DIAMOND FILMS MADE BY DC PLASMA JET ①

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ABSTRACT

This paper is about the diamond films fabricated by dc plasma jet method. Scanning electron microscopy (SEM), X-ray diffractometry and Raman scattering spectroscopy have been used to characterize the diamond films deposited under different experimental conditions and different substrates.

Key words: diamond films dc plasma jet SEM XRD Raman scattering spectroscopy

1 INTRODUCTION

Succeeded to high temperature superconductors, diamond film has become a hot topic recently, referred to as "diamond fever". This "diamond fever" derives from the superlative properties of diamonds: high hardness, high Young's modulus, high thermal conductivity (4 times of copper), large band gap and hole mobilities, resistance to damage from intense radiation and high transparence over a broad range of wavelengths. All these properties suggest their wide applications fields, such as abrasives and cutting tools, acoustics, "heat sinks", semiconductors, and optics. At present, a variety of CVD methods have been successfully used to synthesis diamond or diamond films. Among these, dc plasma jet method is most promising for its high deposition rate and high quality[1].

2 EXPERIMENTAL

Fig. 1 shows a schematic diagram of the deposition apparatus used for the synthesis of the diamond films. A dc plasma jet was produced by a plasma torch. Methane or acetylene was added downstream of the plasma jet, and was decomposed into various radicals in the high temperature plasma stream.

The radicals are transported towards a water-cooled substrate. Diamond films can be deposited at the substrate by specific experimental parameters. In the experiments, diamond films were deposited on four different materials, molybdenum, tungsten, silica glass and silicon wafer, using either methane or acetylene as a carbon source gas. There are three regions in the plasma jet when methane or acetylene was introduced. The inner part of the jet is red, the intermediate part is blue, and the outer part is green, as shown in Fig. 2. The position of the substrates for deposition is in the intermediate part or near the outer part of the jet. It was found that the blue light was emitted by CH radical[2], and the temperature in this region is over 2000 ℃. Typical experimental conditions are listed in Table 1.

3 RESULTS AND DISCUSSION

Figs. 3(a), (b) show two Raman spectra of the diamond films on the molybdenum substrate using methane and acetylene as a carbon source gas respectively. The spectra

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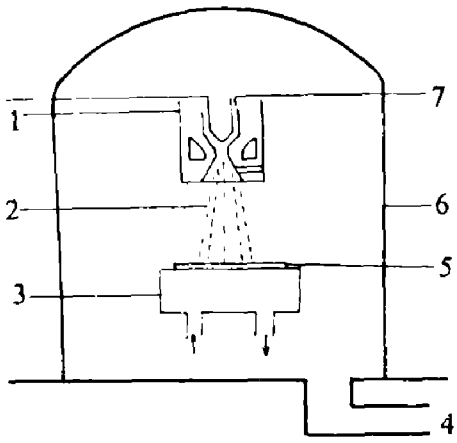

Fig. 1 A schematic diagram of dc plasma jet CVD apparatus

1—power system; 2—plasma jet; 3—substrate holder; 4—vaccum system; 5—substrate; 6—vacum chamber; 7—gas inlet

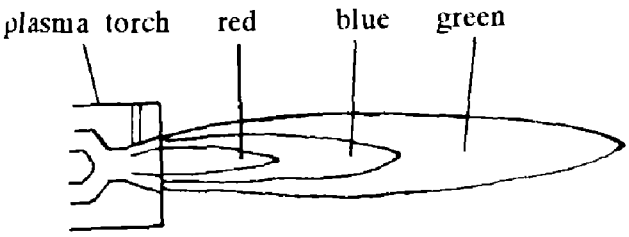

Fig. 2 Three regions of a typical plasma jet

Table 1 Typical experimental conditions

Current	30～70 A
Voltage	35～80 V
CH_4/H_2	0.1～5 Vol.-%
Argon gas flow rate	6～20 SLM
Total pressure	5.3～27 kPa
Substrate temperature	700～100 C

were measured using a Spex 1403 type Raman spectroscopy with an excitation line of $\lambda = 514.5$ nm (Ar^+ laser). Only one sharp peak was detected respectively on each sample at 1 332 cm^{-1} and 1 334 cm^{-1}. This means that the diamond films are of high purity and contain no amorphous carbon or graphite. A set of Raman spectra measurd at different positions of a diamond film is shown in Fig. 4. The four positions measured are distributed equidistantly with 2.5 cm apart along a radial direction of the film. Position 1 is situated at the central point of the film, while position 4 lies in the peripheral part. The spectra corresponding to positions 1 to 3 show only one sharp peak at 1 332 cm^{-1}. This means that the diamond film's quality is very good. The spectrum corresponding to position 4 has one sharp peak at 1 332 cm^{-1} with a slightly lower peak height, and gets a small broad peak around 1 610 cm^{-1}, which means a little amorphous carbon at this position.

A set of SEM photographs of diamond films on different substrates is shown in Fig. 5. As shown, diamond films with diamond crystal habits are deposited on molybdenum, tungsten, silica glass and silicon wafer. The size of diamond crystals are in the range of 5 to 30 μm. Growing steps and spirals on (100) face can be seen in Fig. 6.

X-ray diffraction analyses have been made on substrate and substrate-free diamond films. Fig. 7 (a) shows an X-ray diffraction spectrum of a free-standing diamond film. The observed and standard values of interplanar distances of diamond are listed in Table 2. The values observed are in good agreement with the values reported in JCPDS 6-0675. Fig. 7 (b) is an X-ray diffraction spectrum for a typical diamond film on molybdenum substrate. Besides the X-ray diffraction peaks of diamond and molybdenum substrate, there are peaks of molybdenum carbide phase, Mo_2C. Other carbide phases are observed in tungsten and silicon wafer substrates as well. These results clearly show the existence of a layer of carbide phase between the diamond film and the substrate, and the diamond films grow on the carbide layers.

To ensure high deposition rate of the diamond films, it is necessary that the carbon source gases are fully decomposed, and the decomposed active radicals are transported to

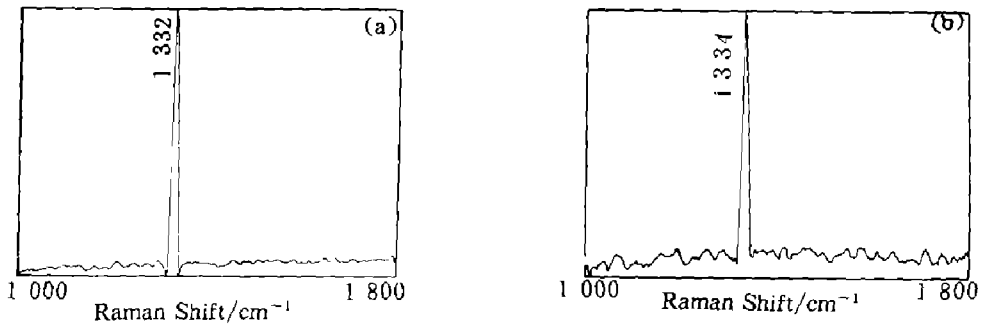

Fig. 3 Raman spectra for two typical diamond films deposited on molybdenum substrate
(a)—methane(1 h); (b)—acetylene(0.25 h)

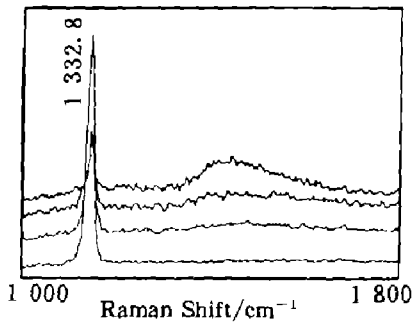

Fig. 4 Raman spectra measured at different positions of a diamond film

the substrate surface as quickly as possible. The dc plasma jet method possesses these conditions. Due to temperatures in the plasma jet are thousands or even ten thousands degree centigrade, the carbon source gas injected into the plasma jet can be totally decomposed, and can be transported to the substrate by high velocity plasma jet, so a high deposition rate can be obtained in this method. In these experiments, the deposition rate of diamond films was 65 μm/h.

Experiments show that the ratio of hydrocarbons and hydrogen has important role on the deposition process. When the ratio is too high, deposits contain lots of amorphous carbon or graphite, while the ratio is too low, growth rate of the deposits will be reduced. It is because atomic hydrogen in the plasma jet has much greater etching action for graphite than for diamond. Pure diamond deposits can be obtained when the hydrogen concentration in the plasma jet is high. However, it is important to keep a proper proportion of hydrocarbon when high deposition rate and high quality are required.

Table 2 A comparison of measured and reported interplanar distances(d)

Observed d /nm	Reported(JCPDS 6-0675) d /nm (hkl)
0.2060	0.2060 (111)
0.1261	0.1261 (220)
0.1075	0.10754 (311)
0.0891	0.08916 (400)

When the total pressure of the chamber is reduced, the plasma jet will be lengthened

Diamond films with good quality were deposited when substrate temperature was in the range of 700 C to 1100 C. When the temperature of substrate is too low the deposit is mainly in amorphous carbon. When substrate temperature is higher, over 1200 C, graphite is the main deposits. X-ray diffraction analyses have been made on diamond films deposited on the same kind of substrate at different temperatures. The diamond films' texture coefficients have been calculated listed in Table 3. and The above mentioned three regions will enlarged accordingly. Influence of the distance between the plasma torch and the substrate on the quality of deposits will not be so sensitive, so, it is easy to control the process. It was found that the

Fig. 5 SEM micrographs of diamond crystals
(a)—tungsten substrate, CH_4, 1 h; (b)—molybdenum substrate, CH_4, 1 h; (c)—silica glass substrate, CH_4, 0.25 h; (d)—silicon wafer substrate, CH_4, 0.67 h.

Fig. 6 Growing steps and spirals of diamond crystals

orientation of diamond films altered from (100)→(111)→(110) when the substrate temperature was decreased from 1 000 to 700 C.

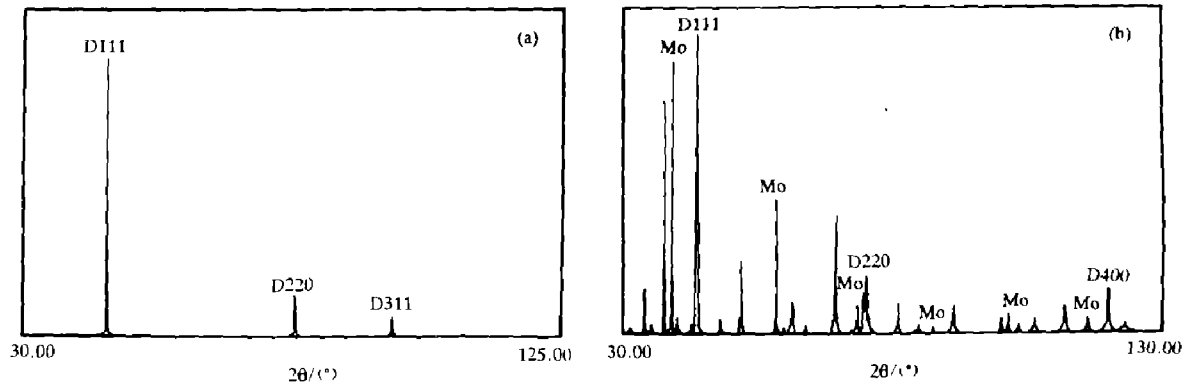

Fig. 7 X-ray spectra

(a)—a free-standing diamond film; (b)—a diamond film on molybdenum substrate, CH_4, 1 h

Infrared transmission spectra of substrate-free diamond films have been measured by Analect RFX-65 model FTIR spectrometer. Fig. 8 are IR transmission spectra corresponding to the diamond films before polishing, after polishing and chemically treated after polishing, respectively.

The IR transmittance of diamond films has been raised after polishing. The enhancement in IR transmittance shows the reduction in diffused reflection of the film due to the reduction of surface roughness. Surface roughness for diamond films before and after polishing are $R_z = 6 \sim 9\,\mu m$ and $R_z = 0.2 \sim 0.4\,\mu m$ respectively. Further enhancement in IR transmittance, shows the effectiveness of chemical treatment in removing impurities in the film.

Table 3 Texture coefficients of diamond films at different substrate temperatures

	(111)	(220)	(311)	(400)
1000 °C	1.15	0.89	0.65	1.31
850 °C	1.45	1.29	0.63	0.63
700 °C	1.31	1.61	0.68	0.40

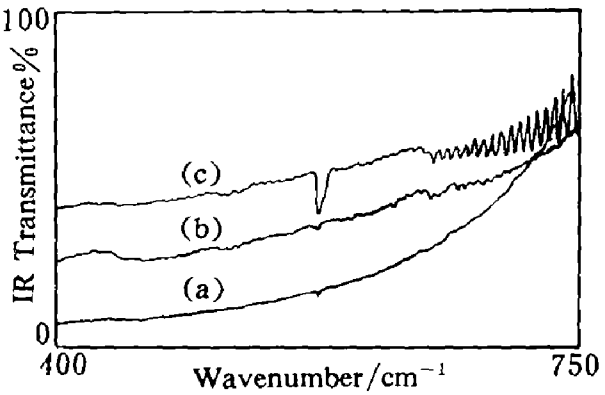

Fig. 8 Infrared transmittance of substrate-free diamond films

(a)—non-treatment; (b)—after polishing; (c)—polishing+chemical treatment

4 CONCLUSIONS

(1) High quality diamond films can be deposited on molybdenum, tungsten, silica glass, and silicon wafer by dc plasma jet CVD process.

(2) Nucleation and growth of diamond films are on the base of a layer of carbide phase when the substrates are carbide-forming materials.

(3) Substrate temperature, composition of reactive gas, gas flow rate and the position where substrates were fixed in the plasma jet are some key factors affecting the nucleation and growth of diamond.

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