

# Growth of diamond particles from methane–hydrogen gas

SEIICHIRO MATSUMOTO, YOICHIRO SATO, MASAYUKI TSUTSUMI,  
NOBUO SETAKA

*National Institute for Research in Inorganic Materials, 1-1 Namiki, Sakura-mura,  
Niihari-gun, Ibaraki-ken 305, Japan*

Microcrystals of diamond were grown on non-diamond substrates including silicon, molybdenum and silica, as well as on diamond by chemical vapour deposition. Deposition was carried out by passing a mixture of hydrocarbon and hydrogen gases through a heated reaction chamber in which a hot tungsten filament was held near the substrates. The deposit was identified by reflection electron diffraction and Raman spectroscopy. The effects of experimental conditions on the growth features were studied.

## 1. Introduction

Diamond is a unique and fascinating material because of its high hardness, good thermal conductivity, high electrical resistance and chemical inertness. The method of diamond synthesis from the gas phase has some advantages in preparing fine particles and thin films. So far, various methods, such as chemical vapour deposition (CVD) [1, 2], ion-beam deposition [3, 4], sputtering [5] and plasma CVD [6–9] have been applied for the purpose of preparing diamond films. Diamond particles with well-defined habits were synthesized by Derjaguin, Spitsyn and their co-workers [10, 11] by chemical transport using excess atomic hydrogen, but experimental details have not been reported. In the present investigation, in a flow system using a hot tungsten filament, diamond particles could be grown from hydrocarbon–hydrogen mixtures. This paper reports the details of the synthetic method and conditions.

## 2. Experimental details

Fig. 1 shows a schematic illustration of the apparatus. The substrates (silicon wafers, molybdenum plates and silica glass plates, etched or washed with CP4, dilute hydrochloric acid and aqua regia, respectively) were put on a silica cell and placed in a silica glass tube. A tungsten filament of 0.15 mm diameter  $\times$  30 mm, and 20 turns was set

above the substrates. After evacuation, a gas mixture of hydrocarbon (mainly methane) and hydrogen was introduced to a predetermined pressure and then an electric furnace held at a high temperature was put in position. The filament was then heated with a stabilized d.c. source.

Methane and hydrogen were mixed using two flowmeters (methane to hydrogen ratio was 0.05–0.005) and were introduced near the substrates through an alumina rod. The total flow rate was 4–200 cm<sup>3</sup> min<sup>-1</sup> at STP. The pressure of the reaction chamber, 0.5–750 Torr, was measured with a Pirani gauge or with a diaphragm gauge. The substrate temperature was monitored by a Pt–PtRh 13% thermocouple set just below the quartz cell. This temperature will subsequently be called the “heating temperature”, and the measured value was 600–1000°C. When the filament was lit, the input power of the furnace was decreased to maintain the heating temperature at a preset value. Owing to the radiation from the filament, the temperature on the substrate surface must have been higher than this heating temperature, but no effort was made to measure the surface temperature. The filament temperature was checked without the furnace by an optical pyrometer under the flow of the reactant gas. The filament temperature was not measured during deposition; the filament current which gave a

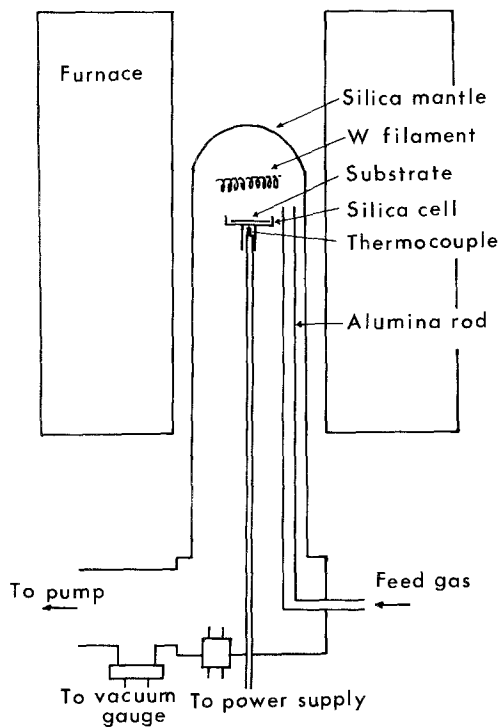


Figure 1 Schematic illustration of the apparatus.

temperature of 1700–2000° C in the absence of the furnace, was used.

Typical deposition conditions were as follows: methane concentration 1%, heating temperature 700–1000° C, filament temperature 2000° C, total gas pressure 10–100 Torr, and the reaction time 3 h. After the deposition, the reaction product was observed by optical microscopy, scanning electron microscopy (SEM), electron diffraction and Raman spectroscopy. Raman spectra were measured with a Spex Ramalog 1401 spectrometer using the 488 nm line of an argon ion laser for excitation.

### 3. Results and discussion

The reaction product was obtained on the substrates as particles up to 5  $\mu\text{m}$  in size. Interplanar spacings ( $d$ ) determined by reflection electron diffraction (Fig. 2) were in good agreement with those of cubic diamond [12]. The Debye–Scherrer rings in Fig. 2 show that no epitaxial relation exists between the deposit and substrate.

Raman spectra of these specimens (Fig. 3) showed a sharp peak at 1334.5  $\text{cm}^{-1}$  which is very close to the value of 1332.5  $\text{cm}^{-1}$  reported for natural diamond. The full widths at half maximum (FWHM) of these samples were found to be about

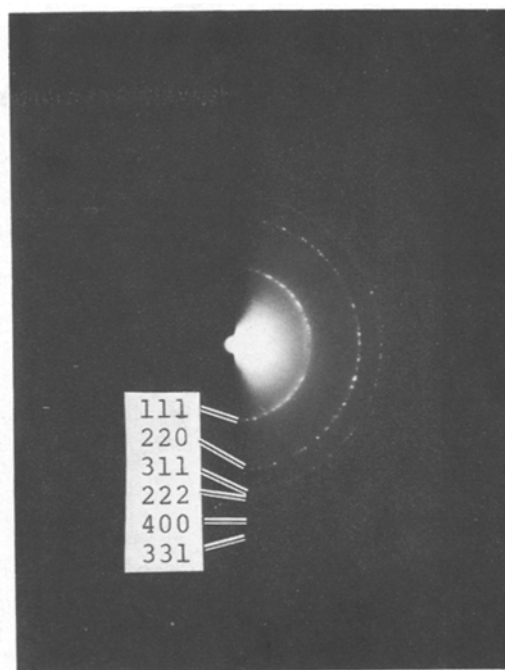


Figure 2 Reflection electron diffraction pattern of particles deposited on Si (111) at 880° C under 32 Torr  $\text{CH}_4$  (1%)– $\text{H}_2$ .

10  $\text{cm}^{-1}$  (measured at a spectral slit width of 2  $\text{cm}^{-1}$ ), which is about three times as large as that reported for natural diamond [13]. In some specimens, a broad peak due to highly disordered graphite was also observed at 1500–1600  $\text{cm}^{-1}$ .

These results indicate that the deposit was cubic diamond, although it may have some defects as compared with natural diamond.

SEM observation revealed that the particles were cubo-octahedral and multiple-twinned particles consisting of 20, 5, 2 single crystal units. The particles grown on silicon, molybdenum and silica glass were half-polyhedral, that is, they were deposited on these substrates with relatively large contact areas. These results agree with those reported by Spitsyn *et al.* [11]. The number of the particles greatly depended on the material and surface perfection of the substrates. The growth rate of each particle was influenced by the number of particles as well as by growth conditions.

#### 3.1. Effect of methane concentration

At 35 Torr total pressure, the equilibrium concentration of methane is roughly estimated to be about 0.5–0.05% at 700–1000° C from the equilibrium constant [14] of the reaction,  $\text{C}(\text{graphite}) + 2\text{H}_2 =$

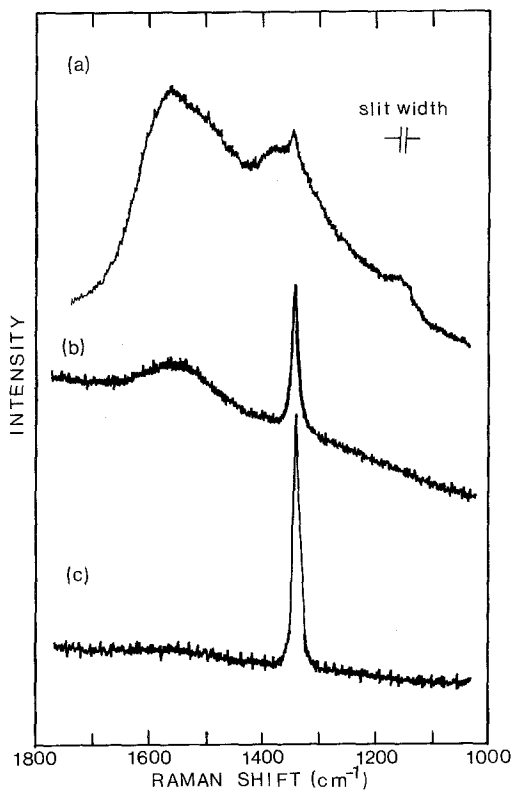


Figure 3 Raman spectra of deposits on molybdenum substrates. Three typical examples are shown which were observed with specimens prepared under different conditions. The sharp peak at  $1334\text{ cm}^{-1}$  is due to diamond while broad peaks centred about  $1560$  and  $1360\text{ cm}^{-1}$  are due to graphitic structures. The amount of graphitic structure apparently decreases in going from (a) to (c).

$\text{CH}_4$  (the concentrations of other hydrocarbons are low). Although the deposition of carbon from a few percent of methane was not prompt on the substrates used, a hot filament accelerated the deposition greatly. This fact suggests that the filament decomposes not only the hydrogen molecule but also hydrocarbons. Therefore, appropriate concentrations of hydrocarbon must be used. At  $700\text{--}1000^\circ\text{C}$ , a methane concentration of about 1% was used. As the concentration of methane increased, the morphologies of particles turned from euhedral, through blocky (Fig. 4a), to ball-like (see Fig. 5e). The ball-like particles showed peaks due to disordered graphite in the Raman spectrum. Lower concentrations decreased the number and size of the deposit (Fig. 4d). In addition, the ratio of the area of the (111) plane to that of the (100) plane decreased with decreasing methane concentration.

### 3.2. Effects of filament temperature and filament-substrate distance

The rate of diamond growth increased to a certain level with increasing filament temperature if the concentration of methane was appropriate (Fig. 5a-c). However, at high concentrations of methane, higher filament temperatures favoured the formation of graphitic carbon (Fig. 5d-f). Fig. 5f shows black carbon film.

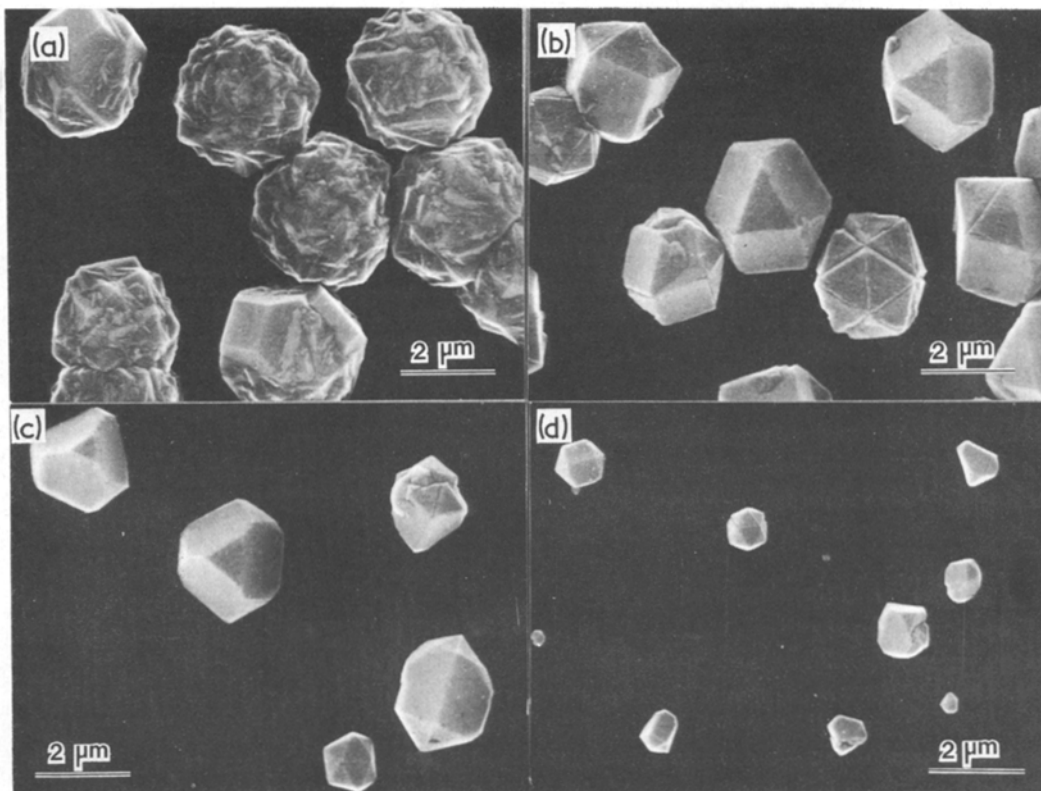
In most of the experiments the filament was placed about 10 mm above the substrate. The growth rates were suppressed by increasing the distance, probably because of the increase in the frequency of collisions between active species produced by the hot filament. SEM observation could not detect any particles with habits after the reaction at 12 Torr (1% methane) and  $925^\circ\text{C}$  by keeping the distance at 30 mm.

### 3.3. Effect of flow rate

In this equipment, it was necessary to flow gases slowly. As Fig. 6 shows, a slow flow rate ( $8\text{ cm}^3\text{ min}^{-1}$  STP) gave diamond particles with a well-defined habit, while a higher flow rate ( $160\text{ cm}^3\text{ min}^{-1}$ ) resulted in the formation of large ball-like particles co-deposited with graphitic carbon. This fact shows that higher flow rates accelerate the deposition of carbon. In this flow system, the C/H ratio in the gas phase seems to be close to the starting composition.

### 3.4. Effect of heating temperature

As described above, the surface temperature of the substrate was higher than the heating temperature. The value of the former was not known exactly. Nevertheless, under the same conditions used for other parameters, three effects of the heating temperature appeared, as Fig. 7 illustrates. 1. Lower temperatures decreased the number and size of the diamond particles formed. In contrast, at higher temperatures, deposition of blocky particles resulted (Fig. 7f). 2. On a cubo-octahedron or a decahedral-Wulff-polyhedron (a crystal composed of five twinned tetrahedra and truncated by five (100) planes), the ratio of the area of (100) to that of (111) increased with increasing temperature (Fig. 7a, c, d). At  $610^\circ\text{C}$ , in addition to cubo-octahedra with predominant (111) planes, the formation of octahedra was observed locally (Fig. 7b). Furthermore, at  $600\text{--}700^\circ\text{C}$ , grooves



*Figure 4* Effect of methane concentration on diamond particles deposited at 800° C under a total pressure of 36 Torr. Methane concentrations are (a) 2%, (b) 1%, (c) 0.67%, (d) 0.5%.

appeared between the (100) planes of a decahedral–Wulff–polyhedron; the grooves are believed to be composed of (111) planes (Fig. 7a, c). On the contrary, at about 900° C, grooves appeared between the (111) planes of an icosahedron (a crystal composed of twenty single crystal units). These grooves may consist of (100) planes.

3. Twin formation seems to be enhanced by increasing temperatures under the present experimental conditions.

The experiments on thermal desorption of hydrogenated diamond powder [15, 16] suggest that the thermal stability and reactivity of the growing surface of diamond depend on temperature. Also, the supersaturation of carbon increases with increasing temperature in this equipment. This effect can increase the area of (111) planes as discussed in Section 3.1. Nevertheless, the (100) planes predominated at high temperatures. This fact suggests that the reaction of hydrocarbon radicals produced by the hot filament have a greater influence on the growth of diamond than the decomposition of the hydrocarbons on sub-

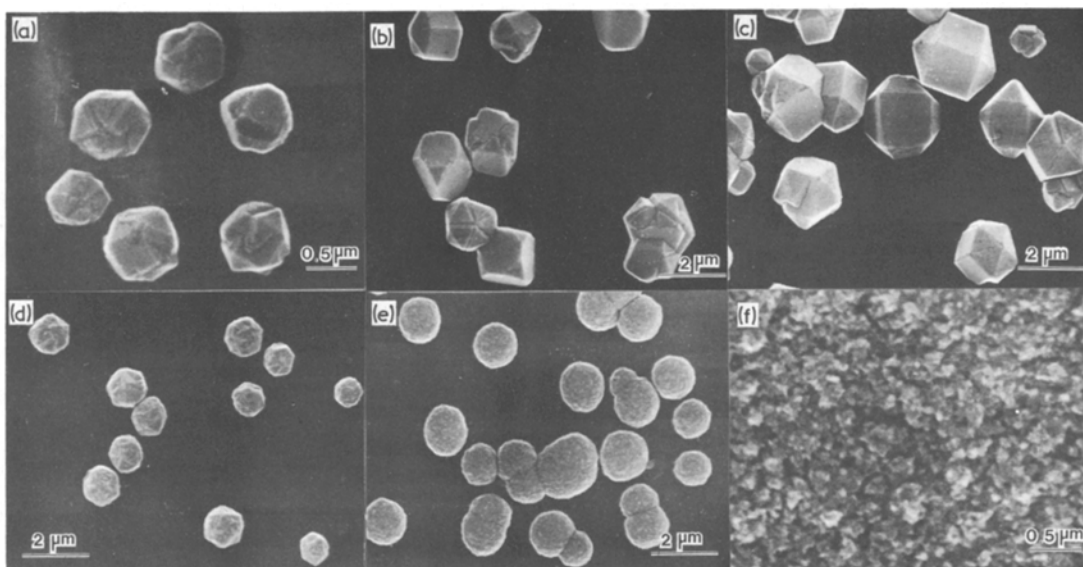
strate and, that the concentrations of the hydrocarbon radicals do not change appreciably with heating by the furnace.

### 3.5. Effect of pressure

At 800–900° C heating temperature, even at 0.5 Torr total pressure (1% methane) traces of diamond particles could be observed on silicon. However, they are small (0.1–0.3 μm) and did not have well-defined habits. At several tens Torr, densely populated and large (up to 5 μm) particles were observed. At 1 atm, however, only a small amount of chip-like deposit was formed which was not identified as diamond. It is not clear at the present stage why a pressure of 1 atm was too high to obtain diamond.

### 3.6. Effects of source gases

Experiments with ethylene instead of methane, gave similar results. In addition to heating by furnace, decomposition of hydrocarbons with a hot filament may decrease the effect of the type of source gas.



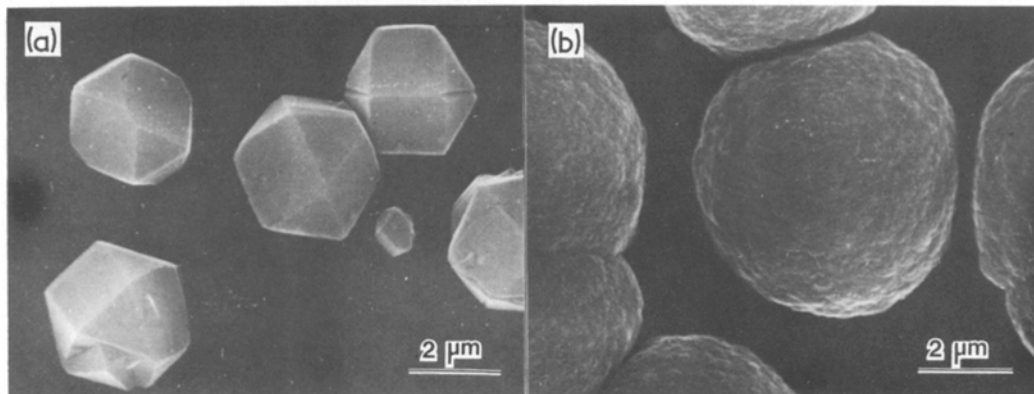
**Figure 5** Effect of filament temperature on the deposits prepared at 800° C under 37 Torr CH<sub>4</sub> (1%)–H<sub>2</sub> (a)–(c), and at 850° C under 10 Torr CH<sub>4</sub> (3%)–H<sub>2</sub> (c), (d). Filament temperatures are: (a) 1850° C, (b) 2050° C, (c) 2150° C, (d) 1850° C, (e) 2000° C, (f) 2100° C.

### 3.7. Effect of substrate

Experiments with silicon and molybdenum substrates gave products having similar morphologies and dimensions. Although the nucleation rate was much smaller on silica glass than on silicon and molybdenum, the particles obtained were also half-polyhedral. On (1 1 1) planes of natural diamond, polycrystalline films of diamond with the same orientation as the substrate, appeared. These results agree with those reported by Spitsyn *et al.* [11].

The relative rates of the growth of diamond and graphitic carbon seem to be determined by three reactions: 1. the formation of carbon-carbon bonds which are sp<sup>3</sup> or sp<sup>2</sup> hybridized by

decomposition of hydrocarbons on substrates and by deposition of active species produced by a hot filament. The calculation of the equilibrium compositions hydrocarbons at 2000° C [17] suggests that CH<sub>3</sub>, C<sub>2</sub>H and C<sub>2</sub>H<sub>2</sub> are probable as the active species. In addition, CH<sub>2</sub> and CH may be formed by interaction of CH<sub>4</sub> with a hot filament; 2. the transformation of the diamond surface into graphite in a hydrogen atmosphere; 3. the reaction of atomic hydrogen or hydrogen ions produced by a hot filament with graphitic carbon. Calculation with an equilibrium constant [14] of the reaction H<sub>2</sub> = 2H, indicates that about 20% hydrogen molecules dissociate in equilibrium at



**Figure 6** Effect of flow rate at 900° C under 35 Torr CH<sub>4</sub> (1%)–H<sub>2</sub> gas. Flow rates are (a) 8 cm<sup>3</sup> min<sup>-1</sup>, (b) 160 cm<sup>3</sup> min<sup>-1</sup>.

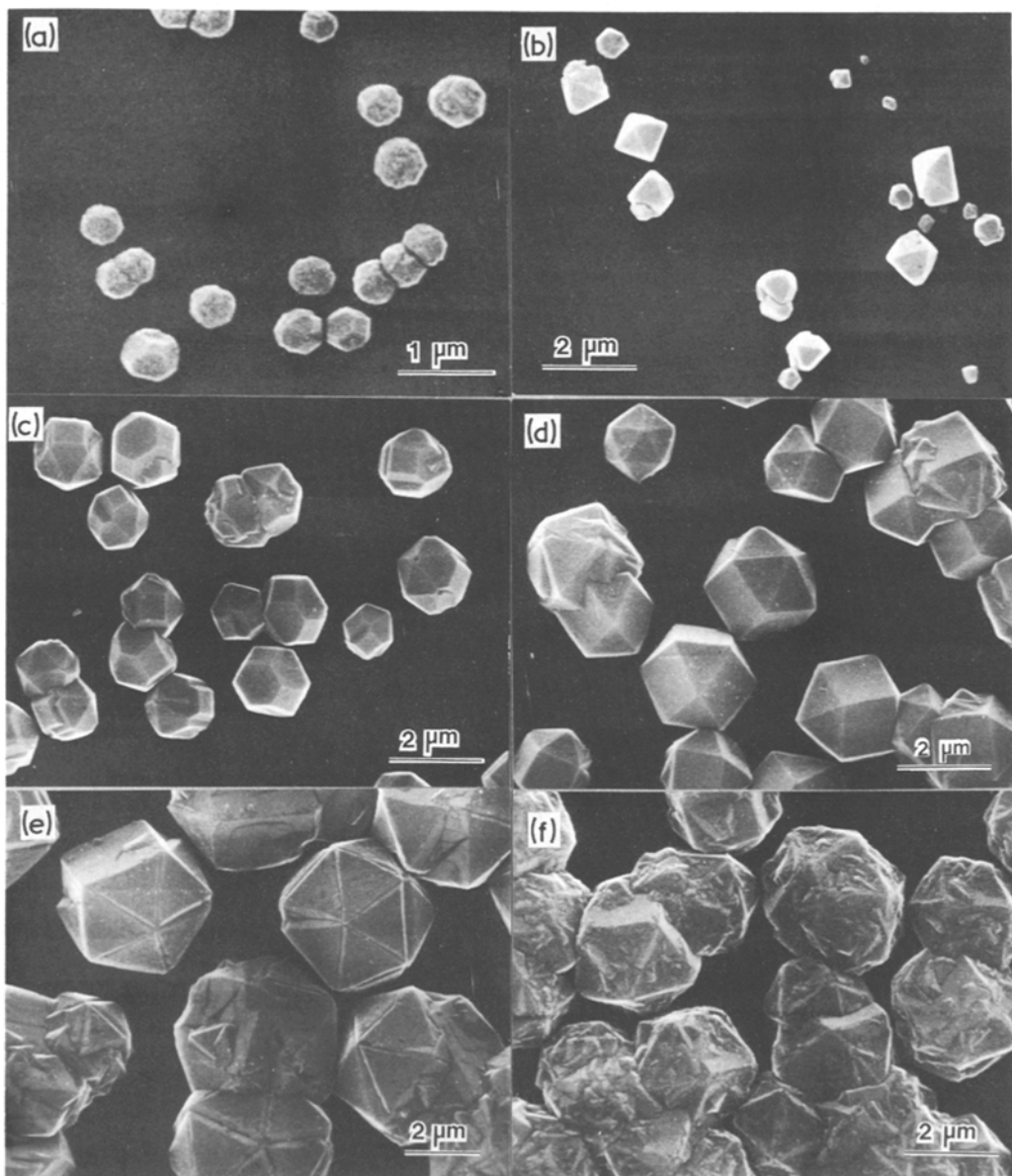


Figure 7 Effect of "heating temperature" under  $\sim 33$  Torr  $\text{CH}_4$  (1%)– $\text{H}_2$ . (a), (b)  $610^\circ\text{C}$ , (c)  $700^\circ\text{C}$ , (d)  $790^\circ\text{C}$ , (e)  $880^\circ\text{C}$ , (f)  $970^\circ\text{C}$ .

$2000^\circ\text{C}$  and at 35 Torr. Atomic hydrogen is believed to have a high reactivity with unsaturated or graphitic carbons and makes it possible to grow diamond selectively as Spitsyn *et al.* indicated [11]. In addition to atomic hydrogen, some sorts of hydrocarbon radicals may also participate in changing unsaturated carbon atoms into saturated ones forming C–C bonds. These three reaction rates are affected by the concentrations of hydrocarbons, active hydrocarbon radicals and atomic hydrogen, as well as by the substrate

temperature and pressure. Experiments are needed which can vary these factors independently to investigate the reaction mechanism in detail.

The present experiments showed that diamond particles can be grown on non-diamond substrates in a flow system. In contrast to the deposits obtained by the ion-beam method and plasma CVD, those prepared by this method were well crystallized, in cubic form, and had definite habits. In addition, though experimental results are not presented in this report, growth of diamond films

on non-diamond substrates was also possible. Raman spectra showed that the deposits have some imperfections. Detailed characterization is now being undertaken.

### Acknowledgements

The authors wish to express their thanks to Professor Akio Kato for valuable discussions and comments and to Dr Fujio Izumni for his critical reading of the manuscript.

### References

1. W. G. EVERSOLE, US Pat. 3030187 and 3030188 (1958).
2. J. C. ANGUS, H. A. WILL and W. S. STANKO, *J. Appl. Phys.* **39** (1968) 2915.
3. S. AISENBERG and R. CHABOT, *ibid.* **42** (1971) 2953.
4. E. G. SPENCER, H. P. SCHMIDT, D. C. JOY and F. J. SANSALONE, *Appl. Phys. Lett.* **29** (1976) 118.
5. G. GAUTHERIN and CHR. WEISMENTAL, *Thin Solid Films* **50** (1978) 135.
6. D. S. WHITMELL and R. W. WILLIAMSON, *ibid.*

7. L. HOLLAND and S. M. OJHA, *ibid.* **38** (1976) L17.
8. D. A. ANDERSON, *Phil. Mag.* **35** (1977) 17.
9. S. BERG and L. P. ANDERSSON, *Thin Solid Films* **58** (1979) 117.
10. B. V. DERYAGIN, B. V. SPITSYN, L. L. BUILOV, A. A. KLOCHKOV, A. E. GORODETSKII and A. V. SMOL'YANINOV, *Sov. Phys. Dokl.* **21** (1976) 676.
11. B. V. SPITSYN, L. L. BOUILOV and B. V. DERJAGUIN, *J. Crystal Growth* **52** (1981) 219.
12. ASTM X-ray powder data file 6-675.
13. A. SOLIN and A. K. RAMDAS, *Phys. Rev.* **B1** (1970) 1687.
14. "JANAF Thermodynamical Tables" (NBS, Washington, 1971).
15. S. MATSUMOTO and N. SETAKA, *Carbon* **17** (1979) 485.
16. S. MATSUMOTO, Y. SATO and N. SETAKA, *ibid.* **19** (1981) 231.
17. B. LERSMACHER, H. LYDTIN, W. F. KNIPPENBERG and A. W. MOORE, *ibid.* **5** (1967) 205.

Received 25 January  
and accepted 1 March 1982