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Synthesis of Carbon Nanotubes by Thermal CVD under High Magnetic Field

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High magnetic fields up to 10 Tesla are applied to chemical vapor deposition (CVD) for carbon nanotube synthesis in order to control the nanotube morphology. Although changes of the nanotube morphology in the presence of magnetic field were not obviously discernible in the SEM images, an increase in the onion-like nano-carbons due to magnetic field was discernible in TEM images. It suggests that the magnetic field influences on formation processes of nano-carbons as well as carbon nanotubes via magnetic effects on metal catalysts.
Key words: carbon nanotubes, thermal CVD, high magnetic field, SEM, TEM

1. INTRODUCTION

Carbon nanotubes have been synthesized using various kinds of methods [1-3] and mass production of carbon nanotubes has been already reported as well. However, morphology control of nanotubes is still an important issue. In order to control tube morphology, we have carried out nanotube synthesis by arc discharge in the presence of high magnetic fields up to 10 Tesla (T) [4,5]. In this case, an external magnetic field gave rise to macroscopic phenomena such as an effective increase in the arc current due to plasma confinement during the arc discharge. Since the discharge process involves highly energetic collisions, microscopic phenomena, i.e., quantum effects such as a spin polarization effect, may have been concealed. This result indicates that a softer synthesis process is favorable to distinguish the polarization effects. Thermal chemical vapor deposition (CVD) is a mild synthesis technique compared with arc discharge. Accordingly, thermal CVD under high magnetic field has been attempted to the nanotube synthesis.

2. EXPERIMENTAL

Synthesis of carbon nanotubes under high magnetic field up to 10 T was carried out using a magnetic-field-proof furnace (MP-furnace) as shown in Fig. 1. The MP-furnace was prepared as follows: an Fe-Cr wire with a diameter of 0.5 mm was wound on the outer surface of the quartz tube (30 mm in diameter) with the bifilar-technique. The six-turn heater coil was molded with alumina cement. After the cement was dried, it was covered with a heat insulating material. Finally, the quartz tube covered with the insulating material, i.e., MP-furnace, was inserted into a Cu cylinder with a Cu cooling tube.

Catalytic metal (Fe, Ni or Fe + Ni) films of about 30 nm thick were deposited by magnetron sputtering on the amorphous (a-)SiO_2 and crystalline (c-) Si substrates. The a-SiO_2 and c-Si substrates were put into the quartz tube of the MP-furnace. The substrates in the MP-furnace were placed at the maximum field of a superconducting magnet. The magnetic field was parallel to the quartz tube axis. After the magnetic field reached a certain value, the furnace was evacuated by a rotary pump and the heater was turned on. The ammonia (NH_3) gas for surface etching was introduced into the quartz tube, when the furnace temperature reached 800 °C. The flow rate and pressure of NH_3 gas were 30 standard cc (cm^3)/min (sccm) and 100 Torr, respectively. This etching procedure with the NH_3 gas was conducted for 10 min. and formed nanometer-sized grains on the surface [3]. After the NH_3 gas was evacuated, an acetylene (C_2H_2) gas was introduced and thermally decomposed for 10 min. at 700 or 800 °C by the aid of nano-sized metal catalysts. The deposits were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS).

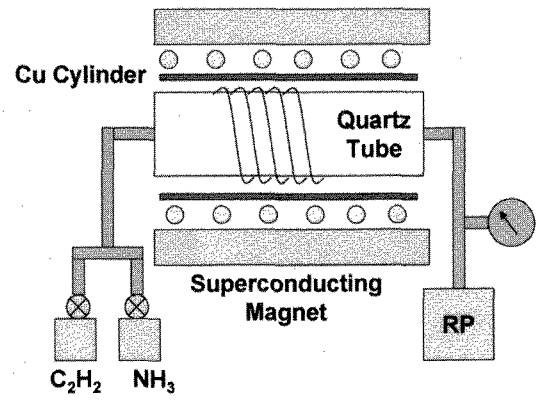

Fig. 1. Schematic diagram of the experimental setup.

3. RESULTS AND DISCUSSION

Carbon nanotubes and nanowires were synthesized on a-SiO_2 substrates under a C_2H_2 gas pressure of 30 Torr at 800 °C in the presence of magnetic field as well as in the absence of magnetic field, as shown in Figs. 2 (a) 0 T, (b) 1 T, (c) 5 T and (d) 10 T, where an arrow indicates the direction of magnetic field. Thinner and thicker linear structures in Fig. 2 are identified as nanotubes and namowires, respectively. The growth directions of the nanotubes and nanowires were randomly oriented in all the cases. The spatial distribution of Ni grains evaluated by the electron reflection images was almost equal to each other. This result indicates that the surface etching with NH_3 gas under the high magnetic fields is not different from the etching in the absence of magnetic field. Similar SEM and reflection images were obtained for the deposits synthesized on c-Si substrates. It is difficult by SEM to precisely evaluate changes of tube length and production yield in the presence of magnetic field. Roughly saying, such quantitative changes were scarcely discernible. It is expected that the effect of magnetic field on the nanotube synthesis is enhanced lowering synthesis temperature and gas pressure.

Figures 3 (a) and (b) show SEM images for the deposits on a-SiO_2 substrates under the conditions of 10 Torr and 700 °C in the absence of magnetic field (a) and in the presence of magnetic field (10 T) (b). In Fig. 3, it is again difficult to recognize the changes of tube length and production yield. However, an increase of onion-like structures was discernible in TEM images, as shown in Fig. 4. The production yield of the deposits under the magnetic field decreased in the case of Fe as the catalyst, whereas the Ni catalyst did not cause such a magnetic effect.

In a viewpoint of magnetic property, a primary difference between Ni and Fe is Curie temperature, which is 358 °C for Ni and 769 °C for Fe. Since the synthesis temperature was 800 or 700 °C, Curie temperature of Ni is much lower than the synthesis temperatures, while that of Fe is close to the synthesis temperatures. Ferromagnetism of the Fe catalyst should be maintained at the synthesis temperature of 700 °C. The relationship between synthesis temperature and

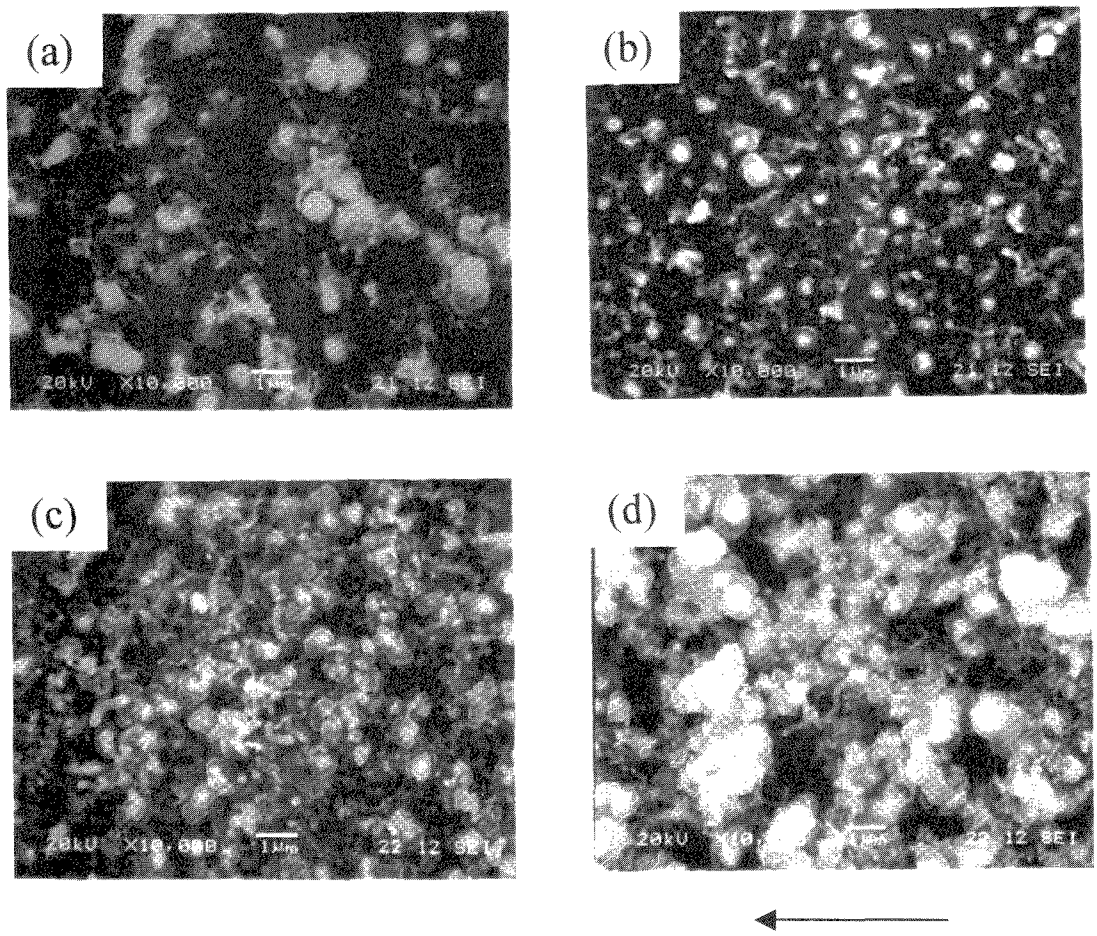

Fig. 2. SEM images of the deposits using Ni as a catalyst synthesized on the a-SiO_2 substrates at 800 °C under 0 T (a), 1 T (b), 5 T (c) and 10 T (d). C_2H_2 gas pressure was 30 Torr.

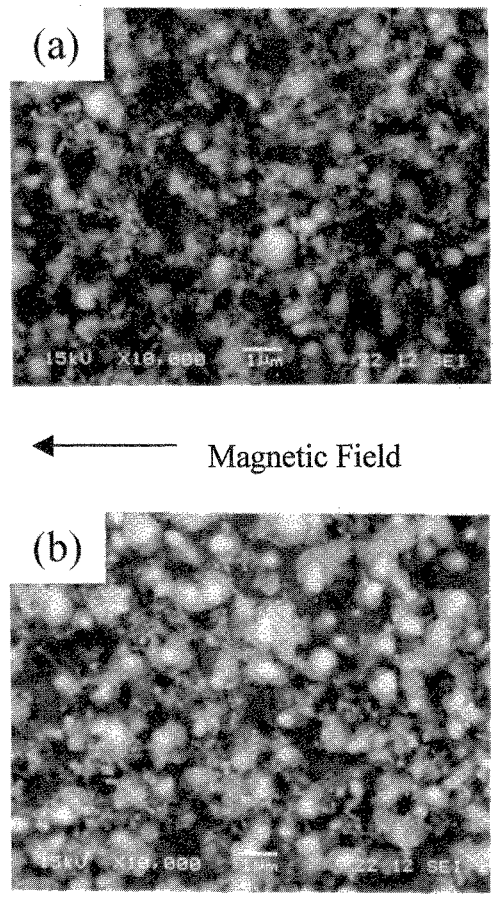

Fig. 3. SEM images of the deposits using Ni as a catalyst synthesized on the a-SiO_2 substrates at 700 °C under 0 T (a) and 10 T (b). C_2H_2 gas pressure was 10 Torr.

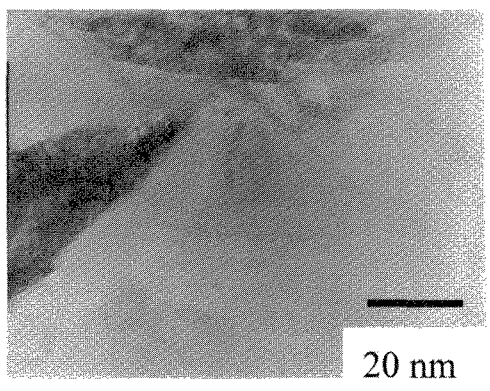

Fig. 4. TEM images of the deposits for using Ni as a catalyst synthesized on the a-SiO_2 substrates at 700 °C under 10 T. C_2H_2 gas pressure was 10 Torr.

Curie temperature may explain that the effect of magnetic field on the nanotube synthesis is scarcely distinguished in the case of Ni, but that the effect is discernible in the case of Fe. It is suggested that the magnetic field influences on formation processes of carbon nanotubes via magnetic effects on metal catalysts. This suggestion is consistent with the result obtained by TEM, i.e., an increase in the production yield of onion-like structures, where onion-like nano-carbons consist of curvature structures rather than linear structures.

4. SUMMARY

Carbon nanotubes have been synthesized by thermal CVD under high magnetic fileds up to 10 T. The production yield and tube length in the presence of magnetic field were scarcely discernible by SEM in the case of using Ni as a catalyst, but the production yield in the presence of magnetic field decreased in the case of using Fe as a catalyst. The TEM images showed an increase of onion-like structures for the deposits synthesized under the magnetic field. These results can be explained in terms of magnetic effects of metal catalysts, taking account of the Curie temperatures of the catalysts and synthesis temperatures. Further study of magnetic field effects on the nanotube growth is underway for an effective use of magnetic field.

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References

[1] W.Z. Li, S.S. Xie, L.X. Qian, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao and G. Wang, *Science* **274**, 1701 (1996).

[2] 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).

[3] S.H. Tsai, C.W. Chao, C.L. Lee and H.C. Shih, *Appl. Phys. Lett.* **74**, 3462 (1999).

[4] H. Yokomichi, H. Sakima, M. Ichihara, F. Sakai, K. Itoh and N. Kishimoto, *Appl. Phys. Lett.* **74**, 1827 (1999).

[5] H. Yokomichi, F. Sakai, M. Ichihara and N. Kishimoto, Extended Abstract of Int. Conf. Superlattices, Microstructures, and Microdevices 2000, Kyongju, Korea (2000).

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