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Room-temperature growth of ion-induced carbon nanofibers: Effects of ion species

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Abstract

Graphite surfaces were bombarded with Ne^+, Ar^+ and Xe^+ ions at 450 eV–1 keV to induce the carbon nanofiber (CNF) growth at room temperature, and the dependence of size and numerical density of ion-induced CNFs on the ion species and ion energy was investigated in detail. The ion-sputtered surfaces were covered with densely distributed conical protrusions and aligned CNFs grew on the tips, except for the low-energy Xe^+-sputtered surfaces. Longer CNFs grew by lighter-mass-ion irradiation, and finer CNFs formed by heavier-mass-ion bombardment. In addition, the higher the ion energy, the longer the length of the ion-induced CNFs. Because the size and numerical density were controllable by the ion-irradiation parameters, ion-induced CNFs were believed to be quite promising for myriad of applications such as high-resolution scanning probe microscope cantilevers, bio-cell manipulators and field emission source operating at low voltage.

Keywords: Amorphous carbon; Nanofibers; Ion bombardment; Sputtering

1. Introduction

1-dimensional carbon materials, such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs), have attracted great attention in nanomaterials science and nanoelectronics technology since the discovery of CNTs by Iijima [1]. They have been conventionally synthesized from a gas phase at growth temperatures higher than 500 °C [2–6]. However, for a wider range of applications, especially for flexible devices using non-heat-tolerant plastics as substrates, synthesis at lower temperatures, ideally at room temperature, needs to be achieved.

In the previous papers, we have demonstrated that CNFs grew on carbon coated metals, semiconductors and plastics as well as on bulk carbon plates by the Ar^+ ion irradiation to the sample surfaces without any catalyst even at room temperature [7–9]. Those Ar^+-ion-induced CNFs can be used as flexible electron emission sources [10,11] and CNF probes for atomic force microscopes [12,13]. Since those device properties strongly depend on the CNF size in the practical applications, the establishment of the method to control their size is indispensable. In the present work, we tackled this important subject in terms of the ion species and ion energy.

2. Experimental procedure

Samples employed were polycrystalline graphite plates, 20 mm × 20 mm × 1 mm (thickness) in size (Toyo Tanso Co., Ltd.). In order to enhance the formation of conical structure, thin porous carbon film was deposited onto the samples prior to the ion irradiation [9–11]. For the growth of CNFs, the sample surfaces were irradiated with Ne^+, Ar^+ and Xe^+ ions at 45° from the normal to the surface using a Kaufman-type ion gun (Iontech. Inc. Ltd., model 3-1500-100FC). The oblique Ar^+ bombardment is known to be suitable for ion-induced CNF growth, compared with Ar^+ sputtering at normal incidence [14,15]. The diameter of the ion beam was 6 cm. Ion irradiations at 450 eV, 600 eV and 1 keV were done at room temperature for 60 min. The basal and working pressures of the CNF-growth chamber were 1.5×10^{-5} Pa and 2×10^{-2} Pa, respectively.

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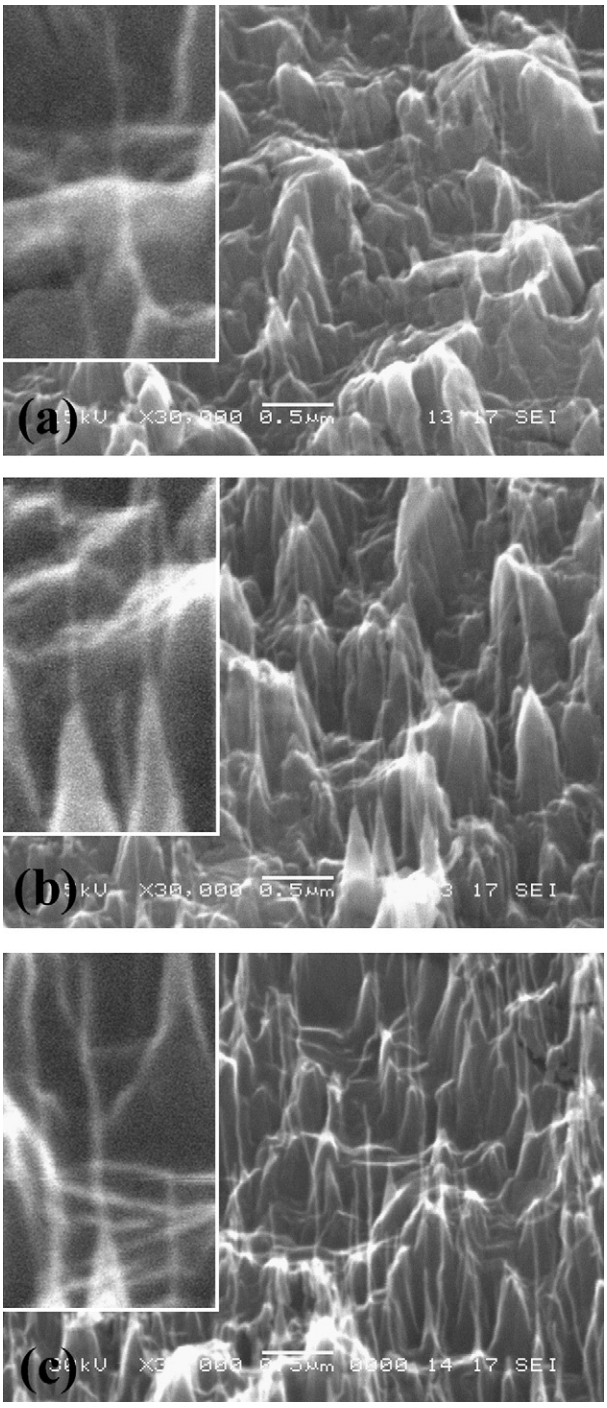

Fig. 1. SEM images of a graphite plate surface sputtered with Ar^+ ions at (a) 450 eV, (b) 600 eV, and (c) 1 keV. Insets: Magnified SEM images.

After sputtering, the topography of the sample surfaces and the crystalline structure of CNFs thus grown were carefully observed by scanning [SEM (JEOL; JEM-5600)] and transmission electron microscopes [TEM (JEOL; JEM-3010)], respectively. For TEM, the thin edges of graphite foils (80 μm in thickness; TYK Co., Ltd.) were ion-irradiated under the above-described conditions, and were directly mounted on a TEM sample holder without any post-treatment.

3. Results and discussion

Fig. 1(a) shows an SEM image of a graphite plate surface sputtered with Ar^+ ions at 450 eV, exhibiting that the whole surface was covered with conical protrusions and that aligned CNFs grew on the tips. No CNF grew without cone bases, and more than one CNF never grew on the respective cone tips. Both basal cones and CNFs pointed in the ion-beam direction. Those topographical features were similar to those observed previously for the Ar^+-sputtered bulk graphite and carbon films deposited onto the various kinds of substrates [7–9]. The averaged diameter, length and numerical density of CNFs were ~25 nm, ~0.5 μm and $\sim 1.5\times10^6$ mm^{-2}, respectively. Graphite surfaces irradiated with Ar^+ ions at 600 eV and at 1 keV were also characterized by the CNF-tipped cone structures [Fig. 1(b) and (c)]. CNFs increased in length and in numerical density with an increase in ion energy, while their average diameter was ~25 nm, almost independent of the ion energy. The sizes of CNFs thus formed by various sputtering conditions are tabulated in Table 1.

Fig. 2 shows SEM images of graphite plate surfaces sputtered with Ne^+ ions at 450 eV, 600 eV and 1 keV. Similar to the Ar^+-sputtered graphite, the surfaces were covered with CNF-tipped cones. For Ne^+ case also, both length and numerical density of the ion-induced CNFs increased with an increase in ion energy, while their average diameter was ~25 nm, almost independent of the ion energy. Compared with CNFs fabricated by Ar^+ sputtering, longer and larger amount CNFs formed by Ne^+ sputtering. The maximum length and numerical density, ~2.5 μm and $\sim 3.0\times10^6$ mm^{-2}, respectively, were obtained for the surface irradiated with Ne^+ ions at 1 keV (see also Table 1).

The surface morphology induced by sputtering, in general, depends on the sputter-ion species and energy. In case of metal thin films, for instance, sputtering with heavier ions at lower energy yields smoother surface [16]. It was also the case for the present graphite surfaces. For graphite surfaces sputtered with Xe^+ ions at 450 eV and 600 eV, the conical structure was not prominent and CNF was not observed [Fig. 3(a)]. A graphite surface sputtered with Xe^+ ions at 1 keV was featured by rippled structure and CNFs, as shown in Fig. 3(b). Compared with CNFs formed by Ar^+ and Ne^+ ions, Xe^+-induced CNFs were shorter in length (0.3 μm–0.6 μm) and finer. The average and the finest diameter observed were ~12 nm and ~8 nm,

Table 1
Comparison of size and numerical density of CNFs grown by Ne^+, Ar^+ and Xe^+ ions

Ion energy	Ion species	Ne^+	Ar^+	Xe^+
450 V	Length (μm)	1.0–1.2	0.5	Non-growth
	Average diameter (nm)	25	25	
	Density (10^6/mm^2)	3.1	1.7	
600 V	Length (μm)	1.2–1.9	0.55	Non-growth
	Average diameter (nm)	25	25	
	Density (10^6/mm^2)	3.0	2.3	
1 keV	Length (μm)	1.0–2.5	0.5–0.9	0.3–0.6
	Average diameter (nm)	25	25	12
	Density (10^6/mm^2)	3.2	3.3	2.0

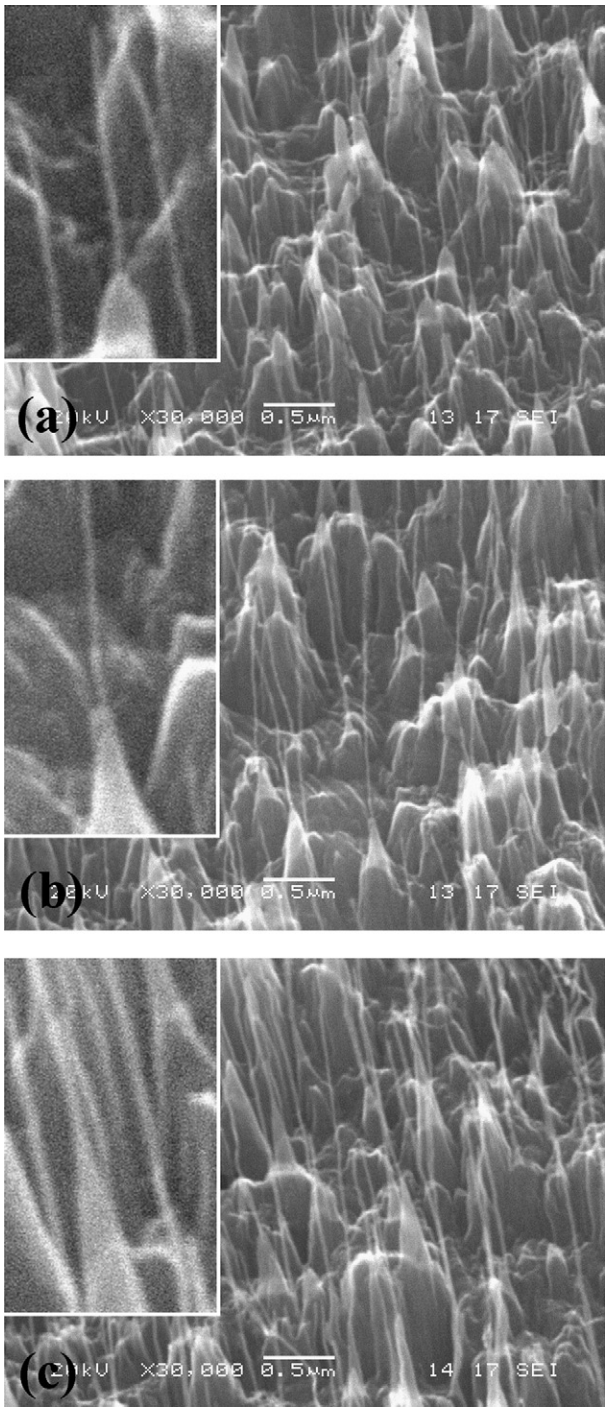

Fig. 2. SEM images of a graphite plate surface sputtered with Ne^+ ions at (a) 450 eV, (b) 600 eV, and (c) 1 keV. Insets: Magnified SEM images.

respectively. A careful inspection revealed that the CNFs grew from tips of very tiny cones, but not from the ground directly [inset of Fig. 3(b)].

A comparison of CNF sizes grown by Ne^+, Ar^+ and Xe^+ ions is tabulated in Table 1. In this table, it is clear that the CNF growth is enhanced by the lighter-mass ion bombardment and that the fine CNFs and the smoothly sputtered surfaces are attained by the heavy-mass ion bombardment. In addition, the higher the ion energy, the longer the length of the ion-induced CNFs. The longest CNF (~2.5 μm in length) and the finest CNF (~8 nm in diameter) grew under the Ne^+ bombardment at 1 keV and Xe^+ bombardment at 1 keV, respectively.

As was demonstrated previously [7,15], Ar^+-induced CNFs possessed no hollow structure and characterized by the amorphous-like nature. In addition, no clear boundary between a CNF and a conical tip was recognizable. This may be evidence that CNFs grew via diffusion of carbon atoms to the conical tips. These structural features were also confirmed for Ne^+- and Xe^+-induced CNFs. Hofmann et al. also demonstrated that CNTs synthesized by plasma-enhanced chemical vapor deposition at 120 °C were low in graphitization quality [17]. Thus, the amorphous structure may be a feature common to 1-D carbon nanomaterials grown at low temperatures.

The growth mechanism of ion-induced CNFs is thought to be as follows [12]: (i) Formation of conical protrusions, (ii) re-deposition of carbon atoms sputter-ejected from the surface onto the sidewall of the conical protrusions, and (iii) the surface diffusion of the re-deposited carbon atoms toward the tips during sputtering. The formation of the conical structures is known to be triggered by several factors including the initial surface roughness, grain orientations, crystalline defects and impurities (so-called "seeds") [18–20]. And the formation of conical protrusion is in general ascribed to the dependence of sputtering yield on the

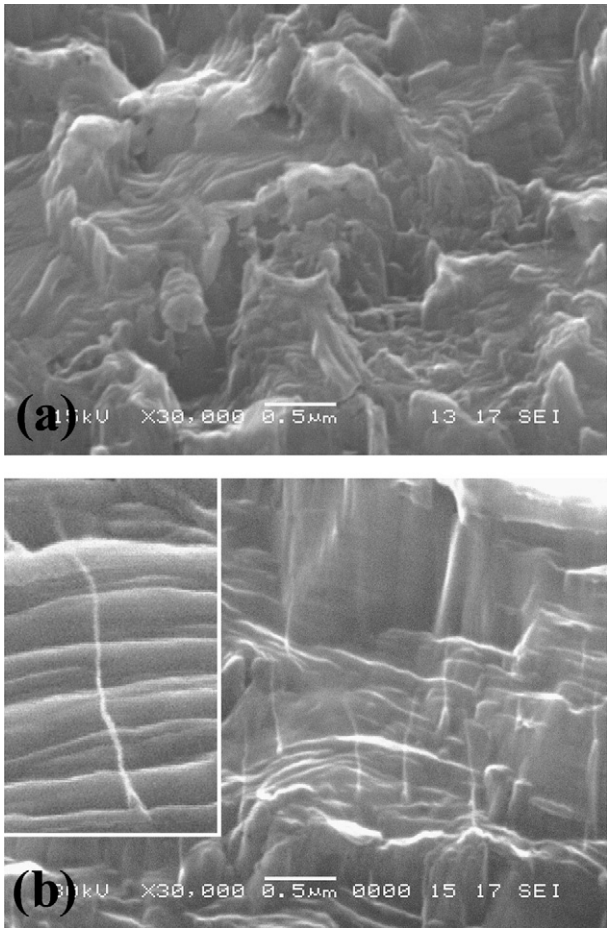

Fig. 3. SEM images of a graphite plate surface sputtered with Xe^+ ions at (a) 450 eV, and (b) 1 keV. Insets in (b): Magnified SEM image.

incidence-angle of ion-beam [18]. In the present study, since the samples employed were the polycrystalline graphite plates with the porous carbon pre-coating, the above-described factors except for impurities would have triggered the cone formation. (The impurities whose sputtering yield is lower than that of matrix are known to be responsible for the cone formation. Since carbon is, however, one of the materials of the lowest sputtering yield, the factor of the impurity will be ruled out.) In the growth mechanism of the ion-induced CNFs, the radiation-induced diffusion of carbon atoms at the surface region must play an important role in the CNF growth. Because Xe^+ ion is the largest in size and also the heaviest in mass among the inert gas ions, the ion-penetration depth is the shortest among the ion species tested here. In other words, defect rich region where the diffusion is enhanced is shallowest for Xe^+-ion irradiation, resulting in the smallest amount of carbon atoms to diffuse. This will be the reason why the CNF growth was suppressed and fine CNFs grew for Xe^+ case.

As demonstrated above, the size and numerical density were controllable by the ion-irradiation parameters. Thus, the application fields of ion-induced CNFs will be further extended: For example, lengthened CNFs are necessary for the SPM probes for the precise analysis of high aspect ratio samples and for bio-cell manipulation, while fine CNFs are indispensable for high-resolution SPM applications and for field emission sources. The former will be realized by Ne^+-induced CNFs and the later will be achieved by Xe^+-induced CNFs. Experiments along these lines are now being undertaken and the result will be treated in forthcoming papers.

4. Conclusion

The dependence of size and numerical density of ion-induced CNFs on the ion species and ion energy was investigated in detail for graphite surfaces irradiated with Ne^+, Ar^+ and Xe^+ ions at 450 eV–1 keV. The lighter-mass-ion bombardment yielded longer CNFs, and heavier-mass-ion bombardment generated finer CNFs. In addition, the higher the ion energy, the longer the length of the ion-induced CNFs. The reduction in size of the CNFs formed by Xe^+ ion bombardment was explained in terms of the suppressed diffusion of carbon atoms.

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