## A Study of Single-Walled Carbon Nanotube Cap Structure Using Field Emission Image

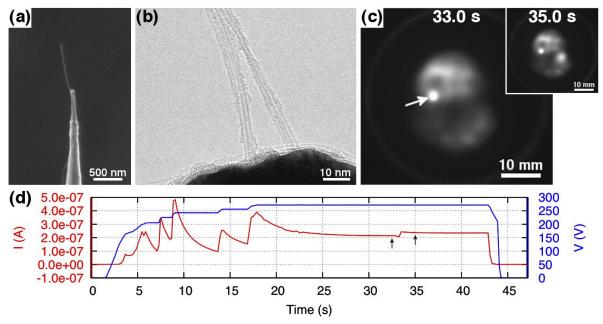
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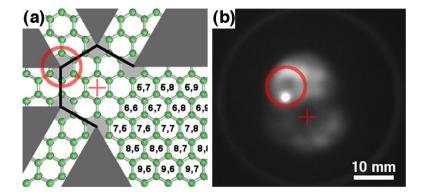
A single-walled carbon nanotube (SWNT) is a nanoscale cylinder composed of one single-layer sheet of carbon atoms. As-grown SWNTs by chemical vapor deposition have a cap at one end and a catalyst particle at the other end. In the application of SWNT to scanning tunneling microscopy tip [1], electron source [2], etc., the SWNT cap structure needs evaluation for precise control. Furthermore, it is important to observe the cap structure to reveal the SWNT growth mechanism. Although field emission microscopy (FEM) images of SWNT caps have been studied by Dean *et al.* [3], no systematic relationships between field electron emission (FE) images and cap structures were found. So far, FE from a structure defined SWNT has not been explored yet because of the difficulty in the sample treatment [2]. We need a series of observations of the same SWNT by scanning electron microscopy (SEM), FEM and transmission electron microscopy (TEM) to understand the relationship between FEM images and the SWNT cap structure.

We have observed FE images from a capped SWNT with defined length and diameter that were determined by SEM and TEM as shown in Fig. 1. The length of SWNT was 800 nm as shown in Fig. 1 (a). However, the sample processing for TEM caused the SWNT tip bent and adhesion to the W tip as shown in Fig. 1 (b). Accidentally this made stable TEM observation possible; otherwise vibration of the tip hindered observation of the tip at a high magnification. The TEM image in Fig. 1 (b) clearly shows that the SWNT tip is a four-SWNT bundle with the average SWNT diameter of 1.73 nm. The isolated SWNT kept being extruded on the W tip until the SEM observation performed after FEM observation as shown in Fig. 1 (a). We believe that an isolated SWNT would be extruded from the bundle of SWNTs.

FEM images are presented in Figure 1(c). The FE current from SWNT behaved like Fig. 1 (d). We observed these data at the same time. Each snapshot of FEM image in Fig. 1 (c) corresponds to the arrows indicated on the I-t curve in Fig. 1 (d). The FE current exhibits a sawtooth-like transient behavior when the applied voltage was changed as shown in Fig. 1 (d). A stable current of  $2.2 \times 10^{-7}$  A was obtained with a low applied voltage of 270 V, which is an advantage of SWNT tip. The FEM image shows the electron emission sites on the SWNT cap. However, adsorption of gas molecule affects the image as seen in the image at 35.0 s in Fig. 1(c). The FE current change with gas adsorption was  $0.2 \times$ 10<sup>-7</sup> A at 270 V. On the other hand, the image at 33.0 s is free from gas adsorption and reflects the cap structure. The center part appears dark and there are six dim patterns around the dark center. The dark center suggests existence of a 6-membered ring and dim patterns may reflect the location of 5membered rings [4, 5]. Thus, a six-fold structure can be a candidate of the observed cap. Figure 2 (a) shows a development view of near six-fold structures: the "+" indicates the center 6-membered ring and the sixth 5-membered ring can be set at the one of the indexed-positions that determines the SWNT chirality. Due to distortion of the near six-fold cap structure, the 5-membered ring marked with the circle protrudes. Those features coincide with the FEM pattern as shown in Fig. 2 (b). By knowing the diameter and the symmetry of the FEM image, the detailed cap structure can be estimated.



**Figure 1.** Multifaceted observation results of the SWNT tip. (a) SEM images of the SWNT tip after FEM. (b) TEM images of the SWNT tip observed after FEM at the root part. (c) Snapshots of the FEM image. The arrow shows a defect of micro-channel plate. (d) Time variation of I and V. The arrows in (d) correspond to each snapshot of FEM image. The FEM image is strongly related to the FE current.



**Figure 2** An interpretation of the FEM image. (a) A development view of near six-fold structures. The gray areas show five 5-membered ring positions and the deep gray areas show the cut out areas. A selection of sixth 5-membered ring position determines SWNT chirality. (b) The FEM image from SWNT cap shown in Fig. 1 (a). The "+" shows the center 6-membered ring and the circle shows the 5-membered ring position.

## References

- [1] M. Irita, Y. Homma, and T. Miura, e-J. Surf. Sci. Nanotech 11 (2013) 105.
- [2] M. Irita and Y. Homma, Surf. Interface Anal. (submitted).
- [3] K. Dean and B. Chalamala, J. Vac. Sci. & Tech. B 21 (2003) 868.
- [4] Y. Saito, K. Hata, and T. Murata, Jpn. J. Appl. Phys. 39, 271 (2000).
- [5] C. Oshima *et al.*, Phys. Rev. Lett. 88, 038301 (2002).