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RESEARCH ARTICLE

Effects of enhanced nucleation on the growth and thermal performance of diamond films deposited on BeO by hot filament CVD technique

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Abstract A method of controlling the feeding concentration of methane was applied in a hot-filament chemical vapor deposition (HFCVD) in order to improve the nucleation of diamond on the beryllium oxide substrates. The nucleation density and the morphologies of diamond were investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM) while the thermal conductivities of substrates and the composites were detected by laser-diathermometer. The results show that the diamond thin film is in larger grain size with lower roughness when CH_4 and H_2 enter the chamber, respectively, rather than as a mixture, and the composites' conductivity soared by 21%–31% compared with BeO substrates. At the conditions of separated gas entry, several projects with changes of the CH_4 flux during depositing were designed to discuss the influence of CH_4 concentration on diamond nucleation. The uniform and compact diamond thin films were acquired when the ratio of CH_4:H_2 at nucleation stage was in the range of 4%–8%.

Keywords enhanced nucleation, HFCVD, diamond thin film, BeO, thermal conductivity

1 Introduction

Among the several kinds of high thermal conductivity (TC) ceramics, beryllium oxide (BeO) is considered to be the most promising material for high frequency and high power applications because of its mature technique for production, high TC at low temperature and low dielectric permissivity [1]. Numerous studies about improving the TC of BeO have been conducted by scientists through preparation control [2–4]. However, the advancements on TC are still limited.

Diamond possesses the highest TC as we know [5,6]. It is possible to improve the integral TC by depositing a layer of diamond thin film on the BeO substrate. Nucleation is the first and critical step for chemical vapor deposition (CVD) diamond growth. The control of nucleation is essential for optimizing the diamond properties such as grain size, orientation, adhesion and roughness that are necessary for targeted applications [7,8]. Several methods of nucleation enhancement have been widely investigated by researchers in recent years, such as, scratching the substrate surface with diamond powder and other abrasive powders [9] and impositions of an electric bias on the substrate to enhance nucleation [10]. Many studies have been carried out on the nucleation and growth of diamond films, especially the effect of pressure during deposition [11] and the reactant concentration [12]. High methane concentration is propitious to cause massive nucleation. However, it will be too high to yield high quality diamond growth [13].

In this paper, a new method of enhancing nucleation in a hot filament chemical vapor deposition (HFCVD) system was designed by entering CH_4 and H_2 separately. Based on this, the scheme of stepping reactant concentration was adopted by changing CH_4 flux at different phases in the process of deposition.

2 Experimental

In the experiment, diamond films were synthesized by HFCVD as described elsewhere [14]. The depositions were performed on 99% BeO ceramic which were pre-

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Table 1 Detailed deposition processing of diamond thin films

Projects	Ways of gas entering	Nucleus stage (CH_4 flux/sccm, time/min)			Grow-up stage
		Stage I	Stage II	Stage III	Stage IV
		CH_4 flux (time)	CH_4 flux (time)	CH_4 flux (time)	CH_4 flux (time)
A-1	mixed	5(2)	1(2)		1.5(300)
A-2	separated				
B-1	separated	5(0.5)	3(3)	1(1)	1.5(120)
B-2	separated	5(1)			
B-3	separated	5(1.5)			

treated by 5 μm diamond powder- scratching with gas mixtures of CH_4 and H_2 at sub-atmospheric pressures (4 kPa). Before deposition, the substrates were etched by H_2 for 10 min.

The detailed deposition processing is shown in Table 1. In group A, the compared experiments have been conducted with the different ways of gas feeding. A-1 was deposited by CH_4 and H_2 mixed before entry into the chamber (Fig. 1(a)) while A-2 was produced by CH_4 and H_2 inputted separately (Fig. 1(b)). The gas flow for CH_4 and H_2 is shown in Fig. 1 according to hydrodynamics. In group B, different initial CH_4 concentration was obtained by controlling the time of gas entry (in stage I) in a gas-separated entry system. Knowing that high methane concentration is propitious to cause massive nucleation but influence the quality of diamond, we used high CH_4 flow for the first few minutes and then lowered it.

The morphologies and the nucleation density of diamond were investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively, while the thermal conductivities of substrates and the composites were detected by laser-diathermometer.

3 Results and discussion

3.1 Ways for reactant entry

3.1.1 Surface morphologies

The influences of two different ways of gas inlet on diamond morphologies were studied. The surface morphologies of diamond is shown in Fig. 2 by SEM. The surface of diamond thin film produced by gas mixture (Fig. 2 (a)) is less uniform and compact than that deposited by CH_4 and H_2 entering the chamber separately (Fig. 2 (b)). Compared with the microstructures of diamond acquired by gas mixture, which has a lot of irregular grains at the surface (Fig. 2 (a)), diamond deposited by inputting CH_4 and H_2 respectively has a much larger grain size and the facet is clear (Fig. 2 (b)).

For mixed gas entry, the concentration of CH_4 is equal everywhere in active chamber as the gas is mixed before entry (shown in Fig. 1(a)). However, in a separated gas entry system, the concentration of carbon source near the filaments and the substrate was higher for the distance of CH_4 inlet and the gas outlet is nearer than the mixed gas entry system (shown in Fig. 1(b)). In the process of

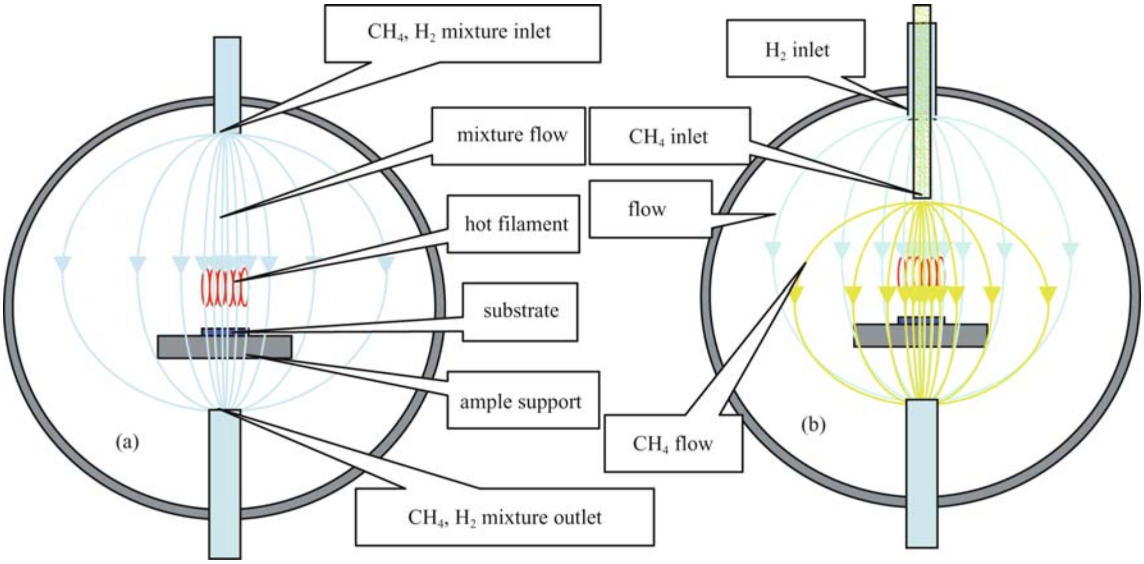

Fig. 1 Diagrammatic sketches for two different gas entry methods: **(a)** gas mixed entering; **(b)** gas separated entering

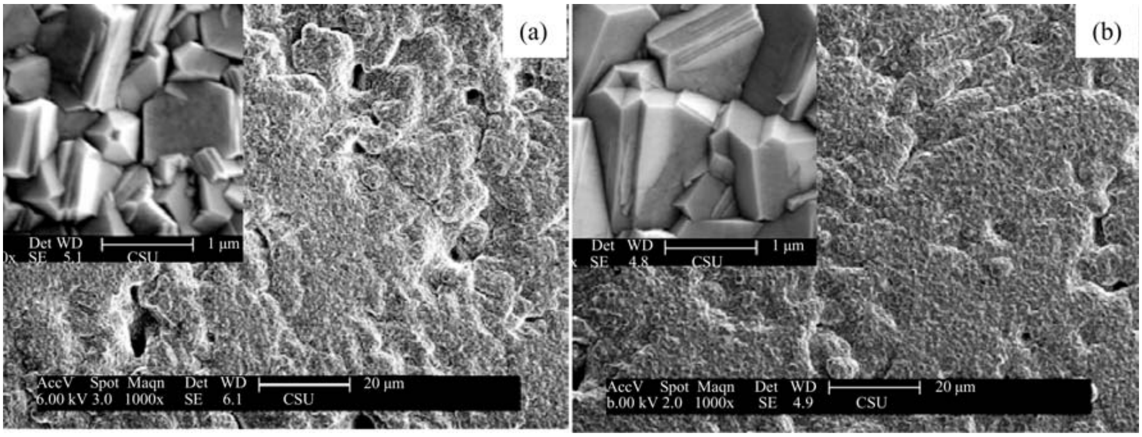

Fig. 2 SEM micrographs of samples for gas **(a)** mixed (sample A-1) and **(b)** separated (sample A-2) before entry (diamond micro-morphologies are shown at both the top left corners)

Table 2 Thermal performances of substrate and deposition samples

Samples	Thermal diffusion coefficient/cm^2·s^{-1}	Heat conductivity/J·cm^{-1}·K^{-1}·s^{-1}	Increased/%
substrate	0.70	2.094	–
sample A-1	0.85	2.543	21.44
sample A-2	0.92	2.75	31.33

HFCVD, some activated particles like CH_4, CH_3-, CH_2-, $CH-$, H^+ and H_2, play a great role for diamond nucleation and growth during deposition [15–17]. It is generally accepted that the roles of atomic H and H^+ ions are crucial for diamond nucleation by means of increasing the purity of diamond through reacting with or etching graphite and stabilizing the diamond surface [18,19]. By entering CH_4 and H_2 separately, the rate of dissolution for both CH_4 and H_2 can be increased as their flows are in different directions toward the filament. The concentration of CH_4 around the hot filament is higher and the radical hydrocarbon will increase, which leads to a more compact diamond film and larger grain size. Simultaneously, the atomic H and H^+ ions increase by entering the reactants respectively, so that the rate of reaction and etching for both graphite and small grain diamond speeds up. As a result, there are little small grains of diamond on the surface with clear facets.

3.1.2 Thermal properties

Thermal diffusion coefficients are measured by laser-dia-thermometer and the heat conductivities were calculated by using the equation [20]:

$$K = \alpha \cdot \rho \cdot C_V \tag{1}$$

where K is the heat conductivity, α stands for thermal diffusion coefficient, ρ and C_V are constants which represent density and thermal capacity, respectively.

The thermal performances of substrate and deposition samples are shown in Table 2. The thermal performance of sample A-2 is better than that of sample A-1. The dominating mechanism for thermal conductivity of diamond is the lattice vibration [21]. Compared with sample A-1, heat flow encountered less resistance in sample A-2 of which the diamond films are more compact with fewer holes which can only conduct the heat by radiation. Thus, sample A-2 has a higher thermal diffusion coefficient and heat conductivity.

3.2 Concentrations of carbon source

The nucleation and the growth of diamond are two basic steps during the process of CVD diamond deposition. It is

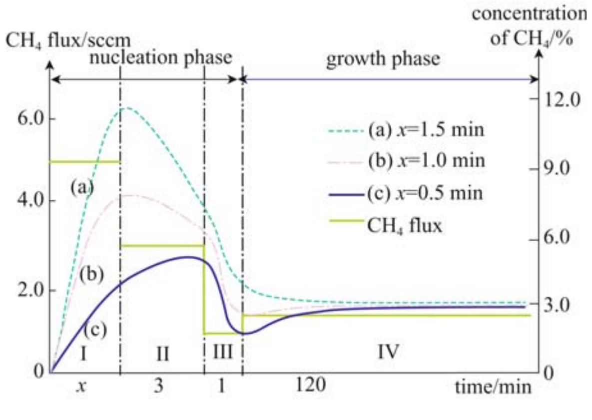

Fig. 3 The flux and the effective concentration of CH_4 at the process of deposition

well known that a higher carbon source concentration is propitious to enhance the nucleation of diamond while influencing the quality of films [13]. In this paper, projects of higher CH_4 flux at nucleation phase and lower at growth phase are designed to acquire high quality diamonds with a higher nucleation rate. Figure 3 gives the fluxes and the effective concentrations of CH_4 at different period of deposition.

Figure 4 shows the morphologies of diamond films deposited with different time of duration at high CH_4 flux (5 sccm) at the beginning of deposition. It can be seen that the diamond films become more continuity with the increase of duration. The obtained diamond films with the duration of 0.5 min at high CH_4 flux were non-sequence after deposition for 2 h and the nucleation of diamond were not uniform (Fig. 4(a)). Compared with it, with the duration of 1 min at high CH_4 flux, a continuous diamond film with certain crystal form was formed after deposition for 2 h, and the facet of obtained diamond films was clearer (Fig. 4(b)). With the duration time at high CH_4 flux expanding to 1.5 min, the obtained diamond film was also continuous, but the surface of the film became rough and integrality was not good (Fig. 4(c)). The nucleation densities of samples are shown in Fig. 5. The density of diamond nucleation increased with the increase of carbon source.

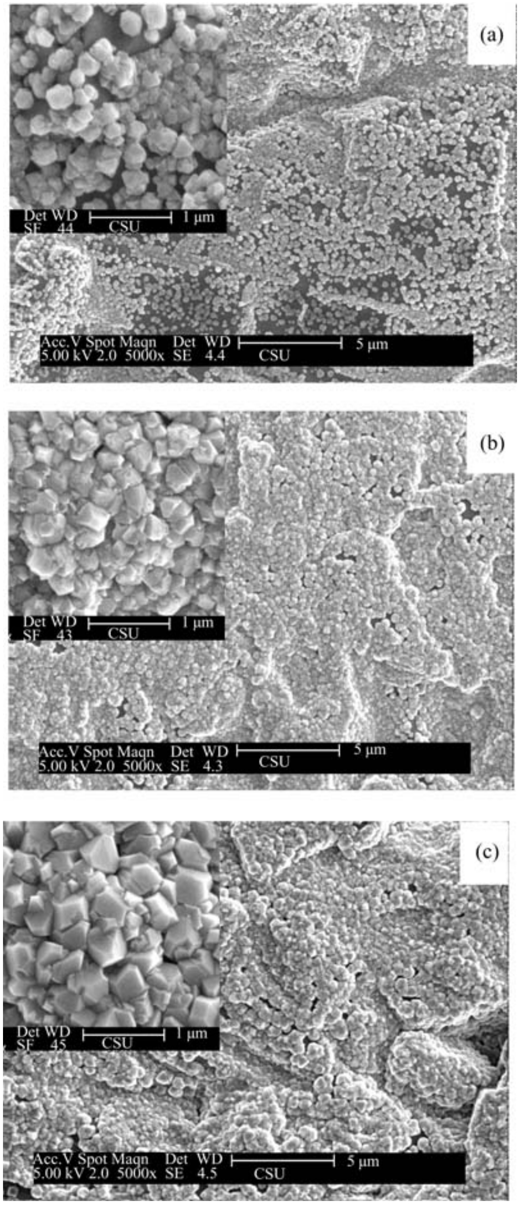

Fig. 4 The morphologies of diamond films deposited with different time of duration at high CH_4 flux (5 sccm): **(a)** 0.5 min (sample B-1); **(b)** 1 min (sample B-2); **(c)** 1.5 min (sample B-3) (diamond micro-morphologies are shown at the top left corners)

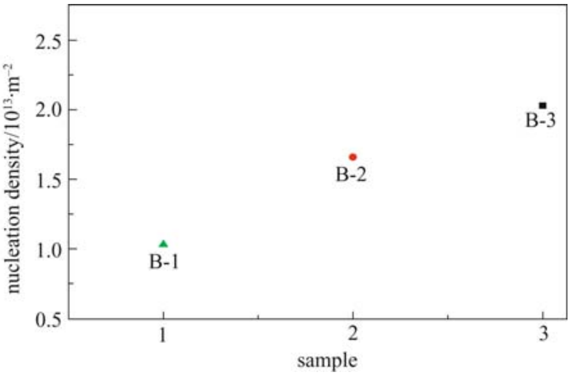

Fig. 5 The nucleation density of different samples

AFM images of different durations at the CH_4 flux of 5 sccm at the beginning of deposition are shown in Fig. 6. The mean grain size of sample B-2 is 158.16 nm with a roughness of 33.411 nm, while sample B-3 has a larger grain size and roughness, which are 225.663 and 67.792 nm, respectively.

As described in Fig. 4, a more compact diamond film was obtained with a higher concentration at the nucleation stage because of the enhanced motivity for diamond nucleation and growth with the increasing of the radical of hydrogen and hydrocarbon which came from CH_4. However, when the concentration of CH_4 increased more than 8% (Fig. 3(a), II), the hydrogen around the filament was reduced. There was too much hydrocarbon for atomic H to react with or etch. As a result, some diamonds grew to a big scale while others were diminished or disappeared. Thus, the roughness increased as was described in Fig. 6. For sample B-2, the concentration of CH_4 is 4%–8% at the stage of nucleation (Fig. 3(b)). It is enough for diamond nucleation and growth with enough hydrogen to decompose. Thus, the surface of diamond is compact and uniform with lower roughness.

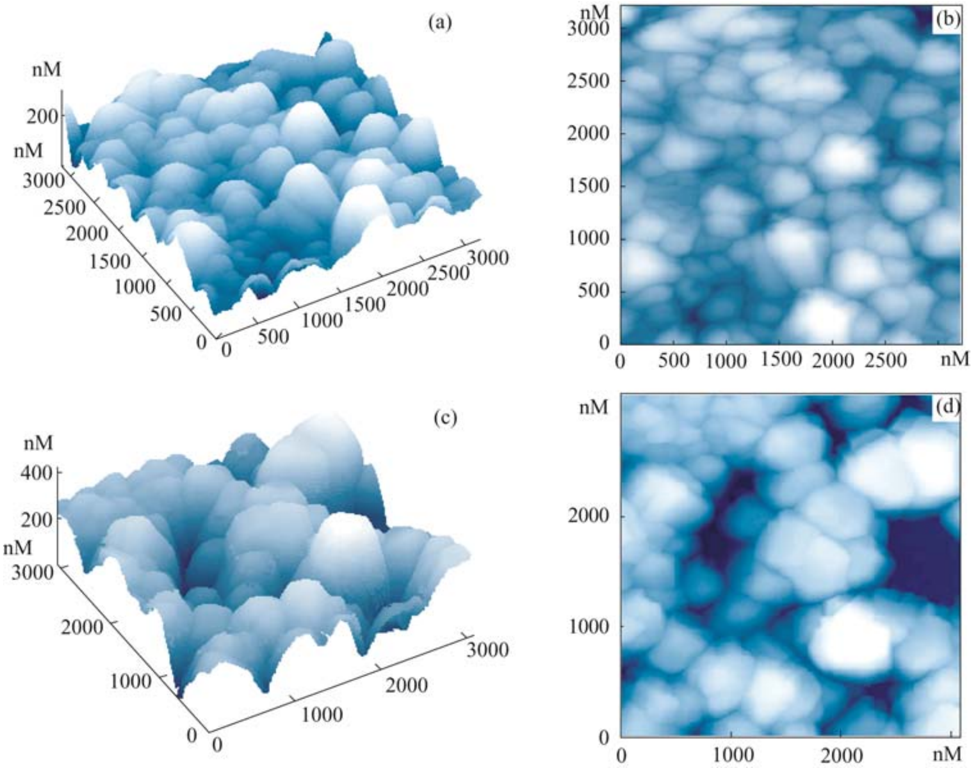

Fig. 6 AFM images of different duration for 5 sccm CH_4 at the beginning of deposition: **(a)(b)** 1 min (sample B-2); **(c)(d)** 1.5 min (sample B-3)

4 Conclusions

The enhanced nucleation method by inputting CH_4 and H_2 separately in an HFCVD system is an effective way to improve the rate of diamond deposition. Besides, the film quality and thermal conductivity were improved by increasing the radical of hydrocarbon and hydrogen. A uniform and compact diamond thin film is acquired when the ratio of CH_4:H_2 at nucleation phase is 4%–8%.

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