

Electronic structure of carbon nanotubes studied by photoelectron spectromicroscopy

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The electronic structure of multiwalled carbon nanotubes aligned perpendicularly on a Si substrate was studied by means of photoelectron spectromicroscopy. The valence band and the C 1s spectra, measured systematically from spatially selected regions along the tube axes, were the fingerprint for lateral variations in the electron density of states and in the band bending, respectively. It was found that the tips have a larger density of states near the Fermi level than the sidewalls, whereas band bending, which would explain such a spectral difference, was not observed. It is suggested that the different density of states near the Fermi level is due to a larger dangling bond density at the tips.

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I. INTRODUCTION

The electronic structure of carbon nanotubes has attracted much attention because of their nanometer-scale highly one-dimensional structure.¹ Moreover, a specific electronic structure is expected at the tips of nanotubes, where the graphene cylinders are closed by hemispherical caps. Recently, investigation of the electronic structure at the tips has also become important for understanding the electron-field-emission properties of nanotubes.² Although the low threshold field is generally attributed to the large field enhancement factor at the tips, a precise understanding of the mechanism of field emission from nanotube tips is still lacking. It is not clear which electronic states are responsible for the emission: the Fermi sea in metallic tubes or localized states at the tips induced by the insertion of the five-member rings in the graphene network.³ Theoretical calculations also suggest that the dangling bond states near the Fermi level largely increase the emission for open-ended tubes.^{4,5}

In a previous paper, we have measured the electronic structure of tips of aligned multiwalled carbon nanotubes (MWNT's) and of sidewalls of random MWNT's.⁶ The interpretation of our results has been obscured by the fact that the two types of samples were grown with different methods. However, employing high-resolution cross-sectional photoemission microscopy, we were now able to investigate the electronic structure of tips and sidewalls of the *same* MWNT sample aligned perpendicularly on a Si substrate. Systematic measurements of spatially selected photoemission spectra along the tube axes unambiguously revealed that the density of states near the Fermi level at the tips is considerably larger than at the sidewalls. It was also revealed that the position-dependent electronic density of states cannot be explained by

band bending, but because the tips have a characteristic density of states near the Fermi level.

II. EXPERIMENT

The MWNT's aligned perpendicularly on a Si substrate were grown using microwave plasma-enhanced chemical vapor deposition (MPE-CVD) with Co as a catalyst. A typical cross-sectional scanning electron microscope (SEM) image of a cleaved sample is shown in Fig. 1. The diameter and the length of the nanotubes were about 30 nm and 10 μm , respectively. The catalytic Co particles are encapsulated at the bottom of the nanotubes.⁷ Details of the synthesis and of the structural properties of these MWNT samples are given elsewhere.^{7,8}

Photoelectron spectromicroscopy experiments were performed with the scanning photoelectron microscope (SPEM) at the ESCA microscopy beamline at the ELETTRA synchrotron radiation light source in Trieste, Italy. The microscope consists of a photon focusing system (a combination of a Fresnel zone plate lens and an order sorting aperture),

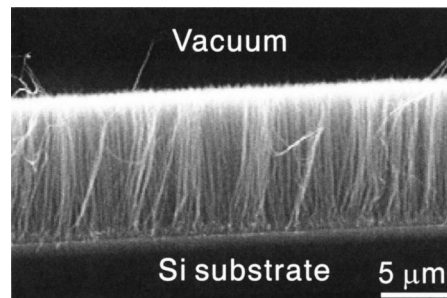


FIG. 1. Cross-sectional SEM image of the aligned MWNT's.

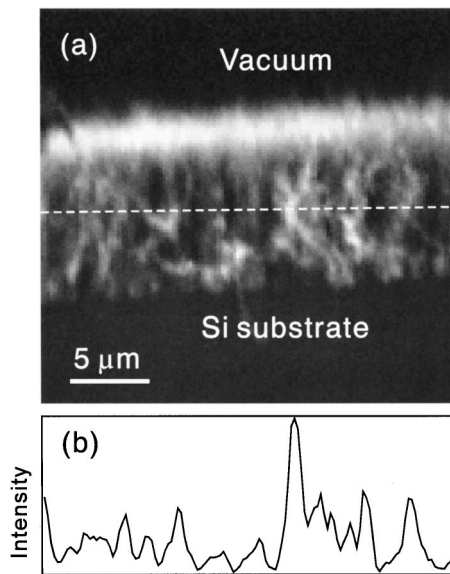


FIG. 2. (a) Cross-sectional C 1s photoelectron spectromicroscopy image of the aligned MWNT's and (b) C 1s photoelectron intensity profile along the dashed line in (a).

specimen positioning and scanning system, and a hemispherical capacitor electron analyzer with a 16-channel detector. The angle between the incident light (normal to the sample) and the electron energy analyzer is 70° . The instrument works in imaging mode and spectroscopy mode. Detailed descriptions of the beamline and the measurement station are given elsewhere.^{9,10} All cross-sectional spectromicroscopy measurements reported here were carried out with lateral resolution of 90 nm and energy resolution of about 0.3 eV (photon energy 497.0 eV). Under these conditions, the probing depth of our experiments is a few nanometers (an order of ten graphene layers).

The MWNT sample was cleaved in air and then annealed at about 200°C for 12 h in the preparation chamber (base pressure $\sim 5 \times 10^{-10}$ Torr) in order to remove physisorbed molecules. We investigated the electronic change induced by surface contamination.¹¹ Before annealing, several atomic percent of oxygen are detected by core-level x-ray photoemission spectroscopy (XPS). The oxygen is due to physisorbed molecules and can easily be removed by annealing. After annealing, no other element than carbon is detected by XPS.¹¹ For the experiments, the sample was transferred into the analysis chamber (base pressure $\sim 1 \times 10^{-10}$ Torr) where the SPEM measurements were carried out at room temperature.

III. RESULTS AND DISCUSSION

Figure 2(a) shows a cross-sectional image of the cleaved MWNT sample obtained by collecting the C 1s photoelectrons. The contrast is dominated by surface topography. The grazing acceptance angle of the analyzer enhances the topographic effects. In fact, otherwise it would be difficult to distinguish the nanotubes, because as will be shown below they all emit in the same C 1s range. Brighter parts are seen around the tips and also in some middle parts with disor-

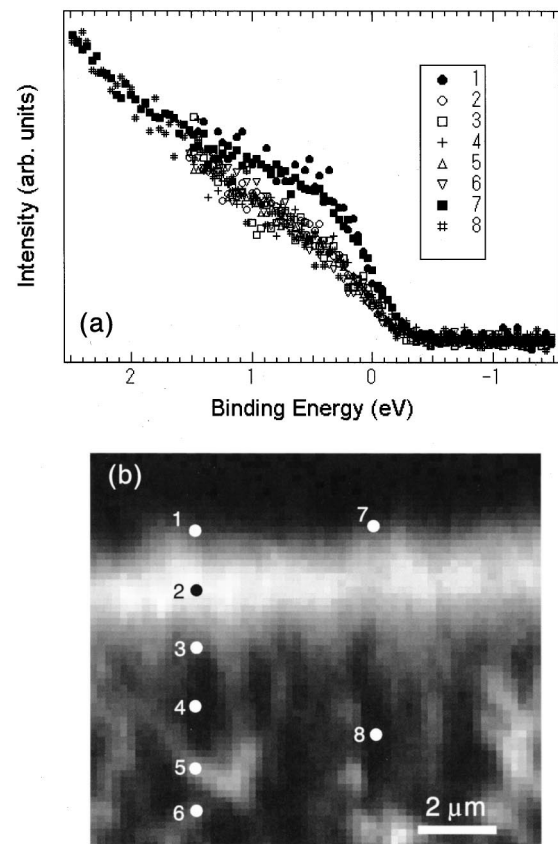


FIG. 3. (a) Valence-band photoemission spectra in the vicinity of the Fermi level from spatially selected regions. The positions of the measurements are shown in the C 1s photoelectron spectromicroscopy image in (b).

dered nanotubes (the disorder is probably a result of the cleavage). On the other hand, some middle parts appear very dark due to a shadowing effect by neighboring nanotubes. Figure 2(b) shows a photoelectron intensity profile measured along the broken line shown in Fig. 2(a). Photoelectron intensity peaks having widths of several hundred nanometers can be clearly observed, corresponding to the diameter of bundles of the MWNT's.

The valence-band spectra in Fig. 3(a) were measured in spots along the nanotube axes as indicated in Fig. 3(b). Although the overall valence-band spectra from the tips and sidewalls were very similar, a distinct difference was observed in the vicinity of the Fermi level. Spectra 1 and 7 were obtained from the tip regions and all others from the sidewall regions, including the bright and dark parts, as denoted in the image in Fig. 3(b). The spectra from the sidewall positions are reasonably similar to each other. However, the two tip positions show a substantially larger spectral intensity in the energy range down to ~ 1 eV below the Fermi edge. This is clear evidence that the MWNT tips possess a larger density of states in the vicinity of the Fermi level than the sidewalls.

Figure 4 shows the C 1s spectra of tips and sidewalls. Some oxidized components at a binding energy about 1 eV above the main peak and at higher energies were observed in previous XPS studies.^{12,13} However, no such component is

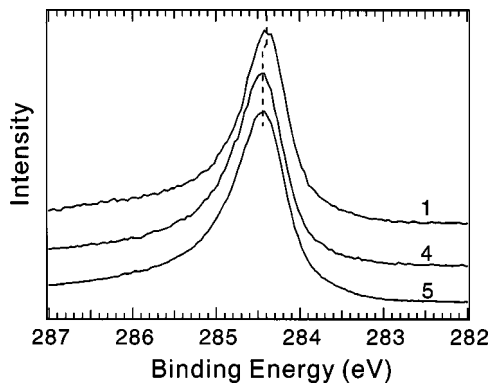


FIG. 4. C 1s photoemission spectra from spatially selected regions. The numbers correspond to the measurement positions indicated in Fig. 3(b).

observed in Fig. 4, although the spectra were obtained at a much higher energy resolution than conventional XPS. Thus we conclude that the surface of the MWNT's was not oxidized.

There is a reproducible slight shift of the C 1s spectra from the tips to a lower binding energy by about 50 meV. This slight shift might be due to band bending near the tips. In such a case, the Fermi level is located inside the valence band at the tips. This will slightly increase the density of states at the Fermi level at the tips. However, the large spectral difference between the tips and sidewalls shown in Fig. 3(a) cannot be explained by a Fermi level shift of only 50 meV at all (we estimate that a shift of 0.2 eV would be necessary). Thus we can conclude that the tips have a characteristic enhancement in the density of states near the Fermi level, which is not caused by band bending. In our previous study, the overall electronic structure of the tips of the aligned MWNT's including the valence band and C 1s states showed a slightly (0.1–0.2 eV) higher binding energy than those of the sidewalls of random MWNT's. With the data available now (and presented here) we can conclude that the spectral shift does not directly originate from the electronic structural difference between tips and sidewalls, but probably due to a difference in the tube diameters (the tube diameters of random MWNT's grown by thermal CVD were more widely distributed than those of the aligned MWNT's grown by MPE-CVD).

Also, the insertion of five-member rings and the curvature at tips cannot satisfactorily explain the enhanced density of states near the Fermi level. If the observed large density of states at the Fermi level were due to a relatively large curvature at the tips of the MWNT's, thin single-walled nanotubes (SWNT's) should also show a large density of states at the Fermi level. This is inconsistent with our previous result that SWNT's have a very small density of states at the Fermi level.⁶ This is also inconsistent with our recent finding that the sidewalls of MWNT's showed a larger density of states near the Fermi level than the sidewalls of SWNT's did, although their radius of curvature is larger.⁶ Furthermore, in this case, it is unlikely that the electronic structure at the tips is largely affected by the insertion of five-member rings, be-

cause the diameter of the MWNT's was about 30 nm. From a simple geometrical consideration, the five/six member ring ratio at the tips can be estimated to be approximately 1/4500. Therefore, the contribution of the five-member rings can be neglected.

Our previous transmission electron microscopy (TEM) study also revealed that MWNT's are considerably defective (graphene sheets are often broken in MWNT's).¹⁴ Furthermore, our previous study have shown that after Cs deposition the aligned MWNT's are intercalated by Cs.¹¹ This is further evidence for their defective nature. These results are somewhat consistent with the existence of an edge state that has been theoretically predicted. Previous calculations on a stepped graphite surface¹⁵ and graphene ribbon^{16,17} have predicted that a localized state that makes a sharp peak in the density of states at the Fermi level is formed on an edge with a zigzag shape. Thus, if we assume that the density of the breaks of the graphene sheets is larger at tips, the edge state would account for a local increase in the density of states at the Fermi level and the almost no band bending along the tube axes. However, the edge state cannot explain the observed enhanced density of states in a relatively wide energy range (approximately 1 eV), because the edge state will not show any characteristic density of states except for just at the Fermi level.

However, the obtained results can be interpreted assuming a higher density of dangling bonds at the tips, consistent with the defective nature of the MWNT's as discussed above (note that the edge state does not originate in the dangling bonds). Indeed, our TEM study has revealed that most of the graphene sheets in deintercalated MWNT's had a continuous length of only ~ 10 nm.¹⁸ Supposing that this is the typical size of the graphene sheets in a MWNT, the dangling bond density will be $\sim 5 \times 10^{21}$ cm⁻³. Such a large density will be enough to cause a spectral change like that shown in Fig. 3(a). Thus we suggest that a spectral difference near the Fermi level is observed, because the dangling bond density is larger at the spherically curved tips than at the cylindrically curved sidewalls, although details of the defect formation mechanism is not clear yet. This explains also the relatively large density of states near the Fermi level at the sidewalls of MWNT's with respect to SWNT's, observed in our previous study.⁶ SWNT's seem to have much less defective structures than MWNT's, because doping into the inner hollow space of SWNT's can be carried out only through opened tube ends.¹⁹ Thus the spectral difference between the sidewalls of MWNT's and SWNT's can also be attributed to a difference in dangling bond densities. The slight spectral shift of the C 1s spectra in Fig. 4 may be due to a contribution from carbon atoms having localized dangling bonds, not due to band bending, because the localized dangling bond states may cause a slight chemical shift of the C 1s level.

IV. CONCLUSIONS

We have measured the spatially resolved electronic structure of aligned MWNT's along the tube axes. We found that the tips have a larger density of states, which expands down

to approximately 1 eV below the Fermi level, whereas there is only a very small shift of the C 1s core-level energy of about 50 meV between the tips and sidewalls. This difference in the photoemission spectra is attributed to the strong influence of structural defects on the electronic structure of MWNT's: namely, the higher dangling bond density at the spherically curved tips than at the cylindrically curved sidewalls. We suggest that the observed larger electronic density of states at the tips of aligned MWNT's may play an important role for their field-emission properties.

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¹S. Iijima, *Nature (London)* **354**, 56 (1991).

²W. A. de Heer, A. Chatelain, and D. Ugarte, *Science* **270**, 1179 (1995).

³J. M. Bonard, H. Kind, T. Stockli, and L. O. Nilsson, *Solid-State Electron.* **45**, 893 (2001).

⁴S. Han and J. Ihm, *Phys. Rev. B* **61**, 9986 (2000).

⁵Ch. Adessi and M. Devel, *Phys. Rev. B* **62**, 13 314 (2000).

⁶S. Suzuki, Y. Watanabe, T. Kiyokura, K. G. Nath, T. Ogino, S. Heun, W. Zhu, C. Bower, and O. Zhou, *Phys. Rev. B* **63**, 245418 (2001).

⁷C. Bower, O. Zhou, W. Zhu, D. J. Werder, and S. Jin, *Appl. Phys. Lett.* **77**, 2767 (2000).

⁸C. Bower, W. Zhu, S. Jin, and O. Zhou, *Appl. Phys. Lett.* **77**, 830 (2000).

⁹M. Marsi, L. Casalis, L. Gregoratti, S. Günther, A. Kolmakov, J. Kovac, D. Lonza, and M. Kiskinova, *J. Electron Spectrosc. Relat. Phenom.* **84**, 73 (1997).

¹⁰M. Kiskinova, M. Marsi, E. Di Fabrizio, and M. Gentili, *Surf.*

Rev. Lett. **6**, 265 (1999).

¹¹S. Suzuki, Y. Watanabe, T. Kiyokura, K. G. Nath, T. Ogino, S. Heun, W. Zhu, C. Bower, and O. Zhou, *Surf. Rev. Lett.* (to be published).

¹²H. Ago, T. Kugler, F. Cacialli, W. R. Salaneck, M. S. P. Shaffer, A. H. Windle, and R. H. Friend, *J. Phys. Chem. B* **103**, 8116 (1999).

¹³E. Frackowiak, S. Gaucher, S. Bonnamy, and F. Beguin, *Carbon* **37**, 61 (1999).

¹⁴S. Suzuki and M. Tomita, *J. Appl. Phys.* **79**, 3739 (1996).

¹⁵K. Kobayashi, *Phys. Rev. B* **48**, 1757 (1993).

¹⁶K. Nakada, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. B* **54**, 17 954 (1996).

¹⁷M. Fujita, K. Wakabayashi, K. Nakada, and K. Kusakabe, *J. Phys. Soc. Jpn.* **65**, 1920 (1996).

¹⁸Zhou, R. M. Fleming, D. W. Murphy, C. H. Chen, R. C. Haddon, A. P. Ramirez, and S. H. Glarum, *Science* **263**, 1744 (1994).

¹⁹K. Hirahara, K. Suenaga, S. Bandow, H. Kato, T. Okazaki, H. Shinohara, and S. Iijima, *Phys. Rev. Lett.* **85**, 5384 (2000).