10. Applied Science

10-1. Electronic Structure at Carbon Nanotube Tips

Since the first discovery of carbon nanotubes, naotubes have attracted much attention of both material scientists and engineers because of their interesting new phenomena and their potential use in nanoscale devices: quantum wires, transistors, molecular memory devices, and electron field emitters. The most unique features of nanotubes arise from their electronic properties. Especially, a specific electronic structure is expected at their tips, where the graphene cylinders are semi-spherically terminated. Investigations of the electronic properties of nanotube tips are important for understanding the electron field-emission properties of nanotubes. Photoemission spectroscopy can measure the electronic structure over a wide energy range. Furthermore, photoemission spectroscopy can directly determine the work function, which is crucial for understanding the field-emission properties.

Synchrotron-radiation photoemission spectros-



Figure 1.

Photoemission spectra in the vicinity of the Fermi level of aligned and random MWNT's and the SWNT's.

copy has been employed to measure the work function, valence band structure, and C 1s spectra of vertically aligned and randomly distributed multiwalled carbon nanotubes (MWNT's) grown on Si substrates [1]. The length and diameter of the nanotubes are 10 µm and 30 nm, respectively. The spectra from the aligned and random MWNT's are considered to be dominated by photoemission from their tips and sidewalls, respectively. The experiment was performed at BL-1C. Figure 1 shows the spectra in the vicinity of the Fermi level of the aligned and random MWNT's. For a reference, the spectrum of random single-walled carbon nanotubes (SWNT's) is also shown. For the aligned MWNT's, the existence of the Fermi edge is obvious. A Fermi-edgelike feature is also slightly observed in the random MWNT's, although the spectral intensity at the Fermi level is apparently lower than that of the aligned MWNT's. On the other hand, the SWNT's show a very small spectral intensity at the Fermi level. These results strongly suggest a specific electronic structure at the tips of the aligned MWNT's. Figure 2 shows the secondary-electron threshold spectra of the aligned and random MWNT's. The work function of the random MWNT's was determined to be



Figure 2.

Secondary-electron threshold spectra of aligned and random MWNT's.

about 4.6 eV. This value is close to the value for graphite obtained in our previous study (4.6–4.7 eV) [2] and in other photoemission studies (4.6 eV). On the other hand, the work function of the aligned MWNT's was determined to be 4.4 eV, which is smaller than those of the random MWNT's and graphite. It is worth noting that this result is consistent with a previously reported paper which showed that the threshold voltage of electron field emission of aligned MWNT's is lower than that of random MWNT's [3]. Furthermore, the work function of the SWNT's, in contrast to the aligned MWNT's, was found to be 4.8 eV in our previous study [4], which is a slightly larger value than that for graphite. These results can be explained by assuming that the Fermi level is slightly shifted upward and located inside the conduction band at the tips of the MWNT's. We suggest that the electronic structure at the tips of the MWNT's is considerably affected by defects.

Y. Watanabe and S. Suzuki (NTT Basic Research Laboratories)

References:

S. Suzuki, Y. Watanabe, T. Kiyokura, K. G. Nath,
 T. Ogino, S. Heun, W. Zhu, C. Bower, and O.

Zhou, Phys. Rev. B. 63 (2001) 245418.

- [2] S. Suzuki, C. Bower, Y. Watanabe, and O. Zhou, Appl. Phys. Lett. 76 (2000) 4007.
- [3] C. Bower, O. Zhou, W. Zhu, A. G. Ramirez, G.
 P. Kochanski, and S. Jin, in Amorphous and Nano-Structured Carbon, edited by J. Robertson,
 J. Sullivan, O. Zhou, B. Coll, and T. Allen,
 Mater. Res. Soc. Symp. Proc. No. 593 (Materials Research Society, Pittsburgh, 2000), p. 215.
- [4] S. Suzuki, C. Bower, T. Kiyokura, K. G. Nath, Y. Watanabe, and O. Zhou, J. Electron. Spectrosc. Relat. Phenom. 114-116 (2001) 225.

