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Room-temperature growth of carbon nanofibers induced by Ar^+-ion bombardment

M. Tanemura[1,a], T. Okita[1], J. Tanaka[1], H. Yamauchi[1], L. Miao[1], S. Tanemura[1], and R. Morishima[2]

[1] Department of Environmental Technology, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan
[2] Toyota Motor Corporation, Higashifuji Technical Center 1200, Mishuku, Susono, Shizuoka 410-1193, Japan

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Abstract. Glassy carbon plates, a Ni mesh coated with a carbon film and mechanically polished graphite plates were Ar^+ ion-bombarded with and without a simultaneous Mo supply at room temperature. Conical protrusions were formed on the sputtered surfaces, and in some cases carbon nanofibers (CNFs) 0.2–10 μm in length and 10–50 nm in diameter grew on the tips. The growth of CNF-tipped-cones was optimized in terms of the ion-incidence angle and the rate-ratio of sputtering and seeding. Oblique sputtering was proved to be quite effective to grow the CNF-tipped-cones. Thus, the redeposited massive carbon atoms onto cones were thought to diffuse toward the cone tips, resulting in CNF formation. This growth mechanism was confirmed by transmission electron microscope (TEM) observation disclosing the boundary-less structure between conical bases and CNFs. TEM observation of CNF-tipped-cones also revealed no-hollow structure and an amorphous nature of CNFs. Since this sputtering method is a room-temperature process and quite straightforward, ion-induced CNFs promise to have myriad applications, such as field emission sources for flat panel displays.

PACS. 81.05.-t Specific materials: fabrication, treatment, testing and analysis – 79.20.Rf Atomic, molecular, and ion beam impact and interactions with surfaces – 61.82.Rx Nanocrystalline materials – 81.10.-h Methods of crystal growth; physics of crystal growth

1 Introduction

The synthesis of low-dimensional materials, such as carbon nanotubes (CNTs) [1] and carbon nanofibers (CNFs), is one of the current topics in materials science and microelectronics technology. The ion bombardment of solid surfaces sometimes entails the formation of nano- to micro-sized surface structures, taking such forms as ripples, pyramids, conical protrusions and whiskers, depending on the sputtering parameters [2,3]. Thus, ion bombardment is a fascinating fundamental principle for the fabrication of a desired type and size of structure on any solid substrate. In addition, during the ion bombardment, a simultaneous supply of so-called "seed" materials, which differ from the surface-constituent materials, is known to enhance the surface texturing. Based on these fundamentals, we have constructed a nanoprotrusion fabrication system consisting of a differentially pumped micro-beam ion gun and a seed-atom supply source, both of which operate under an ultra-high vacuum (UHV) ambient [4,5], and its scaled-up version for large substrates.

In the previous paper, we demonstrated that oblique Ar^+ ion bombardment with a simultaneous Mo supply on a glassy carbon surface induced the growth of conical protrusions 0.2–1 μm in the base-diameter, and either aligned or non-aligned CNFs about 50 nm in diameter and 0.2–10 μm in length grew thereon even at room temperature [5]. Since the temperature higher than 500 °C is required for the synthesis of CNFs and CNTs in the conventional growth methods such as arc discharge [1], laser ablation [6], chemical vapor deposition (CVD) [7–9], room-temperature growth of ion-induced CNFs will be promising to have myriad applications. In the preset work, the crystalline structure of CNFs, which has yet to be revealed, was investigated in detail. In addition, ion-induced CNF growth was optimized in terms of the rate ratio of sputtering and seeding, and ion-incidence angle.

2 Experimental

Two types of the experimental systems, *i.e.*, a UHV-system for the fundamental studies and a practical system for the large-scale fabrication, were employed. The UHV-system comprises a differentially pumped micro-beam ion

[a] e-mail: tanemura.masaki@nitech.ac.jp

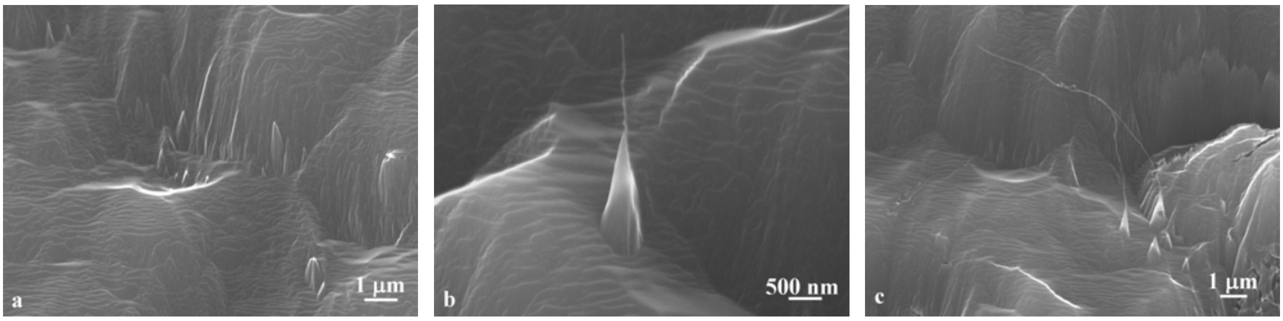


Fig. 1. SEM images of glassy carbon surfaces sputtered (a) at $S/D = 100$, and (b), (c) at $S/D = 125$ for 100 min in the UHV-system.

gun (JEOL; MIED) and an arc-plasma gun (ULVAC; APG-1000) [10] serving as a seeding source [4,5]. In brief, the ion gun and the arc-plasma gun, both of which operate under a UHV ambient, are located on the same plane, with their incidence angles at 55° from the normal to the surface. 3 keV Ar^+ ions, 380 μm in diameter and 88 to 264 $\mu A/cm^2$ in the ion current density, were used for sputtering. The corresponding sputtering rates (S) were 10 to 30 nm/min. As a seeding metal, Mo was employed. The deposition rate (D) of Mo was kept constant at 0.2 nm/min throughout the course of the experiments. The chamber was pumped down to $\sim 10^{-7}$ Pa, and the pressure remained at 10^{-6} Pa during the experiments. For the scaled-up system, a Kaufman-type ion gun (Ion Tech. Inc. Ltd., model MPS 3000 FC) is installed instead of the micro-beam ion gun. The beam diameter, energy of Ar^+ ions and sputtering rate employed were 6 cm, 1 keV and 25 nm/min, respectively. The pressures of achieved and during sputtering were 1.5×10^{-5} Pa and 2×10^{-2} Pa, respectively. Every experiment was carried out at room temperature.

Samples used were glassy carbon plates (Tokai Carbon Co., Ltd.), a Ni mesh (200 mesh; Nilaclo Co., Ltd.) coated with a carbon film and mechanically polished graphite plates (Tokai Carbon Co., Ltd.). After sputtering, the topography of the sample surfaces and the crystalline structure of CNFs thus grown were carefully observed by scanning electron microscope [SEM (JEOL; JEM-5600)] and TEM (JEOL; JEM-3010), respectively. For TEM, the CNF-grown Ni mesh was directly mounted on a sample holder without any post-treatment.

3 Results and discussion

Glassy carbon is known as the material on which ion-induced whisker hardly grows [11]. (Whiskers are rather larger in size than CNFs.) In fact, no ion-induced CNF was observed on it after sputtering at the rate-ratio $S/D < 125$. The sputtered surface was characterized by both the rippled grains and small cones with a sharp tip grown mainly at grain boundaries (Fig. 1a). On a surface sputtered at the rate-ratio $S/D = 125$, by contrast, several cones possessed CNFs of various lengths (0.2–5 μm) on the tips (Figs. 1b and 1c). The short CNFs tended to grow linearly in the cone-growth direction (that is, ion beam direction), whereas long ones bent. Very interestingly, the diameter of CNFs was almost identical (about 50 nm) despite a large difference in the CNF length, and more than one CNF never grew on their respective tips. Further increase in the S/D ratio led to a remarkable increase in the CNF length. Some CNFs reached as much as 10 μm in length at $S/D = 150$. Thus, ion-induced CNFs grew at room temperature under the optimum sputtering condition even on a glassy carbon surface.

CNFs grown on the glassy carbon surface, unfortunately, were not mountable onto a TEM sample stage. Alternatively, for the determination of the crystalline structure of CNFs, a carbon coated Ni mesh was ion-bombarded with seeding at the optimum S/D ratio determined above; $S/D = 125$. Similar to the glassy carbon surface, CNF-tipped-cones grew on the C-coated Ni surface. Figure 2 shows a TEM image of typical CNF-tipped-cones thus grown. In Figures 2a and 2b, no hollow structure was recognized in the CNF, identifying it as different from CNTs. The CNF was almost uniform in diameter in their growth direction ($\sim$10 nm) and had a round tip with radial curvature of $\sim$5 nm. Figures 2c and 2d show electron diffractions (EDs) from the conical base and the CNF, respectively. Both EDs displayed the spotty Debye rings corresponding to Mo (110) and Mo (200), indicating the polycrystalline nature of Mo. Less-transparent grains in Figures 2a and 2b may correspond to Mo. (Some of them are indicated by arrows in Fig. 2b.)

Another TEM example of CNF-tipped-cones is presented in Figure 3, also disclosing no hollow structure in the CNF. The tip region of the CNF produced an ED consisting of broad hallow rings (Fig. 3d), clearly proving the amorphous structure of the CNF. Hofmann et al. also demonstrated that CNTs synthesized by plasma-enhanced CVD at 120 °C were low in graphitization quality [12]. Thus, the amorphous structure may be a feature common to carbon nanomaterials grown at very low temperatures. Another important finding which should be stressed here is that no boundary between the CNFs and conical tips was recognizable (Figs. 2a, 2b, 3a and 3b). This point will be discussed latter.

Strangely, no diffraction spot originated from Mo was detected in Figure 3d. This may imply that ion-induced CNFs grow without seeding. In order to confirm this,

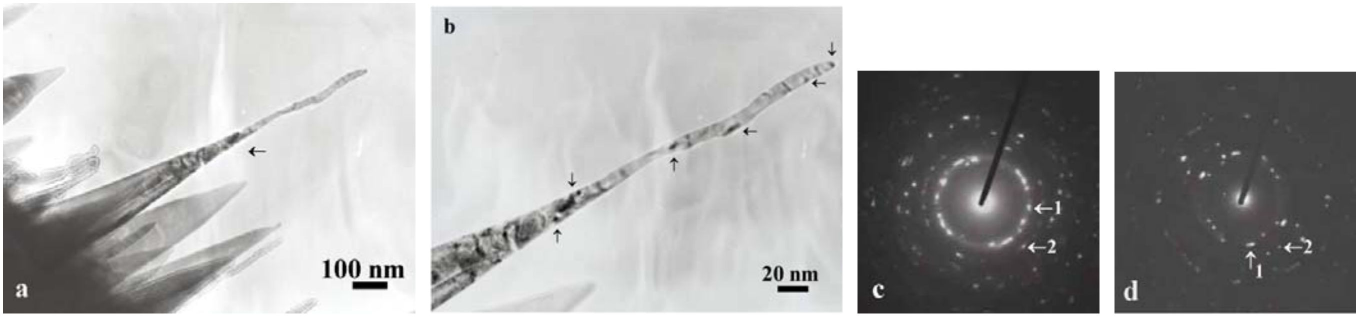
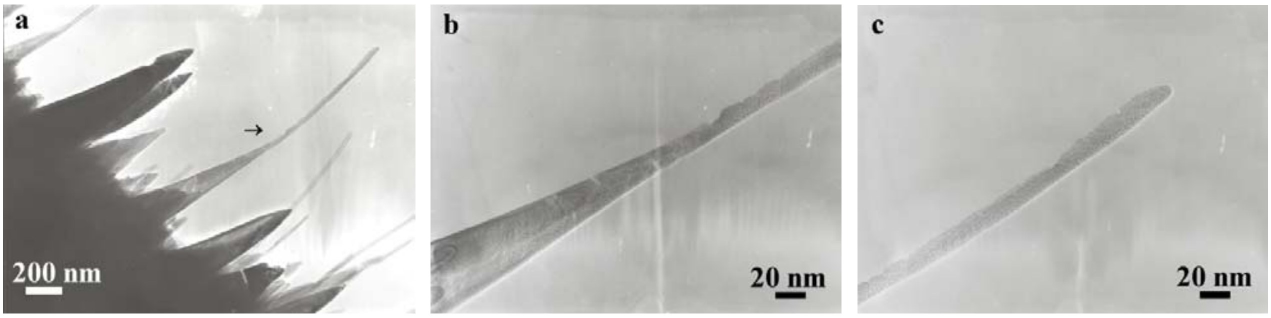


Fig. 2. (a) TEM image of typical CNF-tipped-cones grown under the condition of $S/D = 125$ in the UHV-system. The sputtering time: 100 min. (b) Enlarged image of the arrow-indicated cone in Figure 3a. Arrows in Figure 3b, see text. EDs from (c) the conical region and (d) the CNF tip of the arrow-indicated cone in Figure 3a. Arrow-1 and arrow-2 in Figures 3c and 3d indicate Mo(110) and Mo(200) Debye rings, respectively.



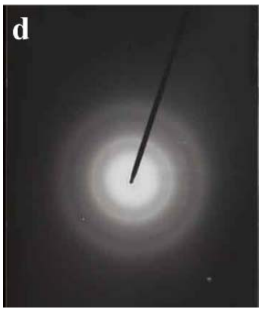


Fig. 3. (a) TEM image of typical CNF-tipped-cones grown under the condition of $S/D = 125$ in the UHV-system. The sputtering time: 100 min. Enlarged images of (b) a boundary region between the cone and the CNF and (c) the CNF tip of the arrow-indicated cone in Figure 4a. (d) ED from the CNF tip of the arrow-indicated cone in Figure 4a.

sputtering without seeding was carried out for graphite surfaces, on which sputter-induced carbon whiskers are known to be readily formed by Ar^+ sputtering at normal incidence [11,13,14]. (Carbon whiskers are rather larger in size than CNFs.) In addition, dependence of CNF growth on the ion-incidence angle (θ), which has never been revealed so far, was investigated.

Figure 4a shows a SEM image of an as-evacuated sample surface before sputtering, disclosing that the surface was almost flat with sparsely distributed small depressions. After sputtering at the normal incidence ($\theta = 0$), the sample surface was characterized by both the rippled structure and small protrusions (Fig. 4b). The small protrusions were less-defined in shape and no CNF grew thereon. It was also the case with a surface sputtered at $\theta = 15°$. On a surface sputtered at $\theta = 30°$, conical protrusions were observed and several tiny cones had single CNFs 0.2–4 μm in length and about 30 nm in diameter on the tips (Figs. 4c and 4d). Interestingly, CNFs fabricated by sputtering at $\theta = 30°$ seemed to be twisted. Figures 4e and 4f show the surface structure obtained with sputtering at $\theta = 45°$. The surface was featured with the CNF-tipped-cones. Compared with CNFs formed at $\theta = 30°$, those grown at $\theta = 45°$ were rather linear in shape and rather small in diameter (less than 20 nm).

CNFs grew only on the cone tips. This fact strongly suggests that cone formation is a prerequisite for CNF growth. As is well-known, oblique ion bombardment often enhances ion-induced cone formation more than does normal-incidence sputtering, and entails a large amount of redeposition of sputtered particles onto the side body of cones, especially at their acute angle side between the growth-direction of cones and the substrate plane [2,3]. Thus, the redeposited massive C atoms would diffuse toward the cone tips, resulting in CNF formation. This will be a reason why CNF growth occurred only under the oblique sputtering conditions in the present experiments. The boundary-less structure between the conical bases and CNFs observed by TEM (Figs. 2 and 3) will be a direct evidence of the above-described growth mechanism based on the diffusion of C atoms.

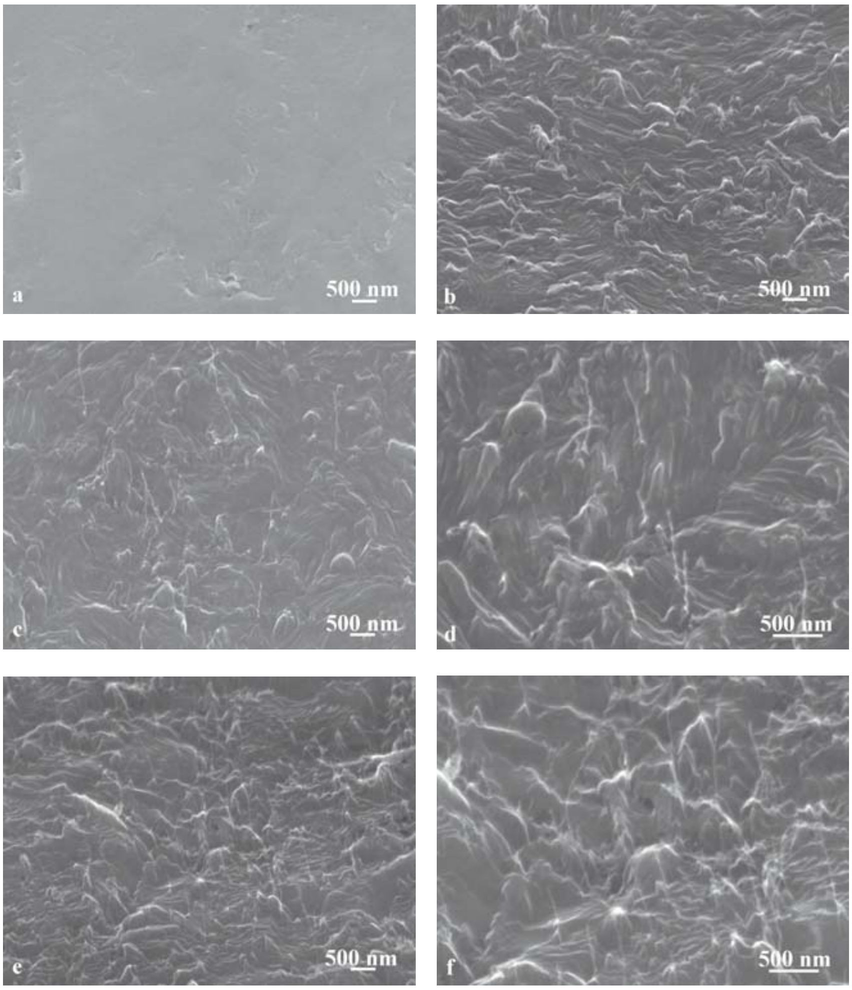


Fig. 4. SEM images of (a) an as-evacuated graphite surface, and surfaces Ar^+-sputtered without Mo seeding for 30 min (b) at $\theta = 0°$ (normal incidence), (c), (d) at $\theta = 30°$ and (e), (f) at $\theta = 45°$, in the scaled-up system. (d), (f) Highly magnified SEM images of (c) and (e), respectively.

4 Conclusion

The growth of sputter-induced CNF-tipped-cones was optimized in terms of the ion-incidence angle and the rate-ratio of sputtering and Mo seeding for various carbon samples. Oblique sputtering was proved to be quite effective to grow the CNF-tipped-cones. CNF formation was ascribed to the surface diffusion of the redeposited massive carbon atoms toward the cone tips. TEM observation of CNF-tipped-cones revealed no boundary between the conical bases and CNFs, supporting this growth mechanism. From the TEM observations, no-hollow structure and an amorphous nature of CNFs were also demonstrated.

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