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Electron Emission Sites on Carbon Nanotubes and the Energy Spectra

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Two kinds of electron emission sites on carbon nanotubes have been clarified; one is a nanoprotrusion exhibiting deformed honeycomb structures composed of carbon hexagons,pentagons and possibly heptagons. The other is either an edged species or adsorbates. The emission spectra show two characteristic features; a broad main peak as compared with theoretical curves based on Fowler-Nordheim theory, and an additional shoulder at about 0.5 eV from E_F, of which the features are observed independent of the emission direction. The broad main peak may indicate that energy band bending occurs near the emission sites.

KEYWORDS: carbon nanotube, field emission, field ion microscopy, field emission spectroscopy

Because of stable electron emission even in relatively poor vacuum, carbon nanotubes have received much attention as a promising electron source for flat panel displays.[1] The long lifetime of the carbon nanotube emitter under ion bombardment and reaction with residual gases originates from strong chemical C–C bonds constructing a honeycomb structure at the surface. Recently, Saito *et al.* reported clear emission patterns with five or sixfold rotational symmetries from clean end caps of carbon nanotubes and discussed the possibility of electron emission sites and carbon pentagon structures.[2] In spite of the importance of clarifying the stable emission character, no one has observed the surface atomic structures of end caps of carbon nanotubes to date far based on the data of field ion spectroscopy (FIM). In this work, therefore, we applied FIM, field emission spectroscopy (FES) and field emission microscopy (FEM) in order to obtain information on the atomic structures and electronic states of local emission sites on the end caps. We have found tiny protrusions of about 0.5 nm in radius and sharp spotty areas on the end caps, and also observed broad energy distributions as compared with those of refractory metal tips.

The fabrication of the emitter used in this experiment was described in a previous paper.[2] The multiwall carbon nanotubes (MWCNT) were prepared by carbon arc discharge in helium or hydrogen gases. A bundle of as-grown nanotubes was fixed on a hairpin-shaped tantalum filament (0.3 mm in diameter) using conducting carbon paste. The detector composed of microchannel plates and a screen for FEM and FIM was placed 50 mm from the electron emitter. A cylindrical energy analyzer of the electrostatic type was also installed, and its energy resolution is about 10 meV. The FE spectra were measured by rotating the tip direction for adjustment of the emission directions, and the electrons passing through the probe hole, 5 mm in diameter at a distance of 30 mm from the emitter were analyzed by means of a cylindrical electrostatic energy analyzer. The main vacuum chamber for FIM, FEM and FES experiments was connected in series to the second chamber of specimen storage and the third chamber for an air-lock specimen-exchange system. About 30 minutes after the emitter introduction into a vacuum, we started FEM, FIM and FES experiments at 10^{-9} Pa. The emitter surface was cleaned by flash heating up to 1000 K by resistive heating; both the emission patterns and the emission currents became stable after the repeated heat treatments. All the experiments were performed at the emitter temperature of 60 K.

Figures 1(a) and 1(b) show typical FIM and FEM patterns obtained from the same carbon nanotube end cap. It should be noticed that inhomogeneous and nonsymmetrical electric fields exist on the end cap, of which the features are different from those of conventional metal tips with a spherical radius of several hundreds nm such as tungsten, platinum, or molybdenum. Hemispherical shapes of conventional tips produce highly symmetrical FIM patterns, which reflect the crystal orientations. In Fig. 1(a), two kinds of bright areas are observed; one kind are atomically resolved areas exhibiting either carbon hexagon or deformed honeycomb structures indicated by H1 and H2. The other kind are relatively small spots without any atomic images indicated by the letters O, P and Q. Figure 1(b) shows a FEM pattern from the same end cap exhibiting the FIM pattern shown in Fig. 1(a). The pentagons depicted by white dotted lines in Figs. 1(a) and 1(b) are visual guides indicating almost the same positions on the detector. The validity of the visual guides is partly supported by synchronous changes due to chemisorption in both the FIM and FEM patterns. The areas exhibiting deformed honeycomb structures of H1 and H2 do not emit high currents as compared with the small spotty areas of O, P and Q; namely, the electric fields around the small spotty areas are much higher than those of the atomically resolved areas of H1 and H2. Hence, the small bright spots presumably originate from either adsorbed molecules or end edge species of nanotubes, which vibrate significantly and (or) rotate even at 60 K. This may be the reason why the atomic images did not appear in the spotty areas, although the atomic resolution was obtained in the other areas of this end cap. In addition, there is another possible explanation for the large bright spots; the electric fields around the emission sites change the magnitudes of the spots in the FIM pattern.

In the FEM pattern, some dark strips appear at the boundaries of two low emission areas. The pattern is similar to the one reported by Saito *et al.*,[2] and has been successfully analyzed on the basis of the Young's interference of electrons

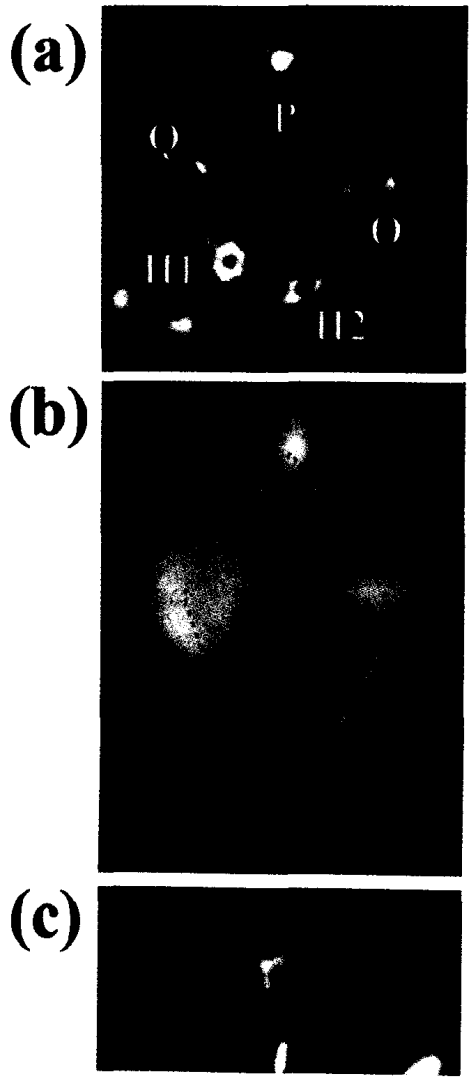

Fig. 1. Typical FIM and FEM patterns. (a) a FIM pattern of a MWCNT, (b) the corresponding FEM pattern. The pentagon appears in the FIM pattern (c) of a different tip.

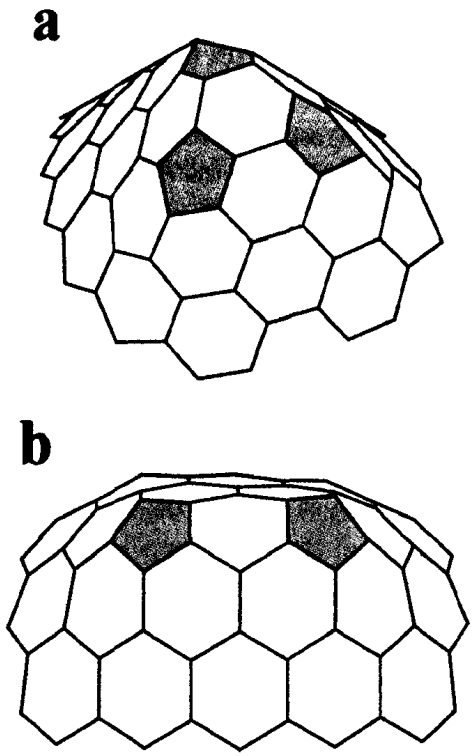

Fig. 2. Atomic structural models of the nanoprotrusions H1 and H2 in Fig. 1. Model (a): The top hexagon surrounded by three adjacent pentagons corresponds to the bright symmetrical hexagon of H1. Model (b): The top hexagon is connected to two adjacent pentagons corresponding to the deformed hexagon of H2.

with the Fermi wavelength.[3] Therefore,those emission sites seem to be located on the same end cap. In this experiment, we observed many atomically resolved areas composed of honeycomb structures as shown in Fig. 1(a), and a carbon pentagon structure was also occasionally detected in the FIM images, as shown in Fig. 1(c). This image was obtained from another nanotube.

The atomically resolved images provide information on atomic structures of the nanoprotrusions. Two protrusions of H1 and H2 seem to be separated by an extremely short distance, if they are situated on the same end cap. Figure 2 shows the possible structural models (a) and (b) corresponding to the protrusion of H1 and that of H2 in Fig. 1(a), respectively. In the other FIM images, we observed the cone-shaped protrusion composed of one carbon pentagon surrounded by a honeycomb structure with 20 carbon hexagons, and noticed a uniform intensity distribution over the 20 hexagons. In the images of H1 and H2, in contrast, only one intensive hexagon appears together with a very weak honeycomb structure. Hence, only the models with high electric fields around the top hexagons are proposed. The top of the model structure in Fig. 2(a) is a carbon hexagon surrounded by three adjacent pentagons and three hexagons. The high electric fields are generated at the edges of the top hexagon as observed in Fig. 1(a). In addition, the bright hexagon of H1 has a threefold rotational symmetry. The images of the carbon hexagon are composed of six lines, which is significantly different from normal FIM images that are composed of bright spots indicating individual atoms. This presumably originates from the anti-bonding π bands spreading over the entire hexagon, because FIM patterns are generated by electron tunneling from the atomic orbital of the imaging gas to the unoccupied π bands.

The protrusion of H2 includes a deformed hexagon and hence, anisotropic electric fields around the protrusion may be induced. The model in Fig. 2(b) is one of the candidates of the protrusion H2; the top hexagon is surrounded by two adjacent pentagons and four hexagons. In the FIM pattern in Fig. 1(a), the distance between the two nanoprotrusions is extremely short, and the heptagons may be situated at the bases of the two nanoprotrusions. The similar protrusions generated by high electric fields have been detected by using transmission electron microscopy.[4]

Figure 3 shows typical emission spectra. The spectrum (a) was obtained from the clean end cap exhibiting the similar FIM and FEM patterns as shown in Fig. 1. The spectrum (b) is a typical spectrum of the same end cap contaminated with residual gases. Even in 10^{-9} Pa, residual molecules adsorb on the surface, and change the emission current, emission pattern,and also the spectrum. We occasionally observed a drastic increase in the local emission current in a part of the emission pattern. The spectrum (b) was obtained for one emission spot,of which the current was enhanced by gas adsorption. The spectrum (c) was obtained from a clean W tip. All of the observed points in the FEM pattern showed the same features: one large peak appears around the Fermi level together

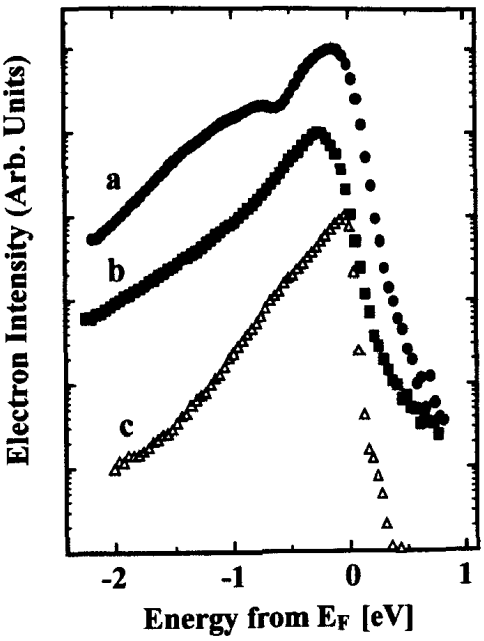

Fig. 3. Typical field emission spectra: Spectrum (a) was measured from the nanotube exhibiting similar FIM and FEM patterns in Figs. 1(a) and 1(b). The spectrum (b) was measured from the same nanotube contaminated with residual gases and spectrum (c) was measured from a clean W tip.

with an additional shoulder at 0.5 eV below E_F. Namely, the spectra did not change with the different orientations. With increasing applied electric fields, the shoulder moves toward the deeper energy range, while the main peak remains at the same energy position. The features are the same as those of the spectra measured from nanoprotrusion W tips.[5] No change in the peak position indicates that the electrons at the main peak come from the nanotube interior, where the energy bands do not change with changing applied electric fields. On the contrary, the shift of the energy position indicates that the emitted electrons are related to the surface electronic states, which are significantly influenced by applied electric fields. Furthermore, the shoulder was very sensitive to the surface conditions; when residual gases are adsorbed on the emission site, the shoulder disappears, as shown in the spectrum (b). Those experimental findings indicate that the shoulder is related to either the surface localized states or excitations of surface collective modes, for instance, electron emission by resonance tunneling through the surface states.[5]

Comparison of the observed spectra with the spectrum (c) of a normal W tip indicates the clear difference in the shape of the main peak; the observed peaks are broad as compared with that of the W tip. Because the energy spectra obtained from the W tips are in good agreement with the curves calculated on the basis of the Fowler-Nordheim theory, the broad peaks in the spectra (a) and (b) show clearly that the high-energy electrons are injected into the end cap from the tube interior and are presumably induced by the penetrating electric fields.[6]

In summary, two kinds of electron emission sites on carbon nanotubes have been found; one is a nanoprotrusion exhibiting atomically resolved images with carbon hexagons, pentagons and possibly heptagons. The other is either an edge species or adsorbates. The main peaks in the emission spectra are broad as compared with the curves calculated with the Fowler-Nordheim theory, and a shoulder appears at about 0.5 eV from E_F. The broad peak indicates that band bending occurs near the emission sites, of which the origin is not clear at this time, but presumably due to the field penetration.

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