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Tetramethysilane-assisted enhancement of diamond nucleation on silicon substrate

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ABSTRACT

This paper describes the effect of tetramethylsilane (TMS) on diamond nucleation on Si substrate under an applied bias voltage of 120 V, performed in a modified microwave plasma chemical vapor deposition (MPCVD) reactor. The introduction of TMS in the CH_4/H_2 plasma leads to a significant enhancement of nucleation density of diamond nuclei, namely from $(3.7 \pm 0.2) \times 10^7/cm^2$ without the introduction of TMS to $(4.7 \pm 0.5) \times 10^{10}/cm^2$ at the TMS flow rate of 4 sccm. On the contrary, further increasing in the TMS flow rate to 8 sccm slightly reduces the nucleation density of diamond nuclei to $(2.1 \pm 0.3) \times 10^{10}/cm^2$, along with the increase in average size of diamond nuclei. High-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) allow us to study the microstructural and chemical composition evolution of Si/diamond interface. The obtained results suggest that bias-enhanced nucleation of diamond on Si substrate exhibits a direct relationship with the TMS flow rate.

1. Introduction

Diamond growth on heterogeneous substrates has received intensive attention due to its important applications, namely ranging from conventional cutting tools to active electronic and/or optical devices. To achieve this growth, it is necessary to form stable nuclei with high density [1, 2]. Over the past decades, several different techniques, such as mechanical abrasion with diamond micro-powders [3, 4] and ultrasonication in diamond powder suspended solutions [5, 6] as well as modification of chemical precursor [7–10], have been widely used to enhance diamond nucleation on various heterogeneous substrates. Compared with these techniques, bias-enhanced nucleation (BEN) has been proved to be a powerful way for the production of diamond nuclei with high density on heterogeneous substrates [11–19].

Generally, applying a suitable voltage to the substrate results in the formation of a bias discharge located on the periphery of the substrate holder, usually originating from two different physical processes: ion bombardment from the plasma and electron emission from the substrate. In this case, the bias discharge can mix with the microwave discharge to form a non-uniform plasma. The interaction between the plasma and substrate surface has a crucial effect on the diamond nucleation behavior [19]. In recent years, the effect of *heterogeneous substrate materials* on the plasma-substrate interaction and subsequent diamond BEN process have been systematically investigated by Arnault et al., using various *in*- and ex-situ surface analysis techniques [14–22].

However, there are few reports about the effect of *the plasma* on the interaction and subsequent diamond BEN process. A possible reason may be that the relevant characteristics of *the plasma* such as ion energy distribution and electronic emission are not measurable and strongly depend on the process parameters [19]. A slight variation in the parameters, such as microwave power, chamber pressure, bias voltage and substrate materials as well as geometrical configuration, can result in remarkable difference in the shape and composition as well as spatial distribution of the plasma.

The aim of this work is to investigate the effect of *tetramethylsilane* (TMS) introduced in the CH_4/H_2 plasma on the diamond BEN on Si substrate. The morphology and microstructure of Si/diamond interface are characterized carefully, followed by a discussion about the evolution with TMS flow rate.

2. Materials and methods

Diamond BEN was performed using a *modified* MPCVD reactor, as shown in Fig. 1. A small graphite substrate holder with diameter of

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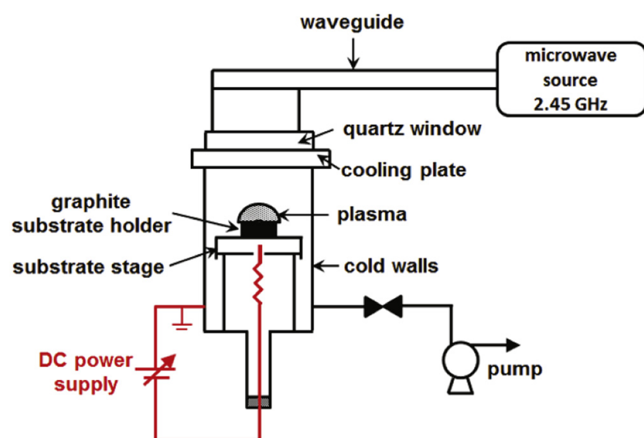

Fig. 1. Schematic diagram of the *modified* MPCVD system for diamond BEN.

15 mm and height of 10 mm was placed on large substrate stage connected to a DC power supply. The substrate stage was insulated from the metallic cold wall, which was maintained at ground potential. Therefore, it was possible to apply a negative voltage to the graphite substrate holder during plasma exposure.

Si substrate was ultrasonically cleaned in piranha solution (H_2SO_4: H_2O_2 = 3:1), followed by washing in deionized water. A microwave plasma discharge pretreatment using pure H_2 at a flow rate of 400 sccm (standard cubic centimeter per minute at STP) was firstly used to clean the Si substrate. The temperature of Si substrate was stabilized to be about 775 °C after the plasma exposure for 10 min. Before the BEN process, a bombardment pretreatment in pure H_2 plasma was performed for 5 min at a bias voltage of 120 V. The temperature of Si substrate was slightly increased to be about 805 °C at the end of bombardment pretreatment. After then, the methane with a flow rate of 14 sccm and the TMS (diluted in H_2) with a *variable* flow rate were simultaneously introduced to begin diamond nucleation. The bias current between substrate holder and metallic chamber wall decreased slightly from 23 mA to 20 mA, and the temperature of Si substrate increased gradually from 805 °C to about 830 °C. Note that the change in both bias current and substrate temperature did not exhibit the dependence on the TMS flow rate. After 5 min, the bias voltage and microwave as well as reactive CH_4/TMS gases were closed at the same time. During the diamond BEN process, microwave power and chamber pressure were set at 1000 W and 25 Torr, respectively. As-obtained samples were thus named as TMS_x, in which symbol x represented the TMS flow rate introduced.

Surface topography of as-obtained samples was observed using field-emission scanning electron microscopy (FESEM, Zeiss Ultra 55). The average nucleation density N and surface coverage S of diamond nuclei were extracted using the *Image J* software from five FESEM micrographs for each sample. HRTEM (FEI Tecnai G2) was employed to examine the detailed microstructure of the interfaces between diamond nuclei and Si substrate. XPS measurements (Thermal VG/ESCALAB 250) were also carried out with a monochromatic Al Kα source. The binding energy scale was calibrated versus the Au 4f 7/2 peak at 83.6 eV.

3. Results and discussion

Fig. 2 shows typical high-magnification FESEM micrographs of Si surface after diamond BEN process. In the TMS_0 sample, only a few discrete particles can be seen on the Si surface (Fig. 2a). Such a result indicates extremely low nucleation density of diamond. The nucleation density N of diamond is estimated to be only about $(3.7 \pm 0.2) \times 10^7$/cm^2. The surface coverage S is almost negligible. In contrast, large amounts of diamond nuclei with average diameter of 28 nm are clearly seen in the TMS_4 sample (Fig. 2b). The estimated N and S values are as high as $(4.7 \pm 0.5) \times 10^{10}$/cm^2 and 32.6%, respectively. However, in the TMS_8 sample, the N and S values reduce to be about $(2.1 \pm 0.3) \times 10^{10}$/cm^2 and 13.4%, respectively. In the meantime, the average diameter of diamond nuclei increases to be about 60 nm. Consequently, the introduction of TMS in the CH_4/H_2 plasma during diamond BEN process can easily influence the plasma-substrate interaction and further enhance the diamond nucleation. Note that such an enhancement exhibits a significant dependence on the TMS flow rate.

In order to identify possible reason for the TMS-assisted enhancement of diamond nucleation on Si substrate, cross-sectional HRTEM characterizations were carried out to observe the detailed microstructure of Si/diamond interface. Fig. 3 shows the typical HRTEM micrographs for each sample. The first remarkable change is the preferential etching of Si surface, thus leading to form triangular surface profile, which is in accordance with the previous reports [2, 23, 24]. More importantly, such an etching behavior can be clearly enhanced with increasing the TMS flow rate, and the peak-to-valley roughness of the triangular Si surface profile increases from about 2 nm in the TMS_0 sample to about 7 nm in the TMS_8 sample. Then, let us turn our attention to the interfacial region between Si surface and diamond nuclei. In the TMS_0 sample, there is almost no clear crystalline phase in the interfacial region, indicating the formation of amorphous phases on the surface of Si substrate. In the TMS_4 sample, some crystalline phases often appear at the valleys of the triangular Si surface profile, but some amorphous phases are seen at the peaks of the triangular profile. Fourier-transformed diffractograms corresponding to these crystalline phases (ft2 in Fig. 2) reveal that they are cubic silicon carbide (β-SiC). On the contrary, a quasi-continuous β-SiC thin films with the average thickness of 2–3 nm can be formed in the TMS_8 sample (Fig. 3). Finally, in the TMS_4 and TMS_8 samples, crystalline diamond nuclei can be easily observed (Fig. 3b and c), however they are hardly seen in the TMS_0 sample (Fig. 3a). Moreover, the size of diamond nuclei in the TMS_8 sample is larger than that in the TMS_4 sample. These observations are in well accordance with the FESEM observations. It is worth emphasizing that diamond nuclei in the TMS_4 and TMS_8 samples are always preferred to nucleate at the peaks of the triangular Si surface profile. Such behavior for the diamond nucleation has been also observed in previous reports [23, 25]. In short, with increasing the TMS flow rate, several remarkable changes, such as stronger preferential etching of Si surface, larger diamond nuclei formed at the peaks of triangular Si profile and more β-SiC deposited in the interfacial region, can be observed.

XPS measurements have been also performed to study chemical composition evolution of Si substrate after diamond BEN process. From the XPS spectra, one can estimate the surface atomic ratio R of Si to C, based on the integrated peak area and the atomic sensitivity factor. The R value is as high as 0.96 in the TMS_0 sample, and it rapidly decreases to 0.18 in the TMS_4 sample as well as increases slightly to 0.30 in the TMS_8 sample. This result is in well accordance with the changes in the nucleation density N and surface coverage S from the FESEM micrographs and the detailed microstructures of Si/diamond interface from HRTEM micrographs. Fig. 4 shows the high-resolution XPS of C1*s* spectral regions for all the TMS_x samples after a Shirley-background subtraction. In order to obtain the peak positions and relative contributions of each chemically shifted component, a curve-fitting procedure was performed. In each sample, three different contributions can be obtained. A first component (Peak I) located at 282.7 eV corresponds to carbon atoms belonging to the β-SiC phase [15]. Two peaks at 284.5 eV (Peak II) and 285.3 eV (Peak III) can be assigned to sp^3-bonded diamond and amorphous carbon, respectively [15, 17, 18]. In addition, the percentage of each chemical bonding state is calculated and shown in Fig. 4d. It can be seen that the diamond component increases from 50.3% in the TMS_0 sample to 71.2% in the TMS_8 sample. Moreover, there is a competitive relationship between the carbon atoms belonging to the β-SiC and the amorphous carbon. Such a relationship has been also reported in previous works about the diamond BEN [17]. To be

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