Template-free preparation of self-standing porous diamond films by hot filament chemical vapor deposition

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High quality self-standing porous diamond film was prepared by template-free hot-filament chemical vapor deposition (HFCVD) with polyvinylpyrrolidone (PVP) as auxiliary material. The micrometer sized diamond particles were used as seed layer. And it also acted as the nucleation sites for the diamond growth. The carbon source inside the film was partially supplied by the carbonized PVP. This method breaks the bottleneck of chemical vapor infiltration, and achieves the growth of new diamond layer inside the film. Due to the high concentration of atom hydrogen, the prepared diamond porous film only contains little graphite phase. This porous diamond film can be used in many fields, such as heat sinking devices, electronic devices, and so on.

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1. Introduction

As a star in the carbon materials, much more attention has been attracted on diamond for its excellent properties such as high hardness, large Yang's modulus, good thermal conductivity, very low coefficient of friction, wide band gap, high mobility of electrons and holes, high negative electron affinity, high radiation tolerant, chemical inertia, and so on [1-5]. Diamond material, especially diamond film exhibit its great potential in many field, including heat sinks in the microelectronic industry and tribological applications due to its unique properties [6].

Though many groups have reported that they can prepare diamond films *via* simple method [7-9], most films are consisted with nanocrystalline diamond particles, which leads to the loss of heat transfer when the films are used as heat sink materials [10-12]. Moreover, the cost of pure diamond film is expensive, which make pure diamond heat sink in the market not favored by people. Diamond composites, particularly metal-diamond composites, are promising candidate in the actual application of heat sinks due to their exceptionally high thermal conductivity and low-cost. In general, diamond/metal composites are produced *via* powder metallurgy with metal powder as a matrix and diamond particles are embedded in it. When diamond particles are embedded in a metal matrix, the interface of diamond particles plays a crucial role in determining the coefficient of thermal expansion [13-16]. E.A. Ekimov reported that a strong diamond skeleton was formed at pressures and temperatures above 8 GPa and 2100 K with a high percentage of diamond (90-95%) in the composite, leading to enhanced thermal conductivity [17]. But the presence of microstructure defects on the interface of two diamond particles affected the thermal expansion. In order to achieve the best thermal conductive performance, the porous diamond film is the ideal candidate. However, preparing the porous diamond film is a big challenge in the whole world up to now. A. Glaser et al. have investigated the growth of diamond in open porous structures of silicon carbide using hot filament chemical vapor infiltration (CVI), which is the preliminary exploration of the continuous diamond skeleton preparation [18, 19]. A. Floter et al. have investigated the diamond growth in and above the trenches in silicon substrates, but with 'infiltration depths' only up to 5 μm [20]. Eaton et al. showed that the concentration of carbon growth species and atomic hydrogen reduced inside the pores, because of the short mean free path and high combination rates [21]. Considered the short transport distance of hydrocarbon groups and the limitation of pores, solid carbon source exhibits its great potential, which can provide the active species for the diamond growth by the etching process of atom hydrogen. Polymers are the good choice as solid carbon source because of their low-cost and easy carbonization under high temperature.

In this work, the self-standing porous diamond film was prepared using HFCVD with PVP as auxiliary materials. Because no other template was involved in the forming of the pores, this method should be a template-free method. The micrometer sized diamond particles provided the original skeleton of the porous film. The carbon source and nucleation sites in the film were supplied by the carbonized PVP. And the possible mechanism for diamond film growth by HFCVD is discussed in detail.

2. Experimental

A traditional hot filament chemical vapor deposition system was used in our experiment (JZ.CD8A-450, Shen Yang Juzhi Vacuum Equipment Co., Ltd., Liao Ning Province, China), which was mentioned in our previous works [22], and the schematic diagram of the apparatus can be found in the supporting information of the literature [23]. Tungsten wires with diameters of 0.60 mm twisted to a 9-turn coil of 3 mm diameter were used as the filaments. The wires were carbonized in a mixture of methane and hydrogen so as to be stable during the diamond growth process. The (100) n-type silicon was used as a substrate, which was ultrasonically cleaned in ethanol and acetone for 10 min each. The seed layer, prepared by mixing the crushing diamond particles (0.1 g) and the alcoholic solution of PVP (1 ml), was placed on the silicon substrate, and the size of diamond particles is 5~50 μm (Yangzhou Hanjiang Grinding Tools, Jiangsu Province, China). The alcoholic solution of PVP consists of PVP (1 g) and analytically pure alcohol (10 ml), which was stirred for 12 h before mixing with diamond particles. Before the experimental process, the silicon substrate was placed right under the filaments. The filament temperature was 2200 °C measured by an infrared thermometer (Raytek) during diamond deposition. Due to the high temperature and hot electrons emitted from the filament, a plasma region was generated around the filament, which was the main reaction site for the CVD. The substrate temperature, measured by thermocouple below silicon substrate, was maintained at 800 °C. The distance between the filaments and the substrate was set to 8 mm. Hydrogen (99.99%, 200 standard cubic centimeters per minute (SCCM)) and methane (99.99%, 2 SCCM) as reaction gases were introduced into the chamber and the total pressures were maintained at 2000 Pa. The base pressure was 9.0×10^{-4} Pa in the experiment. The treatment process lasted 10 h. As a control experiment, the pure diamond particles as seed layer were also treated by the same procedure. In order to study the influence of different carbon source, graphite powder was used to replace the PVP as the solid carbon source, and other experiment parameters were kept the same with that of PVP/diamond composite.

The morphologies and surface component of the diamond films were investigated by field emission-scanning electron microscopy (FESEM, Hitachi S-4800) and Raman spectroscopy (JY-HR800 micro-Raman, with a 532 nm wavelength yttrium aluminum garnet laser), respectively.

3. Results and discussion

It has been reported that the epitaxial diamond prepared by CVI is only deposited on the diamond particles distributed on the surface of the film [18]. This can be explained by the transport of the gas species participating in the growth processes. The growth rate is decreased with the amount of atomic hydrogen and other species, which can be described by the Knudsen number. The Knudsen number is given by

$$K_n = \lambda_k/d \tag{1}$$

with

$$\lambda_k = RT/(\sqrt{2}\,\pi d_{m,k}^2 PN_A) \tag{2}$$

where λ_k is the mean free path of the gas species, d is diameter of the pores, R, T, $d_{m,k}$, P and N_A refer to the gas constant, temperature, molecular diameter of component k, pressure and the number of Avogadro, respectively. The calculated λ_k of atom hydrogen under the deposition conditions is approximately 160 μm and about sixteenth times as large as that of other activated species (e.g. CH_3).

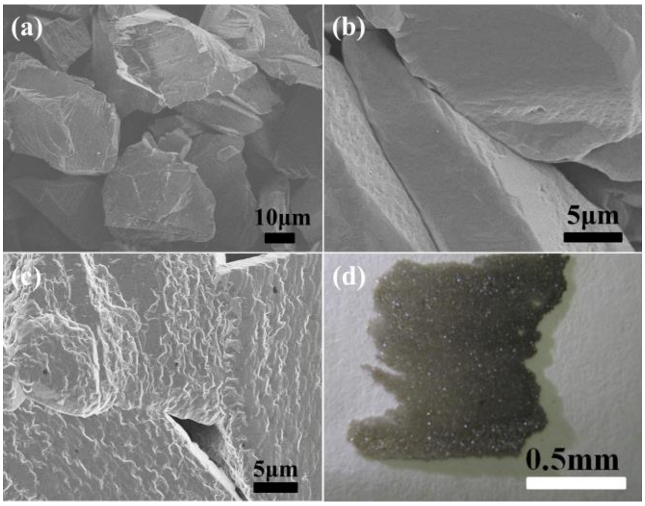

Fig. 1. SEM images of: a) initial diamond particles, b) diamond particles after conventional HFCVD treatment; and (c) the SEM images of the porous diamond film with PVP as auxiliary carbon sources, d) the photograph of self-standing porous diamond film peeled off from the substrate.

Therefore, the carbonaceous active groups can diffuse only several micrometers, which results in low concentration of carbonaceous groups and low growth rate inside the pores. Meanwhile, the small amount nucleation sites also affect the diamond growth on the diamond particles [22]. Fig. 1a is the morphology of the initial diamond particles. It is obviously that the commercially available diamond particles have high surface roughness, a large number of surface defects and uneven edges. Fig. 1b shows the SEM image of the diamond particles treated by conventional CVD method. Smooth surfaces are obtained, which is agreed well with our previous reports [22]. Fig. 1c demonstrates the surface SEM images of porous diamond film prepared by HFCVD with PVP as auxiliary carbon source. And Fig. 1d is the picture of the obtained self-standing porous diamond film, which is the macro image of Fig. 1c. From the SEM images, it can be seen that the surface of diamond particles in PVP/diamond composite is rougher than the diamond particles treated by conventional CVD method, which may be caused by the carbonization of PVP. Because the carbonized PVP can act as carbon source and nucleation sites in the film, the growth of new diamond layer would carry out quickly, which make the coalescence of the grains is stronger than the PVP-free diamond film.

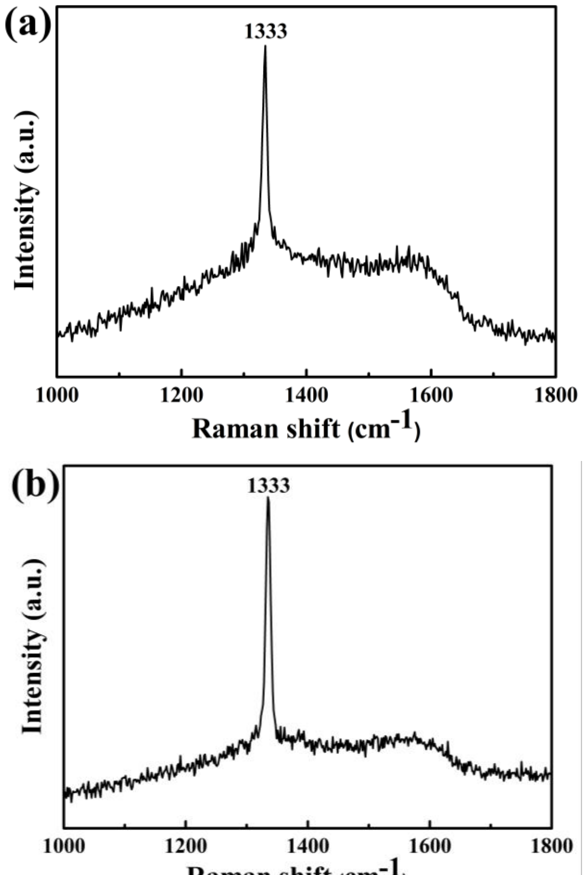

Fig. 2. Raman spectra of the diamond particles after conventional CVD treatment and self-standing porous diamond film prepared with PVP as auxiliary carbon sources.

Raman spectroscopy is a powerful and widely used method for the characterization of sp^2 and sp^3 hybridized carbon atoms in the carbonaceous materials. Fig. 2 displays the Raman spectra of the samples. The peak at 1332 cm^{-1} is the characteristic peak for diamond phase. The broad peak at 1595 cm^{-1} corresponds to the G peak of sp^2 bond. Because the sensitivity of the Raman signal for graphite phase is 50 times higher than diamond phase, the signal of graphite phase can be observed obviously in the Raman spectrum if a little graphite phase exists in the sample. For easily comparing the change of the graphite phase content, we define the I_{dia}/I_{gra} is the ratio of the signal intensity for the diamond phase and graphite phase. Compared with the diamond particles treated by the conventional HFCVD method (I_{dia}/I_{gra} = 2.29), the sp^2 carbon signal in self-standing diamond film is weaker (I_{dia}/I_{gra} = 3.91). This result may be caused by the high content of atom hydrogen inside the film and the quality of second nucleation.

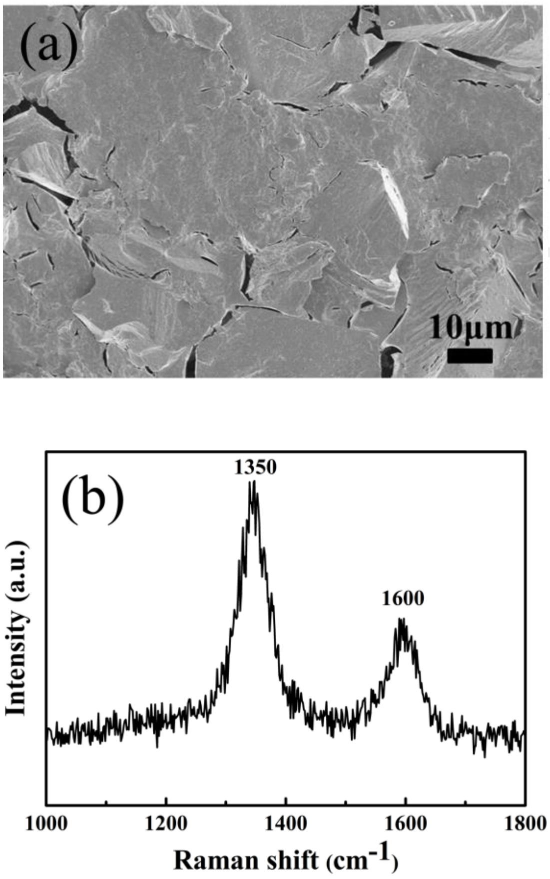

Fig. 3(a) SEM images of porous diamond film prepared by HFCVD with graphite powder as auxiliary carbon sources, (b) Raman spectrum of porous diamond film prepared by HFCVD with graphite powder as auxiliary carbon sources.

To study the influence of different auxiliary materials on the quality of obtained diamond film, graphite powder was used as auxiliary material to replace PVP. The surface SEM image of the obtained diamond film is shown in Fig. 3(a). From the SEM image, a porous diamond film can also be observed, but the surface is rough. However, due to the weak connection among diamond particles, the self-standing diamond film cannot be obtained. The Raman spectrum of the diamond film prepared with graphite powder as auxiliary material is shown in Fig. 3(b). The peaks at 1350 and 1600 cm^{-1} are corresponding to the characteristic peaks of graphite phase, and almost no signal of diamond phase can be found. On the one hand, the signal sensitivity of graphite phase in Raman spectra is much higher than that of the diamond phase. On the other hand, the graphite phase still exists in the mixture because the graphite powder in the mixture cannot be etched completely by the small content of atom hydrogen.

According to the above results, the possible growth mechanism of self-standing porous diamond film by HFCVD is presented in Fig. 4. Carbonaceous materials etched by H plasma can form CH, CH_2, and CH_3 radicals during the growth process. Some radicals will escape from the film, and some radicals will be absorbed by the diamond particles. Under high temperature and hydrogen plasma environment, new diamond layers can be grown on the diamond particles caused by the second nucleation process. The new diamond layers are grown around the diamond particles and connect the surrounding particles. Consequently, a porous diamond film is formed, as shown in Fig. 1c. But graphite phase can also be formed because the concentration of carbonaceous groups is higher than that of atom hydrogen (with graphite powder as auxiliary material) [22]. In the early stage of growth, PVP would dehydrate, carbonize and then play the role of nucleation sites and carbon source. Due to the high content of atom hydrogen, the new diamond layer would contain a small amount of graphite phase. Because only the diamond particles at the top layer can grow effectively and be linked into a whole block, the obtained self-standing diamond film can be peeled from the substrate. Owing to the high thermal conductivity and high mobility of electrons and holes, the porous diamond film can be used in many related field, such as heat sink devices, support body of resistant materials and so on.

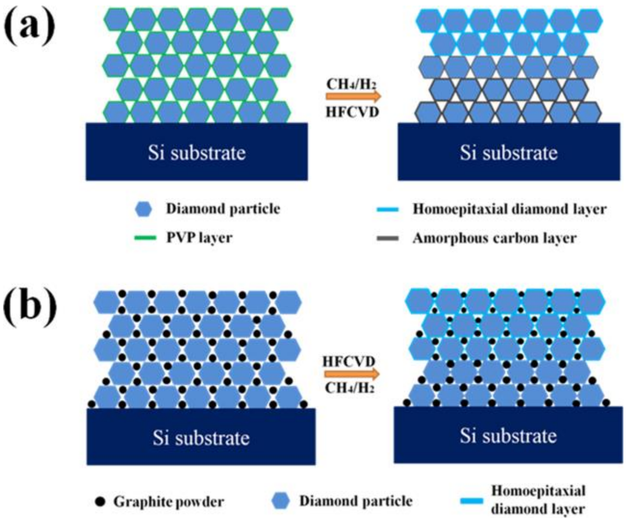

Fig. 4. The possible mechanisms of the porous diamond film prepared by HFCVD with PVP and graphite powder as auxiliary carbon source.

4. Conclusions

In summary, self-standing porous diamond films were prepared by HFCVD with PVP as an efficient auxiliary material. Compared to the conventional diamond growth process, the auxiliary carbon source provides more carbonaceous groups and nucleation sites inside the diamond particle film, which breaks the bottleneck of CVI that the epitaxial process can carry out only in the surface of the film. Due to the high concentration of atom hydrogen, the prepared diamond film only contains a small amount of graphite phase. This self-standing porous diamond film can be used in many field, especially in heat sink devices.

Acknowledgments

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