APPLIED PHYSICS LETTERS **86**, 113107 (2005)

Field electron emission from sputter-induced carbon nanofibers grown at room temperature

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(Received 4 November 2004; accepted 27 January 2005; published online 9 March 2005)

Graphite, carbon-coated silicon, and carbon-coated nickel surfaces were bombarded with obliquely incident Ar^+ ions at room temperature. The sputtered surfaces were covered with conical protrusions, $\sim 2.5 \times 10^5$ mm^{-2} or higher in numerical density, and partially aligned single carbon nanofibers (CNFs), ~20 nm in diameter and 0.3-2 μm in length, grew on the tips. They were characterized by the amorphous nature and the boundaryless structure between the CNF and the conical base. The field electron emission measurements for the CNFs thus grown on the carbon-coated silicon substrate showed the threshold field of 1.8 V/μm with a current density of 1 μA/cm^2, and the field enhancement factor was estimated to be 1951 from the Fowler-Nordheim plot assuming the work function of 4.6 eV for graphite. The morphological structure of CNFs grown on conical bases was thought to be effective to reduce the screening effect due to sufficient distance between adjacent CNFs. Thus, the sputter-induced CNFs were concluded to be quite promising as a field electron emission source. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1884749]

Due to their high aspect ratios, small tip radii of curvature, and high chemical stability, carbon nanomaterials such as carbon nanotubes (CNTs)[1] and carbon nanofibers (CNFs) are expected to be very promising as field electron sources; for example, for flat-panel displays.[2,3] For the practical application of CNTs and CNFs to field electron sources, their synthesis on large substrates is indispensable. In the conventional synthesis methods, such as arc discharge,[1] laser ablation,[4] chemical vapor deposition (CVD),[5–7] growth temperatures higher than 500 °C are generally required. Such a high growth-temperature is, however, a serious drawback for commercialization: They should be grown at lower temperatures, ideally at room temperature. Thus, plasma-enhanced CVD at and below 120 °C has been recently attempted.[8,9]

In the previous paper, we demonstrated that oblique Ar^+-ion bombardment on a glassy carbon surface induced the growth of sparsely distributed conical protrusion, and partially aligned CNFs grew on some of the tips even at room temperature.[10] CNFs thus grown sparsely were about 50 nm in diameter and 0.2 to 10 μm in length. Very interestingly, no CNF grew without cone bases, and more than one CNF never grew on the respective cone tips. Since their formation is a room-temperature process, they will be very fascinating for emission-source applications, if they are synthesized with an enough numerical density. In addition, as is well known, in field electron emission (FEE), the excess numerical density of emitter-tips leads to the saturation in total emission current due to the so-called "screening effect" of adjacent tips.[11] The CNFs grown on conical bases will be also advantageous to prevent the excess of emission-site density, and hence diminish the screening effect. In the present study, we tackled the large-area synthesis of densely distributed sputter-induced CNFs on several kinds of substrates at room temperature, and their FEE properties were investigated.

Three kinds of samples were prepared in the present work. (i) A mechanically polished graphite plate, 20 mm $\times$ 20 mm in size (Toyotanso Co., Ltd.): Sputter-induced carbon whiskers, which are rather larger in size than CNFs, are known to be readily formed thereon by Ar^+ sputtering at normal incidence.[12–14] (ii) A C-coated Si (C/Si) plate, 10 mm $\times$ 10 mm in size: From a standpoint of the practical application of sputter-induced CNFs to flat-panel displays, they should be grown on any solid substrate at room temperature. Si is the most popular material used in the microelectronics. (iii) A C-coated Ni mesh for the determination of crystalline structure of CNFs by transmission electron microscope (TEM).

These samples were bombarded with Ar^+ ions using Kaufman-type ion gun (Iontech. Inc. Ltd., model MPS 3000 FC). Since the oblique Ar^+ bombardment is more suitable for ion-induced CNF growth than sputtering at normal incidence,[10] the incidence angle of the ion beam was set at 45° from the normal to the surface. The diameter and energy of the ion beam employed were 6 cm and 1 keV, respectively. Sputtering was done at room temperature for 60 min. The basal and working pressures were 1.5×10^{-5} Pa and 2×10^{-2} Pa, respectively.

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-covered Ni mesh was directly mounted on a sample holder without any post-treatment.

The FEE characteristics were measured for the applied voltage range of 0 to 3500 V at 5.0×10^{-4} Pa under a parallel-plate configuration with a polished metal anode of 10 mm in diameter. The gap distance between the anode and cathode (sample) was kept constant at 1 mm.

Figure 1(a) shows a SEM image of a sputtered graphite surface, revealing that the whole surface was covered with uniformly distributed cone clusters [see arrow A in Fig. 1(a)], which are composed of more than 10 large conical protru-

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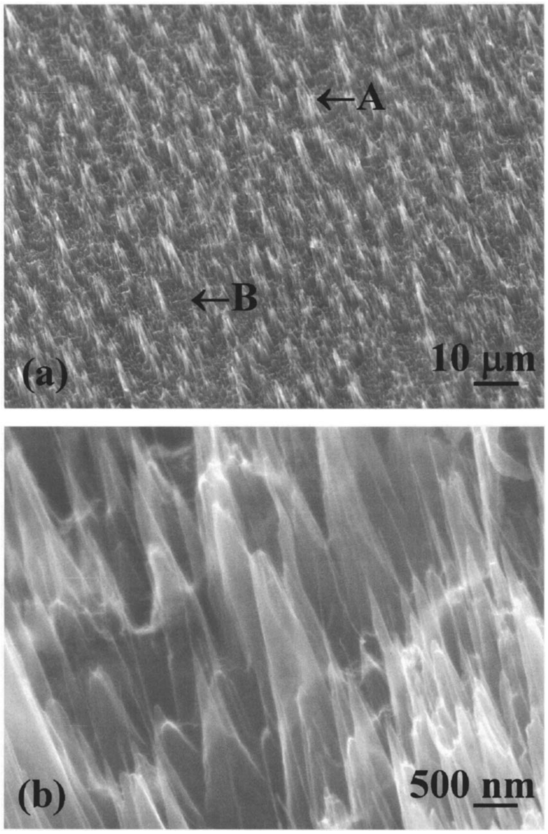

FIG. 1. (a) Overall view of a mechanically polished graphite surface after ion bombardment. (b) Highly magnified SEM image of one of the largest cone clusters. Arrows A and B in (a) indicate a typical cone-cluster and the inter-cone-cluster surface, respectively.

sions. The respective cluster-containing cones are larger than 500 nm in base diameter and several micrometers in length. The numerical density of cone clusters was estimated to be $2.5\times10^{4}\ \mathrm{mm}^{-2}$. A careful inspection of Fig. 1(a) disclosed that the sputtered surface between cone clusters [see arrow B in Fig. 1(a)] was also covered with densely distributed tiny cones, much smaller than 1 μm in length. These cluster-consisting and tiny cones were pointed in the ion-beam direction. It should be noted that CNFs aligned in the ion-incidence direction grew on almost all of the cones, as seen in Fig. 1(b). Similar to CNFs sparsely grown on a sputtered glassy carbon surface,[10] single CNFs grew on the respective cone tips, and no CNF formed without cone bases. CNFs ranged from 0.3 to 2 μm in length independently of the size of the cone base, whereas they were almost uniform in diameter (20 nm). Thus, the sputter-induced CNFs densely grown on a graphite surface were almost identical in dimension with those on glassy carbon.

Strangely, the apex angle of basal cones on which CNFs grew was about 15°. The formation of conical protrusion is, in principle, ascribed to the dependence of sputtering yield (S) on the incidence-angle of ion-beam (θ) measured from the normal to the surface. S increases with increasing θ up to a critical angle θ_m and then decreases rapidly with the further increase in θ (Fig. 2). This S-θ variation implies (see the inset of Fig. 2) that the etching rate of a plane that inclines at θ_m to the ion beam is the highest, resulting in the formation of conical protrusions with an apex angle of $2(\pi/2-\theta_m)$. Since θ_m is, in general, known to be 70°–75° for Ar^{+} sputtering at the keV range,[15] the apex angle of cones should be

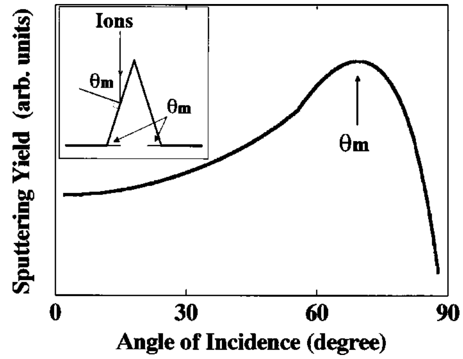

FIG. 2. Schematic representation of the dependence of sputtering yield (S) on the incidence angle of ion beam (θ). Inset: A model of cone formation based on the S-θ variation.

in the range of 30°–40°. The excess surface diffusion of C atoms on the sidewall of cones to the tip, which is the basic mechanism of CNF growth, may be a possible reason for the formation of cones with more acute apexes.

As described earlier, sputter-induced CNFs should be grown on any solid substrate at room temperature for the application to flat-panel displays. Figure 3(a) shows a SEM

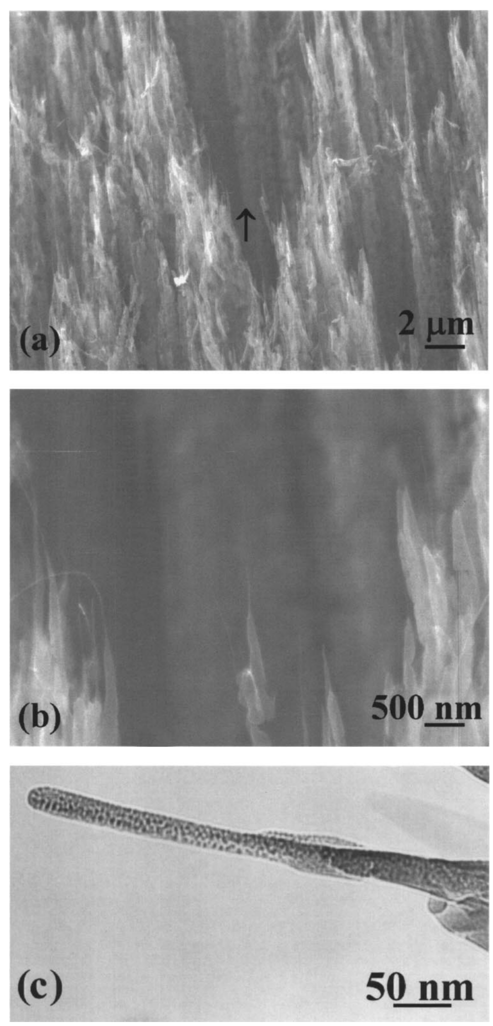

FIG. 3. Typical SEM images of a C-coated Si surface after sputtering, taken at (a) low and (b) high magnifications. (b) In order to highlight the shape of CNFs, the image was taken at a boundary region of microspatula-like structures [arrow indicated in (a)] where CNFs were less densely distributed. (c) TEM image of a typical CNF-tipped cone grown on a C-coated nickel mesh.

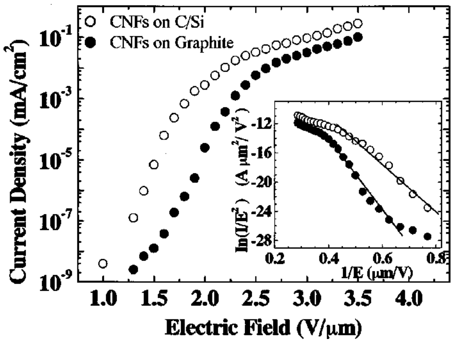

FIG. 4. *I-V* characteristics of CNFs grown on graphite and C/Si surfaces. Inset: Corresponding FN plot.

image of typical CNFs grown on a C/Si wafer. The whole sputtered surface was covered with microspatula-like structures consisting of needle-like projections. The numerical density of the microspatula-like structures on the C/Si surface was higher than that of cone clusters on a graphite surface. A close-up SEM image of the microspatula-like structures is presented in Fig. 3(b), revealing that partially aligned CNFs grew on the tip of respective needles. The grown CNFs were about 20 nm in diameter, agreeing with the dimension of CNFs grown on a graphite surface.

Figure 3(c) shows a TEM image of a typical CNF grown on a C-coated Ni mesh. It should be noted that no clear boundary between a CNF and a conical tip was recognizable. This may be evidence that CNFs grew via surface diffusion of C atoms to the conical tips. No hollow structure was observed in CNFs, identifying them as different from CNTs. CNFs had a round tip with the radial curvature of $\sim$10 nm. Figure 3(c) also disclosed the amorphous structure of CNFs. Hofmann *et al.* also demonstrated that CNTs synthesized by plasma-enhanced CVD at 120 °C were low in graphitization quality.[9] Thus, the amorphous structure may be a feature common to carbon nanomaterials grown at very low temperatures.

Figure 4 shows the FEE characteristics of CNFs grown on graphite and C/Si substrates. The corresponding Fowler-Nordheim (FN) plot is also shown in the inset of Fig. 4. The current density J was calculated using the anode area (0.79 cm^2). From Fig. 4, the turn-on fields of 1.7 and 1.4 V/μm, and the threshold fields of 2.2 and 1.8 V/μm were estimated for CNFs on graphite and C/Si, respectively. Here the turn-on field and threshold field were defined as the fields at which J reaches 1 nA/cm^2 and 1 μA/cm^2, respectively. These emission characteristics were comparable to those reported for CNTs,[16–19] and were much better than those obtained for CNFs grown at low temperatures.[20,21]

The field enhancement factors (β) calculated from the FN plot were 1310 and 1951 for CNFs on graphite and C/Si, respectively, assuming a work function of 4.6 eV for graphite. These β values were also in the reported range for CNTs. CNFs on C/Si show a better emission property and a higher β value, compared with CNFs on graphite (Fig. 4). This will be attributed to the higher numerical density of CNFs on C/Si, implying that the numerical density is not reached the regime wherein the screening effect dominates the emission property. The morphological structure of a CNF-tipped cone will be quite effective to reduce the screening effect due to a sufficient distance between adjacent CNFs. Thus, the sputter-induced CNFs grown at room temperature were concluded to be quite promising as a FEE source for a variety of applications.

In summary, we demonstrated a very simple method to grow CNFs on any substrates at room temperature using an obliquely incident Ar$^+$-ion irradiation, and the FEE properties of the CNFs thus grown were investigated. The sputtered surface was covered with densely distributed conical protrusions, and partially aligned single CNFs, about 20 nm in diameter and 0.3 to 2 μm in length, grew on the tips. CNFs were characterized by the amorphous nature and the boundaryless structure between the CNF and the conical base. For the further exploitation of this promising material as an FEE source, detailed measurements of the number density of the emitters will be necessary.

The authors express sincere thanks to Dr. M. Hirakawa, ULVAC Japan, Ltd., for his excellent assistance in the measurement of FEE properties. This work was partially supported by the Japan Society for the Promotion of Science (JSPS; Grants-in-Aid for Scientific Research B, No. 15360007), and a grant from the NITECH 21st Century COE Program "World Ceramics Center for Environmental Harmony."

[1] S. Iijima, Nature (London) **354**, 56 (1991).
[2] Y. Saito, K. Hamaguchi, S. Uemura, K. Uchida, Y. Tasaka, F. Ikazaki, M. Yumura, A. Kasuya, and Y. Nishina, Appl. Phys. A: Mater. Sci. Process. **67**, 95 (1998).
[3] W. B. Choi, D. S. Chung, J. H. Kang, H. Y. Kim, Y. W. Jin, I. T. Han, Y. H. Lee, J. E. Jung, N. S. Lee, G. S. Park, and J. M. Kim, Appl. Phys. Lett. **75**, 3129 (1999).
[4] 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).
[5] 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).
[6] 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).
[7] M. Tanemura, K. Iwata, K. Takahashi, Y. Fujimoto, F. Okuyama, H. Sugie, and V. Filip, J. Appl. Phys. **90**, 1529 (2001).
[8] B. O. Boskovic, V. Stolojan, R. U. A. Khan, S. Haq, and S. R. P. Silva, Nat. Mater. **1**, 165 (2002).
[9] S. Hofmann, C. Ducati, J. Robertson, and B. Kleinsorge, Appl. Phys. Lett. **83**, 135 (2003).
[10] M. Tanemura, T. Okita, H. Yamauchi, S. Tanemura, and R. Morishima, Appl. Phys. Lett. **84**, 3831 (2004).
[11] D. Nicolaescu, V. Filip, and F. Okuyama, J. Vac. Sci. Technol. A **15**, 2369 (1997).
[12] *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.
[13] J. A. Floro, S. M. Rossnagel, and R. S. Robinson, J. Vac. Sci. Technol. A **1**, 1498 (1983).
[14] J. A. Van Vechten, W. Solberg, P. E. Batson, J. J. Cuomo, and S. M. Rossnagel, J. Cryst. Growth **82**, 289 (1987).
[15] *Ion Bombardment Modification of Surfaces*, edited by O. Auciello and R. Kelly (Elsevier, Tokyo, 1984).
[16] M. Tanemura, V. Filip, K. Iwata, Y. Fujimoto, F. Okuyama, D. Nicolaescu, and H. Sugie, J. Vac. Sci. Technol. B **20**, 122 (2002).
[17] H. Murakami, M. Hirakawa, C. Tanaka, and H. Yamakawa, Appl. Phys. Lett. **76**, 1776 (2000).
[18] W. Zhu, C. Bower, O. Zhou, G. Kochanski, and S. Jin, Appl. Phys. Lett. **75**, 873 (1999).
[19] M. Chhowalla, C. Ducati, N. L. Rupesinghe, K. B. K. Teo, and G. A. J. Amaratunga, Appl. Phys. Lett. **79**, 2079 (2001).
[20] S. Hofmann, C. Ducati, B. Kleinsorge, and J. Robertson, Appl. Phys. Lett. **83**, 4661 (2001).
[21] R. C. Smith, J. D. Carey, C. H. P. Poa, D. C. Cox, and S. R. P. Silva, J. Appl. Phys. **95**, 3153 (2004).