Synthesis of oriented textured diamond films on silicon via hot filament chemical vapor deposition

Qijin Chen,[a] Jie Yang, and Zhangda Lin
State Key Laboratory of Surface Physics, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603-8, Beijing 100080, People's Republic of China

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Oriented diamond films were achieved on Si(001) and Si(111) substrates via hot filament chemical vapor deposition (HFCVD) with the orientation relationship of dia⟨110⟩//Si⟨110⟩ and dia(001)//Si(001) for Si(001), and of dia⟨110⟩//Si⟨110⟩ and dia(111)//Si(111) for Si(111). The substrates were negatively biased relative to the filament during the nucleation stage. The as-grown films were characterized by scanning electron microscopy (SEM) and Raman spectroscopy. The role of negative bias is discussed in light of the differences between HFCVD and microwave plasma CVD. In conclusion, the importance of the electron emission from the diamond coating on the substrate holder is highlighted, while the ion bombardment is eliminated as a main factor based on our experiments. © *1995 American Institute of Physics.*

Great progress has been made in heteroepitaxy of diamond on Si in hopes of utilizing the promising applications of diamond film in electronics[1] since Spitsyn *et al.*'s report in 1981.[2] To attain this goal, it is necessary to get high-density oriented nucleation without any possible damage to the Si surface by pretreatment, which usually causes randomly oriented nucleation. Applying negative bias to the substrate during the nucleation stage has been proven to be an effective method in microwave plasma chemical vapor deposition (MPCVD). With this method, Jiang *et al.*,[3] Wolter *et al.*[4] and Stoner *et al.*[5] have obtained oriented and/or local epitaxial diamond films on Si(001) and/or β-SiC. However, as a major method of diamond deposition, hot filament CVD (HFCVD) has not been reported to bring similar results despite its advantages as compared with other methods. For example, the HFCVD apparatus is much simpler, and it is much easier to enlarge the deposition area in HFCVD at a much lower cost. Recently, Yang *et al.*[6] reported observation of localized epitaxy of diamond directly on Si(001) through high resolution transmission electron microscope (HRTEM). This sheds some light on diamond heteroepitaxy on Si, but they did not acquire uniformly large area oriented diamond films. Although many researchers have tried the negative bias enhanced nucleation method in HFCVD system, no oriented diamond growth by HFCVD has been reported as yet. Zhu *et al.*[7] reported that nucleation enhancement occurred only along the edges of the Si wafer by simply negatively biasing the substrate. They did not get oriented diamond film, either. In order to make full use of the advantages of HFCVD, it is necessary to achieve oriented or epitaxial growth of diamond films on Si.

In this letter, the authors report oriented diamond films on single crystal either Si(001) or Si(111) wafers by negative bias nucleation method in a conventional HFCVD apparatus. Although our results are quite similar to those of Jiang[3] and Wolter,[4] we believe that this is the first report of oriented textured growth of diamond films on Si substrates via HFCVD. Because there are great differences between the HFCVD system and MPCVD system, this work sheds some light on the role of negative bias for nucleation. Our results are of great significance since HFCVD has many advantages in diamond films growth as compared with other deposition methods.

In this work, the diamond films were deposited in a typical HFCVD apparatus, which is quite similar to that of Chu *et al.*[8] Cooling water was used to adapt the substrate temperature to desired values. Mirror-polished *p*-type both Si(001) (sample I) and Si(111) wafers (sample II) were used as substrates, cleaved into the size of 8×10 mm^2. The substrates were ultrasonically cleaned in acetone for 10 min and then rinsed in 30 vol. % HF for 1 min before loaded into the deposition chamber. The substrates were placed on a molybdenum substrate holder. The dc negative bias was applied to this Mo holder while the filament was dc grounded. Our chamber was pre-evacuated to 10^{-3} Torr, then the mixture of H_2 and CH_4 was fed into the deposition chamber. The filament temperature was measured by a pyrometer. The substrate temperature was measured by a thermocouple (PtRh), which was carefully arranged to contact the backside of the substrate. The filament-to-substrate distance was fixed at 8 mm. Sample I was taken out of the chamber to take a SEM photograph of the nucleation pattern immediately after the nucleation stage, then it was reloaded for subsequent growth. The as-grown films were analyzed by SEM and Raman spectroscopy. The parameters are listed in Table I.

Figure 1 is the SEM image of sample I immediately after the nucleation stage. Obviously, some of the nuclei joined each other after 1 h bias. Although the nuclei appear to be unfaceted, the overall nucleation pattern is quite unusual, different from those reported by other researchers.[9,10] It seems that the nuclei were undergoing a two-dimensional expansion (gray areas in Fig. 1) from their initial nucleation points (white spots) along the Si surface, suggesting the possibility of epitaxy during nucleation. The nucleation density is measured to be higher than 10^9 cm^{-2}.

Figures 2(a)–2(b) show the SEM micrographs of the surface of the overgrowth on sample I at different magnifica-

[a]Electronic mail: linzd@aphy01.iphy.ac.cn

TABLE I. Experimental conditions.

Parameters	Sample I	Sample II
Flow rate (sccm)	200	200
CH_4 concen. (nucl.) (vol.%)	1.4	2.0
CH_4 concen. (growth) (vol. %)	1.4	0.6
Filament temperature (°C)	2000	1950
Substrate temperature(°C)	800	750
Pressure (torr)	40	40
dc bias (V)	−260	−260
Emission current (mA)	200	200
Bias time (min)	60	20
Growth time (h)	6.0	6.0

tion. Figure 2(c) shows that of sample II. In contrast with the result of Zhu *et al.*,[7] diamond films were realized across the Si surfaces by simply applying negative bias to the substrates. Both the diamond (001) squares in Figs. 2(a)–2(b) and the diamond (111) triangles in Fig. 2(c) are almost uniformly oriented. The arrows in Figs. 2(b) and 2(c) indicate the direction of Si⟨110⟩ and Si⟨$\bar{1}$10⟩, respectively. From the shape of the diamond crystals, we conclude that the uniformly oriented diamond films are in the orientation relationship of dia(001)//Si(001) plus dia⟨110⟩//Si⟨$\bar{1}$10⟩ for Si(001) [Fig. 2(b)], and dia(111)//Si(111) plus dia⟨110⟩//Si⟨$\bar{1}$10⟩ for Si(111) [Fig. 2(c)]. It is believed that the diamond film is epitaxial on Si or on SiC intermediate epilayers. This conclusion conforms to the reports of Wolter *et al.*[4] and Jiang *et al.*[3]

Furthermore, there exist various small angles between different crystallites, as shown in Fig. 2(b). Some of them resulted from the large lattice mismatch (diamond: 3.5667 Å, Si: 5.4301 Å) between Si and diamond. However, some other angles, e.g. those between grain A, B and C in Fig. 2(b), is speculated to have resulted from the stress from neighboring crystallites, e.g. grain D, E, F, etc. since they are as small as 1°. On the other hand, for some crystallites in Fig. 2(b), the two perpendicular edges of their (001) facets do not make a right angle in this picture; these (001) facets are not exactly parallel with the substrate surface. For example, crystallite F makes an angle of 91.0°, crystal G makes 96.4°. We believe that there also exists a small range of the misorientation angle between Si(001) and dia(001) plane. They cannot be attributed to only the Si/diamond lattice mismatch, but to a combination of the mismatch and the stress among the diamond grains.

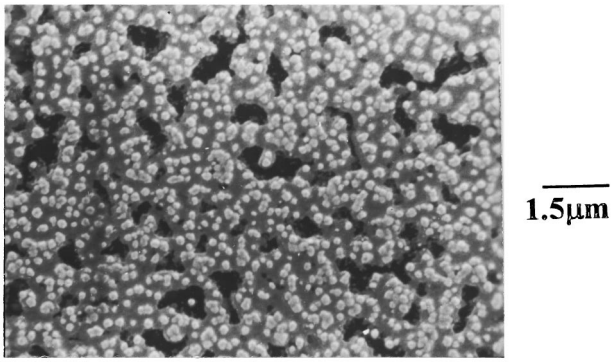

FIG. 1. SEM image of sample I after 1 h biased nucleation.

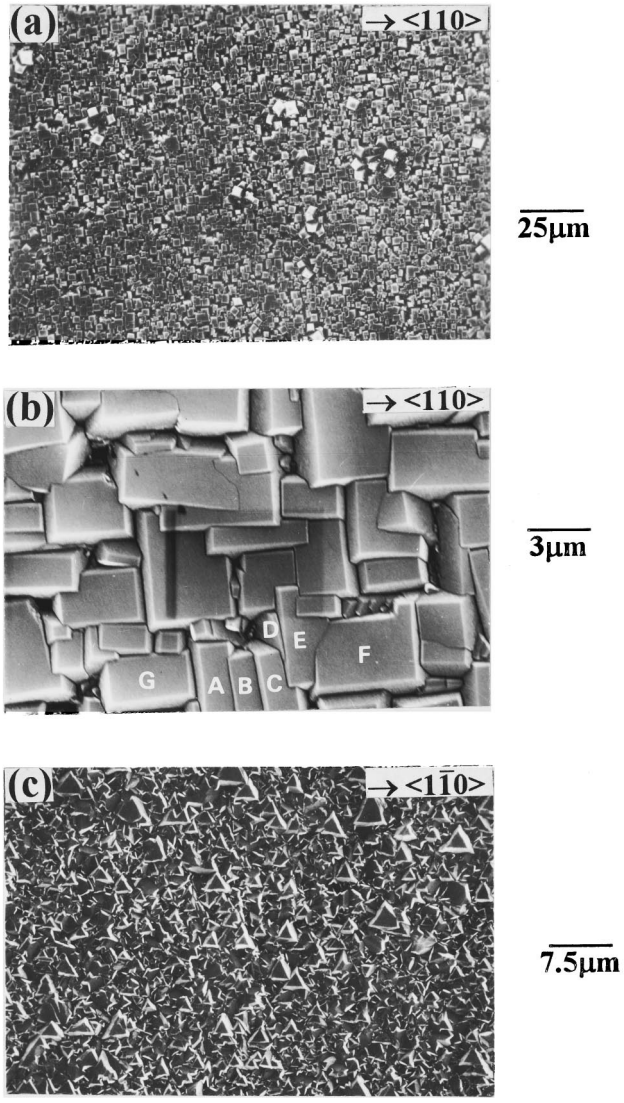

FIG. 2. SEM images of the diamond films on (a)-(b) sample I and (c) sample II. (b) is with higher magnification compared with (a).

Figure 3 gives the Raman spectrum of the film on sample I, that of sample II is quite similar. Obviously, the diamond peak at 1333 cm^{-1} is strong, though it is slightly greater than 1332 cm^{-1} in a stress-free case, demonstrating the existence of internal compressive stress in the film. Meanwhile, the broad peak centered at about 1520 cm^{-1} is very weak, indicating little nondiamond carbon. Accordingly, the quality of the diamond film is high.

As of today, the role of the negative bias during nucleation has given rise to controversy. By the MPCVD method, Yugo *et al.*[11] argued that negative bias of the substrate accelerated various ions in the plasma to the substrate surface and enhanced the nucleation. Jiang *et al.*[10] claimed that the bias-enhanced ion bombardment improved the adatom diffusion and was responsible for the diamond nucleation. In comparison with MPCVD, however, there exists much less in the amount of ions in HFCVD. This is a great difference between these two systems. Yet we achieved similar results

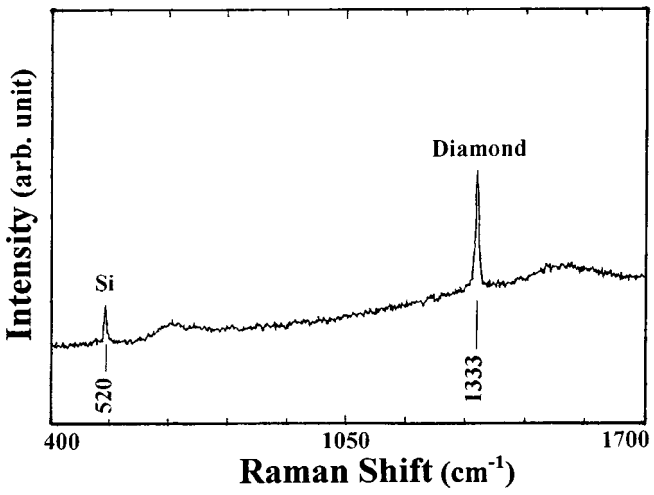

FIG. 3. Raman spectrum of the as-grown diamond film on sample I.

with HFCVD as to those with MPCVD. In a separate paper, we reported high density nucleation realized within as short a time as 8 min at a higher substrate temperature and with a higher methane concentration.[12] Accordingly, we can rule out the role of the ions in our experiments to a great extent. We believe there exist some fundamental mechanisms common to both HFCVD and MPCVD.

Stoner *et al.*[13] put forward two possible mechanisms for negative bias nucleation. One was material transport from the diamond coating on the Mo substrate holder to the substrate surface during the bias nucleation stage. They reported decreasing electron emission current from the diamond coating and accordingly the etch of the coating by electron emission. However, we find that the emission current can be rather steady or even slightly increase at a higher CH_4 concentration and higher substrate temperature. Therefore, the material transport mechanism seems not to be true.

The other mechanism showed that the increased nucleation resulted from an increased concentration of dissociated hydrogen and/or hydrocarbon radicals near the substrate surface, caused by electron emission from the diamond coating. In fact, the electron emission was confined outside the sample, as could be seen clearly because the emission presented a blue color. The electrons collided with the H_2 molecules and various hydrocarbon species and helped to dissociate them. Consequently, the concentration of atomic hydrogen and dissociated hydrocarbon radicals greatly increased. Owing to the diffusion, these hydrogen atoms and hydrocarbon radicals moved onto the substrate surface, added to the supersaturation of carbon and, eventually, led to nucleation. This is why nucleation occurred from the outer to inner area. Meanwhile, we have found that almost no nucleation occurred over a long time (say, 10 h) in the case that only negative bias was applied but without electron emission; the greater the emission current, the higher the nucleation rate. Therefore, we conclude that the electron emission played a critical role during nucleation.

In summary, oriented textured diamond film on both Si(001) and Si(111) wafers as achieved by HFCVD. As far as the HFCVD method is concerned, this is the first report of oriented growth of diamond films on silicon as of today. The orientation relationship is Si$\langle 1\underline{1}0\rangle$//dia$\langle 1\underline{1}0\rangle$ plus Si(001)// dia(001) for Si(001), and Si$\langle 110\rangle$//dia$\langle 110\rangle$ plus Si(111)// dia(111) for Si(111) substrate, respectively. The mechanism of negative bias nucleation is discussed. The importance of the electron emission from the diamond film coating the Mo substrate holder is underlined while the ion bombardment is rule out of the main factors for nucleation in our experiments.

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