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Determination of the chiralities of isolated carbon nanotubes during superplastic elongation process

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The structural changes in an isolated carbon nanotube during superplastic elongation are studied using a *in situ* transmission electron microscopy equipped with a nanomanipulation system. Nanobeam electron diffraction reveals the chiral indices of the nanotube decrease by (1, 1) when tensile stress and electroresistive heating are simultaneously applied. The change in the chiral indices corresponds to the migration of just two pairs of defects in the nanotube walls. The experiment allows the dynamics of plastic deformation to be understood at the atomistic level, which will be beneficial for constructing advanced devices with utilization of nanotubes. © 2010 American Institute of Physics. [doi:10.1063/1.3473823]

Carbon nanotubes (CNTs) are currently one of the most attractive materials in nanotechnology. CNTs are believed to possess great potential for realizing miniature electronic devices by using them as wiring. Although various electronic devices utilizing CNTs have been studied recently,¹⁻³ it is essential to establish technologies not only to operate individual nanotubes but also to process them using actions such cutting, plumbing and bending, to give the CNTs the features required for installation in devices. Several fundamental papers concerning the machining processes of individual CNTs have been reported.^{4–8} Individual CNTs have undergone plastic deformation by simultaneously employing mechanical deformation and electroresistive heating, namely Joule heating, as the driving forces. In particular, Huang et al. has reported the superplastic deformation behavior of CNTs. According to their report, a CNT was elongated by more than 200% by simultaneously applying tensile stress and a small amount of Joule heating. It should be noted that such a deformation process would require a significant amount of reconstruction of the atomic arrangement in the individual CNT, which may affect the electronic properties of the deformed CNTs. The atomic arrangement of a CNT is defined by a pair of integers (n,m) called the chiral indices. According to theoretical⁹ and experimental¹⁰ research, CNTs show metallic behavior when n-m is a multiple of 3, otherwise they exhibit semiconducting behavior. Therefore, it is essential for realizing CNT-based electronic devices to investigate the atomistic-scale structural changes in CNTs caused by deformation processes.

Transmission electron microscopy (TEM) is an essential tool for the processing of single CNTs, because it allows the whole process to be closely monitored. However, direct visualization of chirality and defects is still difficult for most conventional TEMs because of the limit of spatial resolution ($\sim 0.2 \text{ nm}$) and the light weight of carbon atoms, although some specially-tuned TEMs containing aberration correctors have been developed.^{11,12} In this paper, we demonstrate that nanobeam electron diffraction (NBED) can be used as an

effective alternative to atomic-resolution imaging to investigate the structural changes of individual CNTs during deformation processes. NBED has been used previously for characterizing individual CNTs.^{13–17} It enables tiny structural changes that are difficult by conventional TEM imaging to be examined in a specific area of a CNT, even during deformation.

In the present study, isolated CNTs were deformed by using a manipulator (TEM- scanning tunneling microscope (STM) system, Nanofactory Ins.) assembled in a TEM (JEM-2500SE, JEOL, Japan) operated at an acceleration voltage of 90 kV. The manipulator contained an inertia-driven mobile stage, which allowed a needlelike probe to be operated three dimensionally at sub-nanometer accuracies and/or introduce a current as in a STM. In the present experiment, a tungsten needle was attached onto the mobile stage. CNTs were arranged protruding over the edge of a fixed stage made of a thin flake of silicon wafer coated with platinum. An isolated and straight CNT was chosen and bridged to the tip of the tungsten needle. The experimental setup is illustrated in Fig. 1(a). The CNT was preheated by inducing rather higher current than the following experiment to eliminate existing defects in the tube walls as well as organic contaminations on the surface. Figure 1(b) shows a TEM image of a CNT bundle forming a bridge between the tungsten tip and the substrate. An isolated double wall CNT (DWNT) was protruding approximately 300 nm from the end of bundle. It is noted that the DWNT was elastically bent by being pushed to keep close contact when the DWNT is fixed to the tip of needle, but no structural anomalies such as kinks, buckling and other topological changes due to the bending was not observed in the walls of DWNT. The tip of the protruding DWNT was fixed to the tungsten needle using electron irradiation-induced coalescence of small amount of fullerene molecules, which were deposited on the surface of the needle in advance (details of this process are reported in Ref. 18). In Fig. 1(b), the image contrast of the nanotube is blurred because of the slight vibration at room temperature. Though such blurring makes it difficult to visualize the lattice images as well as the detailed features of the DWNT, the chirality of the structure can be analyzed using NBED. Figure 1(c)

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FIG. 1. (a) Schematic showing the arrangement of experimental setup. An isolated CNT forms a bridge between the tip of the tungsten needle and platinum/silicon substrate. (b) TEM image of an isolated DWNT bridge. (c) NBED pattern taken from the circled region in (b). (d) and (e) show a TEM image and corresponding diffraction pattern of the same area after deformation.

shows an NBED pattern taken from an area of approximately 10 nm in the middle portion of the isolated DWNT as circled in Fig. 1(b). The chiral indices of DWNT were determined from the NBED pattern as follows. The diffraction intensities in Fig. 1(c) are represented by two sets of diffracted lines, which are called "layer-lines,"¹⁷ because of their discrete translation invariance along the tube axis. The diffraction intensity along a layer-line becomes diffuse and oscillates due to the finite width of the CNT. These pseudo-oscillation periods are directly linked to the diameter of the nanotube. For example, two types of layer-lines are highlighted by pairs of white and black arrows. The diameter of DWNT is estimated by measuring the oscillations along these layerlines, so it was decided that the diffraction intensities indicated by white and black arrows are from the outer and inner tubes of the DWNT, respectively. In addition, two types of periodicities can be seen in the diffraction intensity along the central layer-line indicated by a pair of black arrowheads. These correspond to the inverses of the mean diameter and interlayer distance. Furthermore, the peak maxima of each line are originated in the hk-type diffraction spots of a graphene sheet. It was recognized early on that the rotational angle of the line passing by the diffraction center and these maxima with respect to the tube axis are closely related to the chiral angle.¹⁹ From the structural information obtained from the NBED pattern as well as the tilt angle of the DWNT with respect to the incident electron beam, the chiral indices can be determined with the aid of simulation.¹⁷ In the case of the DWNT examined in the present experiment, the

initial chiral indices of the inner and outer tubes were determined to be (16, 11) and (21, 16), and the DWNT can be designated as (16, 11)@(21, 16).

The (16, 11)@(21, 16) DWNT was pulled by operating the mobile stage of the manipulator on the side of the needle. Current was simultaneously applied, providing the DWNT with the activation energy for undergoing plastic deformation. The circumferential current density was approximately 1.0 μ A/nm. The DWNT was then straightened as shown in Fig. 1(d) by the applied tension. The NBED pattern shown in Fig. 1(e) was recorded in the same area as the region on the unstretched DWNT circled in Fig. 1(b). Analysis of the NBED pattern determined the chiral indices to be (15, 10)@(20, 15). This means that the indices of both inner and outer tubes have decreased by (1, 1). This is the experimental result demonstrating that such a small change in chirality of a single CNT can be elucidated at the initial stage of plastic deformation. Such a change in chiral indices indicates that DWNT diameters have decreased by 0.13–0.14 nm, and that the DWNT has elongated by 6%. Structural information for the DWNT before and after deformation is summarized in Table I.

In the present experiment, the activation energy for structural change was supplied by applying current during the whole process of deformation. The amount of the energy supplied was very small; less than that required for the sublimation of carbon atoms that constitute the CNT.⁶ Hence it can be considered that the carbon atoms in the DWNT do not sublimate during deformation. Instead, the structural changes are thought to occur by switching of carbon bonds as theoretically suggested by Yakobson et al.²⁰ According to their model, in the first step of tensile deformation a couple of topological defects consisting of five- and seven-membered rings of carbon atoms (5-7 defects) initially arise in the middle of the graphitic wall. The 5-7 defect migrates to relax the stress by switching neighboring carbon bonds in an ordered process, which causes the CNT to elongate as well as altering the chiral index. The plastic deformation observed in the present study can be explained by the migration of just two five to seven defects. One defect migrates along the Burgers vector (1, 0) and the other along (0, 1). Although Yakobson et al. suggested that defect migration is preferred along the (0, 1) direction rather than the (1, 0), which means that chiral CNTs prefer to convert to zigzag-type CNTs, the present experiment indicates that both paths were followed. To understand the difference between the experimental results obtained in this study and theoretical calculation, several factors must be considered. One is the activation energy provided. Although a small amount of current was carefully applied for Joule heating, it may still be above that required for propagation in both the (1, 0) and (0, 1) directions. Some additional experimental results obtained exhibited a similar tendency. Figure 2 shows chiral maps showing modulation

TABLE I. Chiral indices of the DWNT determined in the present experiment and structural parameters calculated from the indices.

	Outer tube			Inner tube			Interlover
	Chiral indices	Diameter (nm)	Chiral angle (deg)	Chiral indices	Diameter (nm)	Chiral angle (deg)	distance (nm)
Initial	(21, 16)	2.52	25.6	(16, 11)	1.84	23.9	0.34
After deformation	(20, 15)	2.38	25.2	(15, 10)	1.71	23.4	0.335



FIG. 2. (Color) Chiral maps indicating modulation paths of chiral indices of a SWNT, DWNT, and TWNT in the plastic elongation process. The chiral indices of DWNT is also shown in Table I. In every CNTs, propagation of five to seven defects was suggested to take both dislocation directions with Burgers vectors b = (0, 1) and b = (0, -1).

paths of chiral indices of a SWNT, DWNT, and triple-wall CNT (TWNT) determined by NBED, where the DWNT is the same one examined in Fig. 1. We can see that every tubes has taken dislocation direction with Burgers vectors (1, 0)and (0, 1). The other factor to be considered is that DWNT was used in this experiment rather than a single walled CNT, which may change the situation. The inner and outer tubes of the initial DWNT fitted together with a 0.34 nm interlayer spacing due to Van der Waals interactions. This means that the deformation processes of both tubes must restrict each other. Indeed, the present experimental data indicated that both the inner and outer tubes decreased their chiral indices by same numbers: (1, 1). What interesting is that we observed similar behavior with the outermost and middle tubes in the TWNTs shown in Fig. 2. In the initial TWNT, outer and middle tube walls fitted together with spacing approximately 0.38 nm, while the middle and inner tube wall rather separated by >1.2 nm. After the large deformation, the outer and middle tubes showed similar numbers of changes in chiral indices, and chirality of the inner tubes likely had less correlation to the other two tubes. This fact suggests the existence of structural crosstalk between tube layers during the deformation process when the neighboring layers fit each other in multiple wall CNTs. Although only several deformation steps were examined in this study, additional experiments are underway to elucidate the dynamics further by examining the structural changes in a single CNT in continuous steps during the whole deformation process.

In summary, the small change in the chiral indices of an isolated CNT during the primary step of plastic deformation was investigated by means of NBED with the aid of a nanomanipulation system and a TEM. *In situ* experiments using the method presented in this paper will open doors to elucidating the dynamics of materials under various types of plastic deformation processes at the atomistic scale.

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