

# Oriented and textured growth of (111) diamond on silicon using hot filament chemical vapour deposition

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## Abstract

A very low pressure (13 Pa), high substrate temperature and a.c. discharge for the nucleation stage have been applied. Uniformly oriented and textured growth of (111) diamond (dia) with dia(111)//Si(111) and dia<1 $\bar{1}$ 0> //Si<1 $\bar{1}$ 0> has been achieved on not only well polished but also scratched silicon substrates using hot filament chemical vapor deposition. A probable explanation, heteroepitaxy, was hypothesized. The as-grown diamond films were characterized by Raman spectroscopy, scanning electron microscopy, and X-ray analysis.

*Keywords:* Chemical vapour deposition; Diamond; Epitaxy; Nucleation

## 1. Introduction

The promising applications of diamond thin films in electronics have been made clear [1]. Since its prospective electronic properties are based on the bulk properties of diamond, it is necessary to produce large-area single-crystal thin films [2]. Homoepitaxial growth of diamond has been reported. Unfortunately, no substrates of sufficient size are available economically. Therefore, heteroepitaxial growth of diamond has been an important goal of the researchers. Owing to the very small lattice mismatch between cubic boron nitride (cBN) and diamond (1.3%) [3], it has been reported that diamond can be epitaxially grown on micrometer-sized cubic boron nitride crystals [4–7]. However, cBN substrates of enough size are quite difficult to acquire, making the heteroepitaxy of diamond on them impractical. Another candidate is monocrystalline silicon, and many efforts have been made to achieve the epitaxy of diamond on it.

Usually, diamond films grown on silicon substrates by chemical vapor deposition (CVD) are polycrystalline and non-oriented because of the use of the ex-situ pretreatment to enhance the nucleation such as: (i) mechanical scratching with diamond powder [8], (ii) production of defects and sharp edges on the substrates [9], and (iii) predeposition of carbonaceous precursors or non-diamond carbon such as diamond-like carbon (DLC) [10,11], pump oil [12] or graphite

[13]. Epitaxial growth of (100) diamond on mirror-smooth silicon substrate using microwave plasma CVD (MPCVD) has been reported by Jiang et al. by negative bias [14–16]. Oriented and textured growth of (100) diamond on Si and  $\beta$ -SiC has also been reported by other research groups [17–19]. Zhu et al. have found direct epitaxy on  $\beta$ -SiC [19]. All these results have been achieved by MPCVD and only mirror-polished Si substrate has been used. Recently, using hot filament CVD (HFCVD), Yang et al. observed local direct epitaxy of (100) diamond on Si wafer through high-resolution transmission electron microscopy (HRTEM) [20]. However, highly oriented large-area growth of either (100) or (111) diamond film has not yet been reported. One reason is that it is difficult to obtain high-density nucleation on a mirror-polished Si substrate. It is necessary to investigate whether or not the HFCVD method is suitable for large-area oriented or epitaxial growth of diamond film. Another fact is that no oriented growth of diamond on scratched Si wafers has been reported by either HFCVD or MPCVD. It is generally taken for granted that well-polishing Si wafers is a prerequisite for heteroepitaxy, but there is no direct evidence as yet.

In this paper, the authors report the oriented and textured growth of (111) diamond on both well-polished and scratched Si substrates (by 0.5  $\mu$ m diamond powder) by a conventional HFCVD method. No bias was applied during either the nucleation phase or the growth process. But in the nucleation stage, a very low chamber pressure (13 Pa) and high substrate temperature were employed in our experi-

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ments. In the meantime, due to the very low pressure in the chamber, an a.c. discharge automatically occurred between the filament and the substrate. This discharge is critical for nucleation in our experiments, as discussed below.

## 2. Experimental details

A  $\phi$  140 mm and 500 mm long quartz tube was used as the deposition chamber, and a copper platform of 80 mm in diameter was used to support the samples.  $\phi$  0.2 mm tungsten wires winding into coils 2.5 mm in diameter were used as filaments with their temperature measured by a two-colour optical pyrometer. Three  $5 \times 8 \text{ mm}^2$  and 0.5 mm thick n-type (111) silicon wafers were used as substrates. Cooling water was also used to adjust the substrate temperature. Samples I and III were mirror-polished while sample II was scratched by 0.5  $\mu\text{m}$  diamond powder. The temperature of the substrates was measured by a type-K thermocouple directly in contact with the backside of the substrates. The source gas was diluted  $\text{CH}_4$  in hydrogen with the total flow rate of 100 sccm. The distance between the filament and the substrates was fixed at 6 mm. The substrates were chemically cleaned with acetone in an ultrasonic bath for 10 min, followed by a 1 min rinse in 30 vol.% HF solution. The sample surfaces remained mirror-smooth after this rinse. The nucleation stage lasted for 5 min, during which an a.c. discharge (50 Hz), mainly consisting of the electron emission from the hot filament at very low pressure, occurred, though not confined exactly, between the filament and the substrate. The filament-to-substrate a.c. electrical potential difference was typically 50–60 V, i.e. the filament heating voltage; the discharge current ranged from 0.5 A to 1.0 A. The subsequent deposition lasted for 12 h. Then the samples were analyzed with SEM to see the micro-morphology, Raman spectroscopy to determine the quality, and X-ray diffraction to find the texture of the overgrowth. For the other parameters, please see Table 1.

## 3. Results and discussion

Fig. 1(a) and 1(c) show the SEM images of the as-grown diamonds on samples I–III, respectively. The diamond par-

ticle size is up to 3  $\mu\text{m}$ . It is clear that uniformly oriented (111) diamonds have been achieved as shown in Fig. 1(a) and 1(b), where the triangular diamonds are separate. When the triangles combine, their shape will become irregular, and thus their orientation will not be clear, as in Fig. 1(c). However, it is clearer when viewed with a lower magnification, and especially when viewed with an optical microscope. The only difference in condition for sample I and sample III is the  $\text{CH}_4$  concentration, as shown in Table 1. Due to the higher  $\text{CH}_4$  concentration corresponding to Fig. 1(c), the nucleation and deposition speed were higher. So the diamonds in Fig. 1(c) expanded and joined one another, while those in Fig. 1(a) and 1(b) remained separate. In Fig. 1(b), the arrow in the Si  $\langle 1\bar{1}0 \rangle$  direction indicates that the diamonds may be locally epitaxial directly to Si with  $\text{dia}(111)//\text{Si}(111)$  and  $\text{dia}\langle 1\bar{1}0 \rangle // \text{Si}\langle 1\bar{1}0 \rangle$ . One scratch mark can be seen in the lower part of Fig. 1(b), as indicated by an arrow in this figure. It is interesting to note that the scratches did not affect the orientation of the (111) diamonds. This result is quite unusual as it has been generally believed that scratching the substrate surface usually disturbs the orientation of the diamond nuclei though it does enhance the nucleation. If the diamonds were hypothesized epitaxial to the substrates, this result would be explained satisfactorily, for it is believed that only in the epitaxial case can the grown diamonds be uniformly oriented and that only epitaxy can result in the uniform orientation in spite of the scratches. This hypothesis is also supported by the X-ray results.

Fig. 2(a) and 2(b) shows the Raman spectra obtained in back-scattering geometry with the spot size of approximately 80  $\mu\text{m}$  in diameter, corresponding to samples I and III, respectively. The Raman spectrum of sample II is the same as that of sample I. The diamond peak at  $1332 \text{ cm}^{-1}$  is strong. The broad peak of graphite centered at  $1580 \text{ cm}^{-1}$  and that of amorphous carbon at  $1545 \text{ cm}^{-1}$  are very weak. This indicates high quality of the diamond films. It is obvious that the diamond intensity in Fig. 2(b) is stronger than that in Fig. 2(a). This is because that the film on sample III is continuous (Fig. 1(c)) while that on sample I is not, i.e. the triangular (111) diamonds have not joined one another (Fig. 1(a)).

X-ray diffraction was used to analyze the texture of the as-grown films. Fig. 3(a) and 3(b) shows the X-ray diffraction results of the sample III. The results of samples I and II are

Table 1  
Experimental conditions

	Nucleation stage			Growth stage		
	Sample I	Sample II	Sample III	Sample I	Sample II	Sample III
Substrate	Polished	Scratched	Polished	Polished	Scratched	Polished
$\text{CH}_4$ concentration (vol.%)	0.8	0.8	1.5	0.8	0.8	1.5
Filament temperature ( $^\circ\text{C}$ )	2 200	2 200	2 200	2 100	2 100	2 100
Substrate temperature ( $^\circ\text{C}$ )	900	900	900	820	820	820
Pressure (Pa)	13	13	13	2 660	2 660	2 660

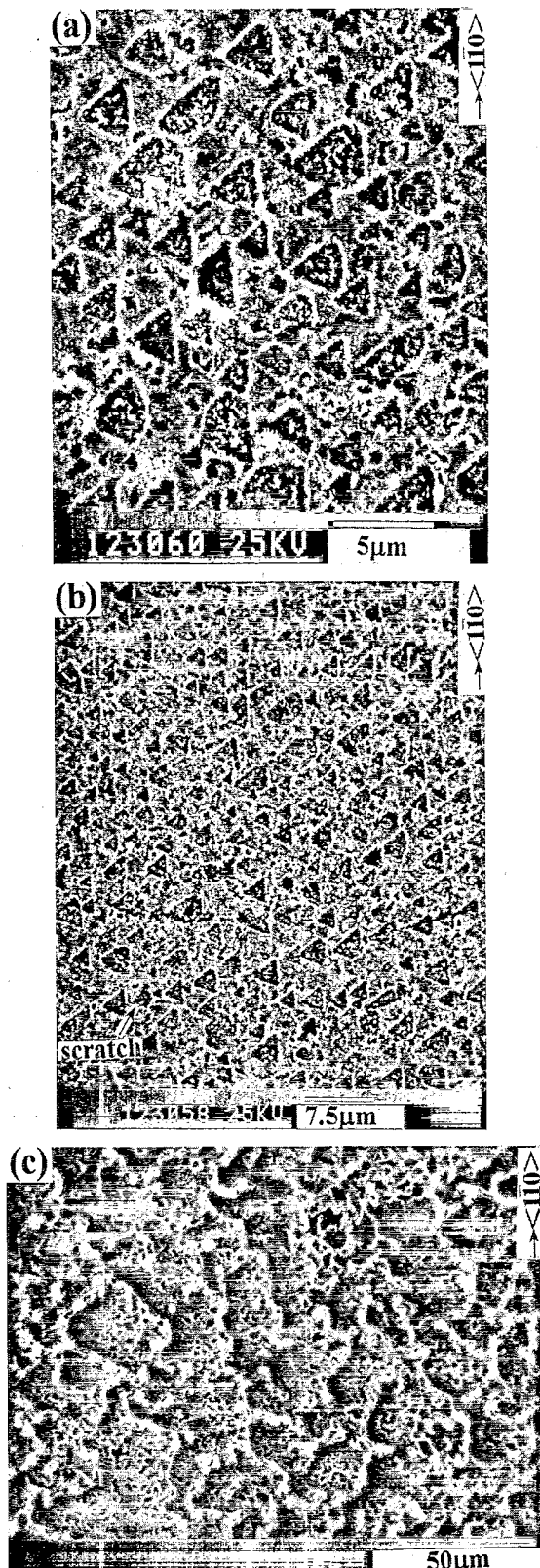


Fig. 1. SEM micrographs of the as-grown diamond films on sample (a) I, (b) II and (c) III after 12 h deposition.

quite similar to Fig. 3, except that the intensity of diamond is weaker. Sample III was measured twice, corresponding to Fig. 3(a) and 3(b). It was rotated  $90^\circ$  around the normal of its surface between these two measurements, as shown in Fig. 3(b). In Fig. 3(a), the intensity ratio of dia(111)/

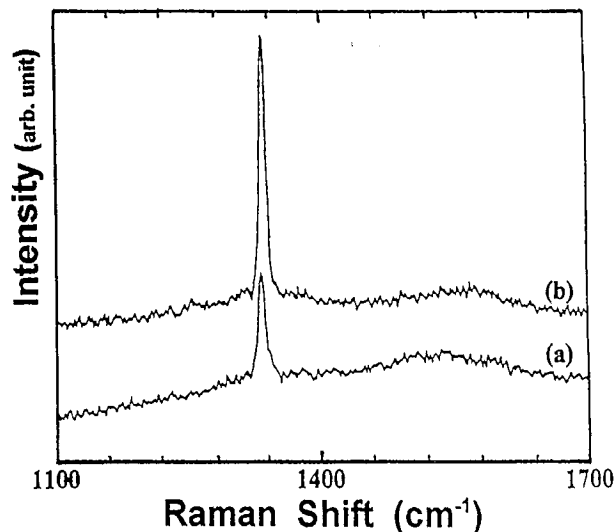


Fig. 2. Raman spectra of the as-grown diamond films on sample (a) I and (b) III, respectively.

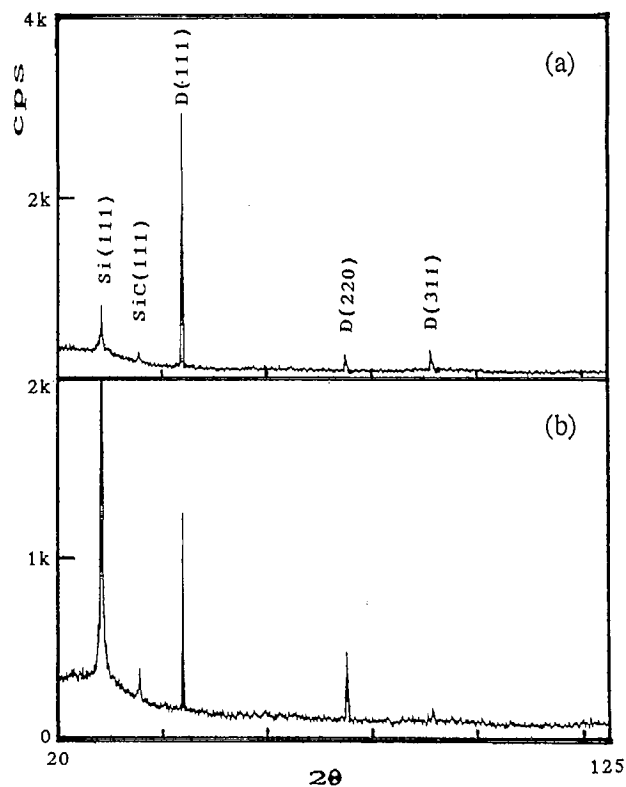


Fig. 3. X-ray results of sample III. After measurement of (a), the sample was rotated  $90^\circ$  around the normal of its surface for measurement of (b).

dia(200) is as high as 14, indicating a strong (111) texture, as shown in Fig. 1. However, this ratio declined to only 3 in Fig. 3(b), less than that in powder case. In contrast, the peak of Si(111) grew surprisingly. The fact that the intensity of Si(111) and that of dia(111) did not change proportionally is speculated to result from the probable misorientation between these two crystal planes owing to the great lattice mismatch (52%) between diamond and silicon. The change in intensity of dia(111) agrees with the uniform orientation of the diamond grains. The weak peak at  $2\theta=35.6^\circ$  is assigned to  $\beta$ -SiC(111). However, from this result, we

cannot say whether or not there exists an epitaxial  $\beta$ -SiC interlayer, though Williams and Glass reported transmission electron microscopy (TEM) results of an epitaxial  $\beta$ -SiC interlayer between the diamond film and the substrate [21]. Nevertheless, the (111) texture of the films conforms to the epitaxy hypothesis very well.

In view of all the figures, it is firmly believed that the diamond films is epitaxial to the Si substrates. Generally, the nucleation stage is critical for epitaxy, and the most important thing is to acquire a clean Si surface. Usually, the Si wafers are covered by non-stoichiometrical oxide layers. These oxide layers are considered deleterious to nucleation and especially epitaxy [22]. As a fact, SiO<sub>2</sub> masks have been widely used as a method of obtaining selected-area nucleation of diamond on silicon [23,24]. Accordingly, researchers have been making efforts to remove these oxide layers. In MPCVD, negative bias has been considered an effective method for this purpose [14–19]. In our experiments, we rinsed the Si wafers before deposition in HF solution, which removed most of the surface oxide. Furthermore, compared with conventional HFCVD, we employed an a.c. discharge between the filament and the substrate at very low pressure in the nucleation stage. This discharge played a role similar to that of negative bias in MPCVD. It helped to decompose the H<sub>2</sub> into H, H<sub>2</sub><sup>+</sup>, H<sup>+</sup> and e<sup>-</sup> and to activate the surface sites of the substrate. In the meantime, very low pressure greatly increased the mean free path of atomic hydrogen and helped to transport H atoms to the substrate surface. All these factors led to the removal of the surface oxide layer, thus a clean Si(111) surface was acquired in situ, as is critical for heteroepitaxial or oriented crystal growth. On the other hand, the a.c. discharge also helped decompose the hydrocarbon species, and, in combination with the long mean free path of these species at very low pressure, greatly increased the concentration of reactive hydrocarbon radicals on/near the Si surface; this high concentration is considered very significant for diamond nucleation. In addition, the substrate temperature for nucleation in our experiment (900 °C) was much higher as compared with the usual values (around 800 °C), adding to the mobility of the ad-species and thus the probability of 2-dimensional (2D) growth, which is very important to epitaxy [25,26]. The ratio of the film thickness (0.5 μm as measured by SEM) to the diamond size (up to 3 μm) agrees with 2D growth.

There is an important difference between our result and those of Glass and coworkers [17–19]. In their results, only 50% of the diamond grains oriented after the negative bias nucleation stage, and the orientation went up to nearly 100% only after the films had grown to several microns thick. On the other hand, in our case, all the (111) diamonds were perfectly oriented, even on scratched substrate, as shown in Fig. 1(a) and 1(b), though the films were still very thin. It seems that it was uniformly oriented just after nucleation. The causes of this difference should be found out as it is crucial to get uniformly oriented nucleation from the beginning in order to achieve single-crystal diamond films.

More important and surprising is that the scratch did not disturb the orientation of the (111) diamonds, as shown in Fig. 1(b). This is challenging. The fine polishing of the substrate seems not necessarily a prerequisite for epitaxy. We believe the exact answer to this issue will help to understand the mechanism of nucleation and growth, especially in epitaxial case.

As demonstrated above, we believe that the HFCVD method is also a hopeful candidate for the heteroepitaxy of a diamond film as well as MPCVD; slightly scratching the substrate does not disturb the orientation of diamond in some cases.

#### 4. Conclusion

In summary, uniformly oriented and textured growth of (111) diamond by HFCVD was obtained on either polished or scratched silicon substrates. Heteroepitaxy is hypothesized to explain the results. A very low pressure, high temperature and a.c. discharge were used for nucleation. We believe that HFCVD is also suitable for diamond heteroepitaxy. Slightly scratching the substrates did not affect the overall orientation during the diamond deposition.

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