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Research Article

Carbon Nanofibers from Carbon Nanotubes by 1.2 keV Ar^+ Sputtering at Room Temperature

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Multi-walled carbon nanotubes (MWCNTs) were irradiated by 1.2 keV Ar ion beams for 15–60 min at room temperature with current density of 60 $\mu A/cm^2$. The morphology and microstructure are investigated by scanning electron microscopy, transmission electron microscopy and Raman spectroscopy. The results show that carbon nanofibers are achieved after 60 min ion irradiation and the formation of carbon nanofibers proceeds through four periods, carbon nanotubes—amorphous carbon nanowires—carbon nanoparticles along the tube axis—conical protrusions on the nanoparticles surface—carbon nanofibers from the conical protrusions.

1. Introduction

Since their discovery by Iijima in 1991 [1], carbon nanotubes (CNTs) have attracted considerable attention due to their high electrical conductivity, high aspect ratio "whisker-like" shape for optimum geometrical field enhancement, and remarkable thermal stability, which makes it possible to use CNTs as conduction wires and building blocks of a variety of nanoscale electronic and optoelectronic devices [2]. The realization of nanoscale devices and interconnections among building blocks with CNTs requires fully exploiting the CNTs potentials and effective methods to tailor CNTs with desired aims. Furthermore, since the devices are often used in an electromagnetic and/or high-energy particle radiation environment, the investigations on structural modification through irradiating CNTs are of great importance for providing insights into interactions between energetic particles and CNTs, for controllably fabricating multifunctional nanodevices, and for controllably protecting and producing radiation damages.

The interactions between high energy particles and CNTs have been extensively studied during the last several years [3–13]. Structural evolution of CNTs irradiated by in situ electron beam performed by Banhart et al. showed that basal planes of CNTs appeared as rupture, tilting, and bending under the irradiation [3, 4]. Other researchers found structural transformations from CNTs to carbon onions [5] or to diamond [6] by electron beam. Wei et al. tailored CNTs that could be tailored by using 30 or 50 keV Ga ion beam of different doses [7]. The transformation of CNTs proceeds from highly ordered pillbox-like nanocompartments and the formation of amorphous rod with hollow structure, without destroying the tubular shape of CNTs after the irradiation-induced amorphization to homogenous amorphous rods. CNTs irradiated by 4 MeV Cl ion beam have been investigated by Kim et al. [8]. They found that morphological transformation from CNTs to nanocompartments with bamboo-like structure inside the tubes was formed at the dose of 3×10^{16} ions/cm^2 and concluded that the nanocompartments with bamboo-like structure were originated from folding of the inner walls. In our previous work [9–11], the interaction between the CNTs and Si ion beam with the energy of 40 keV has been investigated. The result shows that with the increment of ion dose, the CNTs are transformed into semisolid amorphous carbon nanowire with hollow structure, solid amorphous carbon nanowire, and carbon nanowire junctions by the defects assisted the bridging of carbon nanowire. Therefore, CNTs should transform into other carbon nanostructure such as onion, diamond, and amorphous wire by high energy ion sputtering. However, the investigation of the interactions

between CNTs and ion beam with energy that ranged from several ten eV to several keV has not been attention.

Recently, the interaction between the carbon material and ion beam with energy of several keV has been studied, such as diamond [12], graphite and graphite paste [13, 14], glassy carbon [15, 16], and flexible plastic substrate [17–19]. These results show that the carbon nanofiber could form by ion sputtering and carbon nanofiber only grow on the tip of cone. Hence, it is believed that the carbon nanofiber could be formed by ion sputtering carbon nanotube with low energy of several keV. In this paper, carbon nanotubes are irradiated by Ar ion beam with energy of 1.2 keV at room temperature and the structural transformation is investigated.

2. Experimental Details

Multiwalled carbon nanotubes (MWCNTs), synthesized by chemical vapor deposition (CVD), were dispersed in alcohol by ultrasonic waves and dropped onto Si substrates as the samples. Then, the samples were placed in the chamber of Kaufman low energy gas ion source and were irradiated by Ar ion beam at room temperature with energy of 1.2 keV and current intensity of 60 μA/cm^2. The irradiation time was from 15 min to 60 min. The morphology evolution of samples before and after the low energy ion treatment was observed through Scanning electron microscopy (SEM, LEO 1530VP). The characteristic of structural changing of CNTs was investigated by transmission electron microscope (TEM, JEOL 2010F) operated at 200 kV and micro-Raman spectroscopy (Dilor LabRam-1B) at room temperature.

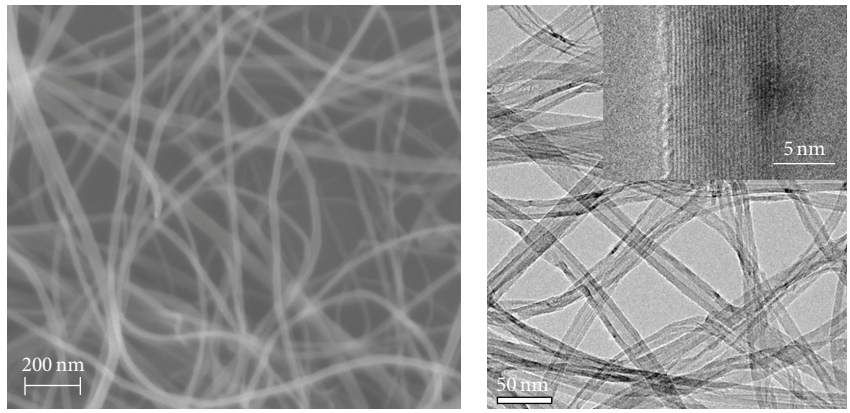
3. Results and Discussion

Figure 1 shows the SEM images and TEM images of the the as-grown CNTs and the inset is the high-resolution TEM (HRTEM) images. The diameters of as-grown CNTs are 18–35 nm. TEM and high-resolution TEM (HRTEM) images show that the as-grown CNTs are well-ordered graphitic sheets in [002] orientation (average plane spacing ~0.34 nm).

Figure 2 shows the SEM images of CNTs irradiated by 1.2 keV Ar ions for 15–60 min. The inset images in Figures 2(b) and 2(d) are the corresponding TEM images and high-resolution SEM images, respectively. After 15 min sputtering, the tube shapes of CNTs are almost intact and the diameters of CNTs are 4–35 nm, and only a few CNTs are broken into several parts along the tube axis; the inset TEM images of typical CNTs show that the CNTs are transformed into amorphous carbon nanowires, consistent with the results of our previous work [9–11]. After 30 min irradiation, the CNTs are separated into some particles with the size from 20–30 nm to 300–400 nm along the tube axis and the surfaces of particles are smooth with no conical protrusion. After 45 min sputtering, the all tube morphology of CNTs on the top layer of CNTs stacks is broken and the tube morphology of CNTs at the bottom of CNTs stacks is almost intact; some protrusions can be observed on the coarse aggregated nanoparticles surface. With 60 min sputtering, all CNTs are broken, and some nanofibers can be observed: the lengths of nanofibers are ranged from several ten nm to several μm. The high-resolution SEM images of typical nanofiber show that the nanofiber grows on the tip of protrusion.

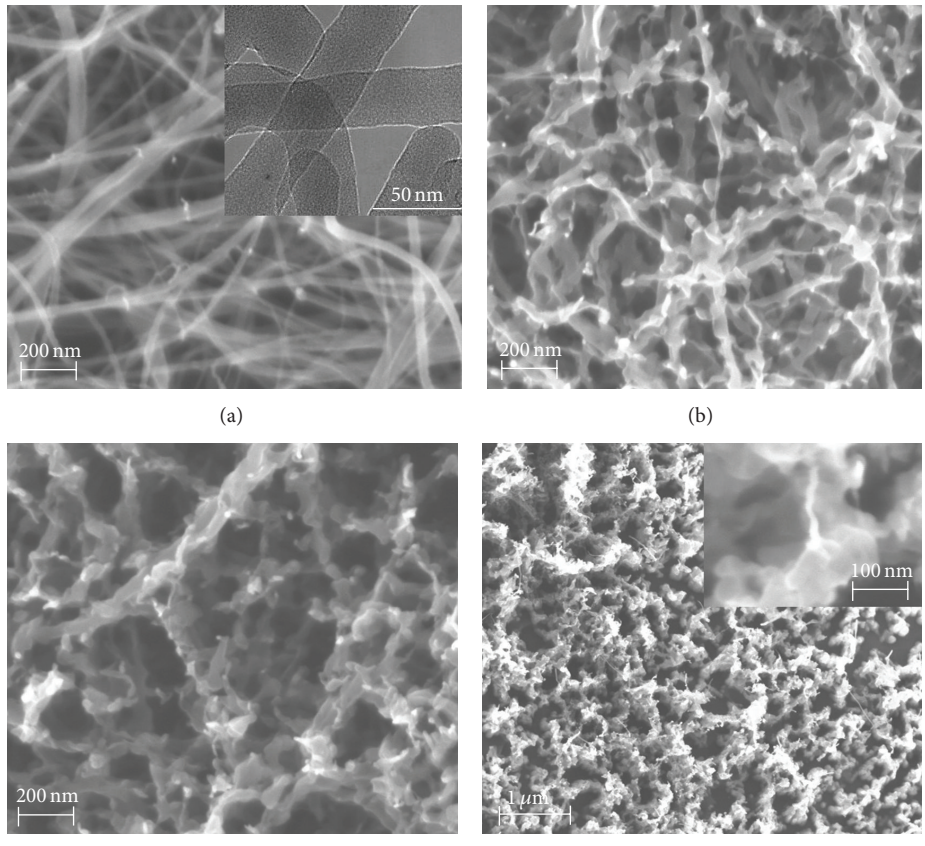
Typical micro-Raman spectra of the as-grown CNTs and CNTs by Ar ion irradiation from 15 min to 60 min are shown in Figure 3. There are two bands between 1000 and 2000 cm^{-1} corresponding to the typical Raman peaks of carbonaceous materials [20, 21]. The peak at 1580 cm^{-1} (G band) corresponds to an E_{2g} mode of graphite and the peak at 1330 cm^{-1} (D band) is associated with the vibration of carbon atoms with turbostratic carbon. The Raman spectrum is considered to depend on clustering of the sp^2 phase, bond disorder, presence of sp^2 rings or chains, and the sp^2/sp^3 ratio. The intensity ratio of the D to G band models (I_D/I_G) represents the amorphous phase content or the degree of crystallinity of the carbonaceous materials. With increasing the sputtering time, the I_D/I_G increases from 0.61 to 0.94 and the G position moves from 1580.9 to 1566.1 cm^{-1}, consistent with that of from carbon nanoparticle of graphene stacks to amorphous carbon provided by Ferrari and Robertson [21].

Based on the investigation of SEM, TEM, and Raman spectroscopy, it is speculated that the formation of carbon nanofiber has four processes: the CNTs are transformed into the amorphous carbon nanowire, the amorphous carbon nanowires are broken into some particles with smooth surface along the tube axis, some protrusions are formed on the particles, and the carbon nanofibers grow from the tip of the protrusions. It is known that the ion-induced surface morphology is accounted for two competitive effects, the roughening process and the smoothing process. The roughening process is caused by the different sputtering yield depending on the curvature of the surface. For a rough surface, the sputtering yield at the trough is higher than that on the crest, which should enlarge the amplitude rapidly. The smoothing process is caused by the thermal or ion-induced diffusion driven by surface energy minimization. In general, the ripple-like or periodic structure [22] is formed on solid surface by the off-normal ion beam irradiation. Habenicht et al. [23] have investigated the topography of graphite surface eroded by a 5 keV Xe^+ ion beam. The investigation result shows that the periodic ripple morphology evolved with the ion fluences of 5×10^{16} ions/cm^2 at the incident angle of 60°, and then large perturbations of the surface topography occurred for rising ion fluences to 2×10^{18} ions/cm^2; even the periodic structure was damaged by the larger perturbations of the surface topography at the ion fluences of 5×10^{18} ions/cm^2. Floro et al. [24] have investigated the formation of cones on graphite by 1 keV Ar^+ bombardment with current density of 2 mA/cm^2. They found that very fine whiskers or leaders became visible after 5 min of bombardment (the ion fluences was ~3.8×10^{18} ions/cm^2). The first 25 min of whisker formation were characterized by a rapid growth process in which whiskers grew to some critical length and radius. Subsequent to the initial growth spurt, length and radius increased slowly with time. The investigations of carbon material (such as glass amorphous carbon, graphite, and diamond) irradiated by Ar^+ with energy of several keV show that the cone or protrusions could form by several ten min sputtering [12–19]. Hence,



(a) (b)

Figure 1: Morphology and structure observations of the as-grown CNTs. (a) A typical SEM image; (b) typical TEM image and HRTEM image (the inset).



(a) (b)

(c) (d)

Figure 2: SEM images of CNTs irradiated by 1.2 keV Ar ions for 15–60 min. (a) 15 min; (b) 30 min; the inset was the typical TEM images of CNTs; (c) 45 min; (d) 60 min; the inset was the high-resolution SEM images.

it is believed that the formation of cone or conical carbon protrusions is contributed to the competitive effects of the roughening process and the smoothing process. This is the formation reason of carbon protrusions in our experiment. The investigations of carbon material irradiated by Ar^+ with energy of several keV also show that carbon nanofibers grow only on the tip of cone or protrusion, the cone or protrusion formation is a prerequisite for carbon nanofiber growth, and the redeposited massive carbon atoms diffuse toward the cone tips, resulting in carbon nanofiber formation. It is also the reason of carbon nanofiber growth in our experiment.

Therefore, the formation process of carbon nanofibers by Ar^+ sputtering CNTs could be speculated. At first, the CNTs are subjected to structural changes due to displacement

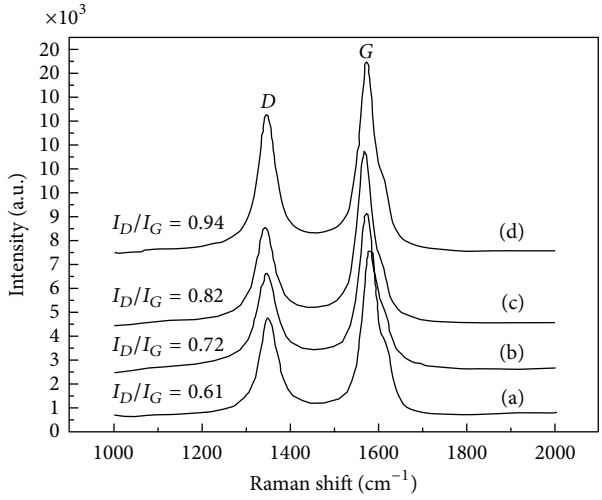


Figure 3: Typical micro-Raman spectra of the as-grown CNTs (a) and CNTs by Ar ion irradiation from 15 min to 60 min; (b) 15 min; (c) 30 min; (d) 60 min.

collisions and collision cascade effect, which generate large quantities of defects (vacancies and interstitials) on the tube walls and between the walls. The concentration of higher defects results in the increment of degree of disorder. With the further generation of defects, the CNTs could even collapse and form amorphous nanowires. Then, due to the different sputtering yield dependent on the curvature of the amorphous nanowire surface, carbon atom on some area are sputtered quickly, CNTs are broken, and some particles are formed along the tube axis. Subsequently, the protrusions are formed due to the competitive effects of the roughening process and the smoothing process. At last, the migration of mass redeposition atom toward the tip leads to the growth of carbon nanofibers on the protrusion.

4. Conclusions

In conclusion, the carbon nanotubes are irradiated by Ar ion beam with energy of 1.2 keV at room temperature with current density of 60 μA/cm^2 and the samples are investigated by SEM, TEM, and Raman spectroscopy. The structural evolution of CNTs by ion beam bombardment shows that the formation of carbon nanofibers proceeds through four periods: carbon nanotubes, amorphous carbon nanowires; carbon nanoparticles aligned along the tube axis; conical protrusions on the nanoparticles surface; and carbon nanofibers from the conical protrusions. The formation of carbon nanofibers is accounted for the competitive effects between the roughening process and the smoothing process.

Conflict of Interests

The authors declare that they have no conflict of interests regarding the publication of this paper.

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References

[1] S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, vol. 354, no. 6348, pp. 56–58, 1991.

[2] C. Dekker, "Carbon nanotubes as molecular quantum wires," *Physics Today*, vol. 52, no. 5, pp. 22–28, 1999.

[3] F. Banhart, "Irradiation effects in carbon nanostructures," *Reports on Progress in Physics*, vol. 62, no. 8, pp. 1181–1221, 1999.

[4] F. Banhart, "The formation of a connection between carbon nanotubes in an electron beam," *Nano Letters*, vol. 1, no. 6, pp. 329–332, 2001.

[5] F. Banhart, T. Füller, P. Redlich, and P. M. Ajayan, "The formation, annealing and self-compression of carbon onions under electron irradiation," *Chemical Physics Letters*, vol. 269, no. 3-4, pp. 349–355, 1997.

[6] B. Wei, J. Zhang, J. Liang, and D. Wu, "The mechanism of phase transformation from carbon nanotube to diamond," *Carbon*, vol. 36, no. 7-8, pp. 997–1001, 1998.

[7] B. Q. Wei, J. D'Arcy-Gall, P. M. Ajayan, and G. Ramanath, "Tailoring structure and electrical properties of carbon nanotubes using kilo-electron-volt ions," *Applied Physics Letters*, vol. 83, no. 17, pp. 3581–3583, 2003.

[8] H. M. Kim, H. S. Kim, S. K. Park, J. Joo, T. J. Lee, and C. J. Lee, "Morphological change of multiwalled carbon nanotubes through high-energy (MeV) ion irradiation," *Journal of Applied Physics*, vol. 97, no. 2, Article ID 026103, 2005.

[9] Z. Ni, Q. Li, J. Gong, D. Zhu, and Z. Zhu, "Structural change of carbon nanotubes produced by Si ion beam irradiation," *Nuclear Instruments and Methods in Physics Research B*, vol. 260, no. 2, pp. 542–546, 2007.

[10] Z. Ni, Q. Li, D. Zhu, and J. Gong, "Fabrication of carbon nanowire networks by Si ion beam irradiation," *Applied Physics Letters*, vol. 89, no. 5, Article ID 053107, 2006.

[11] Z. Ni, Q. Li, L. Yan, J. Gong, and D. Zhu, "Large-scale fabrication of carbon nanowire networks using kilo-electron-volt ion beam," *Diamond and Related Materials*, vol. 17, no. 3, pp. 365–371, 2008.

[12] Q. Li, S. Xue, Z. Li, J. Gong, and D. Zhu, "Carbon nanofibres from diamond film using Ar-ion bombardment and their field emission property," *Micro and Nano Letters*, vol. 4, no. 1, pp. 1–4, 2009.

[13] X. L. Liu, R. Z. Zhang, and Z. M. Zhang, "Near-field thermal radiation between hyperbolic metamaterials: graphite and carbon nanotubes," *Applied Physics Letters*, vol. 103, no. 21, Article ID 203102, 2013.

[14] Y. B. Chen, Y. Hu, M. X. Liu et al., "Chiral structure determination of aligned single-walled carbon nanotubes on graphite surface," *Nano Letters*, vol. 13, no. 11, pp. 5666–5671, 2013.

[15] M. Tanemura, T. Okita, J. Tanaka et al., "Room-temperature growth of carbon nanofibers induced by Ar^+-ion bombardment," *European Physical Journal D*, vol. 34, no. 1–3, pp. 283–286, 2005.

[16] M. Tanemura, T. Okita, H. Yamauchi, S. Tanemura, and R. Morishima, "Room-temperature growth of a carbon nanofiber

on the tip of conical carbon protrusions," *Applied Physics Letters*, vol. 84, no. 19, pp. 3831–3833, 2004.

[17] M. Tanemura, H. Hatano, M. Kitazawa et al., "Room-temperature growth of carbon nanofibers on plastic substrates," *Surface Science*, vol. 600, no. 18, pp. 3663–3667, 2006.

[18] T. T. Tan, H. S. Sim, S. P. Lau, H. Y. Yang, M. Tanemura, and J. Tanaka, "X-ray generation using carbon-nanofiber-based flexible field emitters," *Applied Physics Letters*, vol. 88, no. 10, Article ID 103105, 2006.

[19] H. S. Sim, S. P. Lau, H. Y. Yang, L. K. Ang, M. Tanemura, and K. Yamaguchi, "Reliable and flexible carbon-nanofiber-based all-plastic field emission devices," *Applied Physics Letters*, vol. 90, no. 14, Article ID 143103, 2007.

[20] F. Tuinstra and J. L. Koenig, "Raman spectrum of graphite," *The Journal of Chemical Physics*, vol. 53, no. 3, pp. 1126–1130, 1970.

[21] A. C. Ferrari and J. Robertson, "Interpretation of raman spectra of disordered and amorphous carbon," *Physical Review B*, vol. 61, no. 20, pp. 14095–14107, 2000.

[22] R. M. Bradley and J. M. Harper, "Theory of ripple topography induced by ion bombardment," *Journal of Vacuum Science and Technology A*, vol. 6, no. 4, pp. 2390–2239, 1988.

[23] S. Habenicht, W. Bolse, K. P. Lieb, K. Reimann, and U. Geyer, "Nanometer ripple formation and self-affine roughening of ion-beam-eroded graphite surfaces," *Physical Review B*, vol. 60, no. 4, pp. R2200–R2203, 1999.

[24] J. A. Floro, S. M. Rossnagel, and R. S. Robinson, "Ion-bombardment-induced whisker formation on graphite," *Journal of Vacuum Science and Technology A*, vol. 1, no. 3, pp. 1398–1402, 1983.