Carbon nanofibers (CNFs) as well as carbon nanotubes (CNTs) exhibit unique electrical and thermal properties with high surface area and chemical inertness. An increasing number of potential applications have been reported, such as field emission electron sources, fuel cell electrodes and chemical sensors. For practical applications of CNTs/CNFs, a method of synthesis at low temperatures is essential to allow the direct deposition of CNTs/CNFs on various substrates involving materials with low melting points, and a large number of studies on the low-temperature (<400 °C) synthesis of CNTs/CNFs by plasma-enhanced chemical vapor deposition (PECVD) with various discharge systems have been reported, such as the RF discharge of CH₄, the DC discharge of C₂H₂/N₂H₃, the AC discharge of C₂H₂/N₂H₃/N₂/He, the microwave discharge of CH₄/H₂, and a combination of ECR C₂H₂ plasma with ICP N₂ plasma. In the previous report, we showed that the vertically aligned CNFs could be synthesized at temperatures as low as 90 °C using a low-temperature CO/Ar/O₂ DC plasma system while a more smooth carbon film was obtained in a CO/Ar/H₂ system. To our knowledge, few attempts at low-temperature PECVD of CNTs/CNFs using CO as the carbon source have been made. In general, the advantages of low-temperature plasma CVD using CO instead of hydrocarbons as the carbon source gas are as follows: (1) the deposition of amorphous carbon is suppressed even at low temperatures; (2) the CO disproportionation reaction, CO + CO → CO₂ + C, is thermodynamically favorable at low temperatures; (3) vibrationally excited molecules are formed which enhance reactions at low temperature, such as CO(v) + CO(w) → CO₂ + C; (4) C₂ radicals are known to be formed effectively through the reactions C + CO + M → C₂O + M and C + C₂O → C₂ + CO and can be precursors for the deposition of functional carbon materials. In our subsequent study on the importance of catalyst activities, we found that the CNF growth process is not controlled by the catalyst particle, and that, surprisingly, CNFs can be grown even if no catalyst is used in our CO/Ar/O₂ plasma system. From the viewpoint of process simplification and product purification, this catalyst-free synthesis is attractive. Therefore, in the present study, we tried to synthesize CNFs without any catalyst materials.
reported by some researchers in their catalytic-grown CNFs using carbon monoxide as the carbon source gas.\(^{20-22}\) In the rest of the fibers, those layers were not clearly seen because their directions were random relative to the fiber axis and they overlapped each other [Figs. 2(d) and 2(e)]. However, it can be said that the crystallinity of the carbon fibers was quite high in spite of the low growth temperature.

We have examined the Raman spectra of carbon deposits and it was found that there was no appreciable difference between the Raman spectra in the present study and previous one in which Fe catalyst was used:\(^{11}\) (1) the spectra for all the samples present two peaks of carbon material: the rather sharp G-band peak at approximately 1590 cm\(^{-1}\), which indicates the presence of crystalline graphene layers, and the broad D-band peak at 1350 cm\(^{-1}\), which indicates the existence of defective graphene layers; (2) the D-band decreased with increasing O\(_2\)/CO ratio while the G-band was almost unchanged. Therefore, from the Raman spectroscopic analysis, it is concluded that the deposition of amorphous carbon is selectively suppressed by the addition of O\(_2\).

Although it has not been clearly understood yet, we tried to infer a possible model for the present non-catalytic CNFs growth mechanism. At first, precursor species such as C, C\(_2\)O, and C\(_2\) appear mainly in the negative glow area, in which strong emission from C\(_2\) molecules are observed,\(^{11}\) and diffuse to the substrate. Then, the Volmer–Weber island growth occurs on the substrate. During this nucleation and growth process, the precursor species deposited on the substrate are etched by the oxygen selectively, and only the crystallized carbons on the nuclei remain.\(^{10,14,15}\) Moreover, because of the surface diffusion of the etchant species from the substrate and/or that of the precursor species to the substrate, the growth rate on the nucleus near the substrate is slower than at the tip area, which results in anisotropic growth from the nuclei. After some anisotropic growth of the nuclei, the local deposition of precursor species occurs around the tip area, which also enhances the anisotropic growth. This is because the sticking probability of the precursor species onto the CNF surface is so high\(^{23}\) that almost all of the precursor species are deposited around the tip area and rarely reach the lower fiber surface. In this anisotropic growth process, if the O\(_2\)/CO ratio is optimal, the diameter of CNFs does not increase as the fiber grows, and a fibrous structure can be achieved. However, if the O\(_2\)/CO ratio is slightly lower than its optimum value, the diameter of the CNFs increases as the fiber grows and the CNFs attach to adjacent fibers, which finally extinguishes the fibrous structure. On the other hand, if the O\(_2\)/CO ratio is slightly higher than its optimum value, the diameter of CNFs decreases as the fiber grows or nuclei cannot grow further. This optimum O\(_2\)/CO window is so narrow that this phenomenon would not have been observed until now.

In conclusion, we demonstrated the catalyst-free synthesis of carbon nanofibers by low-temperature DC-plasma-enhanced CVD using a CO/Ar/O\(_2\) system at substrate temperatures as low as 90 °C and presented a possible growth mechanism. The optimum O\(_2\)/CO ratio controls the...
anisotropic linear growth of carbon materials by etching the amorphous carbon selectively, allowing the formation of crystallized carbon nanofibers without catalyst materials. As is well known, high-temperature treatment is usually necessary for the activation of catalyst in the conventional CNFs growth method; our present results could lead to the development of a more viable process for the direct growth of CNFs onto low-temperature substrates like plastics, because no catalyst preparation step would be necessary.

**Acknowledgments** We thank Mr. Hori, Mr. Genseki, and Mr. Koki of the Center for Advanced Material Analysis in Tokyo Institute of Technology for assistance with the SEM and TEM observations.

1. A. V. Melechko, V. I. Merkulov, T. E. McKnight, M. A. Guillorn, K. L. Klein, D. H. Lowndes, and M. L. Simpson: *J. Appl. Phys.* **97** (2005) 041301.
2. M. Tanemura, J. Tanaka, K. Itoh, Y. Fujimoto, Y. Agawa, L. Miao, and S. Tanemura: *Appl. Phys. Lett.* **86** (2005) 113107.
3. M. A. Guillorn, A. V. Merkulov, D. K. Hensley, M. L. Simpson, and D. H. Lowndes: *Appl. Phys. Lett.* **81** (2002) 3660.
4. K. Lee, J. Zhang, H. Wang, and D. P. Wilkinson: *J. Appl. Electrochem.* **36** (2006) 507.
5. L. Li, J. Li, and C. M. Lukehart: *Sens. Actuators B* **130** (2008) 783.
6. B. O. Boskovic, V. Stolojan, R. U. A. Khan, S. Haq, and S. R. P. Silva: *Nat. Mater.* **1** (2002) 165.
7. S. Hofmann, C. Ducati, J. Robertson, and B. Kleinsorge: *Appl. Phys. Lett.* **83** (2003) 135.
8. S.-J. Kyung, Y.-H. Lee, C.-W. Kim, J.-H. Lee, and G.-Y. Yeom: *Carbon* **44** (2006) 1530.
9. K.-H. Liao and J.-M. Ting: *Diamond Relat. Mater.* **15** (2006) 1210.
10. T. M. Minea, S. Point, A. Granier, and M. Touzeau: *Appl. Phys. Lett.* **85** (2004) 1244.
11. S. Mori and M. Suzuki: *Diamond Relat. Mater.* **17** (2008) 999.
12. J. H. Han, S. H. Choi, T. Y. Lee, J. B. Yoo, C. Y. Park, T. W. Jeong, H. J. Kim, Y. J. Park, I. T. Han, J. N. Heo, C. S. Lee, J. H. Lee, and W. K. Yi: *Physica B* **323** (2002) 182.
13. E. Plonjes, P. Palm, G. B. Viswanathan, V. V. Subramaniam, I. V. Adamovich, W. R. Lempert, H. L. Fraser, and J. W. Rich: *Chem. Phys. Lett.* **352** (2002) 342.
14. Y. Muranaka, H. Yamashita, and H. Miyadera: *J. Appl. Phys.* **69** (1991) 8145.
15. J. Stiegler, T. Lang, M. Nyygard-Ferguson, Y. von Kaenel, and E. Blank: *Diamond Relat. Mater.* **5** (1996) 226.
16. M. Capitelli: *Nonequilibrium Vibrational Kinetics* (Springer, Berlin, 1986) p. 33.
17. S. Mori, H. Akatsuka, and M. Suzuki: *J. Nucl. Sci. Technol.* **38** (2001) 850.
18. Yu. Z. Ionikh, I. N. Kostyukevich, and N. V. Chernysheva: *Opt. Spectrosc.* **76** (1994) 361.
19. T. G. McCauley, D. M. Gruen, and A. R. Krauss: *Appl. Phys. Lett.* **73** (1998) 1646.
20. N. M. Rodriguez, A. Chambers, and R. T. K. Baker: *Langmuir* **11** (1995) 3862.
21. H. Murayama and U. Maeda: *Nature* **345** (1990) 791.
22. S.-H. Yoon, S. Lim, S.-h. Hong, W. Qiao, D. D. Whitehurst, I. Mochida, B. An, and K. Yokogawa: *Carbon* **43** (2005) 1828.
23. P. Traskelin, O. Saareoja, and K. Nordlund: *J. Nucl. Mater.* **375** (2008) 270.