

The growth of diamond in microwave plasma under low pressure

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The synthesis of diamond particles in a low pressure plasma has been studied, with emphasis on the investigation of the substrate effect and the plasma conditions. It was found that a special pre-treatment of silicon substrate made it possible to form dense films, and a thickness of about $15\ \mu\text{m}$ could be reached by 20 h discharge. Unfortunately, however, the prepared films had poor adhesion. Observations by scanning electron microscope (SEM) showed that the poor adhesion was due to the fact that the film consisted of large particles with a diameter of about $10\ \mu\text{m}$, and each particle had contacted to the substrate only by a point, not by a face. In addition, the plasma diagnostics of optical and ultraviolet emission spectroscopy (OES, 200–750 nm) revealed that CH and H radicals have come to be criteria for the formation of diamonds, and the ratio of radicals drastically affected the characteristics of the deposits. Nucleation and growth mechanism are also discussed.

1. Introduction

There are two major methods of diamond synthesis: one is the well-known method in the thermodynamic stability region of superhigh pressure and high temperature, and the other is that in the thermodynamically hindered low pressure region.

Many workers have attempted to synthesize diamond in the hindered region during the last decade [1–3]. Recently this method of synthesis has been succeeded by chemical vapour deposition using tungsten filament (filament CVD) [4], followed by the plasma CVD using microwave (MW) or radio frequency (RF) devices [5, 6]. On the other hand, it had been thought that only *i*-carbon films could be grown by ion beam methods [7, 8]. Very recently, however, an ion beam sputtering method and an ionized deposition method were reported to succeed in the synthesis of diamond films [9, 10].

Unfortunately, however, the mechanism of diamond growth is not clear at this stage. To date, the following qualitative explanations have been made. Firstly, the hydrogen atomic radicals are important in order to etch graphite more rapidly than diamond, which results in only diamond remaining on the substrate [3]. Secondly, in the CVD method, the substrate temperature must be raised from about 1000 to 1300 K [4–6]. In this temperature range, the reaction between carbon and hydrogen, which brings about the formation of hydrocarbons, would be negligible [11]. Thirdly, in order to obtain diamond films, the substrate must be polished, or there must be a fine scratch on the substrate surface, which would serve as the nucleation site.

In this paper, therefore, the effects of the substrate surface on diamond formation are extensively examined in order to investigate the nucleation phenomena.

Moreover, plasma diagnostics using optical and ultraviolet emission spectroscopy (OES) have been carried out in order to clarify the plasma conditions needed for diamond formation.

2. Experimental procedures

A schematic drawing of the experimental apparatus is shown in Fig. 1. A quartz tube (40 mm diameter) was set across the microwave guide tube, which served as the plasma deposition furnace. H_2 and CH_4 (a few vol %) were used as reactants and microwave (MW, 2.45 GHz) as plasma power supply. MW power was supplied into the deposition furnace through a set of guide tubes, a power monitor, and a tuner. After power tuning, a plasma was generated and confined in the centre of the quartz tube. A (100) silicon wafer, $20 \times 15\ \text{mm}$, was used as a substrate, which was put on a boron nitride holder vertically set at the end of the guide tube ($x = 30\ \text{mm}$). The substrate temperature was measured from a rear window by an optical pyrometer not hindered by plasma radiation.

The obtained samples were analysed by reflection high energy electron diffraction (RHEED), X-ray diffraction (XRD), Auger electron spectroscopy (AES), and infrared absorption spectroscopy (IR).

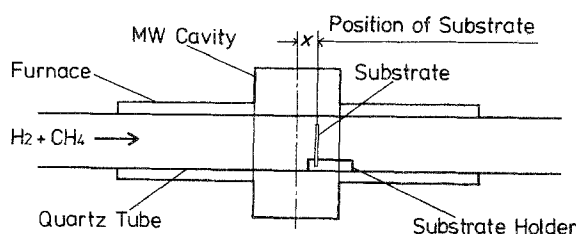


Figure 1 Experimental apparatus. The position of the substrate from the middle of the cavity is denoted by x (mm).

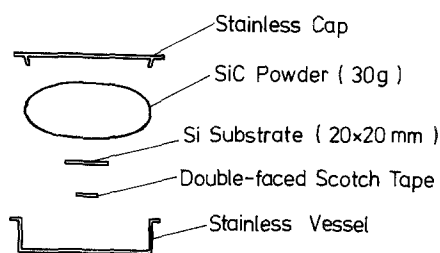


Figure 2 Vessel of substrate treatment. The diameter and height of the vessel are 75 and 20 mm, respectively.

Fig. 2 shows the device used for polishing the substrate. The substrate was fixed on the bottom of the stainless vessel by double-faced Scotch tape, and various particle sizes of SiC powder (#100–#2000, 30 g) were placed on it. Then it was sealed and vibrated for a given time by a mechanical vibrator. By this method the vibration of SiC powder generates fine uniform scratches on the substrate.

The left-hand column of Table I gives the experimental conditions in the case of no treated substrate being used. In this case, the substrate temperature was dependent mainly upon MW supplied power. The right-hand column gives the conditions in the case of the treated substrate being used. Under these conditions, the relation between the features of the deposited diamond and the treated surface conditions were extensively investigated.

Optical and ultraviolet emission spectra in glow

TABLE I Experimental conditions

Parameters	no treated substrate	treated substrate
Total pressure (kPa)	0.1–13	6.7
CH ₄ concentration (vol %)	0.5–5.0	2.0
MW supplied power (W)	300–700	400
Total flow rate (sccm)	60	60
Substrate temperature (K)	1000–1400	1170

discharge were led from the centre of a guide tube to the inlet slit of a monochromator through an optical fibre ST800UV-SY (Mitsubishi Cable Industries), and were detected by the combination of a monochromator JY38P (Seiko) and a photomultiplier R456 (Hamamatu). This system could detect the spectra from 200 to 750 nm, with a resolution of about 0.05 nm.

3. Results and discussion

3.1. Deposition

3.1.1. Preliminary experiments

Particle-like deposits were always grown under the various conditions investigated here (shown in Table I). RHEED patterns of these particles usually consisted of spotty rings, and XRD peaks could be also observed. The calculated values of the interlayer spacings for both XRD and RHEED are in good agreement with the values reported for natural diamond as given in Table II. Moreover, AES spectra showed that the faceted particles were composed of only carbon, except for absorbed surface oxygen. The infrared absorption spectra of the samples have no absorption peak from 4000 to 400 cm⁻¹ and these deposits seemed to be almost transparent to infrared radiation.

However, both diamond and SiC, which were

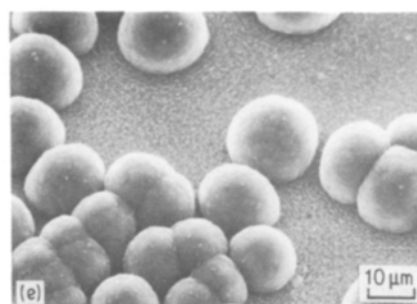
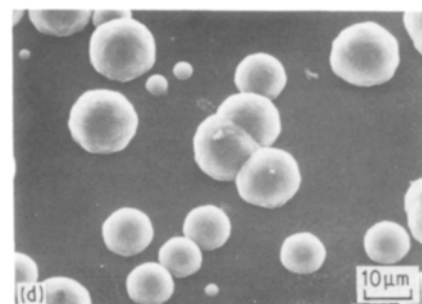
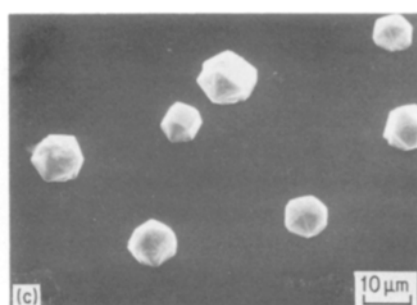
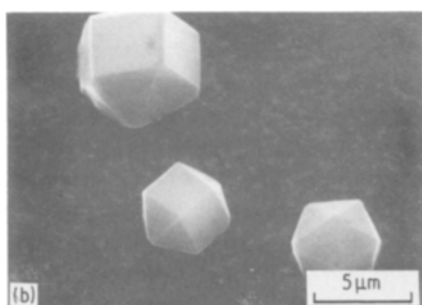
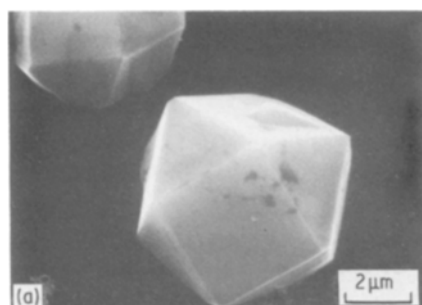


Figure 3 SEM photographs of the deposited particles, which show the influence of CH₄ concentration. (a) 0.5 vol %, (b) 1.0 vol %, (c) 2.0 vol %, (d) 3.0 vol %, (e) 4.0 vol %. Experimental conditions: power, 400 W; pressure, 6.7 kPa; flow rate, 60 sccm; discharge time, 8 h.

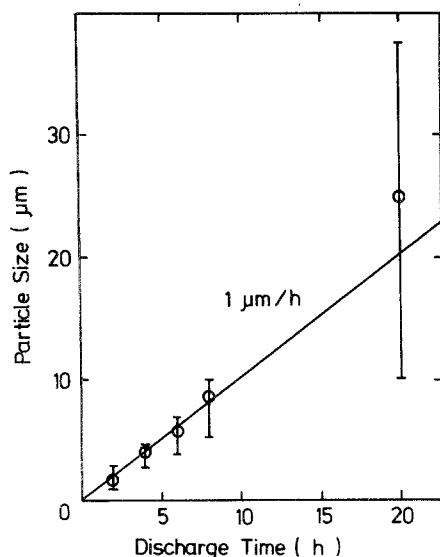


Figure 4 Diamond particle size against discharge time. Bar and open circle show the particle range and the average particle size, respectively. Experimental conditions: power, 400 W; pressure, 6.7 kPa; flow rate, 60 sccm; CH₄ concentration, 2.0 vol %.

confirmed by RHEED, XRD and IR, were formed on the same substrate under the special conditions of high MW power and/or low pressure, for example, at 6.7 kPa and more than 600 W, or at less than 2.0 kPa. The results of RHEED, XRD and IR showed that amorphous SiC was deposited at rather high pressure (a few kPa), but that β -SiC was formed at rather low pressure (a few hundred Pa). The source of silicon was considered to be the quartz tube, because plasma touched the internal source of quartz tube under the above conditions. Accordingly, in order not to eject silicon atoms from the quartz tube, MW power and pressure must be strictly controlled.

Fig. 3 shows the effect of CH₄ concentration on the appearance of diamond. The particles showed the clear-cut habits of cubic crystal at low concentration of CH₄ (less than 2.0%), but at a CH₄ concentration higher than 3.0%, spherical particles were grown although the growth rate became faster. This change of shape would be caused by multi-nucleation on the diamond particles and/or the formation of amorphous carbon between the particles. The shape variation also depended upon MW supplied power, which also affected substrate temperature. The effects of the power on shape showed the similarity to the effects of CH₄ concentration, which would be caused by the fact that the growth rate of diamond was faster at high MW power as well as at high CH₄ concentration. The dependence of pressure on the shape was not evident

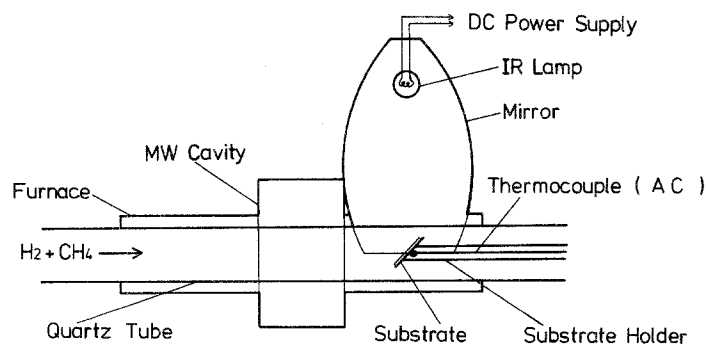


Figure 5 Experimental apparatus for examining the effect of the substrate temperature and substrate position. The substrate is heated by an IR lamp (100 V, 10 A max), and set at the position of $x = 80$ mm compared with the apparatus shown in Fig. 1.

TABLE II Interlayer spacings evaluated by the results of XRD and RHEED. Experimental condition; MW power, 400 W; total pressure, 6.7 kPa; discharge time, 5 h; CH₄ concentration, 2.0 vol %; total flow rate, 60 sccm. (d; lattice spacing (A), I; Intensity).

XRD		RHEED		ASTM 6-675 (diamond)		
d (A)	I/I ₁	d (A)	I	d (A)	I/I ₁	hkl
2.061	100	2.06	S	2.06	100	111
1.261	24	1.27	S	1.261	25	220
1.076	14	1.08	S	1.0754	16	311
		0.90	W	0.8916	8	400
		0.82	M	0.8182	16	331

at this stage, but the density of diamond particles deposited on the substrate had a maximum value at a pressure of about 6.7 kPa. Fig. 4 shows that the diameter of diamond particles was almost proportional to the discharge time, and that the growth rate was about $1 \mu\text{m h}^{-1}$ in this case. As mentioned above, the growth rate was influenced by other parameters, and varied from 1 to $3 \mu\text{m h}^{-1}$.

The other experiments were performed to examine the effects of the substrate temperature and substrate position. The experimental apparatus was almost the same one as shown in Fig. 5, but a substrate heated by an IR lamp was set at the position of $x = 80$ mm, where the substrate was not in contact with the plasma. The experimental condition was the same as that of the left-hand column of Table I. However, the substrate temperature was independently controlled from 900 to 1300 K and measured by a thermocouple. In this case, from the results of RHEED and SEM, most of the deposit was graphite, though diamond was also observed. The formation of diamond seemed to have a tendency to become clear under the conditions of low temperature and low pressure.

In summary, the best conditions for synthesizing pure diamond were as follows: total pressure, 6.7 kPa; CH₄ concentration, 2.0 vol %; MW supplied power, 400 W.

3.1.2. Effects of substrate surface conditions

The depositions were performed under the best plasma conditions obtained by the preliminary experiments (Table I). The diamond particles were deposited on the treated substrate at a higher density than on the untreated one. Some of these samples had particles in a high enough particle density to form diamond film.

Scanning electron micrographs of the samples obtained after 5 h discharge are shown in Fig. 6, as

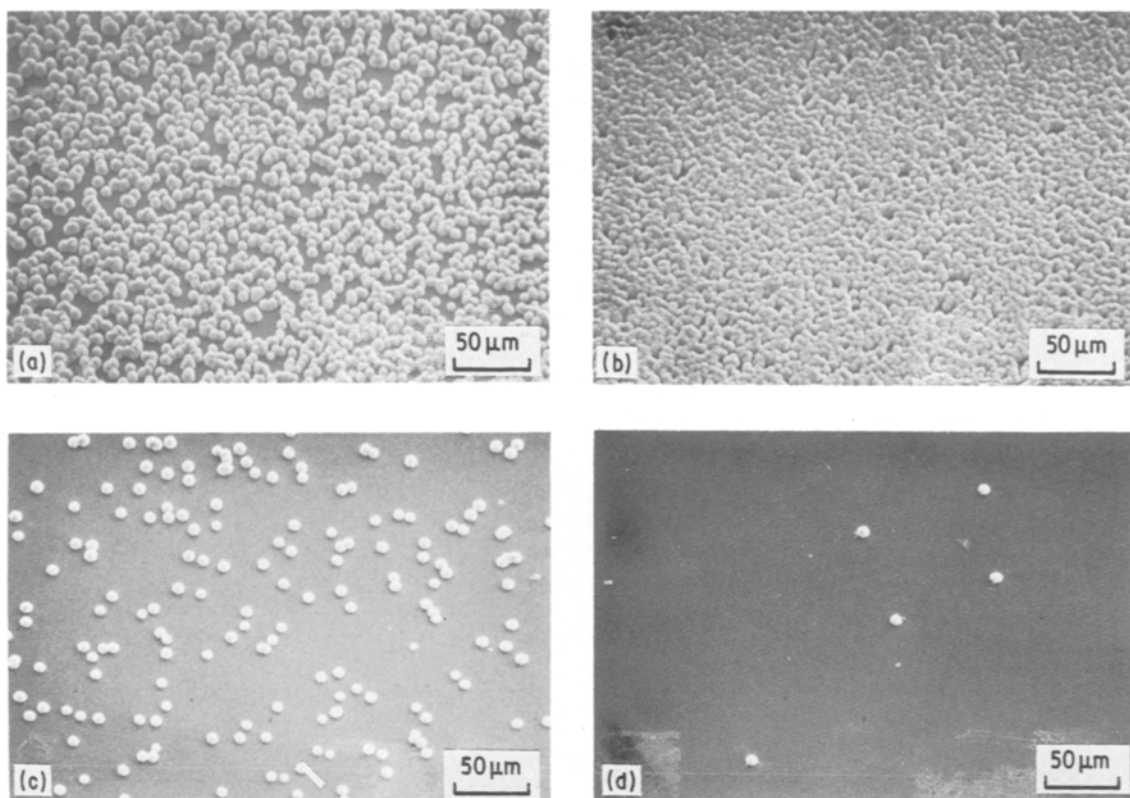


Figure 6 SEM photographs of the deposits, which show the influence of SiC powder size used for the substrate treatment. (a) # 320, (b) # 1000, (c) # 1200, (d) # 2000. Experimental Conditions: power, 400 W; pressure, 6.7 kPa; flow rate, 60 sccm; CH₄ concentration, 2.0 vol %; discharge time, 5 h.

compared with the powder sizes used in one hour substrate treatment, revealing that the best treatment was by # 1000 powder. In this case, diamond particles were grown almost all over the substrate. The rougher or the finer the powder size is than # 1000, the lower density the deposits have. The particle density on the substrate treated by # 2000 powder was almost equal to that on the untreated substrate. The formation of diamond particles on this treated substrate was better than that on the substrate treated by the usual method, in which the substrate is polished by hand using a few μm of diamond paste or powder.

There are apparent differences in the condition of the substrate surface before and after the treatment as shown in Fig. 7. The observed roughness was of the order of 10 nm. However Fig. 6 reveals that only

one or two particles were grown in the area of this photograph, which means that the roughness was not attributed to the nucleation site of the diamond directly, but the surface crystal defects caused by the treatment would be the main factor for the high density deposition.

20 h discharge was performed on the substrate treated by # 1000 powder for 1 h. Scanning electron micrographs of the obtained sample are shown in Fig. 8. The thickness of its film was about 15 μm , and the film consisted of particles with a diameter of about 10 μm . The adhesiveness of the film was so poor that it was removed when this sample was cut by a diamond cutter. The backside surface of the film is shown in Fig. 8b. The vacant space could be clearly seen, though the top surface seemed to be a perfect film.

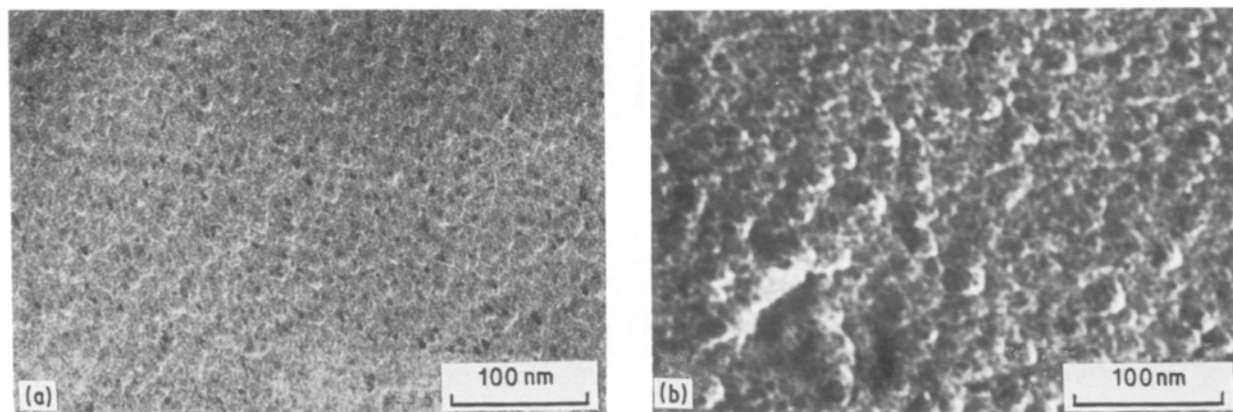


Figure 7 TEM photographs of the replica films, which show the surface condition of the substrate. (a) No treated substrate, (b) treated substrate using # 1000 SiC powder for 1 h.

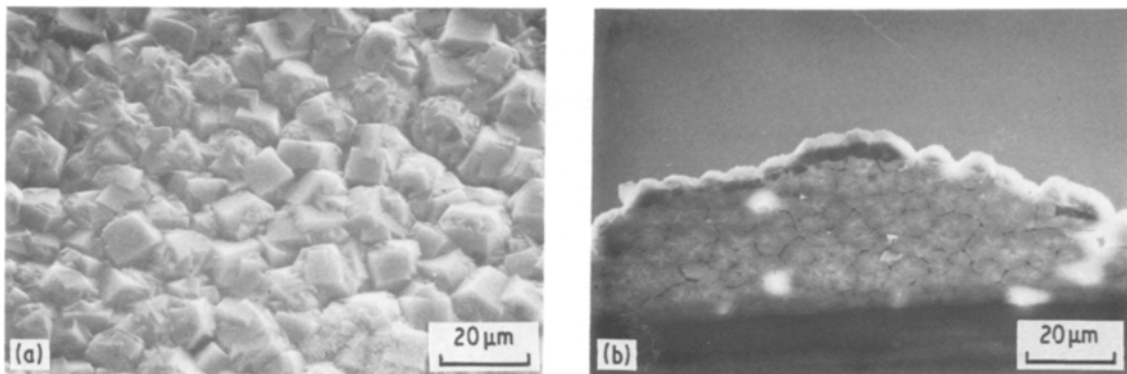


Figure 8 SEM photographs of diamond film deposited for 20 h discharge on the substrate treated by # 1000 SiC for 1 h. (a) Top surface, (b) back surface. Experimental conditions: power, 400 W; pressure, 6.7 kPa; flow rate, 60 sccm; CH₄ concentration, 2.0 vol %.

Accordingly, the following mechanism of film formation could be considered: the growth rate of diamond is faster in diameter at the early stage, and the shape of the diamond particles has the clear-cut habits of cubic crystal, which results in the formation of a vacant space between particles when these particles come into contact with each other. In the next stage, diamonds only grow in a vertical direction to the substrate. This growth mechanism may be attributed to the weak adhesion, because each diamond particle composed of the film was considered to be in contact with substrate at the point which was the vertex of a single crystal.

The treatment time also had an influence on the condition of the deposits. The density of diamond particles became higher in proportion to treatment time, revealing that the number of nucleation sites was

not saturated by the 1 h treatment. Fig. 9 shows scanning electron micrographs of the sample prepared by using substrate treated for 4 h, which shows that the diameter of particles composed of the film was apparently smaller than that of the case in Fig. 8. This means that the treatment of 4 h had more nucleation sites on the substrate than that of 1 h. If the substrate was treated under the appropriate conditions in order to make any nucleation sites, the diamond film would be composed of smaller particles, which would result in the formation of many contact points leading to a good adhesion.

3.2. OES

Table III showed the typical emission spectra observed under the experimental conditions investigated here. Though H₂ spectra were also detected over a wide

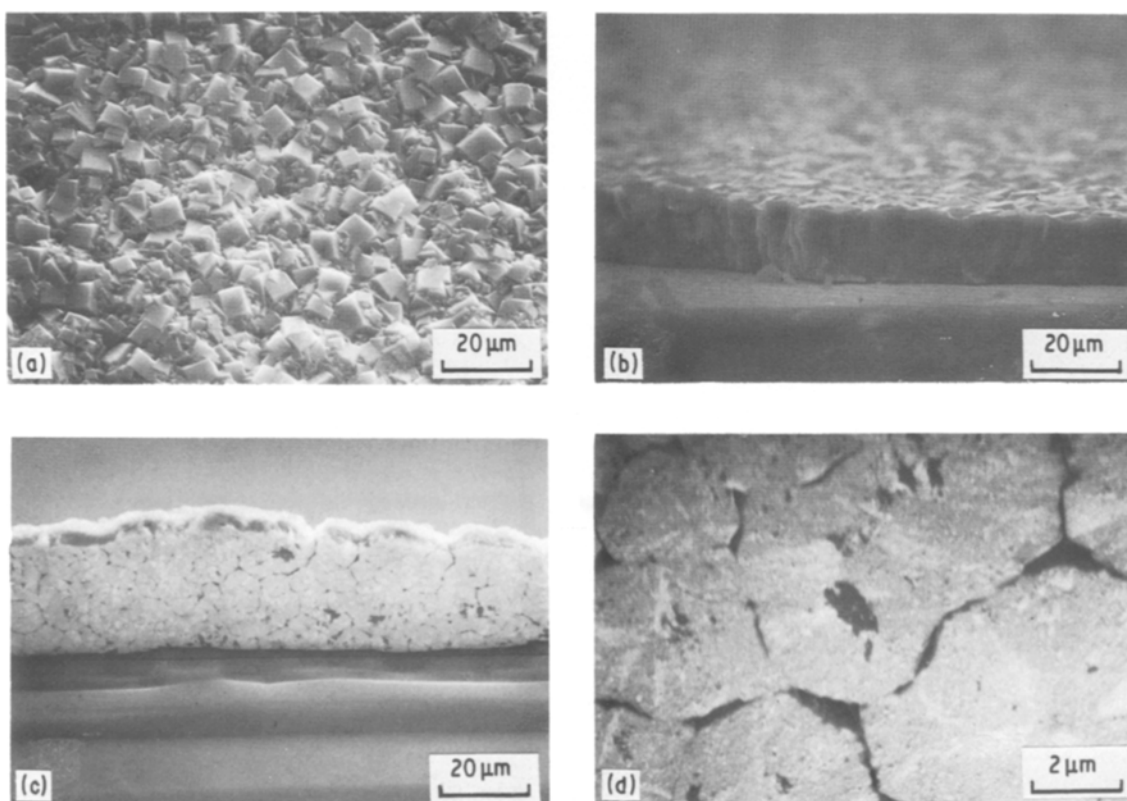


Figure 9 SEM photographs of diamond film deposited for 20 h discharge on the substrate treated by # 1000 SiC for 4 h. (a) top surface, (b) cross section, (c) back surface, (d) expansion of back surface shown in (c). Experimental conditions: power, 400 W; pressure, 6.7 kPa; flow rate, 60 sccm; CH₄ concentration, 2.0 vol %.

TABLE III Identified species in MW plasma from emission spectra

Species	Wavelength (nm)	Band system
CH	314.41	3143A system
CH	387.11	3900A system
CH	431.42	4300A system
H _γ	434.05	Balmer
H _β	486.13	Balmer
C ₂	516.52	Swan
H _α	656.28	Balmer

range of OES, they are ignored in this table, because the H₂ spectrum has few characteristic features, as the rotational structure is so open that there are no band heads or close groups of lines to form anything resembling the usual band structure. Whenever silicon atomic spectra (251.61 and 288.16 nm, etc.) were detected under high power conditions, SiC was also formed on the substrate. As mentioned above, the source of silicon atoms would be the internal surface of a quartz tube, because silicon spectra could be detected without the silicon substrate. The carbon atomic spectrum (247.86 nm) was detected under the conditions of high CH₄ concentration and high power. The spectra of CH_x ($x = 2, 3$), C_x ($x > 2$) and ionic species were not detected. It may be that their concentrations were too low to be detected by our system, or their band spectra were so open that they had no evident peaks. Accordingly, the peak intensities of CH and C₂ radicals were used for the examination of the plasma conditions suited for diamond growth. These radicals could be considered to represent the radical groups of CH_x or C_x. Moreover, in order to investigate the role of H₂ gas, the attention was paid to the emission of hydrogen atomic radical.

By measuring the intensity of these spectra, some necessary plasma conditions for the diamond synthesis were obtained, as given in Table IV. The intensity ratio between CH (314.41 nm) and H_β (486.13 nm) was considered to be the main criterion for diamond synthesis. When this ratio was 5 to 20%, diamond was deposited on the substrate. But diamond has no apparent faceted faces if this ratio is larger than 15%. Even if this condition was satisfied, diamond could not be formed at substrate temperatures below about 1000 K. As mentioned above, if the silicon atomic spectrum (251.61 nm) was detected, both diamond and SiC was formed. Accordingly, the silicon spectrum must not be detected to prepare pure diamond. When the spectra of C₂ radicals were too high as compared with those of CH radicals, graphite was mainly grown. So C_x radicals were considered to be responsible for the formation of graphite. Then the C₂ radical spectrum (516.52 nm) must be much smaller

TABLE IV Diamond synthesis conditions derived from this study

5% < CH(314.41 nm)/H _β (486.13 nm) < 20%
T _{sub} > 1000 K
Si(251.61 nm) negligible
C ₂ (516.52 nm) ≪ CH(314.41 nm)
C ₂ (516.52 nm)/H _β (486.13 nm) < critical point

than the CH radical spectrum (314.41 nm). Moreover, the ratio of C₂ to H_β has an upper limit, namely there should be enough hydrogen atomic radical to etch all the graphite [12]. But the excessive hydrogen radical will etch both graphite and diamond on the substrate. So to deposit pure diamond a plasma must contain the appropriate amount of hydrogen radical. It is considered that this mechanism of diamond formation also gives the lower critical point of the ratio of CH to H.

However, in the case of the substrate set at the position of $x = 80$ mm, as mentioned above, very few diamond particles were observed, although OES was satisfied with all the above conditions given in Table IV. This fact reveals that the role of plasma should be considered not only to generate the effective radicals, but also to enhance the formation of diamond by coming into contact with the substrate.

4. Conclusions

The conclusions of this paper were as follows:

1. Dense diamond films could be successfully deposited on silicon substrate treated by the newly developed special method, and a thickness of about 15 μm could be reached by 20 h discharge.
2. The film consisted of large particles with a diameter of about 10 μm, each particle contacting to the substrate only by a point, not by a face.
3. The adhesion strength between the substrate and the film was relatively weak, and was considered to be dependent upon the number density of the contact points. If particle size is reduced, the film should adhere to the substrate more strongly.
4. From the results of OES, the intensity ratio of CH and H radicals was found to be an important criterion in the formation of diamond, which drastically affects on the characteristics of the deposits.
5. CH_x radicals are related to the diamond formation, while C_x radicals are responsible for the graphite formation.

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