Fullerene formation during production of chemical vapor deposited diamond

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We report a novel method for fullerene formation during diamond synthesis via a hot filament, chemical vapor deposition (CVD) procedure. The fullerenes occur in the soot that forms as a by-product on the edges and rear surface of the substrate holder, where the temperature does not favor diamond deposition. Mass spectrometry of the soot shows a peak having a mass to charge ratio corresponding to C_{60}. From typical concentrations of gaseous species in the diamond-growing CVD chamber, we conclude that hydrocarbon species such as CH_3 or C_2H_2 may be the precursors for the fullerene in the CVD chamber. The atomic hydrogen in the gaseous species is believed to play an important role in removing the hydrogen from hydrocarbon to form the all-carbon fullerene. Our observations also suggest that fullerenes produced in the CVD diamond growth chamber play a role in diamond nucleation on foreign substrates. © *1995 American Institute of Physics.*

In 1985, Kroto *et al.*[1] produced microscopic quantities of fullerenes (most notably C_{60} and C_{70}) in a supersonic molecular beam. Subsequently Kratschmer *et al.*[2] developed a method of producing macroscopic quantities of fullerenes using a carbon-arc apparatus. While these developments led to intense research into the physical and chemical properties of this unique class of carbon molecules, the precise nature of their formation[3] remains controversial. Here we report a new method of forming fullerenes using hot-filament chemical vapor deposition (CVD), which is a standard method for diamond thin-film growth.

The experiments were performed in a conventional hot-filament CVD chamber[4] using a straight 0.75-mm diameter tungsten filament approximately 8 cm in length. The current was maintained between 50 and 55 Å, and the filament temperature was estimated to be ≈2200 °C. The feed gases were 99.8% pure CH_4 mixed with 99.999% pure H_2. The chamber pressure was kept between 30 and 35 Torr. Flow rates were controlled at 0.4 sccm for CH_4 and at 99.6 sccm for H_2. A stainless-steel substrate holder was used, and a scratched Si wafer served as the substrate. Substrate temperatures, as monitored by both thermocouple and pyrometer, were kept between 850 and 900 °C to optimize diamond deposition. Runs lasted between 5 and 24 h. After each diamond deposition, the soot was collected from the substrate holder. Typically 10–75 mg of soot was collected after each run.

Samples of the collected soot (about 100 mg) were analyzed by mass spectrometry using the procedure described by Daly *et al.*[5] The signal at a mass-to-charge ratio of 720 in Fig. 1 indicates the presence of C_{60}. Another set of samples was collected under similar conditions to those described above and laser-desorption time-of-flight mass spectrometry was employed to study the soot. To avoid ambiguous results, we used low laser power density[6] (10^5–10^7 W/cm^2) and we also repeated the measurement with a sample (Antelope coal) that is known to contain only graphitic material and no fullerenes. The results are shown in Figs. 2(a) and 2(b). In addition, we carried out UV-vis absorption spectroscopy of soot dissolved in a CCl_4 solution. After the solution was passed through filter paper, the absorption spectrum was taken with a Perkin–Elmer model No. 552 spectrophotometer. The result illustrated in Fig. 3 shows strong absorption bands at 259 and 328 nm, in agreement with the absorption spectrum of C_{60} reported by Ajie *et al.*[7] in the wavelength range of 255–500 nm. Because of the CCl_4 solvent, no signal can be detected below the 255 nm cutoff wavelength.

In an attempt to increase the yield of fullerene-containing soot, we modified the growth conditions to 2%–5% CH_4 with 95%–98% H_2, and kept the substrate holder at a lower temperature (400–750 °C) by moving the

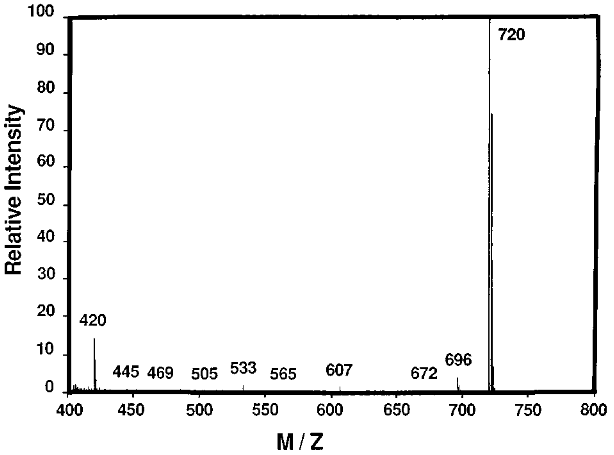

FIG. 1. The mass spectrum of soot collected in the hot-filament CVD diamond-growth chamber.

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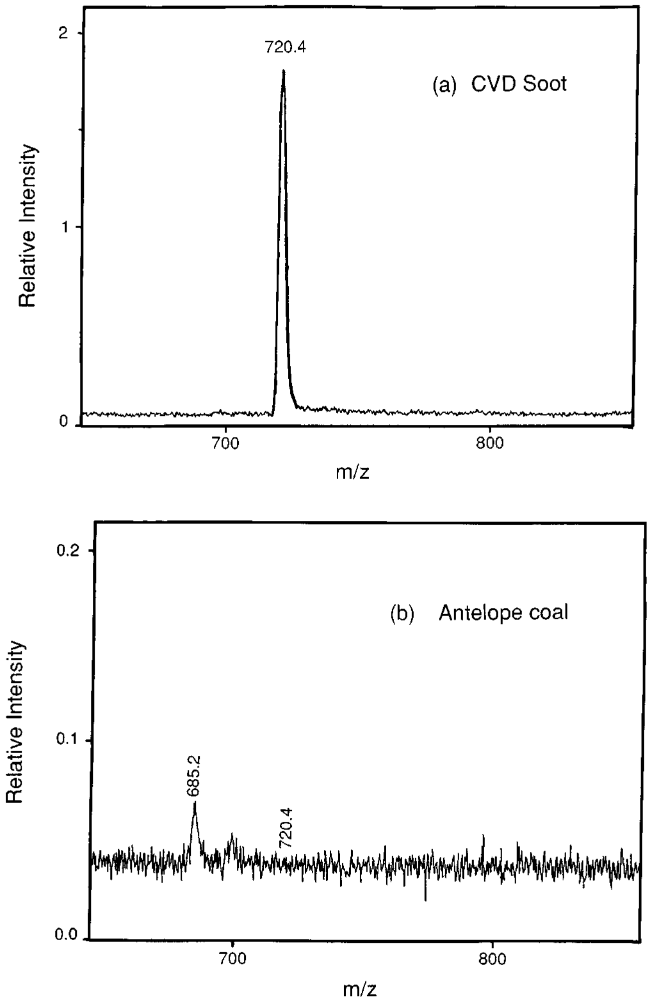

FIG. 2. Laser-desorption time-of-flight mass spectrum of (a) CVD soot, and (b) antelope coal.

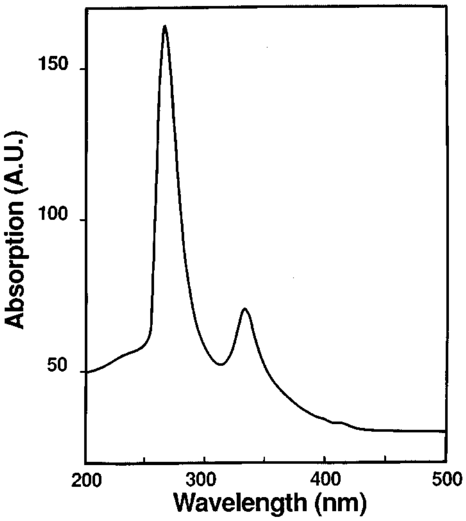

FIG. 3. Ultraviolet-visible spectrum of soot dissolved in CCl_4 solution.

substrate holder away from the filament. Pressure and filament current conditions were unchanged, and the total flow rate remained at 100 sccm. In this way we were able to increase the soot production rate sixfold to about 10–20 mg/h. However, under these conditions diamond was not produced, and mass spectrometry of the soot showed no sign of fullerenes, although some hydrocarbon clusters were present. These results could imply that the atomic hydrogen plays an important role in the formation of fullerene under this condition. It has been shown[8] that the atomic hydrogen concentration decreases as the initial methane concentration increases.

The environment in the hot-filament CVD chamber differs considerably from those during either laser vaporization or carbon-arc synthesis. Under typical diamond-forming conditions of 30–80 Torr of 0.5% CH_4 and 99.5% H_2 and a filament temperature of 2000–2200 °C, the atomic carbon concentration in the CVD chamber is several orders of magnitude lower than most of the hydrocarbon species that are present. Both calculations[9,10] and experimental measurements[11,12] have shown that under such conditions H, C_2H_2, CH_3, and CH_4, in addition to H_2, are the predominating species. It is generally accepted that hydrocarbons like acetylene or methyl radicals rather than carbon atoms are the precursors of diamond growth, and atomic hydrogen plays a major role in etching graphitic material and in promoting the diamond growth.

Here we propose that the C_{60} found in the diamond-forming CVD chamber may also be from hydrocarbon precursors. The process could be similar to the fullerene production in hydrocarbon flames,[13–15] namely, the growth of the hydrocarbon precursors of the fullerene is mainly through the addition of acetylene and hydrogen abstraction. Both atomic hydrogen and acetylene are present in our CVD chamber. Our current operating parameters are optimized for diamond growth, so the formation of C_{60} is clearly a minor effect. A systematic investigation of the conditions under which fullerenes can be formed is now in progress.

One implication of our finding relates to the nucleation of diamond. During CVD diamond growth, Si substrates are normally scratched with diamond powder before deposition in order to increase the diamond nucleation density. However diamond can also be nucleated on an unscratched Si sub-

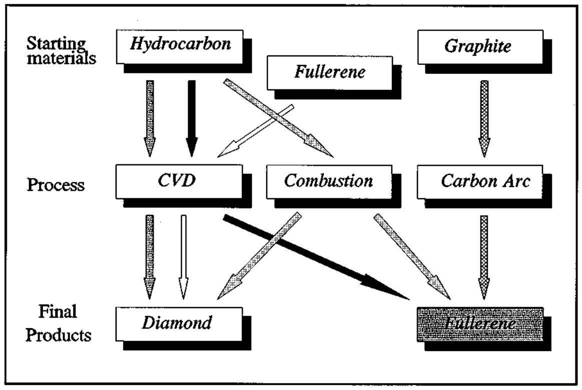

FIG. 4. Several processes using different starting materials to produce diamond and fullerene are shown here. The process reported here is shown by the solid arrows.

strate, although at a much lower rate. It has been proposed that either SiC[16] or some form of graphite[17] acts as the nucleation site when the Si substrate is not prescratched. It was recently found that ion-activated fullerene films on Si substrates increase the diamond nucleation rate by 10 orders of magnitude.[18] This, coupled with our observation of fullerenes in the CVD diamond-forming chamber, could imply that fullerenes or precursors of fullerenes which formed in the CVD chamber may also play a role in the nucleation of diamond on unscratched foreign substrates. Recently, Gruen *et al.*[19,20] have shown that fullerenes can be used as precursors for CVD diamond thin-film deposition. They proposed that C_2, observed in the C_{60} fragmentation process, is the principal growth species under the condition of their experiment. It should be noted that our observation of fullerene formation in the CVD diamond growing chamber reported here is a totally different process from the diamond growth using fullerene as a precursor as reported by Gruen *et al.*[19,20] This difference is perhaps best seen in Fig. 4, where different techniques capable of producing diamond and fullerene, are shown. In Fig. 4, our process is represented by the solid arrow, while Gruen *et al.*'s work is represented by the thin arrow. The figure clearly indicates a strong correlation between the formation processes of diamond and fullerene.

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[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature **318**, 162 (1985).

[2] W. Kratschmer, L. Lamb, K. Fostiropoulos , and D. R. Hoffman, Nature **347**, 354 (1990).

[3] R. F. Curl, Nature **363**, 14 (1993).

[4] W. A. Yarbrough, K. Tankala, and T. DebRoy, J. Mater. Res. **7**, 379 (1992).

[5] T. K. Daly, P. R. Buseck, P. Williams, and C. F. Lewis, Science **259**, 1599 (1993).

[6] P. R. Buseck, S. J. Tsipursky, and R. Hettich, Science **257**, 215 (1992).

[7] H. Ajie, M. M. Alvarez, S. J. Anz, R. D. Beck, F. Diederich, K. Fostiropoulos, D. R. Huffman, W. Kratschmer, Y. Rubin, K. E. Schriver, D. Sensharma, and R. L. Whetten, J. Phys. Chem. **94**, 8630 (1990).

[8] S. J. Harris and A. M. Weiner, J. Appl. Phys. **67**, 6520 (1990).

[9] B. V. Spitsyn, J. Cryst. Growth, **99**, 1162 (1990); B. V. Spitsyn, in *Application of Diamond Films and Related Materials*, edited by Y. Tzeng, M. Yoshikawa, M. Murakawa, and A. Feldman (Elsevier, Amsterdam, 1991), p. 475.

[10] M. Frenklach and H. Wang, Phys. Rev. **43**, 1520 (1991).

[11] S. J. Harris, A. M. Weiner, and T. A. Perry, Appl. Phys. Lett. **53**, 1605 (1988).

[12] F. G. Celii and J. E. Butler, J. Appl. Phys. **71**, 2877 (1992).

[13] J. B. Howard, J. T. McKinnon, Y. Markovsky, A. L. Lafleur, and M. E. Johnson, Nature **352**, 139 (1991).

[14] A. L. Lafleur, J. B. Howard, J. A. Marr, and T. Yadav, J. Phys. Chem. **97**, 13 539 (1993).

[15] C. J. Pope, J. A. Marr, and J. B. Howard, J. Phys. Chem. **97**, 11 001 (1993).

[16] A. Badzian, T. Badzian, R. Roy, R. Messier, and K. E. Spear, Mater. Res. Bull. **23**, 531 (1988).

[17] W. R. L. Lambrecht, C. H. Lee, B. Segal, J. C. Angus, Z. Li, and M. Sunkara, Nature **364**, 607 (1993).

[18] R. Meilunas, R. H. M. Chang, S. Z. Lu, and M. M. Kappes, Appl. Phys. Lett. **59**, 3461 (1991).

[19] D. M. Gruen, S. Liu, A. R. Krauss, and X. Pan, J. Appl. Phys. **75**, 1758 (1994).

[20] D. M. Gruen, S. Liu, A. R. Krauss, J. Luo, and X. Pan, Appl. Phys. Lett. **64**, 1502 (1994).