Structural change at the carbon-nanotube tip by field emission

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Carbon-nanotube tips are plastically deformed during field emission. High-resolution transmission electron microscopy and structural simulations suggest that the deformed structure of the closed nanotube is explained by heterogeneous nucleation of the pentagonal and heptagonal carbon ring pairs, and that of the opened one is represented by sp^3-like line defects in the hexagonal carbon network. It is considered that the changing of the inclination of the Fowler–Nordheim plots corresponds to the structural change in which a tip becomes sharp. The field ion microscope image and the corresponding field-emission pattern suggest that the electron emission from a closed nanotube is not necessarily from pentagonal carbon rings, but from the protrudent carbon network sites on the tip. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1376149]

Much attention has recently been paid to the carbon nanotube as an electron source for flat-panel displays owing to its excellent field-electron-emission characteristic.[1–6] The microstructure and electronic state at the tip are considered to affect the electron emission from a nanotube. A few investigations relating to the electronic states of various tip structures which were applied to a field-emission microscopy and scanning tunneling microscopy[7–11] are available as reference. Direct observation by transmission electron microscopy (TEM) has given us useful information about the nanotube tip structure. However, until now there have been no techniques available for TEM observations at the tip before and after emission. In this letter, we present high-resolution TEM images which show a clear structural change appeared at the nanotube tips after the field emission and then the deformation process is discussed at the atomic level.

Multiwall carbon nanotubes were synthesized by the carbon dc arc-discharge method.[12] In order to use the nanotubes as an electron source, they were bundled and aligned along one direction by drawing using C_{60} crystals of ~ 10 μm diam. The C_{60} crystals were produced by arc discharge and high-performance liquid chromatography. A mixture of C_{60} crystals with 40 mass % nanotubes was packed in a silver sheath and was drawn to produce a multicore wire.[13] The nanotubes were oriented in same direction due to the flow of the refined C_{60} crystals during the drawing. The silver sheath was evaporated by heat treatment at 1243 K for 54 ks and then the nanotubes/C_{60} rod was obtained. The rod specimen was mounted on a copper grid by adhesive and silver paste, as shown in Fig. 1. The nanotubes were sticking out of the fractured surface of the rod. The cross-sectional area of the rod was 7.8×10^{-3} mm^2. The emission current (I) against the applied voltage (V) was measured six times on a sample in a high-vacuum chamber with a base pressure of $\sim 6.5\times10^{-6}$ Pa. The distance between the electrodes was fixed at 200 μm using a maica spacer. The same experiment was also performed on the opened nanotube prepared by oxidation in air at 973 K for 1 min. TEM observations were carried out by JEM-2010E (JEOL).

The nanotubes were aligned along the longitudinal direction of the rod, keeping the angular deviation within 30° (Fig. 1, inset). The $I-V$ characteristics of the closed nanotubes are shown in Fig. 2(a). For the first run, the threshold voltage was high and the current increased quickly. After the second run, the emission began at a rather lower voltage and increased gradually. Fowler–Nordhiem (FN) plots [Fig. 2(a), inset] show that the first run cannot be expressed with a straight line and is separated at some stages. This characteristic emission suggests that the electron emission is affected by the surface conditions, such as gas adsorption or the structural change of the nanotube tips. But, another emission experiment done after exposing the sample to the atmosphere shows no different behavior in the emission. The change of the emission characteristic suggests the structural change of the nanotube tip. Figures 2(b) and 2(c) show a typical tip structure of a closed nanotube (b) before and (c) after field emission. Individual nanotubes can be numbered in TEM observation, so that the same nanotube tip can be observed before and after $I-V$ measurement. The high-resolution

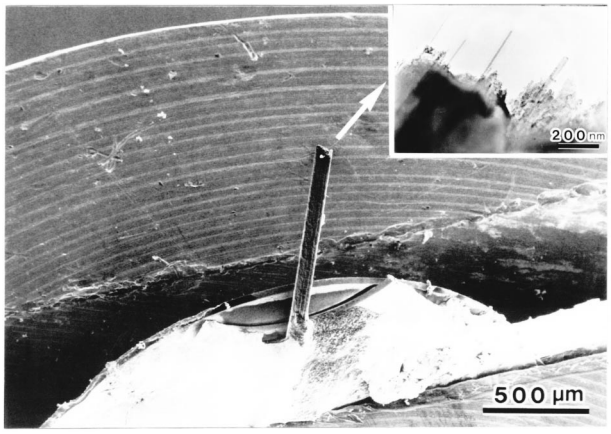

FIG. 1. Scanning electron microscope image of a sample. Inset figure shows the surface morphology at the rod tip. The nanotubes were aligned along the longitudinal direction of the rod within 30°.

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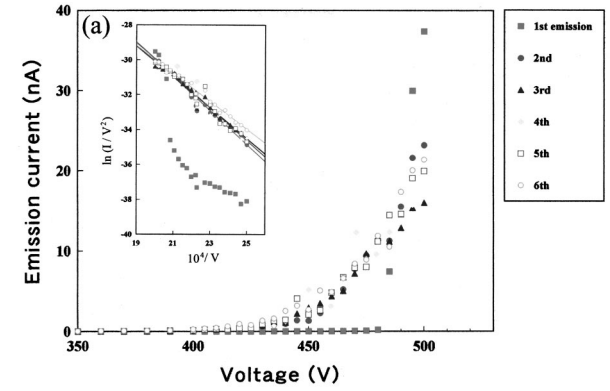


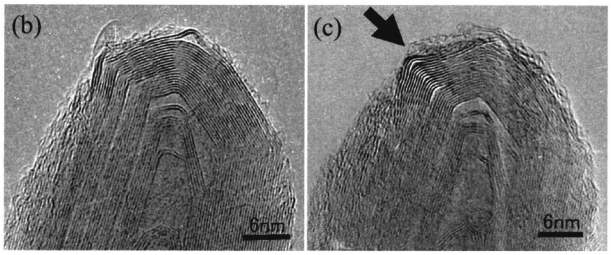
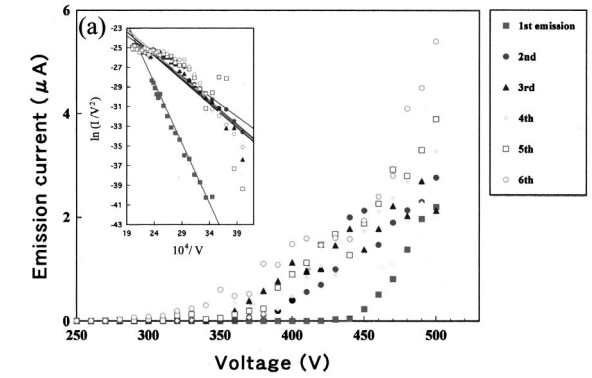


FIG. 2. $I-V$ characteristics of the closed nanotubes (a). High-resolution TEM images of the closed nanotube tip (b) before field emission and (c) after field emission. A protrusion appears toward the electric-field direction, as shown by the arrow in (c).

TEM image revealed that the deformation of the nanotube occurred at a corner in the polyhedral cap and a protrusion was formed along the normal to the electric field, as shown by the arrow in Fig. 2(c).

In the opened nanotubes, the structural change also appeared at the tip. Figures 3(b) and 3(c) show the tip structure



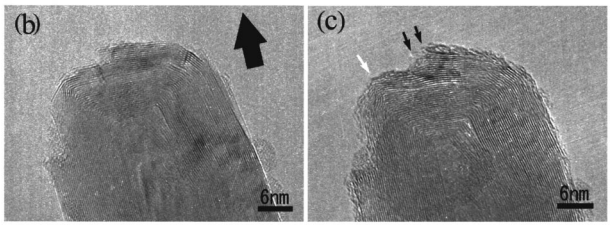


FIG. 3. $I-V$ characteristics of the partially opened nanotubes (a). High-resolution TEM images of the partially opened nanotube tip (b) before field emission and (c) after field emission. At the closed part, the protrusion structure appears toward the electric-field direction as shown by a white arrow in (c). The edge part of the opened layers shows the spread between the layers and turning up of the outer layer, as shown by black arrows in (c).

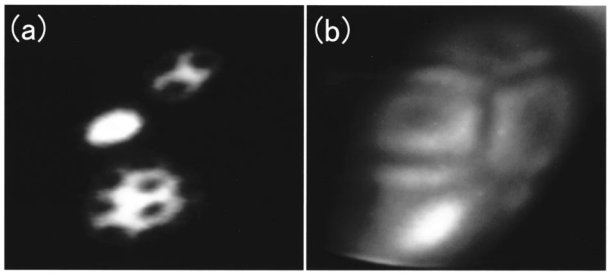


FIG. 4. FIM image (a) and the corresponding FEM image (b). FIM and FEM were performed using a chamber with ultrahigh vacuum of 10^{-9} Pa. The tip voltages of FIM and FEM are 5.5 and -1.4 kV, respectively.

of a partially opened nanotube tip (b) before and (c) after emission. The arrow in Fig. 3(b) shows the anode direction. At the closed region, the protrudent structure is observed in the part shown by the white arrow. The edge part of the opened layers shows the spread between the layers and the turning up of the outer layer shown by black arrows. Although the $I-V$ characteristic shows the same emission behavior as in the case of the closed nanotube, the inclinations of all FN plots tend to decrease gradually with the number of emission times [Fig. 3(a)].

It is assumed that the work function of the nanotube does not change, the decreasing of the inclination of the FN plots corresponds to the structural change in that the tip becomes sharp. TEM observations revealed that the structural change appeared in part of the tips due to the field emission. In the closed nanotubes, the protrusion appeared at the original corner produced by an isolated pentagonal carbon ring. The protrusion with a keenly sharpened structure can hardly be understood in terms of the original structure that consisted of a pentagonal carbon ring. In order to reproduce the protrudent structure, there are two possible ways. One is a replacement of sp^2 bonding state atoms of the nanotube with sp^3 bonding state atoms,[12,14] and the other is nucleation of the pentagonal and heptagonal carbon ring pair in the hexagonal carbon network.[12,15,16] Structural simulations performed by semiempirical molecular orbital calculations (PM3) on a piece of graphene sheet containing a pentagonal carbon ring reveal that introduction of the sp^3 bonding state atoms into the original corner can produce a wedge form protrusion at the tip. In this case, a pentagonal carbon ring is necessarily located at the tip of the protrusion. However, it is rare that the pentagonal carbon ring is observed in field ion microscopy (FIM) images of nanotube tips. Figure 4 shows the FIM image and the corresponding field emission microscopy (FEM) image obtained from a nanotube. In almost all cases, several bright areas of hexagonal carbon rings are observed in the FIM image, as shown in Fig. 4(a). The FEM pattern shown in Fig. 4(b) has four bright rings with a small dark spot in its center, and the interference fringes are also observed in boundary regions between the neighboring the rings.[17] It seems that the observed FEM pattern reflects the bright area sites of the FIM image. These results reduce the likelihood that the bonding state change mechanism might be correct. On the other hand, a kind of bending structure of the nanotube such as buckling is explained by the nucleation of the pentagonal and heptagonal carbon ring pair in the hexagonal carbon network of the cylindrical nanotube wall. If the pen-

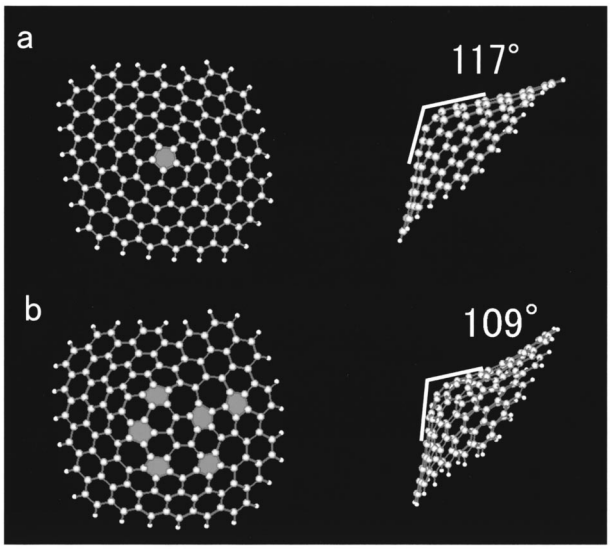


FIG. 5. Proposed deformation mechanisms of the nanotube tips. (a) Hexagonal carbon network with a pentagonal carbon ring (a part of the polyhedral cap), and (b) deformed carbon network formed by introducing pentagonal–heptagonal carbon ring pairs into (a).

tagon and heptagon carbon ring pair is introduced into the hexagonal carbon network around a pentagonal carbon ring by a heterogeneous nucleation mechanism, the protrudent structure of the hexagonal carbon rings can be formed at the tip. Figure 5(b) shows an example of the deformation model produced by the mechanism. As a result of the calculation, the angle of the apex gradually decreased with a pentagonal carbon ring addition. The nucleation mechanism can also reproduce the various deformation structures such as the corrugated structure. The stress caused by the concentration of the electric field and thermal activation due to the temperature increment by the electron emission may contribute to the formation and the motion of the pentagon–heptagon carbon ring.

It has been reported so far that the relative location of pentagonal carbon rings in a tip changes an electronic state of the nanotube, especially since the introduction of isolated pentagonal defects in the nanotube lattice is seen to result in weak acceptor states.[10,11] Recently, Saito, Hata, and Murata have reported that five- or sixfold symmetrical emission patterns were observed, and these were the patterns reflecting the pentagonal carbon ring sites.[17] These reports have suggested that pentagonal carbon rings play a role of the emission site. However, our experimental results differ from their reports. As shown in Fig. 4, the obtained FEM pattern does not necessarily correspond to the pentagonal carbon ring sites. The FEM pattern shown in Fig. 4(b) reflects the bright area sites, including the hexagonal carbon rings rather than the pentagonal carbon rings. It is thought that the obtained emission pattern is the interference fringes of the coherent electron beams, which come out from bright areas, indicating the protrudent sites on a nanotube tip. It is not easy to prove the deformation mechanism of nanotube tips, but it is possible to form the protrudent structure of the hexagonal carbon rings by the heterogeneous nucleation mechanism.

In the opened nanotubes, the deformed structure can be explained by introducing sp^3-like line defects into the hexagonal carbon network.[12,14] It is consider that the spreading and the turning up of the opened nanotube layers were caused by the stress produced by the high-electric-field concentration on each layer, and that is as a result of two or more layers contributing to the electron emission. This is the reason why a high emission current was obtained as compared with the closed nanotube.

In conclusion, we have shown that nanotube tips are deformed during field emission. The Sharp tips caused by deformation contribute to the emission characteristics of the nanotubes. The deformation mechanism is not proved but it can be explained by the heterogeneous nucleation mechanism for the closed nanotube, and by the change in the bonding state from an sp^2- to sp^3-like bonding state for the opened one. The present results suggest that controlling the atomic structure of the tip surface is important to produce field electron emitters.

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