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Uniform coating of CVD diamond on metallic wire substrates

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Diamond was coated onto wire substrates of various transition metals (Mo, W or Ti) of 0.5 mm diameter by the microwave plasma CVD method from a gas mixture of the CO–H_2 system. The CVD conditions for a uniform diamond coating were microwave power, 750–1100 W; total pressure, 2000 Pa; total flow rate, 200 ml min^{-1}; CO concentration, 5 vol %; treatment time, 5 h. The wire substrates were mounted vertically or horizontally on a pyrophyllite susceptor, which was placed parallel to the irradiation direction of microwave power. Homogeneous and fine-grained diamond film was prepared on the whole surface of horizontal W wire substrate with a wire height of 2 mm from the susceptor. To obtain a dense diamond coating, the height has to be as low as possible in the plasma region, where the plasma density is higher at lower substrate temperature. Low pressure and high microwave power were suited for fine-grained coating. Diamond deposition rate was found to be more dependent on pressure than substrate temperature. As the pressure increased, a glassy carbon film was formed instead of diamond.

1. Introduction

Carbon films have been the object of scientific inquiries for many years. Diamond films are becoming increasingly important in several research areas of materials science. Diamond has excellent properties for structural and thermal applications. It has the highest thermal conductivity, hardness and Young's modulus of all materials coupled with an extremely low friction coefficient. Diamond film is needed for coating various shapes for precision working. However, substrate materials and shapes for diamond deposition are limited. In most cases various plates are used as a substrate and there are very few studies of diamond coating onto wire substrates. Drory *et al.* [1] deposited diamond on uniform SiC monofilament of ~200 μm in diameter and 80 mm in length using plasma-enhanced chemical vapour deposition (CVD). Recently, diamond coating on SiC and silica fibres or metallic (Cu and W) wire cores was carried out [2].

We have previously reported that diamond was synthesized by microwave plasma-enhanced CVD in the CO–H_2 reactant system, not only on diamond single crystal [3], but also on the surface of a non-diamond substrate such as cemented carbide substrate [4], molybdenum, tungsten, titanium and other metallic wire substrates [5]. It is estimated that the shapes and spatial arrangement of wire substrates have great influences on the distribution and morphology of deposited diamond in the microwave plasma CVD system. In the present paper, the effects of the arrangement of wire substrates and CVD parameters were investigated in detail for uniform diamond coating.

2. Experimental procedure

The microwave plasma CVD apparatus and major experimental procedure were the same as those described in previous papers [5–7]. Microwave power (frequency 2.45 GHz) was applied to the vertical quartz tube (inside diameter: 48 mm). Wire substrates of various transition metals (Mo, W or Ti) of 0.5 mm in diameter were mounted vertically and horizontally on a pyrophyllite susceptor, as shown in Fig. 1a and b, respectively. A stabilized microwave field was projected parallel to the susceptor surface in the vertical reaction tube. CO–H_2 reactant gases were introduced into the plasma region from the upper side with the desired flow rates. Total gas flow rate was kept constant at 200 ml min^{-1} by mass flow controllers. An ultrasonic microflawing treatment (ultrasonic power: 200 W, treatment time: 30 min) using diamond particles with 0 to 0.25 μm in diameter was carried out on the wire substrates [7]. Microwave power was varied between 550 and 1100 W. The film deposition was carried out for 5 h at total pressures between 2000 and 6000 Pa. The substrate temperature was measured by an optical pyrometer through the observation window attached to the top. The coated wire substrates after CVD treatment were identified by micro-Raman spectroscopy. The surfaces of the coated substrates were observed by scanning electron microscopy (SEM).

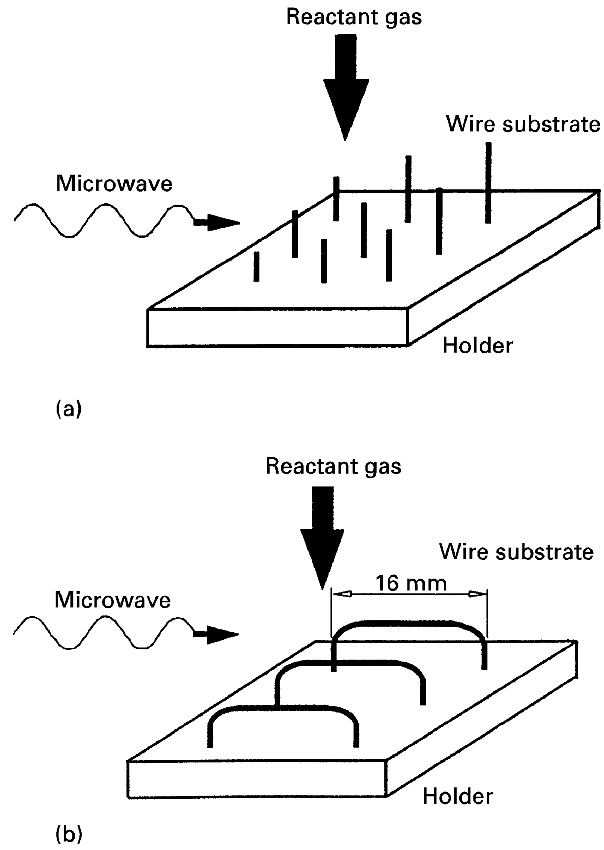


Figure 1 Arrangements of (a) vertical and (b) horizontal wire substrates on a pyrophyllite susceptor.

3. Results and discussion

3.1. Effects of the arrangement of wire substrate on diamond deposition

Fig. 2 shows the morphologies of diamond deposited on surfaces at various heights of W wire substrates, which were mounted vertically or horizontally on a pyrophyllite susceptor. The wire heights of (a) and (b) were 2, 6, and 10 mm with respective vertical and horizontal arrangements, where the height values mean the distance between the surface of susceptor and the positions observed. In the case of the vertical arrangement, substrate temperature had a relatively wide range of about 100 °C between the bottom and the tip. In the horizontal arrangement, however, difference in the substrate temperature was smaller. Wire–substrate height is found to have a great influence on nucleation and morphology of diamond film. A decrease in the deposition rate was observed at the vertical substrate height of 10 mm in spite of the maximum substrate temperature (1050 °C) compared with those at the substrate heights of 2 and 6 mm [5]. Diamond films composed of euhedral diamond crystals were obtained at lower substrate heights. The grain sizes of diamond nuclei were generally larger on the vertical wire substrate than on the horizontal wire substrate, and the distribution of diamond grains were not uniform. On the other hand, homogeneous diamond nuclei were observed in the horizontal arrangement, especially on the substrate with the wire height of 2 mm, where the highest power is projected to the plasma space in the reactor. The correlation between the microwave power and substrate temperature in the CVD system for horizontal arrangement of W wire is shown in Fig. 3. The CO concentration and the pressure were 5 vol % and 2000 Pa, respectively. The substrate temperatures at wire heights of both 2 and 10 mm linearly increased with increasing microwave power. Considering the above results, the horizontal arrangement was adopted in the later experiments for uniform coating of diamond on wire substrates.

3.2. The influence of CO concentration on diamond deposition

Figs 4 and 5 show the scanning electron micrographs and micro-Raman spectra of the coatings deposited on W wire substrates at CO concentrations of 5 and 15 vol % under a pressure of 2000 Pa with microwave power of 750 W. After a deposition time of 5 h, fine-grained diamond with a small amount of amorphous carbon was observed at 5 vol % CO. However, anhedral grains containing much amorphous carbon deposited with 15 vol % CO in the reactant stream. The micro-Raman spectra show a sharp diamond peak at 1333 cm^{-1} at 5 vol % CO, while a broad peak at 1500–1600 cm^{-1}, which is attributed to a low density of amorphous carbon, is observed at 15 vol % CO. It is reported for microwave plasma CVD of the CO–H_2 system [8, 9] that the structure of a-C:H co-deposited with diamond would be a partly crystallized polyacetylene at high CO concentration of 15%, and amorphous polyacetylene at low CO concentration of 1–7%. Active species which participate predominantly in the surface reaction, may be hydrogen atoms and hydrocarbon radicals. Acetylene and methyl radicals are extremely promising precursors for diamond formation [10]. The particles become a spherical type when they contain double-bonded carbons which give such a broad Raman peak. The band is thought to be due to double-bonded carbon such as the conjugated double-bond [11]. It was believed that disordered sp^2-type carbons were contained in the films with increasing CO concentration.

3.3. Morphology of diamond deposited on various wire substrates

Fig. 6 shows the morphologies of the surfaces of diamond films deposited on W, Mo and Ti substrates, where CO concentration was kept constant at 5 vol % for a treatment time of 5 h at a microwave power of 750 W and pressure of 2000 Pa. The wire substrates were mounted horizontally at a constant height of 4 mm. In the case of Ti substrate, the deposited film peeled off or cracks were found on the coated film with the wire being embrittled. Furthermore, regions without deposited diamond were observed in several places. As substrate temperature increased, the diamond film peeled off more, probably because the metal surface was embrittled by the impact of energetic ions and by the attack from the atomic hydrogen during deposition. On the other hand, diamond nucleation was promoted on Mo and W wire substrates with the formation of a diamond film with a fine-grained microstructure. Uniform and euhedral diamond films

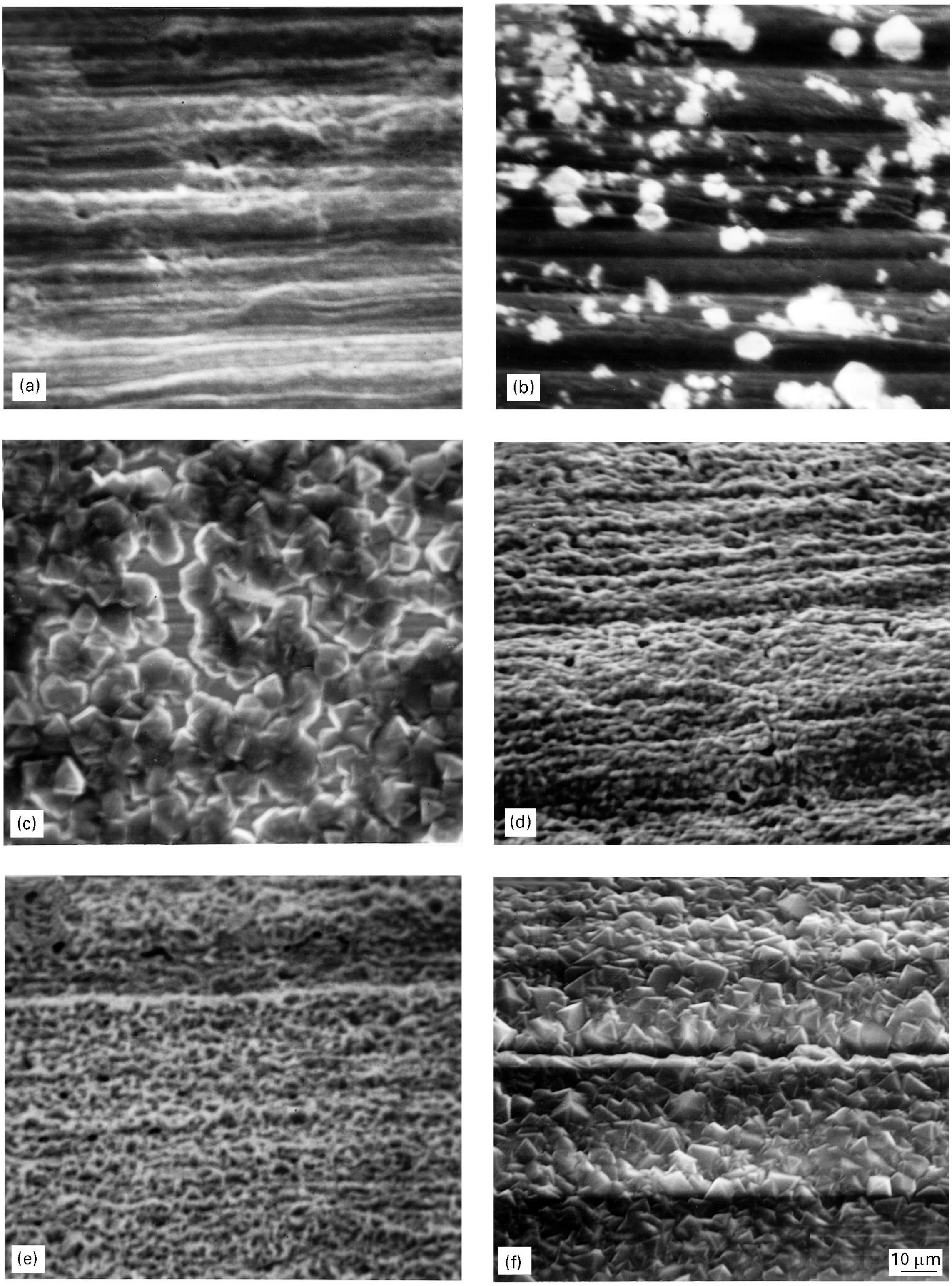


Figure 2 Morphology of diamond deposited on W wire substrates mounted vertically (a, b, c,) and horizontally (d, e, f). CO concentration: 5 vol % treatment time: 5 h, microwave power: 750 W. Wire height: (a) and (d) 10 mm, (b) and (e) 6 mm, (c) and (f) 2 mm.

were found aligned along the scratched lines and grooves of W and Mo substrates in Fig. 6a and b, respectively. The nucleation density on W substrate was higher than that on Mo substrate which can be seen by comparing their features. Furthermore, diamond films on W substrates had a tendency to have better adherence than those on the Mo substrates. This is due to the smaller thermal expansion coefficient of W compared to the other wire substrates and the increased nucleation density which helps the grain boundary to absorb the thermal stress at the film–substrate interface. The difference in the surface morphology of diamond on various wire substrates for the same deposition conditions may be caused by the difference in carbonization behaviour, thermal expansion coefficient and melting point of the metal and carbon system at high temperatures [3].

Fig. 7 shows the micro-Raman spectra of the central and bended portion of the horizontally arranged W wire treated under the above CVD conditions.

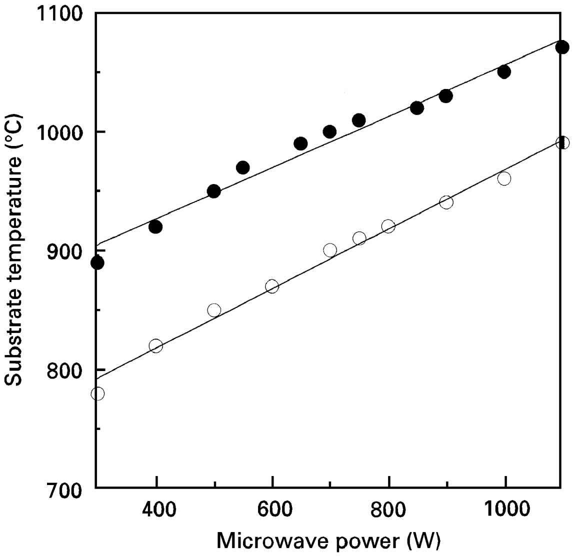
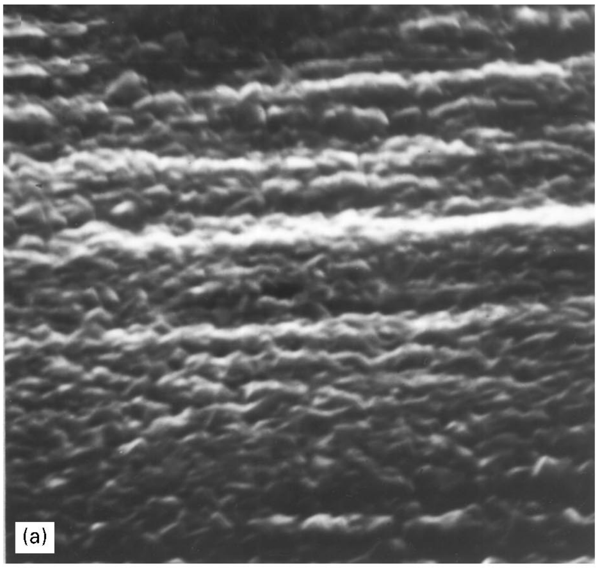


Figure 3 Correlation between the microwave power and substrate temperature of the W wire mounted horizontally. CO concentration: 5 vol %, pressure: 2000 Pa. Wire height; ●:10 mm and ○:2 mm.



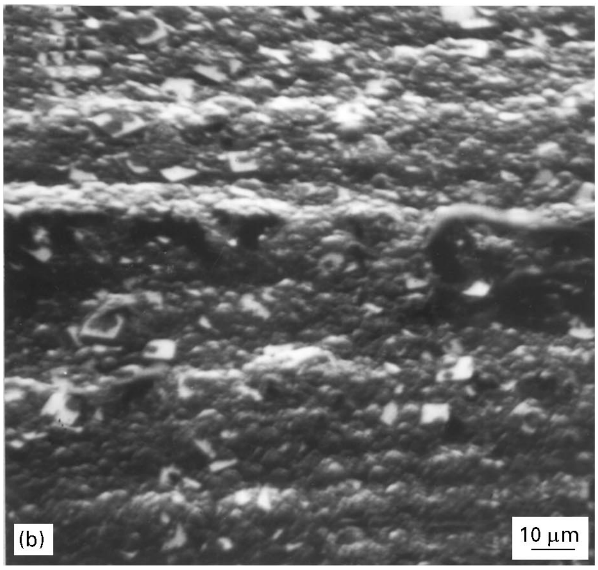


Figure 4 SEM photographs of coatings deposited on W wire substrates. Treatment time: 5 h, microwave power: 750 W, pressure: 2000 Pa. CO concentration: (a) 5 vol % and (b) 15 vol %.

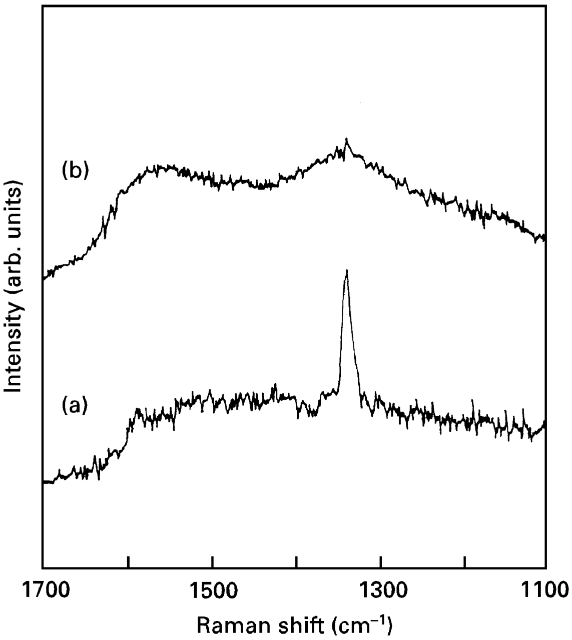


Figure 5 Micro-Raman spectra of the specimens obtained under the same CVD condition as shown in Fig. 4. CO concentration (a) 5 vol % and (b) 15 vol %.

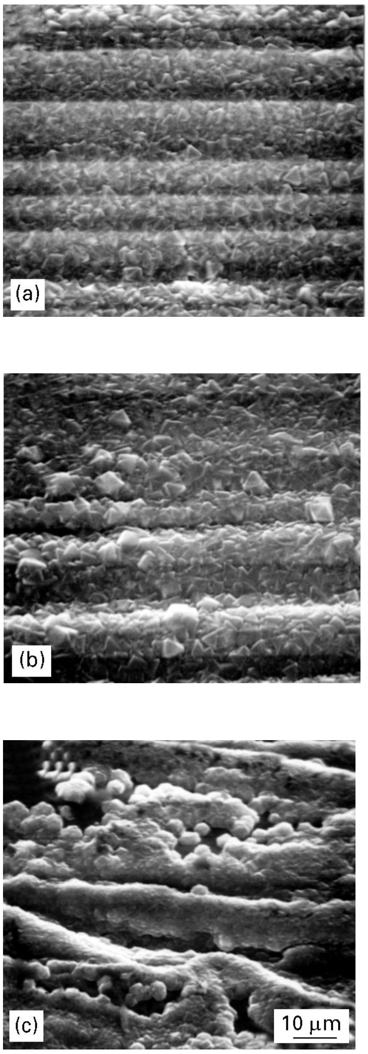


Figure 6 Morphologies of the surfaces of diamond films deposited on (a) W, (b) Mo and (c) Ti substrates. CO concentration: 5 vol %, treatment time: 5 h, microwave power: 750 W, pressure 2000 Pa, wire height: 4 mm.

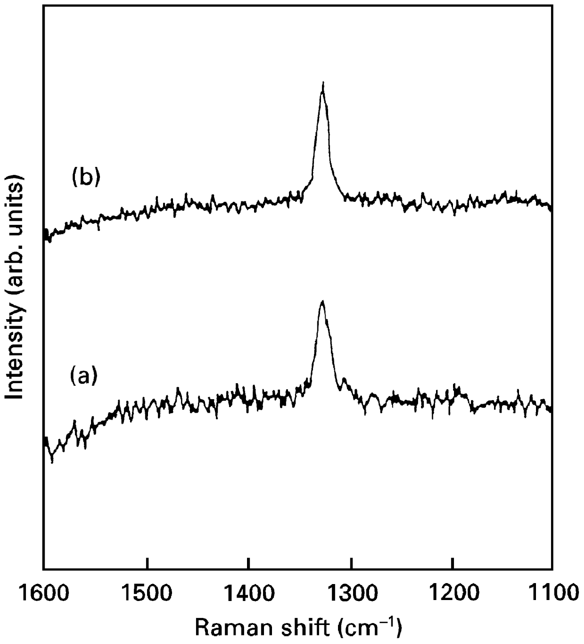


Figure 7 Micro-Raman spectra of (a) central and (b) bended portions of the horizontal W substrate treated under the same CVD conditions as shown in Fig. 6.

Diamond peaks appear at 1333 cm^{-1} on both portions without detection of non-diamond components. Differences in the portion deposited had no influence on the position and shape of the Raman peak, which indicates that the whole wire substrate is coated with a uniform crystalline diamond film.

3.4. Influence of total pressure on diamond deposition

Fig. 8 shows scanning electron micrographs of diamond film deposited on W wire substrate under various pressures of 2000, 4000 and 6000 Pa at 5 vol % CO concentration for a treatment time of 5 h at a microwave power of 750 W. The substrate temperature ranged from 940 °C at 2000 Pa to 1140 °C at 6000 Pa. As pressure decreases, a fine-grained and uniform microstructure is observed without abnormal grain growth. Each crystallite is found to have well-developed (1 1 1) facets whose sizes decreased with decreasing pressure. Grooves along the wire streak mostly disappeared after diamond deposition for 5 h at 2000 Pa. It was found that nucleation density and growth rate of diamond were highly dependent on pressure. When the pressure increased up to 6000 Pa, deposition rate of diamond decreased owing to the lower mean free path of activated species.

Fig. 9 shows a micro-Raman spectrum of the specimen obtained at a pressure of 6000 Pa in Fig. 8. The spectrum corresponding to large single-crystal graphite has a single high-frequency line, the G line, at about 1580 or 1575 cm^{-1} [12, 13]. The G line is assigned to scattering by the graphitic optic zone centre phonon (E_{2g} mode). Polycrystalline graphite exhibits another band at 1355 cm^{-1}, sometimes called the D line. This D line is attributed to scattering from a zone boundary phonon activated by the disorder associated with finite crystallite size [13]. The intensity of the latter is inversely proportional to the effective crystallite size in the graphite plane [14]. In a CO–H_2 microwave plasma CVD system, glassy carbon is known to grow when a high concentration of C or C_2 radical exists in the gas phase [15]. When the substrate temperature is

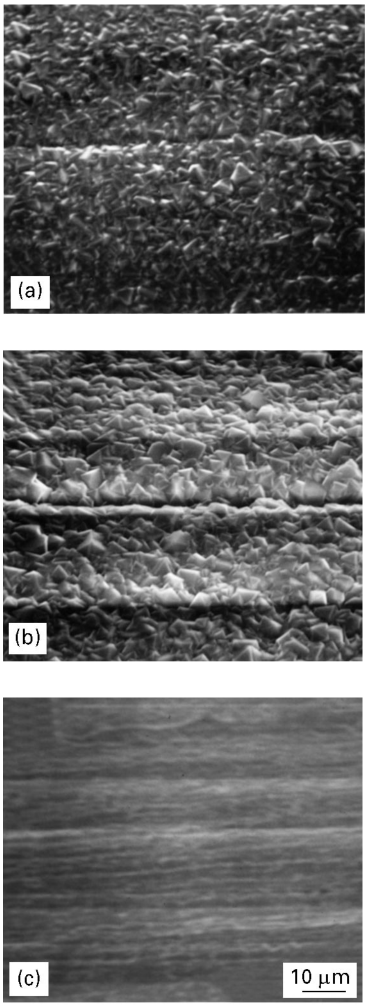


Figure 8 SEM photographs of diamond films deposited on W wire substrates. CO concentration: 5 vol %, treatment time: 5 h, microwave power: 750 W, pressure: (a) 2000 Pa, (b) 4000 Pa and (c) 6000 Pa.

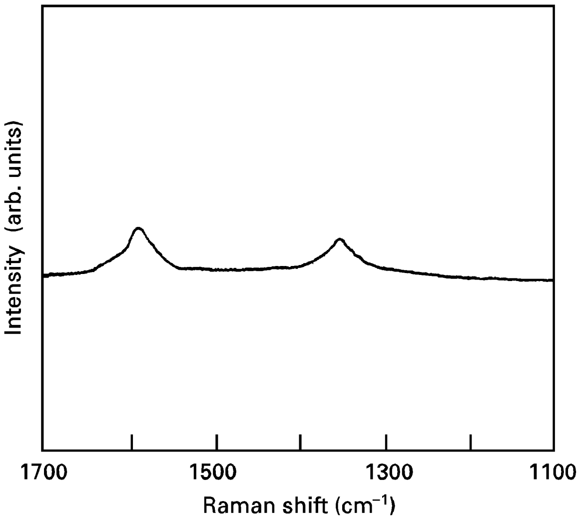


Figure 9 Micro-Raman spectrum of the specimen obtained at the pressure of 6000 Pa in Fig. 8.

changed, e.g. from 800 to 1200 °C with a fixed carbon content, the fraction of sp^2-bonded carbons is found to increase and growth rate goes through a maximum. The increase in sp^2-carbon content with temperature is reasonably explained by decreasing hydrogen coverage of the diamond surface [11]. In practice, the most frequently used lines in Raman spectra to characterize carbon materials are the G and D lines. The intensity ratio $I(\mathrm{D})/I(\mathrm{G})$ is found to increase, going from graphite through glassy carbon to carbon black [16]. Therefore, it is considered from the micro-Raman spectra that these peaks are similar to those of glassy carbon.

4. Conclusions

In this paper, diamond deposition onto wire substrates by the microwave plasma CVD method was investigated by controlling the following deposition parameters independently: wire height, gas composition, pressure and microwave power. A uniform diamond film with homogeneous grain sizes was obtained on wire substrates of W and Mo mounted horizontally on the specimen susceptor. Low pressure and high microwave power were suited to fine-grained coating. To obtain dense diamond coating, the wire height has to be as low as possible in the plasma region, where the plasma density is higher even at lower substrate temperature. Diamond deposition rate was found to be more dependent on pressure than the substrate temperature. When CO concentration increased, the synthesized films contained an amorphous carbon component. As the pressure increased, a glassy carbon film was formed. We suggested that the substrate arrangement in the plasma region is an important factor for the synthesis of uniform diamond film in the microwave plasma CVD system.

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