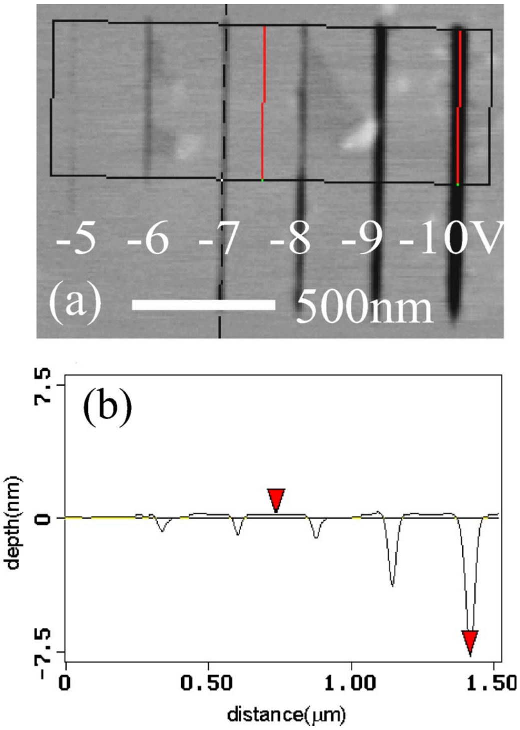

FIG. 2. (a) Tapping-mode AFM image from a cleaved HOPG surface and (b) average cross-sectional profile over the length of each respective etch line inside a rectangular frame depicted in (a). Each etch line was made by a negative voltage tip, on the graphite surface, scanning at a speed of 0.5 μm/s and at a contact force of around 550 nN.

Our experiments of cutting the MWNT's and etching the graphite surface give several interesting results of new concern in common: Only the negatively biased tip can produce cutting and etching in MWNT's and graphite surface layers. As the scanning speed increases and thus the interaction time decreases, the threshold voltage is increased. The threshold voltages are not within the tunneling regime but in the regime of field emission.[17] And the etching depth of the graph-

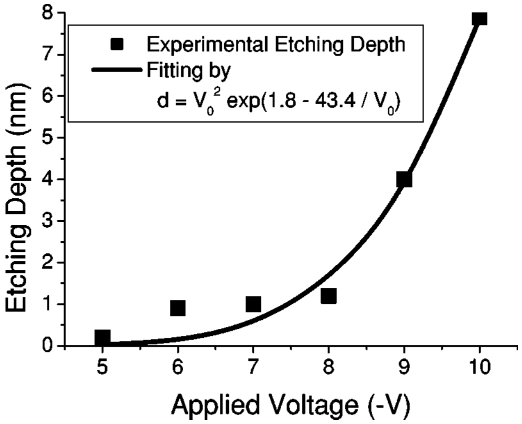

FIG. 3. A best-fit curve to the experimental data of etching depth vs tip voltage.

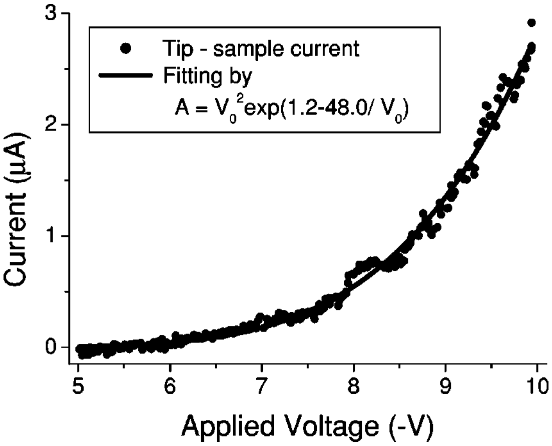

FIG. 4. Experimental data of tip current vs tip voltage and a best-fit curve.

ite surface increases exponentially with the magnitude of the bias voltage, exceeding 20 graphite layers at -10 V. The graphite etching and nanotube cutting are thus encountering the same interaction which occurs only at a negatively biased tip. The threshold voltage depends on the interaction time; that is, the complete interaction needs a threshold total energy to cut the MWNT. The interaction is thus controlled by a voltage-dependent energy factor. This energy function of the etching interaction is then expected to have an exponential dependence on bias voltage. The MWNT cutting may be thus assumed to encounter the same chemical reaction as the graphite etching.

We can assume that the energy for the chemical etching process may be supplied by the field-emission electrons from the AFM tip, where the current density J of field emission is given by the Fowler-Nordheim equation[18] $J = aE^2\exp(-b/E)$ with E representing the electric field. The exponential increase of the field-emission current density J with increasing electric field E would then bring about a corresponding increase of etching depth in the graphite surface.

In Fig. 3 we made use of this formula to best fit the experimental data of etching depth (d) versus applied voltage (V_0) obtained from Fig. 2. The best-fit curve of the etching depth $d(V_0)$ can be represented by a formula $d = a' V_0^2 \exp(-b'/V_0)$, where V_0 is the magnitude of the applied voltage, and a' and b' are the best-fit parameters. Assuming the electric field E is proportional to the applied voltage V_0, the etching depth $d(V_0)$ can be seen to follow the Fowler-Nordheim equation. At very weak etchings of discernible limits discrepancies between experimental data and the fitting curve are apparent due to insufficient samplings for a statistical average. However, this exponential dependence suggests that the graphite surface is also etched by a field-emission current from the negatively biased AFM tip.

The current through a tip to the graphite surface was measured by a current-voltage converter preamplifier while a function generator was supplying negative voltages continuously to the tip, which was scanning on the grounded graphite surface under the same contact force of the graphite-etching experiment. The current was found to flow from the graphite surface to the negatively biased tip and follow exactly the Fowler-Nordheim equation $A = a'' V_0^2 \exp(-b''/V_0)$, as shown in Fig. 4. Therefore, the current flow may well be attributed to the field-emitted electrons from the negatively biased tip.

If b/E of the Fowler-Nordheim equation is set to b'/V_0 of our best-fit formula for the etch depth d, we can estimate the concerned field-emission parameters. In the Fowler-Nordheim equation, we have $b = 6.83 \times 10^7 \phi^{3/2} v(E)$ with ϕ representing the work function so that we may obtain $b = 33.0 \times 10^7$ V/cm at $E = 8 \times 10^7$ V/cm for $\phi = 4.85$ eV (Ref. 19) and $v(E) = 0.45$ eV. We can thus obtain $b/E \simeq 4.13$ at $E = 8 \times 10^7$ V/cm. For $E = 7 \times 10^7$ V/cm we have $v(E) \simeq 0.51$ and $b \simeq 37.2 \times 10^7$ V/cm to obtain $b/E \simeq 5.31$.

On the other hand, from Figs. 3 and 4, we find $b'/V_0 = 4.34$ and $b''/V_0 = 4.80$, respectively, at $V_0 = 10$ V. Both b'/V_0 and b''/V_0 can be seen to take at $V_0 = 10$ V the b/E values corresponding to the electric field $E = 7\text{–}8 \times 10^7$ V/cm. The small difference can be neglected, considering the roughness fluctuation with the tip-surface nm-scale distance and other random conditions to deviate the electric field. The values of b'' and b' are thus close enough to convince us that both the current equation and etch depth equation follow the same Fowler-Nordheim equation. The energy and etch depth thus increase in proportion to the current; therefore, the energy of the graphite etching by the AFM tip in air may be assumed to be supplied by the current of field-emitted electrons from the negatively biased tip.

As the distance between the AFM tip and sample surface is kept at about 1 nm in the contact-mode operation, the electric field between the tip and sample at $V_0 = 10$ V reaches about 10^8 V/cm, close to the electric field 8×10^7 V/cm estimated from b'/V_0 and b/E. Therefore this result also suggests that graphite etching may be provided in energy by the field-emitted electron current from the negative-voltage-applied tip.

If the tip voltage is decreased, the tip size should be reduced to maintain a specific current, following the equation[20] $r = 0.85 V_0^{5/4}/\phi^2$ relating a tip radius r (Å), work function ϕ (eV), and a tip voltage V_0 (V), when the current density will increase accordingly. Therefore, even at voltages smaller than -10 V, the field-emission current density at a nm-size AFM tip can be so large as to etch a graphite surface or cut a thick MWNT.

Because the electric field at a sharp tip end is much larger than at a smooth surface, only the electrons emitted from the negatively biased tip can get so high energy above the threshold as to cut the thick MWNT's at applied voltages smaller than -10 V. But with such small voltages applied to the positively biased nanotip, the electric field at the smooth surface of graphite or nanotubes may not become so high to give the large emission current of electrons required for chemical etching.

In conclusion we could cut 30-nm-diam MWNT's in easy and precise controls by an AFM tip only at a negative bias voltage larger than a threshold. The graphite surface was etched by the same method applied for cutting the MWNT's. The etching current of field emission was measured to verify the microscopic mechanism of cutting by the AFM tip.

Comparing the experimental results between graphite etching and MWNT cutting, we show that both MWNT cutting and graphite etching should be attributed to the same mechanism. The energy required for the chemical etching mechanism[16] for graphite etching is provided by field-emission electrons from the negatively biased AFM tip.

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