JOURNAL OF MATERIALS SCIENCE **34** (1999) 3581–3585

Growth of carbon micro-coils by pre-pyrolysis of propane

XIUQIN CHEN
Faculty of Chemical Engineering, Huaqiao University, Quanzhuo, Fujian, 362011, People's Republic of China

SEIJI MOTOJIMA
Department of Applied Chemistry, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan
E-mail: motojima@apchem.gifu-u.ac.jp

Carbon micro-coils were obtained by the Ni catalyzed pyrolysis of propane as a carbon source which was pre-heated and pre-pyrolyzed at 1000–1100 °C. The obtained carbon micro-coils were mostly irregular double coils with a larger coil pitch of 1–5 μm and larger coil diameter of 5–20 μm than that obtained using acetylene. *© 1999 Kluwer Academic Publishers*

1. Introduction

The helical morphology of proteins or DNA as well as some vine plants provides living bodies with essential and critical functional roles. Thus, we could expect that such 3D-helical-coiled materials may have noble and unique functional properties. However, we can not find materials with a 3D-micro-helical-coiled structure among industrially available materials. In 1953, Davis *et al*. were the firsts to report the vapor growth of thin carbon fibers twisted together in the form of a rope [1]. Since then, other researchers have also reported the growth of micro-coiled carbon fibers from the vapor phase [2–9]. Furthermore, the vapor growth of helically coiled SiC [10–12], SiN [13–16], etc. were also reported. However, the growth of such coiled fibers from the vapor phase was extremely accidential and poorly reproducible. We have found that regularly micro-coiled carbon fibers (referred to as "carbon coils" hereafter) were obtained with high reproducibility by the catalytic pyrolysis of acetylene with a small amount of sulfur or phosphorus impurity, and reported the preparation conditions, morphology, growth mechanism and some properties [18–26].

Many carbon compounds other than acetylene [3, 5], such as CO [2], methane [7], ethylene [4–5], propylene [4], 1-butene [4], cis-2-butene [4], 1,3-butadiene [4], and allene [17], were also used as the carbon source for growing carbon coils. However, when using hydrocarbons other than acetylene, the carbon coils were rarely obtained under any reaction conditions. Metal-catalyzed hydrocarbons usually decompose to form some amounts of acetylene, which are effectively available for growing carbon coils as already reported by us. Among the many hydrocarbons, propane is very advantageous against acetylene from a cost point of view; the cost of propane is about one tenth of acetylene. Accordingly, the use of propane as a carbon source for obtaining carbon coils has a large cost merit, if the same amount of carbon coils as that using acetylene is obtained.

In this study, we prepared carbon coils by the Ni-catalyzed pyrolysis of propane which was pre-heated at high temperatures, and examined the effects of pre-heating conditions on the growth of the carbon coils and the morphologies.

2. Experimental

A schematic of the reactor used is shown in Fig. 1. The horizontal quartz reaction tube (23 mm i.d. and 40 mm long), which has a upper source gas inlet and lower gas outlet, was heated by nichrome elements from the outside. The source gas inlet was separately pre-heated for pre-pyrolyzing of the propane source gas. The graphite plate (15×50 mm^2, on which the Ni powder was dispersed by smearing), was used as the substrate. The gas mixture of propane, hydrogen and thiophene was introduced via the upper gas inlet, maintained at a given pre-heating temperature, into the reaction tube. Propane can undergo pre-pyrolysis by pre-heating before reaching the substrate surface.

3. Results and discussion

Many experiments were carried out without the pre-heating of propane under the following reaction conditions: reaction temperature = 700–950 °C; reaction time = 5–180 min; propane flow rate = 5–100 sccm (standard cubic centimeter per minute); hydrogen flow rate = 10–500 sccm; thiophene gas flow rate = 0.1–1.5 sccm; nitrogen flow rate = 100 sccm. However, no carbon coils could be obtained under these conditions, and only carbon powder and/or straight carbon fibers deposited as shown in Fig. 2A. When using acetylene

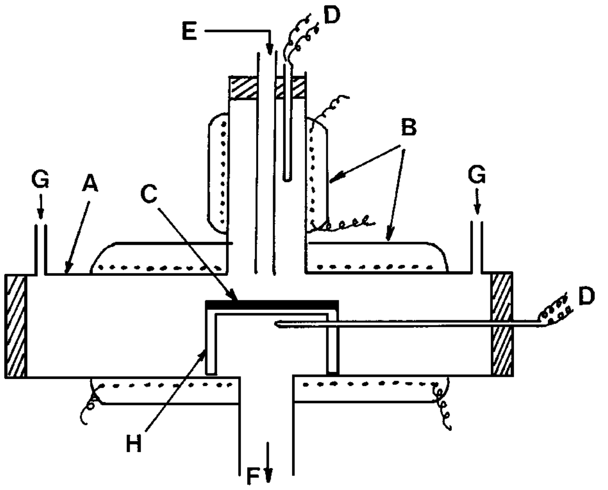

Figure 1 Schematic apparatus: (A) reaction tube (quartz), (B) heater, (C) substrate (graphite plate), (D) CA thermocouple, (E) source gas inlet (C_3H_8, H_2, thiophene), (F) gas outlet, (G) N_2, and (H) susceptor.

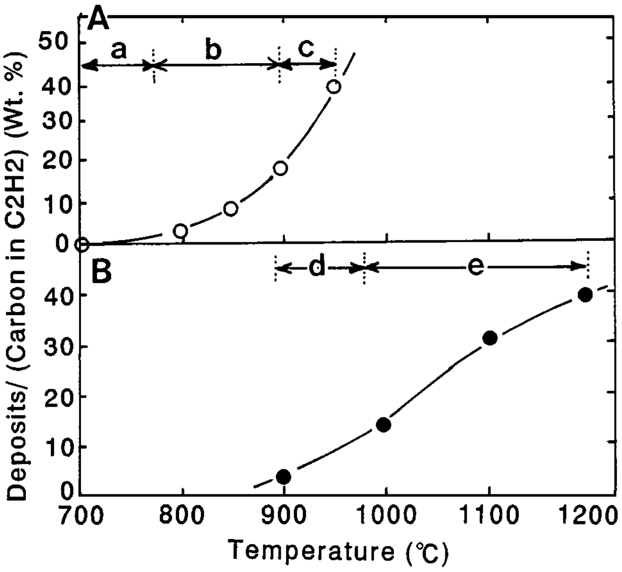

Figure 2 Effect of temperature on the amount and kind of deposits. (A) Without pre-heating, (B) with pre-heating, reaction temperature = 750–780 °C, (a) and (c) carbon powder, (b) carbon powder and straight carbon fibers, (d) straight carbon fibers, (e) straight carbon fibers and carbon coils. Gas flow rate: $C_3H_8 = 10$ sccm, H_2: 60–150 sccm, thiophene: 0.3 sccm.

as the carbon source, the optimum reaction temperature for growing carbon coils is 750–850 °C which depends on the kind of catalyst and impurity [26]. For example, using a Ni catalyst and thiophene impurity, the optimum reaction temperature is about 750–770 °C. Catalytic anisotropy, which is the driving force of coiling of the carbon fibers, between the Ni-C-S-O quaternary compound layers on the surface of the respective crystal faces of the Ni catalyst is considered to be the largest in this temperature range. Accordingly, it may be reasonably considered that the reaction temperature must be maintained within this temperature range for obtaining carbon coils irrespective of the carbon source. However, propane can not be effectively pyrolyzed in this temperature range. Accordingly, propane was pre-heated at high temperatures for the pre-pyrolyzing. The effects of the pre-heating temperature of propane on the kind and amount of the deposits is shown in Fig. 2B, in which the reaction temperature was fixed at 750–77 °C. Straight carbon fibers were deposited at a pre-heating temperature between 900–1000 °C. A small amount of carbon coils mixed with straight carbon fibers were deposited at the pre-heating temperature of 1000–1200 °C directly onto the substrate under the source gas inlet within the region of 6–9 mm diam.

According to Feron [27], when propane undergoes pyrolysis, various chemical species, such as ethylene, acetylene, benzene, etc., can be produced as a function of temperature and residence time. The reactions that occur are as follows:

$$C_3H_8 \rightarrow C_2H_5\cdot + CH_3\cdot$$

$$CH_3\cdot + H\cdot \rightarrow CH_4$$

$$C_2H_5\cdot \rightarrow C_2H_4 + H\cdot$$

$$C_2H_4 + R\cdot \rightarrow C_2H_3\cdot + RH$$

$$C_2H_3\cdot \rightarrow C_2H_2 + H\cdot$$

Acetylene is formed within 0.3 s by the pyrolysis of propane [27]. On the other hand, it was reported that 22% of the propane was pyrolyzed to form acetylene at 903 °C [28], and that the amount of acetylene formed at 1100 °C is larger than that at 1000 °C [29]. Propane can not be decomposed to form a large amount of acetylene at 750–770 °C at which carbon coils can be most effectively obtained from acetylene as the carbon source.

We pre-heated the propane, mixed in a gas mixture of hydrogen and thiophene in the temperature range of 900–1200 °C with and without the substrate, and the formed (exhausted) gases were then analyzed by gas chromatography. The propane and methane as well as hydrogen and nitrogen were observed in the exhaust gas. The dependence of the concentration of acetylene and methane in the exhaust gas at the pre-heating temperature with and without the substrate are shown in Fig. 3. With the substrate, the maximum acetylene concentration in the exhaust gas was obtained at the

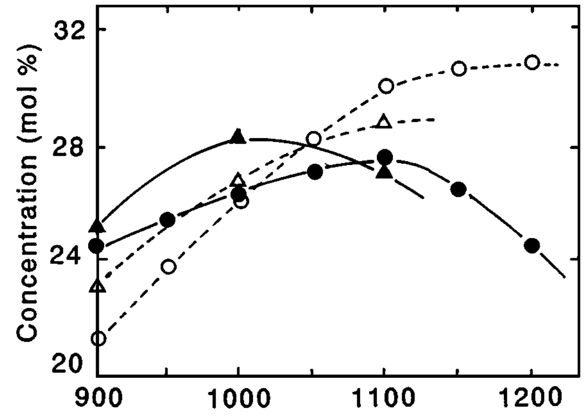

Figure 3 Effect of pre-heating temperature on the concentration of acetylene and methane in the exhaust gas. (○, ●) Without substrate, (△, ▲) with substrate, (●, ▲) acetylene, (○, △) methane. Reaction temperature = 750–780 °C, gas flow rate: C_3H_8= 30 sccm, H_2: 500 sccm, thiophene: 1 sccm.

pre-heating temperature of about 1000 °C, while without the substrate the temperature was 1100 °C. This lowering effect of acetylene formation with the substrate, on which the Ni catalyst was dispersed, may be caused by the catalytic effect of the Ni catalyst on the decomposition of propane. It is considered that when using propane as the carbon source for obtaining carbon coils, the pre-heating of propane is indispensable and the optimum pre-heating temperature is about 1000 °C for the acetylene formation. That is, the growth of carbon coils using propane as a carbon source mainly proceeds via the catalytic pyrolysis of acetylene formed by the pre-heating and pre-pyrolyzing of propane. The SEM image of carbon coils obtained at different pre-heating temperatures are shown in Fig. 4. A small amount of very irregular carbon coils having larger coil diameters of 40–60 μm and larger fiber diameters of 1–2 μm than that obtained using acetylene was obtained at the pre-heating temperature of 1000 °C. On the other hand,irregular carbon coils having a coil diameter of about 20 μm and fiber diameter below 1 μm were obtained at the pre-heating temperature of 1100 °C. The amount of carbon coils obtained at 1100 °C was larger than that obtained at 1000 °C. Almost all of the carbon coils obtained were double-helical coils with irregular shape and large coil pitch as shown in Fig. 5A. Sometimes regular carbon coils with a small coil pitch were obtained for a 2 h reaction time and these representative coils are shown in Fig. 5B. Fig. 6 shows the tip part of the carbon coils obtained with propane and acetylene as the carbon source. Using propane as the carbon source, the representative shape of a Ni catalyst grain observed on the coil tip was hexagonal as shown in Fig. 6A. On the other hand, using acetylene as the carbon source, a rhomb Ni grain, which is a Ni_3C (rhombohedral) single crystal [26], was commonly observed on the coil tip as shown in Fig. 6B, while the hexagonal shaped one was never observed. The reason for the catalyst shape difference is not yet known.

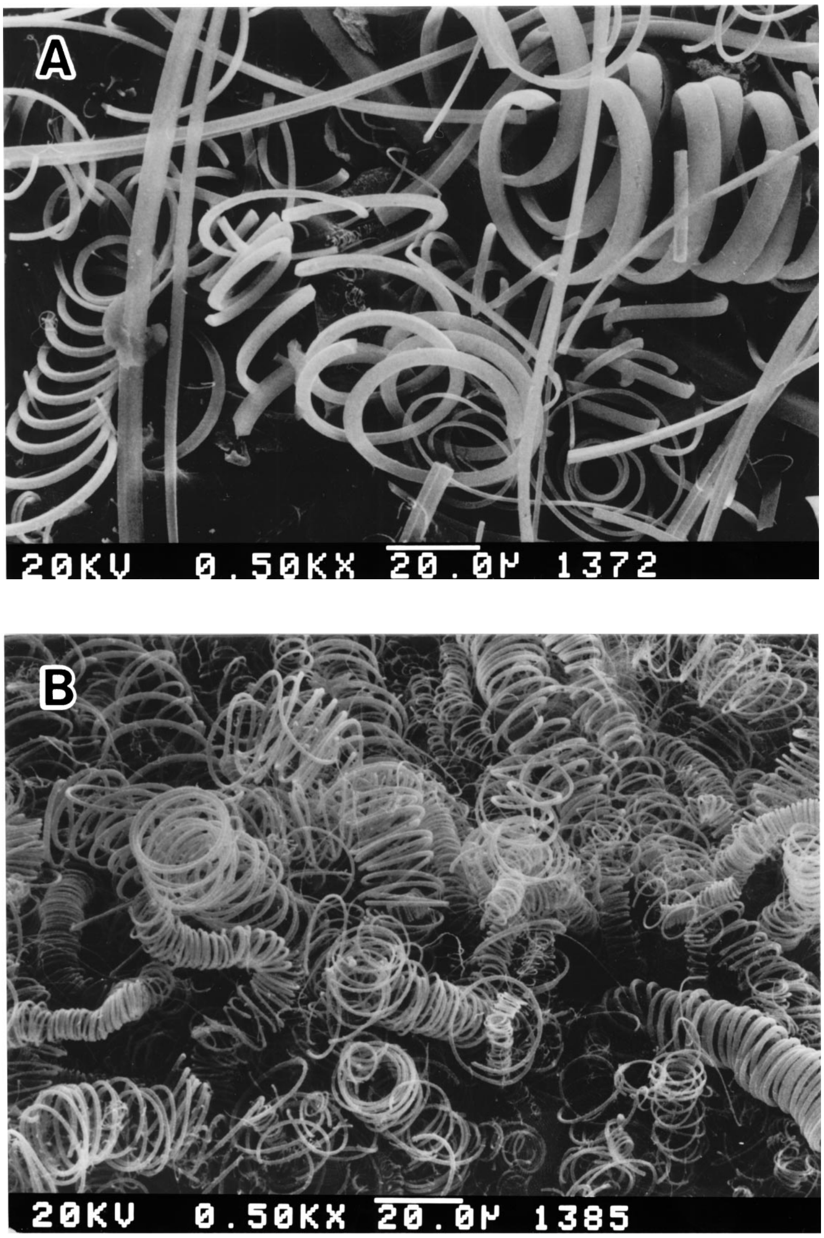

Figure 4 Carbon coils grown at pre-heating temperatures of 1000 °C (A) and 1100 °C (B).

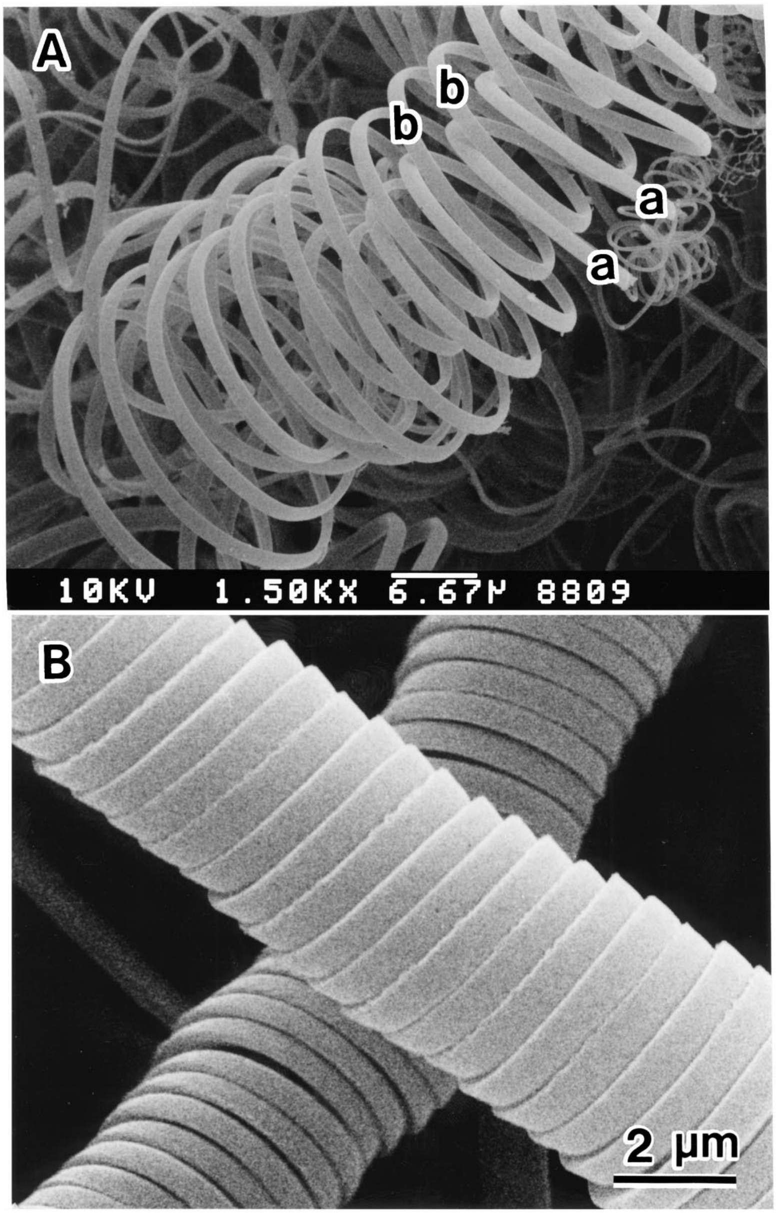

Figure 5 Double helical coils with irregular shape (A) and regular shape (B). (a) and (b) in Fig. 5A indicate two single coils from which double helical coils are formed.

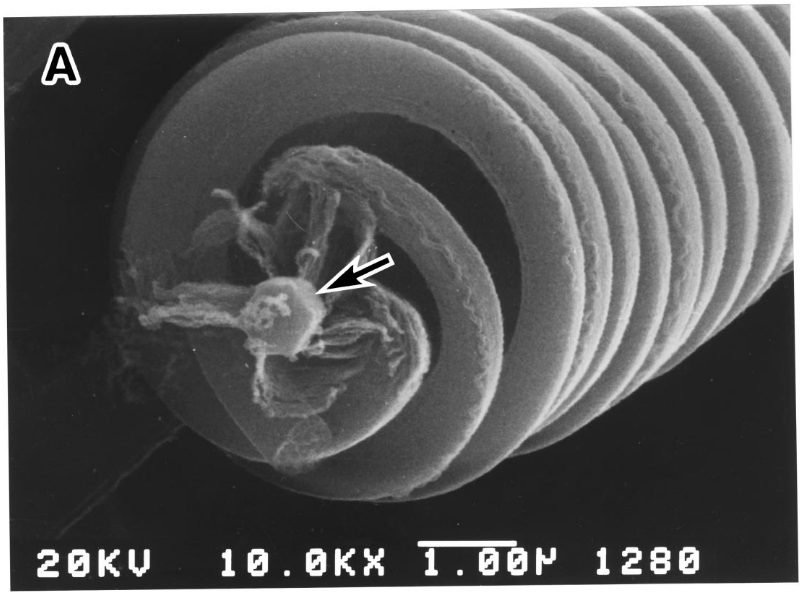

Figure 6 Tip part of the carbon coils. (A) Carbon source: propane pre-heated at 1100 °C, reaction temperature: 750 °C, (B) carbon source: acetylene. Arrow indicates a Ni catalyst grain. (*Continued*)

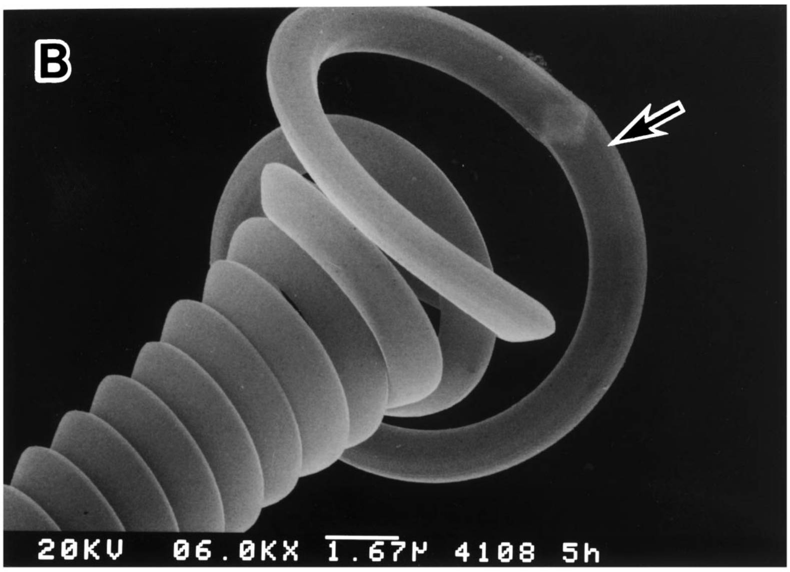

Figure 6 (*Continued*).

4. Conclusions

Propane can be used as the carbon source for obtaining the carbon coils if it is pre-heated and pre-pyrolyzed at 1000–1100 °C to form acetylene. The growth of the carbon coils is considered to occur via the catalytic pyrolysis of acetylene which was formed by the pre-heating and pre-pyrolyzing of propane. The obtained carbon coils obtained were mostly irregular double coils with a large coil pitch of 1–5 μm and coil diameter of 5–40 μm.

Acknowledgements

The authors are very grateful to Miss Y. Fukuda, Mr H. Suzuki, and Mr W. In Huang for their invaluable aid during the experimental programme.

References

1. W. R. DAVIS, R. J. SLAWSON and G. R. RIGBY, *Nature* **171** (1953) 756.
2. *Idem.*, *Trans. Brot. Ceram. Soc.* **56** (1957) 67.
3. R. T. K. BAKER, M. A. BARBER, P. S. HARRIS, F. S. FEATES and R. J. WAITE, *J. Catal.* **26** (1972) 51.
4. L. S. LOBO and D. L. TRIMM, *ibid.* **29** (1973) 15.
5. R. T. K. BAKER and R. J. WAITE, *ibid.* **37** (1975) 101.
6. M. HILLERT and N. LANGE, *Z. Krist.* **111** (1958) 24.
7. J. CALUSZKA and M. H. BACK, *Carbon* **22** (1984) 141.
8. M. AUDIER and M. COULON, *ibid.* **23** (1985) 317.
9. R. A. DALLA BETTA, A. G. PIKEN and M. J. SHELEF, *J. Catal.* **40** (1975) 173.
10. A. ADDAMIANO, *J. Cryst. Growth* **58** (1982) 617.
11. T.-K. KANG, S.-D. PARK, C.-K. RHEE and II.-H.K. KUK, in Proc. 6th Japan-Korea Ceram Seminar (Kobe, 1989) p. 249.
12. S. MOTOJIMA, T. HAMAMOTO and H. IWANAGA, *J. Cryst. Growth* **158** (1996) 79.
13. S. MOTOJIMA, S. UENO, T. HATTORI and K. GOTO, *Appl. Phys. Lett.* **54** (1989) 1001.
14. S. MOTOJIMA, S. UENO, T. HATTORI and H. IWANAGA, *J. Cryst. Growth* **96** (1989) 383.
15. S. MOTOJIMA, T. YAMANA, T. ARAKI and H. IWANAGA, *J. Electrochem. Soc.* **142** (1995) 3141.
16. U. VOGT H. HOFMANN and V. KRAMER, *Key Eng. Mater.* **89–91** (1994) 29.
17. Y. OKADA, K. TAKEUCHI, H. YAMANASHI and H. USHIJIMA, *J. Mater. Sci.* **11** (1992) 1715–1717.
18. S. MOTOJIMA, M. KAWAGUCHI, K. NOZAKI and H. IWANAGA, *Appl. Phys. Lett.* **56** (1990) 321.
19. *Idem.*, *Carbon.* **29** (1991) 379.
20. S. KAWAGUCHI, I. HASEGAWA, M. KAWAGUCHI, N. NOZAKI and H. IWANAGA, *J. Chem. Vapor Deposition* **1** (1992) 136.
21. S. MOTOJIMA, I. HASEGAWA, S. KAGIYA, S. ASAKURA, M. KAWAGUCHI and H. IWANAGA, *J. de Physique* **IV C3** (1993) 599.
22. S. MOTOJIMA, I. HASEGAWA, S. ASAKURA, K. ANDOH and H. IWANAGA, *Carbon* **33** (1995) 1167.
23. S. MOTOJIMA, Y. ITOH, S. ASAKURA and H. IWANAGA, *J. Mater. Sci.* **30** (1995) 5049.
24. S. MOTOJIMA, S. KAGIYA and H. IWANAGA, *Mater. Sci. Eng.* **B34** (1995) 47.
25. S. MOTOJIMA, S. ASAKURA, T. KASEMURA, S. TAKEUCHI and H. IWANAGA, *Carbon* **34** (1996) 289.
26. S. MOTOJIMA, S. ASAKURA, M. HIRATA and H. IWANAGA, *Mater. Sci. Eng.* **B34** (1995) L9.
27. O. FERON, F. LANGLAIS and R. NASLAIN, *Electrochem. Soc. Proc.* **97–25** (1997) 49–56.
28. D. B. MURPHY, R. W. CARROLL and J. E. KLONOWSKI, *Carbon* **35** (1997) 1819.
29. W. BENZINGER, A. BECKER and K. J. HULLINGER, *ibid.* **34** (1996) 957.

Received 30 October
and accepted 23 November 1998