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Influence of periodic magnetic field on the growth of CVD diamond films at lower temperature

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ABSTRACT

A periodic magnetic field (PMF) of $\mathbf{B}=\mathbf{B}_0 \sin \omega t$, where $\mathbf{B}_0=106$ Guass and $\omega=40{,}000$ rpm, was designed and first applied in a special hot-filament chemical vapor deposition (HFCVD) system for diamond synthesis. Different to the conventional HFCVD, an external PMF was introduced for diamond thin film deposition on a Si (1 1 1) substrate. The morphology and cross-section of the film were analyzed by field emission scanning electron microscopy (FESEM) while the bond structure was investigated using Raman spectroscopy. Compared with the conventional HFCVD, the growth rate of diamond film defined as the ratio of film thickness vs deposition time increases by about 7 times at 520 °C with PMF. The I_{Dia}/I_G ratio in Raman spectra indicates that the quality of the diamond film grown with PMF is much higher than that of the film grown by conventional HFCVD. The research shows that the novel technology using PMF may have great practical application potentiality in CVD diamond growth at low temperature and in some relevant fields.

1. Introduction

Because of its high efficiency, convenience to handle and simple requirement on equipments, hot-filament chemical vapor deposition (HFCVD) has been widely used in diamond synthesis. Facilities of HFCVD can easily be upgraded, such as by applying DC bias and DC plasma [1,2]. To meet the requirements in electronic industries, it is necessary to deposit diamond film at lower temperature. Approach to an effective method for diamond growth at low temperature is always an aim for researchers in this field. Many works [3] have been reported that the growth rate of diamond films used by the conventional HFCVD at lower temperature is not satisfying. In order to enhance the growth rate of the films, different methods and gas resources were introduced and some enhancement on the growth rate were achieved, as the growth rate was developed from 0.08 to 0.2 μm/h [4–6]. But diamond film obtained by the conventional CVD possesses high content of graphitic sp^2 phase, showing a comparatively poor quality.

Magnetic field effects are used quite a lot in sputtering systems. They give advantages in sputtering rate and extend ability of operating range, and can reduce electron bombardment at the substrate. For the magnetic fields used in sputtering, which are typically 100 Gauss, only the electrons will be affected, and the purpose of using a magnetic field is to make more efficient use of the electrons, and cause them to produce more ionization [7]; the ions are too massive. Using magnetic field confinement in this way, the magnetic field can also have a considerable effect on the expending operation range and the prompting yield [8]. Considerable experiments have been proven in the magnetron sputtering process.

In order to increase the plasma, magnetic field was introduced into CVD diamond deposition processes. It is reported by Wen et al. [9] and Little et al. [10] recently that diamond film can be deposited under static magnetic field (MF) with an intensity of 10–20 T. Both of them reported that diamond nanoparticles can be synthesized from carbon black under a static high magnetic field, and the yield of diamond increased by 30% with the presentation of magnetic field. According to their analysis, the magnetic field can reduce the surface energy of diamond, and promote the growth rate of diamond film.

A periodic magnetic field (PMF) has been firstly introduced in this article for HFCVD diamond for low-temperature growth. Comparing with the conventional HFCVD, the effect of the PMF on CVD diamond growth has been investigated. This paper focuses on the analysis of the influence of the PMF, while other factors were not included in the discussion.

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2. Experimental details

The PMF applied in this special hot-filament chemical vapor deposition system was designed as shown schematically in Fig. 1. The PMF–HFCVD system consists of a quartz chamber, a three-phase stator winding and an AC transducer.

The PMF, with $\mathbf{B}=\mathbf{B}_0 \sin \omega t$, was generated by the stator winding of a three-phase electric motor, and its angular frequencies (ω) can be adjusted from 3000 to 45,000 rpm. With increase in ω (rpm), the magnetic field declined from 106 to 32 Gauss. The measured variation of the magnetic field along the diameter of the reactive zone is less than 1%. The inner diameter of the pair coils is 210 mm. The vertical gradient of the magnetic field intensity for the pair magnet is as low as 0.135 G/mm, so the PMF in the reactive zone can be considered as even and uniform.

In order to match the PMF, a special HFCVD set was designed as well. A bell-shaped quartz chamber was employed as the depositing reactor. The filament was made of a tungsten wire with a diameter of 0.5 mm and it was twisted to a 5-turn coil with a diameter of 6 mm. The thermocouple was set on the surface of sample to measure the depositing temperature. The temperature gradient was about 20 °C/mm. Due to the large gradient of temperature, the reduction of the substrate temperature in the special HFCVD was achieved by forced cooling. A silicon (111) substrate was used as the substrate, and, before diamond deposition, the substrate was pre-ground with diamond powder of 0.5 μm in diameter and was cleaned in acetone solvents using ultrasonic.

Parameters of the deposition process were set as shown in Table 1. The morphology, cross-section and bond structure of the diamond film were analyzed using FEI Sirion200 field-emission scanning electron microscopy (FESEM) and LabRAM HR Raman spectroscopy with the exciting wavelength of 488 nm. The growth rate was determined by SEM measuring the cross-section image of the diamond films.

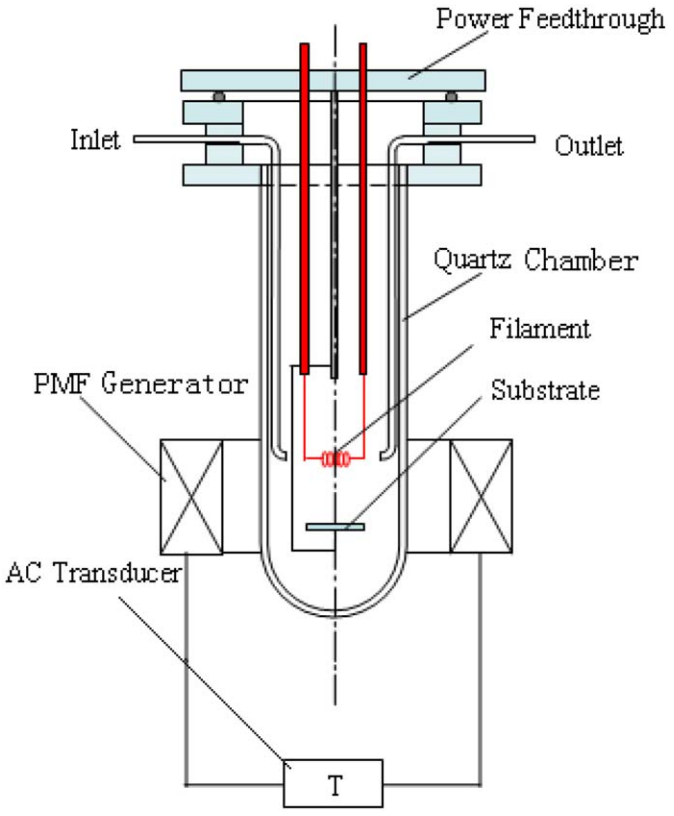

Fig. 1. Schematic diagram of the periodic magnetic field HFCVD system.

Table 1
The parameters of HFCVD diamond.

Parameters	Values
Frequency of the PMF/s^{-1}	40,000
The reactive gas/CH_4:H_2	1%
The total flow rate/sccm	20
Pressure/kPa	2.5
The filament temperature/°C	1900 ± 50
The substrate temperature/°C	520
The deposition time/min	60

3. Results and discussion

Fig. 2 shows SEM images of diamond films deposited with and without the PMF at 520 °C. It can be seen in Fig. 2(a) that the average grain size of diamond deposited without PMF is about

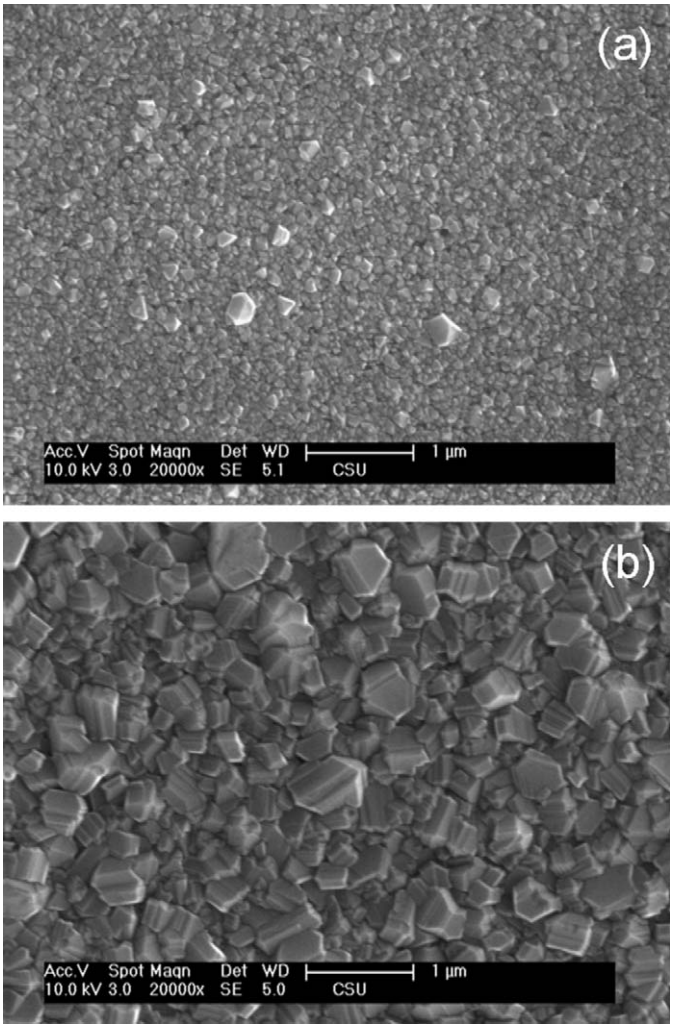

Fig. 2. Typical SEM images of diamond films deposited on Si (111) substrate at 520 °C with (a) conventional HFCVD and (b) the PMF–HFCVD of ω=40,000 rpm.

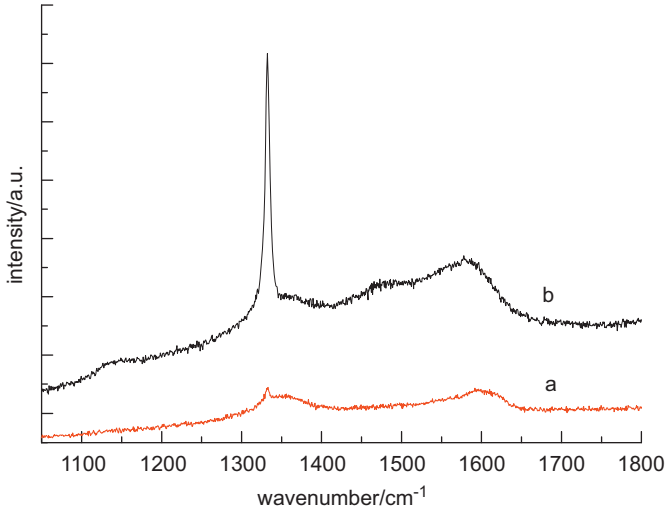

Fig. 3. Raman spectra of the diamond films deposited on Si substrate with (a) conventional HFCVD and (b) the PMF–HFCVD of ω=40,000 rpm.

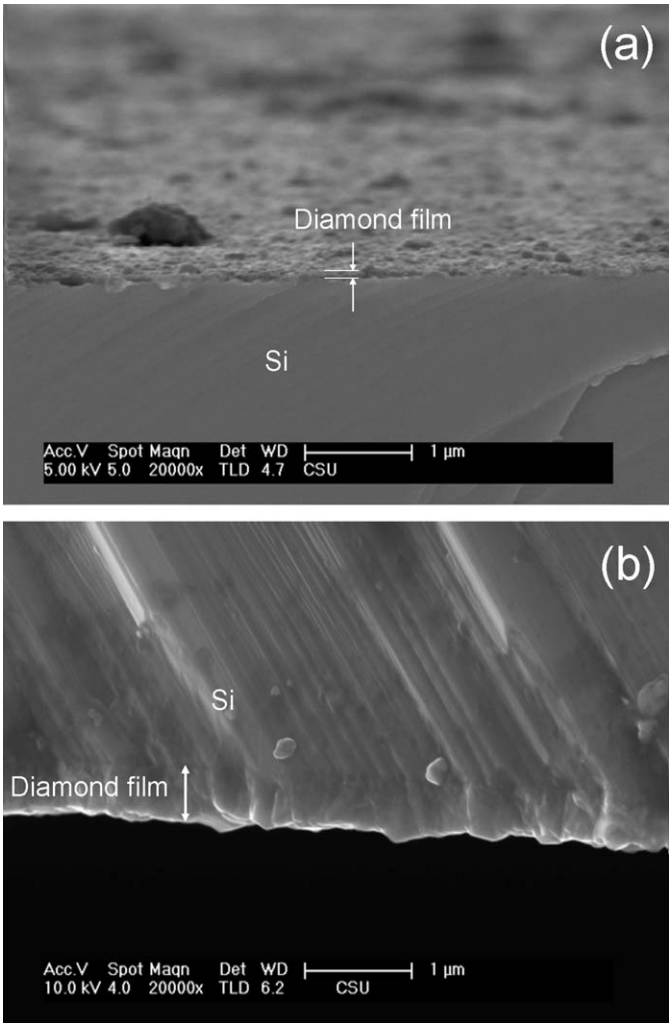

Fig. 4. Cross-section of the typical SEM images of diamond films with (a) conventional HFCVD and (b) the PMF–HFCVD of ω=40,000 rpm.

40 nm while the largest size is around 200 nm. While, in Fig. 2(b), the average grain size of diamond crystals deposited with PMF when ω is 40,000 rpm is about 400 nm, i.e., 10 times as large as that in Fig. 2(a). It indicated that for the conventional CVD method, the growth of crystals at lower temperature is very slow, which this result is similar to the previous works by Ring et al. [6] and Schmidt and Benndorf [11], yet, with the introduction of an additional PMF, the crystals' growth can be significantly improved.

Fig. 3 shows Raman spectra of the diamond films deposited with and without PMF. It can be concluded that, characteristic peak of diamond and graphite can be observed on both spectra at around 1332 and 1550 cm^{-1}, respectively.

It is clear that Raman spectrum of the diamond film deposited with PMF, as shown in Fig. 3(b), has a very sharp peak at 1332 cm^{-1}, which indicates that the deposited diamond is of high quality. On the other hand, a weak peak at around 1332 cm^{-1} appears on the Raman spectrum of the diamond film deposited without PMF (Fig. 3(a)) [12], indicating that the diamond prepared is of poor quality. The ratio of I_{Dia}/I_G [13] for the diamond films deposited with and without PMF, where I_{Dia} and I_G are the intensities of Raman spectrum for diamond and graphite, respectively, is furthermore quite different. Through multi-Gauss fitting, the I_{Dia}/I_G ratio of the diamond films deposited with the PMF is found to be 4.0, while that of the diamond films deposited without PMF is around 0.63. The former is much higher than the latter, indicating that the quality of diamond film deposited with PMF is much better than that deposited without PMF.

Fig. 4 shows the SEM cross-section images of the diamond films deposited in conventional HFCVD and PMF-HFCVD. Fig. 4(a) shows that the as-prepared diamond film is not completely continuous and its thickness is about 80 nm. It is indicated that the average linear growth rate is about 80 nm/h, and this result is similar to the previous report of Schmidt and Benndorf [5]. In Fig. 4(b), a continuous diamond film was obtained, due to a larger growth rate. The mean linear growth rate reached 540 nm/h, i.e., in comparison with that of the film deposited without PMF, the growth rate increased by about 7 times.

According to the report of Mankelevich et al., [14] in a conventional CVD, electrons are soon lost by recombination at the walls or substrate (the energy lost is about 5%) whereas under the PMF, increasing the path length of the electrons before they are collected by the substrate and walls, and of keeping electrons away from the vacuum chamber walls and hence reducing recombination. An electron from the hot filament is traveling along the axis of the discharge will be unaffected, since B and the electron speed (v) will be parallel and so their vector product will be zero. Then it will be subjected to a force ($f = q\vec{v} \times B$) perpendicular to the field. The probability of collisions is increased by the magnetically confined. (Due to f, the electron will then describe circular motion around B at a radius in the vicinity of filament. Therefore, the constriction of the magnetic field is to prevent the electron from the wall and reduce recombination losses. The circular motion is to increase the total path travelled by an electron emitted from the filament , thus enabling it to cause more collisions with other molcular.) When the elastic collision occurs, the momentum of electron will be transferred into the molecule in vapor; whereas the in-elastic collision occurs, the energy of electron will be transferred into the molecule, and the reactive gas may be easily activated and produced more ionization. Hence the deposited yield is prompted [7,16]. At the same time, it is improved that the static magnetic field will cause the non-uniform deposition on the substrates [8]. Meanwhile, the declining of the surface free energy of diamond films also plays an important role in depositing process [9,17], and the increase in the growth rate of diamond films may attribute mainly to the combined affection of the magnetic field and thermal pyrolysis.

4. Conclusion

PMF with $\mathbf{B}=\mathbf{B}_0 \sin \omega t$, where $\mathbf{B}_0=106$ Guass and $\omega=40{,}000$ rpm, was first used in HFCVD diamond deposition. It is found that PMF plays a very important role in enhancing the growth rate of diamond and promoting its quality at a temperature of 520 °C. The linear growth rate of the diamond film deposited with PMF amounts ~540 nm/h, nearly 7 times larger than that under the conventional HFCVD. The I_{Dia}/I_G ratios of the diamond films deposited with and without PMF are 4.0 and 0.63, respectively. The quality of the diamond film deposited with PMF is much better than that deposited without PMF.

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