JOURNAL OF MATERIALS SCIENCE 26 (1991) 3748–3752

TEM observations of diamond films produced by hot filament thermal CVD

Y. OHSAWA, Y. TAMOU, N. KIKUCHI
Central Research Institute of Mitsubishi Metal Corporation, 1-297 Kitabukuro-cho, Omiya, Saitama 330, Japan
K. HIRAGA, T. OKU
Institute for Materials Research, Tohoku University, Katahira, Sendai 980, Japan

Diamond films were provided by a hot filament thermal chemical vapour deposition method with an H_2–CH_4 gas mixture under various reaction conditions: CH_4/H_2 ratios of 0.5% and 1.0%, Si and Cu substrates, a substrate temperature of 750 °C, a pressure of 7 torr and a reaction time of 12 h. TEM observation showed that the films produced have many defects such as twins, stacking faults and large distortion of lattices. These defects, which increase with increasing CH_4 concentration, seem to be introduced during the crystal growth process. Five-fold symmetry twinned crystals were often observed in the diamond films.

1. Introduction

Diamond is the hardest material known and has widely been used in many industrial applications such as grinding tools and polishing powders. In the early stages of diamond applications, only natural diamond was used. Since 1955, diamond has been produced by the ultra-high pressure technique which was developed by researchers at General Electric Co. in the USA [1]. This diamond is in either powder form or a block form, and its applicable areas are rather limited.

Diamond has many useful properties for industrial applications: high electrical resistivity, high thermal conductivity, high optical transparence, high Young's modulus, etc. Therefore, the synthesis processes of diamond, especially for thin film, have been studied by many researchers in order to utilize these useful properties. Spitsyn and Derjaguin [2], Eversole [3], and Angus *et al.* [4] showed that diamond films can be produced by the chemical vapour deposition (CVD) method under a reduced pressure in metastable thermodynamic states. Aisenberg and Chabot [5] also reported that a very hard, optically transparent and high electrical resistance film could be obtained by the ion-beam technique, and they called this film a diamond-like carbon film. This method has been studied by many workers [6–8] and is now one of the most typical methods for making a diamond-like carbon film. These films consist mainly of amorphous carbon, and no method was known for the preparation of crystalline diamond film for a long time.

In 1982, Matsumoto *et al.* [9, 10] reported that thin diamond films could be produced either by a modified thermal CVD method or by a plasma CVD from a low-pressure gas mixture of H_2 and CH_4. Since then, many researchers have studied new synthesis methods [11–13] and on the reaction mechanisms [14, 15]. However, a definite mechanistic model of diamond nucleation and growth of diamond from gas phase has not yet been established.

Transmission electron microscopy (TEM) is one of the most suitable methods to examine the inner structures of thin films. Matsumoto and Matsui [16] examined CVD diamond particles by TEM, and they reported that the typical crystal habit of CVD diamond was cubo-octahedron and also observed twinned crystals. Mar *et al.* [17] also examined diamond particles made by the plasma-assisted CVD by using ultra-high voltage TEM. They observed many line defects inside the diamond particles. As these defects are supposed to be created during the CVD diamond formation, it is important to examine them in detail in order to understand the mechanism of nucleation and growth from gas phases. There are no reports of a detailed study of these defects.

The purpose of this work was to understand the mechanism of nucleation and growth of CVD diamond films by examining its defects in more detail.

2. Experimental procedure

Diamond films were prepared by a hot filament thermal CVD method. Fig. 1 shows a schematic picture of the hot filament thermal CVD apparatus in which H_2 and CH_4 were used as source gases. The inner diameter of the quartz tube is 200 mm and the size of substrate holder, which is made from molybdenum, is 70 mm diameter. Three filaments were made by 0.3 mm tungsten wire wound into 2 mm diameter and 50 turns coils and they were placed over the centre of the substrate holder. They were kept at the centre of the vacuum chamber which can be evacuated to 10^{-3} torr (1 torr = 1.333×10^2 Pa) before reaction. H_2

0022–2461/91 $03.00 + .12

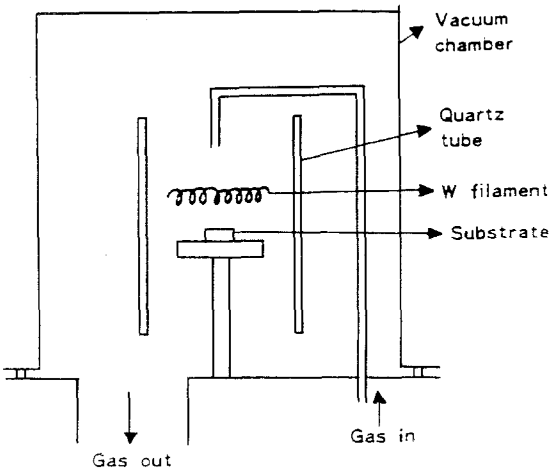

Figure 1 Schematic drawing of the apparatus for CVD of diamond films.

(99.99% purity) and CH_4 (99.9%) were used as reactant gases.

Silicon (Si) and copper (Cu) plates were used as substrates. They were covered by 3 µm diamond powder before use. The substrates were placed on the holder and the chamber was evacuated and then reaction gases were introduced into it at the established pressure for controlling the reaction. The reaction was initiated by heating the filaments up to 2000 °C. During the reaction, the temperature on surface of the substrate was kept at 750 °C with radiation from the filaments. Table I shows the reaction conditions. Only the concentration of CH_4 was varied, i.e. 1% and 0.5%. Scanning electron microscopy (SEM) was used to observe surface morphologies of diamond films. The crystal structure of the diamond films was examined by laser Raman spectroscopy.

Diamond films on the Cu substrates could be peeled off with tweezers, because the adhesive strength of diamond film to Cu is very poor. Diamond films on the Si substrates were obtained by dissolving the substrates with a mixed solution of nitric acid and fluoric acid. These diamond films were transferred on to the microscopic mesh and thinned by ion thinning. TEM observations were performed with a Jeol JEM-200CX type microscope at an accelerating voltage of 200 kV.

3. Results and discussion

Fig. 2 shows scanning electron micrographs of the surface morphology of diamond films which were deposited on the Si substrate at different CH_4 concentrations of 1.0% and 0.5%. At higher CH_4 concentrations (Fig. 2a), the diamond film mainly consists of (1 1 1) planes which are seen to form triangle shapes. At lower CH_4 concentrations (Fig. 2b), the film consists of coagulated diamond particles and the surfaces of these particles are seen to have a mixture of (1 1 1) and (1 0 0) planes.

TABLE I CVD reaction conditions for the deposition of diamond films

Reaction gases	H_2, CN_4 CH_4/H_2:0.5%, 1.0%
Pressure (torr)	7
Substrates	Si wafer, Cu plate
Reaction time (h)	12

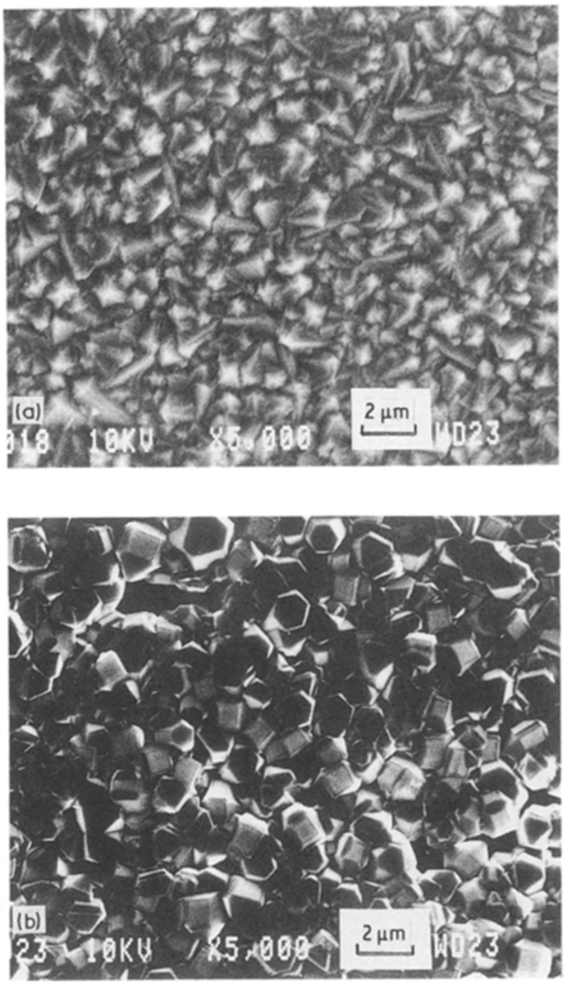

Figure 2 Scanning electron micrographs of diamond films deposited on the Si substrate with CH_4 concentrations of (a) 1.0% and (b) 0.5%.

Fig. 3 shows the results of laser Raman spectroscopy of these diamond films. A broad peak of amorphous C around 1500 cm^{-1} was detected, together with a sharp peak of diamond at 1332 cm^{-1} in the Raman spectrum of a diamond film of high CH_4 concentration (Fig. 3a). As the concentration of CH_4 decreases (Fig. 3b), the amorphous C peak decreases. These results show that amorphous C is produced to a greater degree in the diamond films prepared at high CH_4 concentrations.

Fig. 4 shows transmission electron micrographs of the diamond films which were deposited on the Cu substrate at two CH_4 concentrations. Fine markings which correspond to defects are visible inside the diamond polycrystals, and are more numerous in films at high CH_4 concentrations (Fig. 4a) than in those at low CH_4 concentrations (Fig. 4b). This trend becomes clearer in the diamond films which were deposited on Si substrates. In Fig. 5, transmission electron micrographs of diamond films on Si substrates are shown. The defects are clearly less in diamond films at low

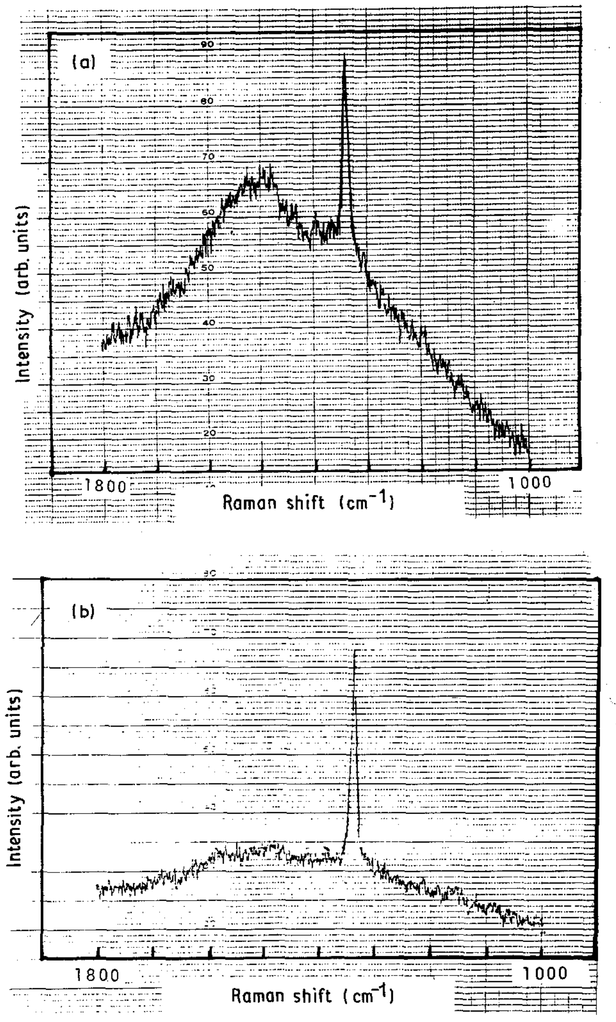

Figure 3 Raman spectra of diamond films prepared on the Si substrate with CH_4 concentrations of (a) 1.0% and (b) 0.5%.

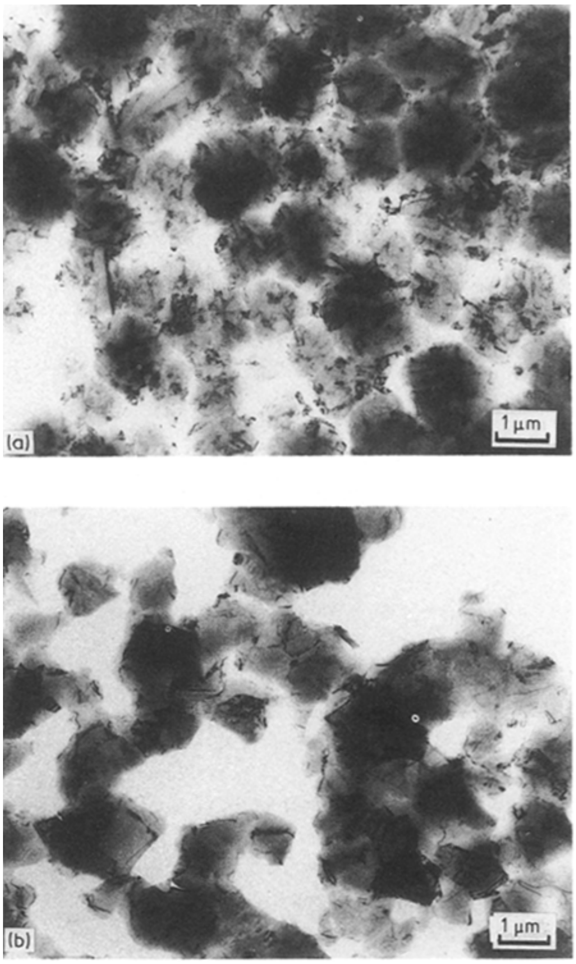

Figure 4 Transmission electron micrographs of diamond films deposited on the Cu substrate with CH_4 concentrations of (a) 1.0% and (b) 0.5%.

CH_4 concentrations (Fig. 5b) than in those at high CH_4 concentrations (Fig. 5a). The grain boundaries of these diamond crystals are relatively clean and no other phases are visible at grain boundaries under all conditions.

Fig. 6 shows high-resolution TEM images of diamond films. Many line defects can be seen consisting of twins and stacking faults (Fig. 5). A straight line (A) in the centre of Fig. 6a is a twin boundary, and the crystal direction is changed on this line and is changed again at the twin boundary (B). These twin couples were observed in many other areas in one crystal, i.e. C and D. Many types of defect, such as stacking faults and dislocations, were also observed, as can be seen at E. In Fig. 6b, a highly disordered region (F) is also seen at the crossing point of twin boundaries. In general,

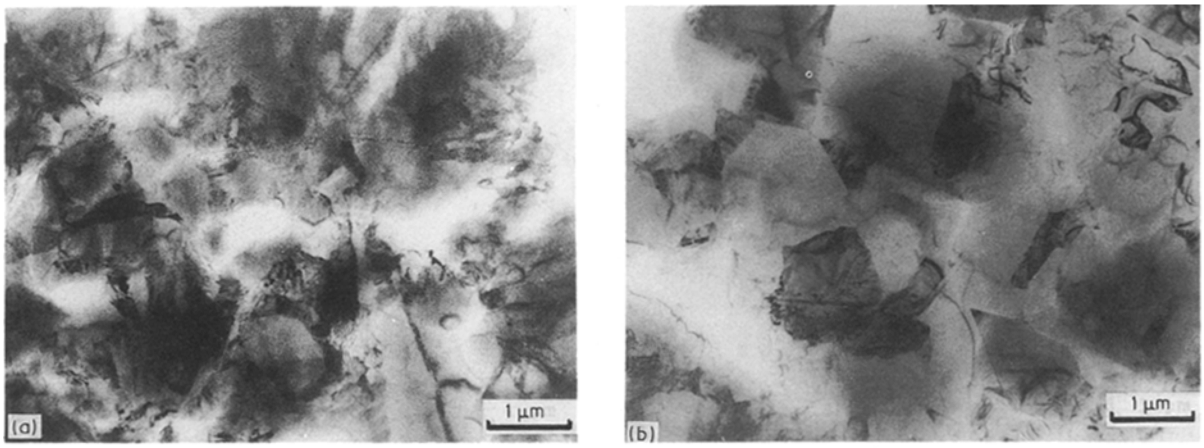

Figure 5 Transmission electron micrographs of diamond films deposited on the Si substrate with CH_4 concentrations of (a) 1.0% and (b) 0.5%.

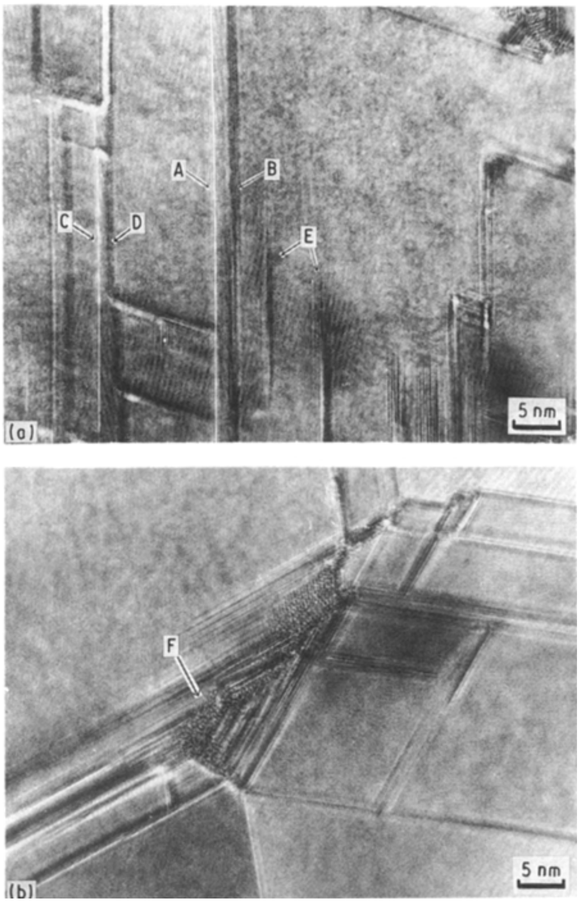

Figure 6 High resolution TEM lattice images of diamond films.

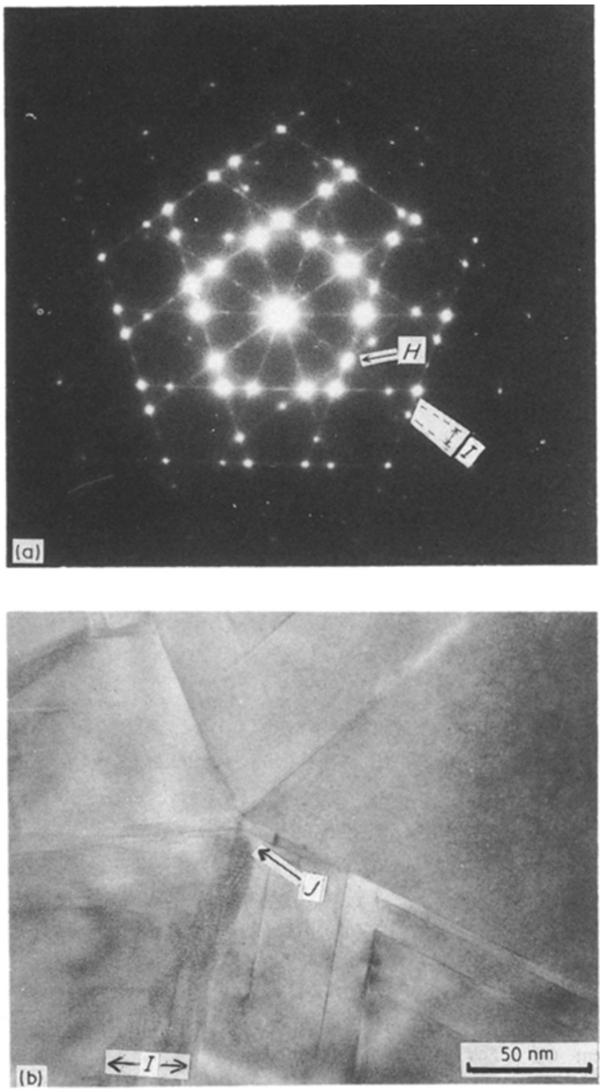

Figure 7 Electron diffraction pattern and TEM picture of five-fold twinned crystals.

twin boundaries are formed in order to relax the stresses which accumulate during grain growth. However, twin boundaries alone are insufficient to relax these stresses, and the highly disordered regions are also induced. From these results, we can suppose that the crystal growth of CVD diamond is not a homogeneous process but rather an inhomogeneous one, i.e. many subgrains which have different directions of crystal growth cross or combine during crystal growth, and highly disordered regions, twins and stacking faults, appear in large single-crystal grains.

In the CVD diamond particles, five-fold twinned crystals have frequently been observed [16]. In general, multiply-twinned particles are often observed in very small metal particles such as Au, Ag, Ni, Co, etc. The maximum size of these particles is about 40 nm because the inner stress of a crystal increases as they grow. This stress is thought to be induced by the elastic deformation to accommodate the misfit angle of 7.20° between the twin units [18]. The size of a multiply-twinned CVD diamond particle is larger than that of metal particles. Matsumoto and Matsui [16] reported that the stress is released at one specific twin boundary and a small gap is produced at one twin boundary [16]. Similar results were obtained in the CVD thin films. Fig. 7 shows a diffraction pattern and TEM picture showing five-fold twinned crystals. In Fig. 7a, a spot (H) is seen to be split. This indicates that a lattice misfit exists at one twin boundary, as can be seen at *I* in Fig. 7b, in which five crystals are separated by five twin boundaries and these twin boundaries are gathered at one point (J) which is the centre of the five-fold symmetry. The angle of twin boundaries at the centre of symmetry is about 70.5° and the angle of misfit of twin boundaries (*I*) is 7.5°. These values are very close to those of the theoretical estimates of twin units and the misfit angle. From these results, we can conclude that the crystal growth of diamond films is very similar to that of particles and a similar mechanism of growth is also operative under high nucleation density conditions.

4. Conclusions

TEM observations of diamond films prepared by a CVD method were performed and the following conclusions were drawn.

1. There are many defects in CVD diamond crystals and these defects increase with increasing CH_4 concentration in the reaction gas mixtures.
2. These defects mainly consist of twins, stacking faults and highly disordered regions which exist at the crossing point of twin boundaries. This indicates that the stresses which are accumulated during the grain growth are released on the formation of these defects.

3. Five-fold symmetry twinned crystals are also observed in the diamond films. This indicates that the crystal growth mechanism of CVD diamond films is essentially the same as that of fine metal particles.

References

1. F. P. BWNDY, H. T. HALL, H. M. STRONG and R. H. WENTORF, *Nature* **176** (1955) 51.
2. B. V. SPITSYN and B. V. DERJAGUIN, USSR Pat. 339 134 (1980).
3. W. G. EVERSOLE, US Pats 3 030 187, 3 030 188 (1962).
4. J. C. ANGUS, H. A. WILL and W. S. STANKO, *J. Appl. Phys.* **39** (1968) 2915.
5. A. AISENBERG and P. CHABOT, *ibid.* **42** (1971) 2953.
6. E. G. SANSALONT, *App. Phys Lett.* **29** (1976) 118.
7. C. WEISSMANTEL, K. BEWILOGA, D. DEITLICH, H. J. ERLER, H. J. HINNEBERG, S. KLOSE, W. NOWICK and G. REISE, *Thin Solid Films* **72** (1980) 19.
8. Y. NAMBA and T. MOHRI, *J. Vac. Sci. Technol.* **13** (1976) 693.
9. S. MATSUMOTO, Y. SATO, M. KAMO and N. SETAKA, *Jpn J. Appl. Phys.* **21** (1982) L 183.
10. S. MATSUMOTO, Y. SATO, M. TSUTSIMI and N. SETAKA, *J. Mater. Sci.* **17** (1982) 3106.
11. A. SAWABE and T. INUZUKA, *Appl. Phys. Lett.* **46** (1985) 146.
12. S. MATSUMOTO, *J. Mater. Sci. Lett.* **4** (1985) 600.
13. T. KOMATSU, H. YAMASHITA, Y. TAMOU and N. KIKUCHI, in “Proceedings of the 8th International Symposium on Plasma Chemistry”, (1987) p. 2487.
14. N. KIKUCHI, T. KOMATSU and H. YAMASHITA, in “Proceedings of the 9th Symposium on Ion Source and Applied Technology”, Tokyo (1985) p. 233.
15. M. TSUDA, M. NAKAJIMA and S. OIKAWA, *J. Am. Chem. Soc.* **108** (1986) 5780.
16. S. MATSUMOTO and Y. MATSUI, *J. Mater. Sci.* **18** (1983) 1785.
17. K. S. MAR, H. KAWARADA, J. SUZUKI, H. MOURI, H. FUJITA and A. HIRAKI, in “Abstracts of Ist International Conference on the New Diamond Science and Technology” (1988) p. 166.
18. S. INO, *J. Phys. Soc. Jpn* **21** (1966) 346.

Received 2 January
and accepted 19 November 1990.