

Fabrication of Two-Dimensional Carbon Nanostructures Using Radio-Frequency Plasma-Enhanced Chemical Vapor Deposition

Mineo Hiramatsu, Kenichi Shiji¹, Hiroshi Amano¹, Yoshinori Ando¹ and Masaru Hori²

Department of Electrical and Electronic Engineering, Meijo University
1-501 Shiogamaguchi, Tempaku, Nagoya 468-8502, Japan

Phone: +81-52-832-1151 E-mail: mnhmrt@ccmfs.meijo-u.ac.jp

¹Department of Materials Science and Engineering, Meijo University
1-501 Shiogamaguchi, Tempaku, Nagoya 468-8502, Japan

²Department of Quantum Engineering, Nagoya University
Furo-cho, Chikusa, Nagoya 464-8603, Japan

1. Introduction

Carbon nanostructures such as carbon nanotubes and nanocrystalline diamond films are of tremendous interest from both a fundamental and an applied prospective. From the point of view of their wide applications, it is desirable to control properties such as the size, shape, and growth direction of surface structures during the growth. Carbon films with different structures, morphologies, and electrical properties can now be fabricated by several different techniques. Recently, fabrication of two-dimensional carbon nanostructures (carbon nanowalls) was reported [1]. The large surface area of carbon nanowall film may provide us various new applications.

In the case of films fabricated by the plasma-enhanced chemical vapor deposition (PECVD) technique, surface morphology can be effectively controlled not only by optimizing the substrate temperature and bias, but also by the inclusion of specific reactive species as appropriate to the film growth and nucleation. Previously, we have demonstrated the formation of diamond crystals using a unique PECVD system that consists of a parallel-plate radio-frequency (rf) capacitively coupled plasma (CCP) assisted by a hydrogen (H) radical source [2,3]. In the present work, carbon nanowalls were successfully fabricated on silicon (Si) substrates without catalyst, using rf PECVD assisted by H radical injection.

2. Experiments

The experimental setup used in this study has been described in detail elsewhere [2,3]. Figure 1 shows a schematic diagram of rf PECVD assisted by a remote radical source, which consists of a parallel-plate rf (13.56 MHz) CCP region and a remote radical source which uses an inductively coupled H₂ plasma (H₂ ICP). The main reaction chamber was equipped with circular parallel-plate electrodes separated by 5 cm, with the rf voltage applied to the upper electrode while the lower one was grounded. Either C₂F₆ or CH₄ as a carbon source gas was introduced into the rf CCP region. H₂ was fed through a quartz tube of 26 mm inner diameter and 20 cm in length. A 5-turn rf coil, which was made of 1/4 inch copper tubing and cooled with flowing water, was mounted on the quartz tube. The rf coil was connected to the rf power generator operating at 13.56 MHz via an impedance matching network. The partial

pressures of C₂F₆ (or CH₄) and H₂ were 20 and 80 mTorr, respectively, and the total gas pressure was 100 mTorr. The rf powers of CCP and ICP were 100 and 400 W, respectively, and the substrate temperature was 500 °C. Substrates used in the growth experiments were 1 cm x 1 cm mirror-polished Si (100) without any catalyst.

3. Results and Discussion

Figure 2 shows the scanning electron microscopy (SEM) image for the carbon nanowalls grown using CH₄ source for 2 hours. The carbon nanowalls grown using CH₄ was rather wrinkled and very thin, and their thickness was less than 10 nm.

Figures 3(a) and 3(b) show the typical SEM images for the carbon nanowalls grown using C₂F₆ source for 2 hours. Two-dimensional carbon sheets were grown vertically on the Si substrate. The thickness of these carbon nanowalls grown was 10-30 nm, and their height was about 300 nm. The aggregation of carbon nanowalls would be useful as templates for the fabrication of other types of nanostructured materials.

The field electron emission characteristics of the films fabricated were measured in a vacuum of 10⁻⁶ Torr. Figure 4 shows the characteristic curve of emission current as a function of the applied field strength for the carbon nanowall film fabricated using C₂F₆ source. The applied field strength denotes the applied voltage divided by the anode-sample distance. The onset field strength of electron emission for the carbon nanowall film was about 5 V/μm. Although the electric field strength needed for the nanowall film was higher than is needed for commonly produced carbon nanotube or nanodiamond films, the field emission properties might be improved by optimizing the growth conditions.

In the case of the deposition without H₂ ICP, on the other hand, carbon nanowalls were not fabricated. The mechanism responsible for the growth of carbon nanowalls is currently not understood. However, H radicals played an important role for forming carbon nanowalls. This implies that radical injection technique enables us to fabricate novel nanometer-scaled functional materials.

4. Conclusion

Carbon nanowalls were successfully fabricated on Si

substrate without catalyst, by using rf-CCP employing C_2F_6 or CH_4 assisted by H radical injection. In the case using CH_4 source, carbon nanowalls were wrinkled and thin (<10nm). In the case using C_2F_6 source, carbon nanowalls were grown vertically on the Si substrate. The thickness of these carbon nanowalls was 10-30 nm, and their height was about 300 nm. In addition, field electron emission was also observed for the carbon nanowall film. The aggregation of carbon nanowalls would be useful as templates for the fabrication of other types of nanostructured materials. In the case of the deposition without H radical injection, on the other hand, carbon nanowalls were not fabricated.

Acknowledgment

This work was supported by 21st century COE program, Nano Factory.

References

- [1] Y.-H. Wu, P.-W. Qiao, T.-C. Chong, Z.-X. Shen, Adv. Mater. 14, 64 (2002).
- [2] M. Ikeda, H. Ito, M. Hiramatsu, M. Hori, T. Goto, Jpn. J. Apl. Phys. 34, 2484 (1995).
- [3] M. Hiramatsu, M. Inayoshi, K. Yamada, E. Mizuno, M. Nawata, M. Ikeda, M. Hori, T. Goto, Rev. Sci. Instrum. 67, 2360 (1996).

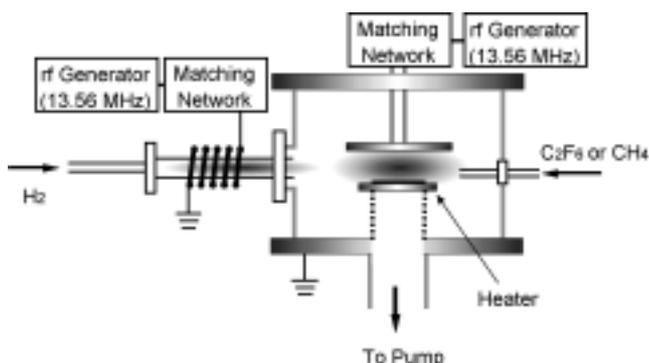


Fig.1. Experimental setup for the formation of carbon nanowalls.

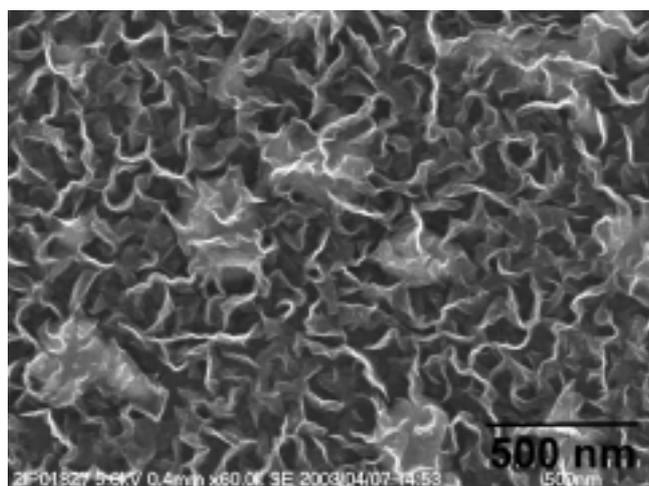


Fig.2. Typical SEM image for the carbon nanowalls fabricated using CH_4 rf-CCP assisted by H radical injection.

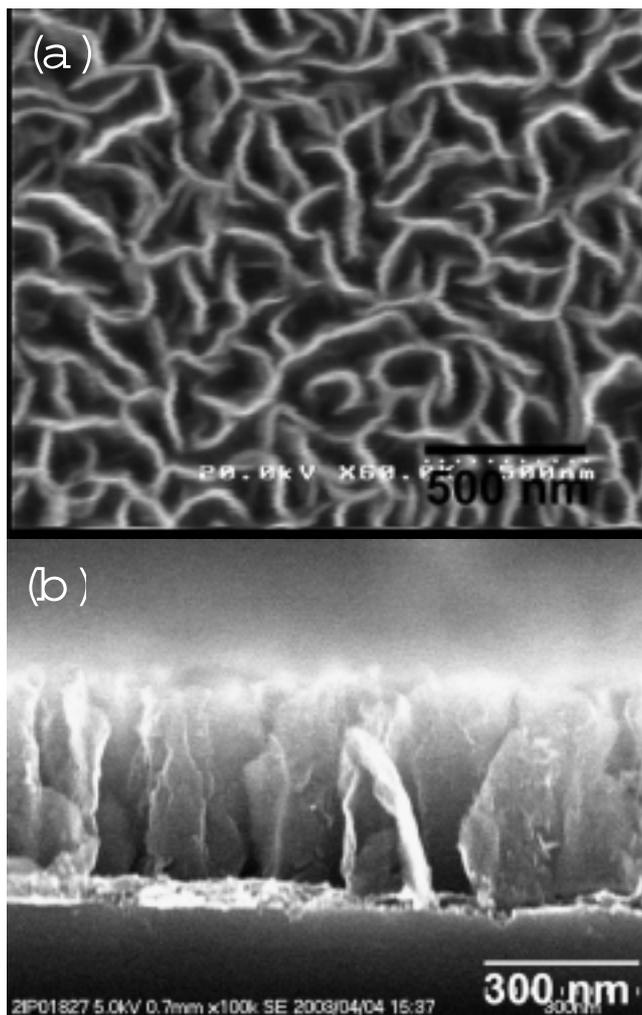


Fig.3. Typical SEM images for the carbon nanowalls fabricated using C_2F_6 rf-CCP assisted by H radical injection, (a) top view, (b) cross-sectional view.

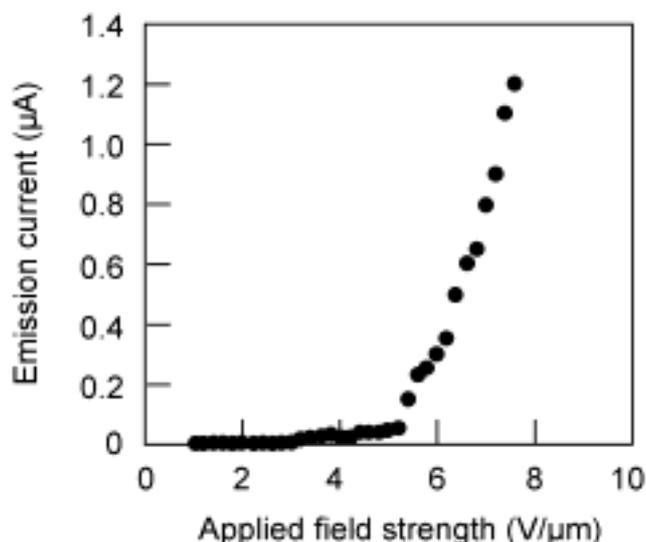


Fig.4. Field emission characteristic of the carbon nanowall film fabricated using C_2F_6 rf-CCP assisted by H radical injection.