Morphology change of multi-walled carbon nanotubes with SiC coating by electron irradiation

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Abstract. The different behaviour between morphology changes of multi-walled carbon nanotube (MWNT) and MWNT with SiC coating was investigated by electron irradiation. High resolution TEM images revealed that deformation of graphitic shells occurred in both MWNT and MWNT with SiC coating by electron irradiation. Electron irradiation began changing the outer and inner diameters of MWNT within 3 minutes exposure, whereas it began changing the diameters of MWNT with SiC coating after 10 minutes exposure. The outer diameter of MWNT increased up to irradiation time of 9 min and then decreased rapidly. On the other hand, the outer diameter of MWNT with SiC coating increased up to irradiation time of 50 min and then was almost saturated. These results lead that the morphology stability of MWNT against electron irradiation can be improved by coating with the SiC layer on MWNT.

1. Introduction
Since carbon nanotubes (CNTs) were discovered in 1991 [1], they are promising materials for nanometer scale electronic-devices, energy storage and nanocomposites because of their unique anisotropic structures and physical properties [2-4]. In particular, CNTs are also expected to be used in radiation environments such as nuclear plants and aerospace. Many researchers have reported electron or ion irradiation studies of CNTs [5-7]. Defects can be generated in CNTs and the morphology of CNTs can be changed by electron or ion irradiation [5-7]. Because these generated defects and changed morphology disrupt the ideal hexagonal network of graphitic shells, the mechanical, electric and optical properties of CNTs alter [8-10]. However, there are few reports about improving the morphological stability against electron and/or ion irradiation.

On the other hand, silicon carbide (SiC) is well known to have excellent morphological stability against electron and/or ion irradiation [11, 12]. So far, we have reported about the synthesis of multi-walled CNTs (MWNTs) coated with SiC layer by the heat treatment of MWNTs with Si powder in a vacuum [13, 14]. In this study, the different behaviour between morphology changes of MWNTs with and without SiC coating by electron irradiation was observed by transmission electron microscopy (TEM). The improvement method of morphological stability of CNT against electron irradiation was investigated.
2. Experimental procedure
MWNTs obtained from Furuuchi Chemistry Corporation (Tokyo, Japan) were used in this study. MWNTs with SiC coating were synthesized by heating MWNTs with Si powder (The Nilaco Corporation, Tokyo, Japan) at 1200 °C for 5h in a vacuum (~10⁻³ Pa). The details of fabrication process and characterization of MWNTs with SiC coating were described elsewhere [11, 12]. Electron beam of energy 200 keV was applied directly from TEM (Model JEM-2100F, JEOL Ltd., Tokyo, Japan) on as-received MWNTs and MWNTs with SiC coating samples at room temperature. The flux of electron beam was 4.2×10¹⁸ e/cm²/s which corresponding to a beam intensity of 0.67 A/cm². The incident electron beam covered an area of 9.6×10⁻¹⁰ cm². Images of the irradiated MWNTs and MWNTs with SiC coating were recorded by a CCD-camera connected with TEM.

![Figure 1. TEM images and the corresponding selected area electron diffraction patterns of as-received MWNT and MWNT with SiC coating before electron irradiation.](image1.png)

3. Results and discussion
Figure 1 shows the TEM images and the corresponding selected area electron diffraction patterns of as-received MWNT and MWNT with SiC coating before electron irradiation. TEM observation revealed that SiC layer was produced on the all regions of outer surface of CNT part in the MWNT with SiC coating. The SiC layer was polycrystalline. The thickness range of SiC layer was

![Figure 2. HR-TEM images of (a), (c), (e), (g) near outer surface and (b), (d), (f), (h) near inner tube of as-received MWNT before and after electron irradiation. Irradiation time: (a), (b) 0 min, (c), (d) 8 min, (e), (f) 20 min, (g), (h) 60 min.](image2.png)
approximately 20 to 40 nm. The as-received MWNT and MWNT with SiC coating irradiated in this study had almost the same outer diameter of CNT part, which were approximately 78 and 79 nm, respectively.

High resolution TEM (HR-TEM) images of the near outer surface and the near inner tube of as-received MWNT before and after electron irradiation are shown in figure 2. According to these TEM images, deformation of graphitic shells occurred by electron irradiation. Interstitial loops were induced between different basal planes. The number of interstitial loops increased with increasing electron irradiation time and seemed to be then saturated. It is well known that temperature effects are of particular importance about morphology change of CNTs [5-7, 15]. At room temperature, an accumulation of defects is observed up to a saturation density which depends on the electron energy and beam intensity [15]. Basal planes were also broken to small segments. The size of segments decreased with increasing irradiation time. It was often observed that different basal planes that were broken to small segments were cross-linked each other as shown in figure 2 (e) and (g). Bending of graphitic walls towards the interior hole near inner tube occurred. The curvature near inner tube by electron irradiation was larger than that near outer surface. The curvature angle near inner tube after 60 min irradiation was over 20° as shown in figure 2 (h).

Figure 3 shows HR-TEM images of the near outer surface and the near inner tube of MWNT with SiC coating before and after electron irradiation. The crystal structure and morphology of SiC layer did not change by electron irradiation because of its excellent morphological stability against electron irradiation. Deformation of graphitic shells in CNT part occurred and interstitial loops were induced as well as as-received MWNT. Basal planes were also broken to small segments. Both of deformation and bending curvature in CNT part of MWNT with SiC coating were smaller than those in as-received MWNT. In particular, the deformation of outer layers in CNT part was constricted because the outer surface in CNT part was bound with the SiC layer. Surprisingly, the bending of inner layers, which were not contacted with SiC layer directly, was also suppressed. The average size of segments of broken basal planes in the MWNT with SiC coating seemed to be larger compared to that in as-received MWNT.

Figure 4 shows the changed ratio of outer and inner diameters of CNT parts in as-received MWNT and MWNT with SiC coating by electron irradiation. Electron irradiation began changing the outer and inner diameters of as-received MWNT within 3 minutes irradiation, whereas it began changing the

![Figure 3. HR-TEM images of (a), (c), (e), (g) near outer surface and (b), (d), (f), (h) near inner tube of MWNT with SiC coating before and after electron irradiation. Irradiation time: (a), (b) 0 min, (c), (d) 8 min, (e), (f) 20 min, (g), (h) 140 min.](image-url)
diameters of MWNT with SiC coating after 10 minutes irradiation. In the as-received MWNT, the outer diameter increased up to the irradiation time of 9 min and then decreased rapidly. The outer diameter swelled at the beginning of electron irradiation because the lattice distance of CNT was widened due to the deformation of graphitic shells and the induction of interstitial loops between different basal planes. It has been reported that all C atoms of single-walled CNT could be ejected by the electron with higher accelerated energy than 139 keV [16]. The energy of electron beam applied in this study was 200 keV. Therefore, the electron irradiation could knock C atoms out from the surface of MWNT. The MWNT contracted rapidly after 9 min irradiation because the effect of knocking out was dominant compared to the widening effect of lattice distance. On the other hand, the outer diameter of MWNT with SiC coating increased up to the irradiation time of 50 min and then was almost saturated. At electron energy of 200 keV, every C atom is susceptible to ballistic ejection [16]. However, in the MWNT with SiC coating, SiC layer that had excellent morphological stability against electron irradiation was coated on the all regions of outer surface of MWNT. It might thereby become hard to knock C atoms out from the outer surface of CNT part. The lattice distance of CNT was widened due to the deformation and the induction of interstitial loops as well as as-received MWNT. These results lead that the outer diameter of MWNT with SiC coating increased with increasing the irradiation time. The changed ratio of outer diameter in MWNT with SiC coating was smaller than that in as-received MWNT.

The inner diameter of as-received MWNT increased rapidly, whereas that of MWNT with SiC coating decreased up to the irradiation time of 80 min and was then saturated. The inner diameters of as-received MWNT and MWNT with SiC coating were approximately 3 and 8 nm, respectively. Banhart et al reported that the stability of nanotubes with diameters below 1-2 nm decreases with decreasing diameter [17]. However, the inner diameters of MWNTs applied in this study were larger than 3 nm. The threshold energy needed to displace C atoms from nanotubes with inner diameters over 2 nm is comparable to that from flat graphite and almost constant against the inner diameter over 2 nm [17]. In spite of these results, the morphological change behaviour of inner diameter in as-received MWNT differed from that in MWNT with SiC coating. The reason is considered that in as-received MWNT it might be easier that C atoms were knocked out from both outer and inner surfaces compared to MWNT with SiC coating. These results lead that the morphological stability of MWNTs against electron irradiation may be improved by coating with SiC layer on the surface of MWNTs.

The changed ratio of wall thickness of CNT parts in as-received MWNT and MWNT with SiC coating is shown in figure 5. The changed ratio of as-received MWNT decreased monotonically. On the other hand, the changed ratio of MWNT with SiC coating increased and was almost saturated after 50 min irradiation. In the as-received MWNT, it might be easy that C atoms were ejected from both the outer and inner surfaces by electron irradiation. Therefore, the wall thickness of as-received MWNT decreased monotonically. On the other hand, it might be harder that C atoms were knocked
out from both surfaces of CNT part in the MWNT with SiC coating due to the existence of SiC coating that had excellent morphological stability against electron irradiation. TEM observation revealed that deformation of graphitic shells occurred and many interstitial loops were induced. Therefore, the lattice distance between basal planes increased with increasing the irradiation time. These results lead that the wall thickness of MWNT with SiC coating increased.

As mentioned above, coating with SiC layer on outer surface of MWNT can bring the facts that the deformation and bending of graphitic shells, the ejection of C atoms from both inner and outer surfaces of CNT part are restrained. Thus, the morphological stability of MWNTs against electron irradiation can be improved by coating with SiC layer.

4. Conclusion
The different behaviour between morphology changes of as-received MWNT and MWNT with SiC coating was investigated by electron irradiation. HR-TEM images revealed that the deformation and bending of graphitic shells occurred in both as-received MWNT and MWNT with SiC coating by electron irradiation. Both of deformation and bending curvature in CNT part of MWNT with SiC coating seemed to be smaller than those in as-received MWNT. Electron irradiation began changing the outer and inner diameters of as-received MWNT within 3 minutes exposure, whereas it began changing the diameters of MWNT with SiC coating after 10 minutes exposure. The outer diameter of as-received MWNT increased up to irradiation time of 9 min and then decreased rapidly. On the other hand, the outer diameter of MWNT with SiC coating increased up to irradiation time of 50 min and then was almost saturated. It might become hard to knock C atoms out from both inner and outer surfaces of CNT part by coating with SiC layer on MWNT. These results lead that the morphology stability of MWNT against electron irradiation can be improved by coating with the SiC layer on MWNT.

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