Room-temperature growth of a carbon nanofiber on the tip of conical carbon protrusions

Masaki Tanemura,[a] T. Okita, H. Yamauchi, and S. Tanemura
*Department of Environmental Technology, Graduate School of Engineering, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan*

R. Morishima
*Toyota Motor Corporation, Higashifuji Technical Center, 1200, Mishuku, Susono,
Shizuoka, 410-1193, Japan*

Glassy carbon was Ar^+-ion bombarded with a simultaneous Mo supply under ultrahigh vacuum conditions using a microprotrusion fabrication system that consists of a differentially pumped ion gun and a seed-material supply source. Conical protrusions were formed by sputtering with a seed supply, and carbon nanofibers (CNFs) grew on the tips even at room temperature. The length of CNFs reached up to ~ 10 μm, and their diameter was almost uniform (50 nm) in the growth direction. The short CNFs aligned in the ion beam direction, whereas the long ones were non-aligned. The CNF growth on a glassy carbon surface was ascribed to the enhanced surface texturing and to the massive redeposition of C atoms onto cones, both of which are specific to the oblique ion bombardment: The former would lead to an increase in the number of possible nucleation sites for the CNF growth, and the C atoms arising from the latter process would migrate toward the conical tips, thus forming CNFs. © *2004 American Institute of Physics.*
[DOI: 10.1063/1.1745109]

Low-dimensional carbon materials, such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs), have attracted great attention in materials science and microelectronics technology since the discovery of CNTs by Iijima.[1] They have been synthesized by several methods, such as arc discharge,[1] laser ablation,[2] chemical vapor deposition,[3–5] and so on. In these methods, in general, temperatures higher than 500 °C are necessary for the synthesis of CNTs and CNFs. For a wider range of applications, however, synthesis at lower temperatures needs to be achieved.[6,7]

Ion irradiation to metals, semiconductors, and also carbon surfaces sometimes induces the formation of various types of surface structures, such as ripples, conical protrusions, rods, and whiskers, with dimensions from nano- to micrometers.[8,9] 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. Thus, ion bombardment with a simultaneous seed supply may have a great potential for fabricating a desired type and size of structure on any solid substrate.

Recently, we constructed a microprotrusion fabrication system [ultrahigh vacuum (UHV) operation] consisting of a differentially pumped ion gun and a seed-material supply source, whose etching and deposition rates are independently controllable,[10] and have launched the systematic experiments on surface modification by ion bombardment for a C–Mo system. In these experiments, we found that oblique Ar^+ ion bombardment with a simultaneous Mo supply induces room-temperature growth of linear and curved CNFs on a glassy

carbon surface, on which no CNF formation has been reported so far.[11] In this letter, we will deal with this morphological modification of a glassy carbon surface.

Our experimental system comprises an UHV-SEM (scanning electron microscope; JEOL; JAMP-10S), a differentially pumped micro-beam ion gun (JEOL; MIED), an arc-plasma gun (ULVAC; APG-1000) serving as a seeding source, and a sample heating stage.[10] The ion gun and the arc-plasma gun, both of which operate under an UHV ambient, are located on the same $X-Z$ plane, with their incidence angles at 55° from the normal to the surface (Fig. 1). 3 keV Ar^+ ions focused into a microbeam 380 μm in diameter with mean ion-current densities of 88–264 μA/cm^2, which correspond to the sputtering rate (S) at the ion-beam center of 10–30 nm/min, respectively, were used for sputtering. Oblique sputtering is often known to enhance the formation of surface roughness, especially for initially nonflat surfaces, compared with the sputtering at normal ion incidence.[9] Thus, the configuration of ion beam used here is quite suitable for the fabrication of microprotrusions. The simultaneous Mo
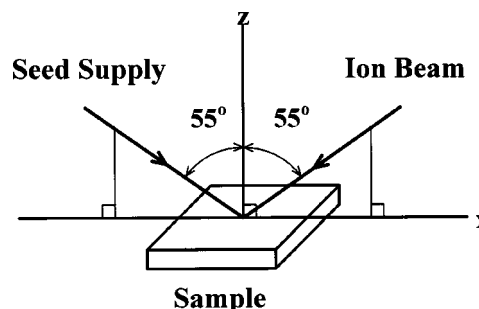

FIG. 1. Geometrical configuration of sample, ion beam, and seed supply source.

[a]Author to whom correspondence should be addressed; electronic mail: tanemura@system.nitech.ac.jp
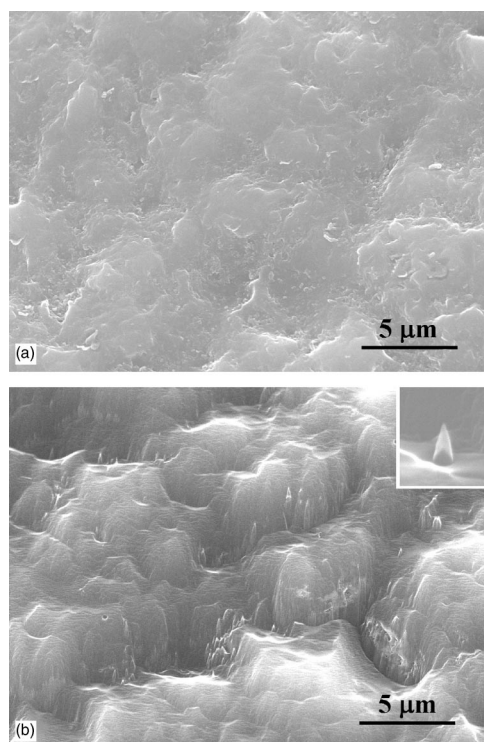
FIG. 2. SEM images of (a) an as-evacuated glassy carbon surface, and (b) a surface Ar$^+$-sputtered with Mo seeding at room temperature. Inset in (b): Enlarged SEM image of a cone. $S = 10$ nm/min, and $D = 0.2$ nm/min.

FIG. 3. Typical SEM images of the surface Ar$^+$-sputtered with Mo seeding at room temperature. $S = 25$ nm/min, and $D = 0.2$ nm/min. Arrowheads A and B in Fig. 3(a): see the text.

seeding was carried out using an arc-plasma gun whose particle evaporation mechanism is based on the pulse-triggered local vacuum-arc discharge generated just around the metal cathode edge (Mo in the present work).[12] The deposition rate (D) of the seeding metal, Mo, was kept constant at 0.2 nm/min throughout the course of the experiments. This D value was employed because it was quite suitable for the nanoprotrusion formation for Si in the previous experiments.[13] The chamber was pumped down to $\sim 10^{-7}$ Pa, and the pressure remained at 10^{-6} Pa during the experiments.

The target material used was a glassy carbon (Tokai Carbon Co., Ltd.). Ion irradiations with a simultaneous Mo supply were carried out at both room temperature and at 120 °C for 100 min. After the experiments, the topography of the sample surfaces was carefully observed by both an UHV-SEM and a conventional SEM (JEOL; JEM-5600).

Figure 2(a) shows a SEM image of an as-evacuated sample surface before sputtering. The sample surface was not flat; wavy grain-boundary like structure was recognizable. After sputtering at $S = 10$ nm/min with a simultaneous Mo seeding at room temperature, the sample surface was sputtered stepwise due to the difference in the sputtering yield of respective grains, as seen in Fig. 2(b). Thus, the sputtered surface resembled abrupt precipices at the grain boundaries, and small cones were sometimes observed there. A careful inspection of Fig. 2(b) revealed fine ripples on the respective grain surfaces. The ripples were aligned perpendicular to the incidence direction of the Ar$^+$ ion beam, as predicted by Bradley and Harper in their linear theory of ripple formation.[14] Room-temperature sputtering at $S = 20$ nm/min with seeding produced an increase in the number and size of grown cones with increasing S value. The formation of clusters or forests of cones was also observed
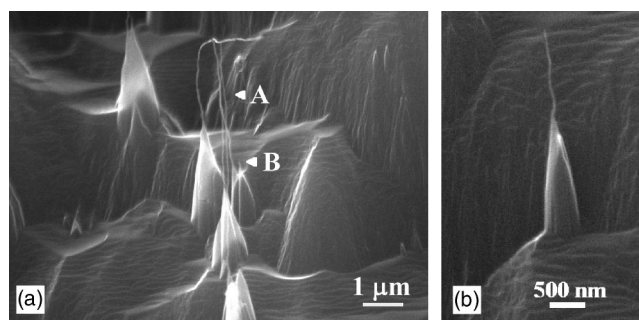
on the sputtered surface. The cones were ideally conical-shaped with a sharp tip and were pointed in the ion beam direction.

Cones formed under room-temperature sputtering at $S = 25$ nm/min with seeding were quite different in morphology from those fabricated at smaller S values (Fig. 3). Several cones had a CNF on their tip. Very interestingly, more than one CNF never grew on their respective tips. In addition, no CNF grew without cone bases. The CNFs ranged from 0.2 to 5 μm in length. The short CNFs tended to grow linearly in the cone-growth direction, whereas long ones bent. No relation between cone size and CNF length was found [compare the length of CNFs indicated by arrowheads A and B in Fig. 3(a)]. It should be noted that the diameter was almost uniform in their growth direction for respective CNFs and was almost identical (50 nm) despite a large difference in the CNF length. The yield of CNF-tipped cones was $\sim 20\%$ under this sputtering condition. Further increase in the population density of cones and in the yield of CNF-tipped cones was not observed for sputtering at a higher rate ($S = 30$ nm/min) with seeding at room temperature, although a remarkable increase in the CNF length was recognized. Some CNFs reached as much as 10 μm in length.

The ion-induced growth of carbon whiskers,[11,15,16] which are rather larger in size than CNFs, was studied by several groups using normal-incident ion beams before the discovery of CNTs, and the following features were discovered. (1) Whiskers exhibit an initial rapid growth process of leads or fine whiskers followed by a slower, diffusion-fed process. (2) All of the fine whiskers point in the incidence direction of the ion beam. (3) Whiskers never grow on diamond or glassy carbon surfaces. Since these investigations focused mainly on the surface modification of graphite surfaces by ion bombardment at rather high ion doses ($>10^{19}$ ions/cm^2), the fine whiskers, which correspond to the present CNFs, have been treated merely as a precursor to ion-induced C-whiskers. For this reason, their features have yet to be fully revealed. As disclosed in the present work, the oblique ion bombardment with a seed supply induced CNF growth even on a glassy carbon surface, and some CNFs were nonaligned in the ion beam direction.

CNFs grew only on the cone tips, as shown in Fig. 3. This fact strongly suggests that cone formation is a necessary condition for CNF growth and that the nucleation site for CNF growth is at the very top of the respective cones. As is well known, oblique ion bombardment often enhances ion-
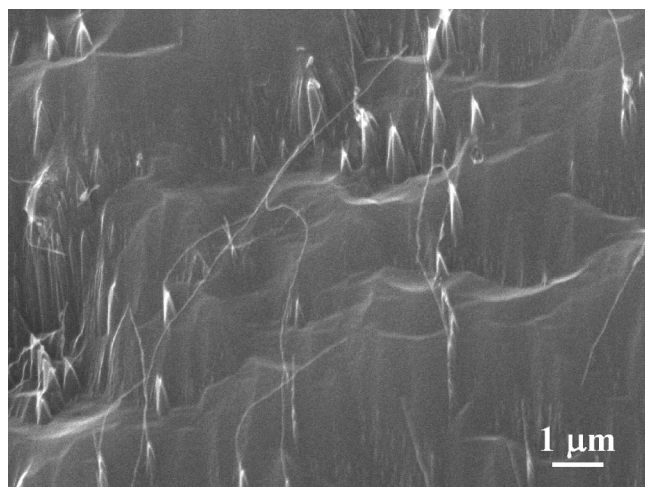
FIG. 4. SEM image of the surface Ar$^+$-sputtered with Mo seeding at 120 °C. $S = 25$ nm/min, and $D = 0.2$ nm/min.

induced surface texturing 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.[8,9] Thus, in the present experiments, the enhanced texturing would lead to an increase in the number of possible nucleation sites for CNF growth on the sputtered surface. Moreover, the redeposited massive C atoms would diffuse toward the cone tips, resulting in CNF formation even on the glassy carbon surface.

In order to enhance surface diffusion, an experiment was also done at 120 °C under one of the best sputtering conditions ($S = 25$ nm/min with a seeding) for CNF growth. The result is shown in Fig. 4. Compared with room-temperature sputtering, the number of cones increased dramatically, and the yield of CNF-tipped cones reached as high as 50%. Strangely, the diameter of CNFs was almost identical, independent of the sputtering temperature. It should be stressed that the length of CNFs grown at 120 °C was much longer than those achieved at room temperature, and that the growth direction of the CNFs was random. Such a dramatic increase in CNF length strongly suggests that surface diffusion plays a key role in sputter-induced CNF growth.

According to Van Vechten *et al.*, ion-induced CNF growth is ascribable to the attachment of migrated C atoms only onto the CNF tops pointing into the ion beam.[16] This is based on the hypothesis that the hydrogen termination of carbon surface arrests CNF growth. In their growth model, during their growth, CNFs are terminated with hydrogen from the residual gas in the sputtering chamber, except at their tops where the continuous bond breaking and ejection of hydrogen adatoms occur by sputtering, so that C atoms never attach onto the CNF walls. Consequently, CNFs should be aligned in the ion beam direction. In the present experiment, the hydrogen termination of CNFs is improbable, because the pressure during the sputtering was sufficiently low (10^{-6} Pa) thanks to the differential pumping of the ion gun. Thus, nonaligned CNF growth may be attributable to the nontermination of the CNF surface with hydrogen. If so, however, why are CNFs uniform in their diameter, indepen-

dent of their growth direction, and why does no branched-off growth occur? In addition, it is still unclear why CNFs grow only at the cone tops. In order to answer these questions and to elucidate the growth mechanism, the structural determination of an interface between a CNF and a conical base by transmission electron microscope may be important. Investigations into this line of questions are now under way. From the standpoint of the synthesis of low-dimensional carbon materials, the present sputtering method is quite simple and has a great potential for their massive synthesis at low temperature. Moreover, since CNFs grow only on the cone tips, they may be applicable for tips of scanning probe microscope.

In summary, oblique Ar$^+$ ion bombardment with a simultaneous Mo supply under UHV condition induces the room-temperature growth of cones with either aligned or nonaligned CNFs on a glassy carbon surface. CNFs were 0.2–10 μm in length and about 50 nm in diameter, and grew only on the cone tops. The yield of CNF-tipped cones and CNF length increased dramatically as sputtering temperature increased, but CNF diameter was almost identical independent of the sputtering temperature. Their growth was ascribed to the enhanced surface texturing and to the massive redeposition of C atoms onto cones, both of which are specific to oblique ion bombardment: The former would lead to an increase in the number of possible nucleation sites for CNF growth, and the C atoms arising from the latter process would migrate toward the conical tips, thus forming CNFs. The present sputtering method is quite promising for low-temperature synthesis of CNFs.

[1] S. Iijima, Nature (London) **354**, 56 (1991).
[2] A. Thess, P. Nikolaev, H. J. Dai, P. Petit, J. Robert, C. H. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Cocert, G. E. Scuseria, D. T. Tomanek, J. E. Fisher, and R. E. Smalley, Science **273**, 483 (1996).
[3] Z. W. Pan, S. S. Xie, B. H. Chang, C. Y. Wang, L. Lu, W. Liu, W. Y. Zhou, and W. Z. Li, Nature (London) **394**, 631 (1998).
[4] Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, and P. N. Provencio, Science **282**, 1105 (1998).
[5] M. Tanemura, K. Iwata, K. Takahashi, Y. Fujimoto, F. Okuyama, H. Sugie, and V. Filip, J. Appl. Phys. **90**, 1529 (2001).
[6] B. O. Boskovic, V. Stolojan, R. U. A. Khan, S. Haq, and S. R. P. Silva, Nature Mater. **1**, 165 (2002).
[7] S. Hofmann, C. Ducati, J. Robertson, and B. Kleinsorge, Appl. Phys. Lett. **83**, 135 (2003).
[8] *Ion Bombardment Modification of Surfaces*, edited by O. Auciello and R. Kelly (Elsevier, Tokyo, 1984).
[9] *Beam Effects, Surface Topography, and Depth Profiling in Surface Analysis*, edited by A. W. Czanderna, T. E. Madey, and C. J. Powell (Plenum, New York, 1998), Chap. 3.
[10] M. Tanemura, H. Yamauchi, Y. Yamane, T. Okita, and S. Tanemura, Nucl. Instrum. Methods Phys. Res. B **215**, 137 (2004).
[11] *Graphite Fibers and Filaments*, edited by M. S. Dresselhaus, G. Dresselhaus, K. Sugihara, I. L. Spain, and H. A. Goldberg (Springer, Berlin, 1988), Chap. 2.
[12] Y. Yamamoto, Y. Agawa, Y. Hara, S. Amano, A. Chayahara, Y. Horono, and K. Fujii, Proceedings of International Conference on Ion Implantation Technology, 1998, p. 1148.
[13] M. Tanemura, H. Yamauchi, Y. Yamane, T. Okita, and S. Tanemura (unpublished).
[14] R. M. Bradley and J. M. Harper, J. Vac. Sci. Technol. A **6**, 2390 (1988).
[15] J. A. Floro, S. M. Rossnagel, and R. S. Robinson, J. Vac. Sci. Technol. A **1**, 1398 (1983).
[16] J. A. Van Vechten, W. Solberg, P. E. Batson, J. J. Cuomo, and S. M. Rossnagel, J. Cryst. Growth **82**, 289 (1987).