Morphological change of multiwalled carbon nanotubes through high-energy (MeV) ion irradiation

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Multiwalled carbon nanotubes (MWCNTs) were expanded by 2.5 times in diameter through high-energy (MeV) ion irradiation. Pristine MWCNTs were synthesized onto SiO2 substrate by chemical vapor deposition. The 4 MeV Cl2+ ions with a dose of 3 x 10^16 ions/cm^2 were irradiated on MWCNTs. From high-resolution transmission electron microscopy (HR-TEM) images, the average diameter of the high-energy-ion-irradiated MWCNTs was ~180 nm, while that of the pristine MWCNTs was ~70 nm. The wall thickness of the pristine and the high-energy-ion-irradiated MWCNT samples was ~20 nm and 40–50 nm, respectively. We observed the clear formation of nanocompartments with bamboolike structure inside the tubes after ion irradiation. The amorphous carbon structure in the ion-irradiated MWCNT shells was observed from Raman spectra. Based on the results of HR-TEM and Raman spectra, the expansion of the systems represents morphological transition from crystalline graphite structure to amorphous carbon or finite sized graphite structure due to the ion impact. We suggest that high-energy ion irradiation can be useful for the modification of MWCNT structures. © 2005 American Institute of Physics.

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ments with bamboolike structure after the high-energy ion irradiation. The expansion of high-energy-ion-irradiated MWCNTs could be caused by the formation of amorphous carbon and finite size graphite with the folding of inner shells by the impact of the high-energy ion irradiation. Wei and coworkers reported the formation of amorphous rods through 30 keV Ga\textsuperscript{2+} ion irradiation,\textsuperscript{15} in which nanocompartments were formed inside nanotubes after 30 keV Ga\textsuperscript{2+} ion irradiation with a dose of $5 \times 10^{15}$ ions/cm\textsuperscript{2}. The inset of Fig. 2(a) shows the magnification of the wall (outer shells) of the ion-irradiated and expanded samples. Most of shells were collapsed into finite graphitic fragments after the ion irradiation, as shown in the inset of Fig. 2(a). The broken and incomplete nanocompartments inside the tubes were observed as shown in Fig. 2(b). Figure 2(c) presents the complete nanocompartments with bamboolike structure inside the tube after the ion irradiation. The nanocompartments with bamboolike structure might be originated from the folding of the inner shells of the MWCNT walls.

Figures 3(a) and 3(b) compare Raman spectra of the pristine and 4 MeV Cl\textsuperscript{2+} ion-irradiated MWCNT samples, respectively. The G-peak at 1580 cm\textsuperscript{-1} and D-peak at 1350 cm\textsuperscript{-1} of pristine MWCNTs were observed as shown in Fig. 3(a).\textsuperscript{19} The shoulder peak at $\sim$1180 cm\textsuperscript{-1} represents $sp^3$ rich phase of pristine MWCNTs implying the existence of defects in the MWCNT walls or amorphous carbon clusters. Figure 3(b) shows Raman spectrum of 4 MeV Cl\textsuperscript{2+} ion-irradiated MWCNT samples. Compared with the Raman spectrum of pristine MWCNTs, the G-peak and D-peak of the ion-irradiated MWCNTs became smoother as shown in Fig. 3(b). The Raman spectrum of the ion-irradiated MWCNTs was decomposed into four subpeaks. From the peak decomposition of the Raman spectra in Fig. 3(b), new peak at $\sim$1490 cm\textsuperscript{-1} and the increase of the shoulder peak at $\sim$1180 cm\textsuperscript{-1} were observed after the high-energy ion irradiation. The increase of peak at $\sim$1180 cm\textsuperscript{-1} and the appearance of the peak at $\sim$1490 cm\textsuperscript{-1} implies that the crystalline graphite wall structure of pristine MWCNTs was changed to an amorphous carbon or finite sized graphite structure.\textsuperscript{20} The area ratio of D-peak to G-peak $[I(D)/I(G)]$ increased from 1.26 for the pristine MWCNTs to 1.69 for the ion-irradiated MWCNTs. The increase of $I(D)/I(G)$ with the appearance of noncrystalline subpeaks implies that the degree of disorder (i.e., amorphization) in the MWCNTs increased with 4 MeV Cl\textsuperscript{2+} ion irradiation. The results were similar with the ion-irradiated graphite or polymer materials.\textsuperscript{12,13} Based on the results of the HR-TEM and Raman spectra, we propose that the high-energy (MeV) ion irradiation caused the number of defects and the amorphous carbon or finite sized graphite,
resulting in the collapse of crystalline graphite shells of the MWCNT walls. These induce the expansion and the formation of bamboolike structure of the high-energy-ion-irradiated MWCNTs.

The structural differences in the SEM images between the pristine and the ion-irradiated MWCNTs were not observed because of the lack of resolution. However, the measured $\sigma_{dc}$ of bulky MWCNTs at RT decreased from $\sim31$ to $\sim16$ S/cm through the high-energy ion irradiation, which supports the increase of degree of disorder in the MWCNTs.

In summary, the multiwalled carbon nanotubes were expanded by $\sim2.5$ times in diameter through 4 MeV Cl$^{2+}$ ion irradiation with a dose of $3\times10^{16}$ ions/cm$^2$. From the HR-TEM images and the analysis of Raman spectra, we observed that the high-energy ion irradiation induces the amorphization of lattice and the formation of defects in the pristine MWCNT shells. As well as the expansion of the diameter in the MWCNTs, the bamboolike structures inside the tubes were formed through high-energy ion irradiation. After the high-energy ion irradiation, the crystalline graphite shells of the MWCNTs were morphologically changed into amorphous carbon and finite sized graphene clusters. The increase of the ratio of the D-peak to G-peak in Raman spectrum was observed for the ion-irradiated MWCNTs, implying the increase of the degree of disorder in the MWCNTs.

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