Epitaxially oriented growth of diamond on silicon by hot filament chemical vapor deposition

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Expitaxially oriented growth of diamond film on Si(001) was achieved using hot filament chemical vapor deposition. The epitaxial relationship between the film and the substrate was confirmed by the observation through scanning electron microscopy and high-resolution transmission electron microscopy (HRTEM) as follows: Dia(001)//Si(001) and Dia⟨110⟩//Si⟨110⟩ with a misorientation angle of 9° between Dia(001) and Si(001). This reports the HRTEM observation of the largest area of the diamond/Si interface (larger than 880 Å). It demonstrates that the intermediate β-SiC layer is unnecessary for achieving diamond epitaxy on Si. Discussion reveals that the value of the misorientation angle between Dia(001) and Si(001) is not unique and should be controlled to deposit single-crystal diamond films on Si. © *1996 American Institute of Physics.* [S0003-6951(96)01302-0]

Great progress has been made in epitaxy of diamond films on Si in the past few years in hopes of utilizing the extraordinary applications of diamond in electronics.[1] In 1992, Wolter *et al.*[2] and Jiang *et al.*[3] achieved oriented diamond film on Si(001). As they reported,[2,4] there existed a β-SiC epitaxial interlayer between the overgrowth and the substrate. They did not get epitaxy of diamond directly on Si. The extremely large lattice mismatch between diamond ($a=3.57$ Å) and Si ($a=5.43$ Å) makes direct epitaxy of diamond on Si difficult. On the other hand, the mismatch between diamond and β-SiC ($a=4.36$ Å) is much smaller. Therefore, many researchers have sought to deposit epitaxial diamond on intermediate β-SiC epilayer. In fact, Stoner *et al.*[5] managed to get oriented diamond film on β-SiC(001) substrate in 1991 in light of this idea. Recently, Yang *et al.*[6] reported observation of epitaxial nucleation of diamond on Si through high-resolution transmission electron microscopy (HRTEM). However, they did not get oriented diamond film. One reason might be that they did not control the deposition parameters well; a large number of microtwins were introduced during their deposition process. Meanwhile, Jiang *et al.*[7] reported observation of epitaxial diamond nucleation on Si in a nearly 3:2 registry through HRTEM. Unfortunately, they presented an epitaxial interface in only a very small area. On the other hand, the misorientation angle between Dia(001) and Si(001) for theirs (nearly zero) is quite different from that for Yang *et al.*'s (7.3°). This deserves careful study; the existence of different misorientation angles adds to the difficulty of achieving single-crystal diamond film growth on Si.

It is also noteworthy that, without exception, the above-mentioned oriented diamond films were achieved by a negative nucleation method using microwave plasma CVD (MPCVD). Using hot filament CVD (HFCVD), we recently presented the first report of synthesis of oriented diamond films on Si by a similar bias nucleation method.[8] Despite all these successes, it is still necessary to achieve large-area epitaxial diamond films directly on Si and make clear the factors affecting the misorientation angle, which are of great significance in both practice and theory.

In this letter, we report HRTEM study of the interfacial structure between an epitaxially oriented diamond film and its Si substrate. Large-area (on a microscale, larger than the whole HRTEM image) direct epitaxy of diamond on Si was observed. The film was prepared by negatively biased nucleation and subsequent growth.

The substrate was a mirror-polished *p*-type Si(001) wafer. It was ultrasonically cleaned in acetone for 10 min and then rinsed in 30 vol % HF solution for 1 min before loaded into the deposition chamber. Our HFCVD apparatus has been described in detail in Ref. 8. To repeat briefly, the substrate was put on a Mo substrate holder that was coated with a diamond film and was negatively dc biased during the nucleation. The filament was dc grounded. The source gas was CH_4 diluted in H_2. The experimental parameters are listed in Table 1. The as-grown film was analyzed by scanning electron microscopy (SEM), Raman spectroscopy, and HRTEM.

Figure 1 shows the SEM image of the obtained diamond film on Si(001). Most of the diamond microcrystals are ori-

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TABLE I. Experimental conditions.

Parameters	Nucleation	Growth
Flow rate (sccm)	100	100
CH_4 concentration (vol %)	5.0	1.0
Filament temperature (°C)	1950	2000
Substrate temperature (°C)	600	750
Pressure (Torr)	20	30
Filament-substrate distance (mm)	13	8
Direct current bias (V)	−200	0
Emission current (mA)	200	0
Time (h)	1	10

ented with the substrate. Similar to the films in other reports,[2,3,8] there are a small portion of the diamond grains which are not oriented. The arrow points to the direction of ⟨110⟩. The epitaxial relationship between the film and the substrate is approximately Dia(001)//Si(001) and Dia⟨110⟩//Si⟨110⟩. Raman analysis has also been performed on the film, and the characteristic diamond peak at approximately 1332 cm^{-1} is very sharp with very weak nondiamond carbon signal, revealing a high diamond quality.

Our HRTEM instrument was JEOL-2010 electron microscopy with a spatial resolution of 1.9 Å. The sample preparation process was the same as described in Ref. 6. Figure 2 is the HRTEM image of the lattice structure of the diamond/Si interface. The picture was projected along ⟨110⟩ direction. Figure 3 gives the corresponding indexed transmission electron diffraction (TED) pattern.

Evidently the lattice of diamond connects directly to that of Si in the left part and from the middle to the right in Fig. 2. There exists a very thin amorphous layer in the region from the left to the middle part. The misfit dislocations are very clear. Meanwhile, the whole interface is extremely smooth. Since the lattices of the overgrowth and the substrate joins each other well at two far separated areas (left and midright) in Fig. 2, and the whole diamond lattice is nearly perfect without microtwins, stacking faults, etc., we believe that the amorphous layer in the middle region was generated by the ion milling in the process of sample preparation, i.e., the diamond lattice grew epitaxially on the Si lattice across at least the whole image. Because of the large lattice mismatch between diamond and Si, there exists great strain in the epitaxial interface, which makes the interfacial lattice vulnerable to the ion milling. It is noteworthy that there exists a dislocation in the Si lattice in the right part of Fig. 2, which may release the interfacial strain to some extent. Therefore, the interfacial lattice in this area can survive the ion milling.

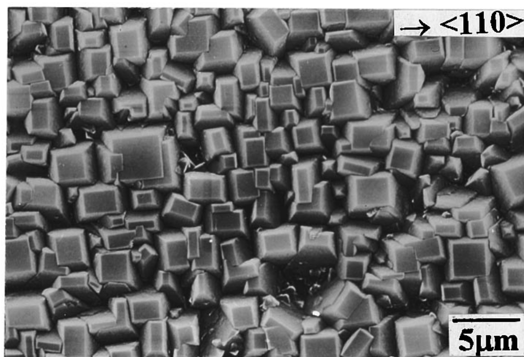

FIG. 1. SEM photo of the as-grown epitaxially oriented diamond film.

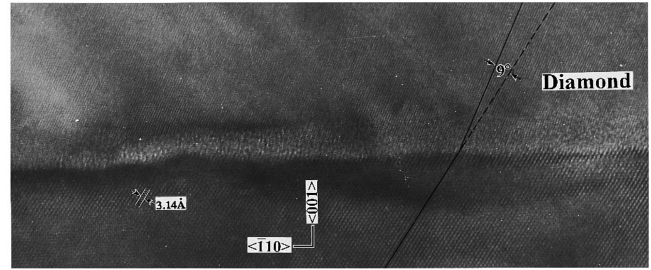

FIG. 2. HRTEM image of the lattice structure of the diamond/Si interface, projected along Si⟨110⟩.

As shown in Fig. 2, the epitaxial relationship can be determined as approximately Dia(001)//Si(001) and Dia⟨110⟩//Si⟨110⟩ with an obvious, though small, misorientation angle between Dia(001) and Si(001). This angle is measured to be about 9° from both Figs. 2 and 3. Dia{111} is rotated slightly about the Si⟨110⟩ direction relative to Si{111}. There is also a slight rotation of the diamond crystal around its ⟨001⟩ axis, i.e., there exists a small angle between Dia⟨110⟩ and Si⟨110⟩, for the diamond {111} layers are clear in only one direction in Fig. 2, and only a few diamond diffraction spots show up in Fig. 3.

Because of the large lattice mismatch between diamond and Si, there exist a large number of misfit dislocations. From the right half of Fig. 2, we work out that 90 Dia{111} layers match 54 Si{111} layers. The proportion is 5:3=1.67. In Yang *et al.*'s report,[6] 40 Dia{111} layers matched 25 Si{111} layers. The proportion was 8:5=1.60. In their case, the misorientation angle between Dia(001) and Si(001) was 7.3°. Verwoerd[9] advanced a model of diamond epitaxy on Si(001) on a 3:2 registry. He did not take into account the misorientation angle probably because 3:2 (=1.50) is quite near 1.52, the ratio of the lattice constant between Si and diamond. Jiang *et al.*[7] observed such an epitaxial mode, for

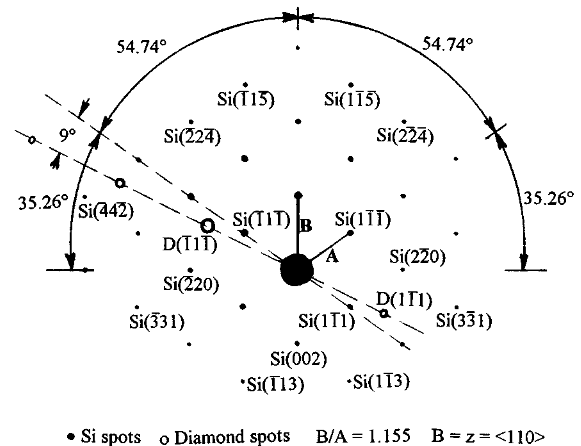

FIG. 3. Indexed TED pattern of the area in Fig. 2. The diamond {111} spots are rotated slightly about Si⟨110⟩ relative to the Si{111}.

which the misorientation between Dia(001) and Si(001) is nearly zero. Accordingly, we conclude that the value of the misorientation angle is not sole; it is speculated that the nearer to 1.52 the above-mentioned proportion, the smaller the misorientation angle. Therefore, we have a larger misorientation angle (9°) than Yang *et al.* (7.3°) since 1.67 deviates farther from 1.52 than 1.60 does, and Jiang *et al.*'s 3:2 leads to an angle of ~0°.

Since different values of the misorientation angle have been observed, it is of great importance to make clear the factors affecting this angle so that one can control it by controlling the experimental parameters. Some parameters may favor one value, others another. The existence of multivalue of this angle will surely add to the difficulty of achieving epitaxial growth of monocrystalline diamond films.

Until recently, many researchers were still making efforts to grow epitaxial diamond films on Si through β-SiC interlayer. They employed a so-called three-step process including *in situ* carburization to generate the intermediate β-SiC layer.[4,10–12] One reason is that the lattice mismatch between β-SiC and diamond is relatively smaller. All the reported interfacial studies of oriented diamond films on Si revealed the existence of intermediate β-SiC layers. On the other hand, SiC can form easily during the nucleation stage. Nonetheless, our result demonstrates that the formation of the β-SiC interlayer is unnecessary, and that it is feasible to deposit an epitaxial diamond film on Si without an interlayer.

Our work indicates that the large lattice mismatch between the overgrowth and the substrate is not an invincible difficulty; it can be overcome by the introduction of misfit dislocations. Verwoerd[9] neglected the possible misorientation in his 3:2 registry for diamond epitaxy on Si(001). However, the ratio of the lattice constant between Si and diamond is not exactly 3:2, which indispensably gives rise to the misorientation angle between Dia(001) and Si(001) and the azimuthal rotation around Dia⟨001⟩. Such misorientation and rotation help to relax the interfacial strain, lower the interfacial energy, and enable the epitaxy.[13] Actually, in Jiang *et al.*'s report,[7] Dia(001) and Si(001) are not exactly parallel to each other, though the angle between them is very close to zero in comparison with our 9°.

As reported elsewhere,[8] we believe that the electron emission from the diamond coating on the Mo substrate holder is responsible for the enhancement of the nucleation. It helps to dissociate the gas and greatly increase the concentration of atomic hydrogen and reactive hydrocarbon radicals. The increased concentration of atomic hydrogen etches any possible residue of the surface oxide, and thus permits the nucleation of diamond directly on Si. The relatively low substrate temperature for nucleation, at which the formation of SiC is very slow, may also contribute to the direct nucleation. Consequently, it is believed that the formation of SiC or amorphous carbon is not a necessary condition for nucleation, and can be avoided by certain measures.

In summary, an epitaxially oriented diamond film was achieved on Si(001), as confirmed by SEM and HRTEM analysis. Large-area (larger than 880 Å) epitaxy of diamond on Si was observed through HRTEM. The epitaxial relationship is Dia(001)//Si(001) and Dia⟨110⟩//Si⟨110⟩. The misorientation angle between Dia(001) and Si(001) is measured to be approximately 9° for the particular crystal grain studied. The existence of the azimuthal rotation of the grown diamond about its ⟨001⟩ axis is also revealed by the HRTEM observation. This is the best HRTEM observation of the epitaxial diamond/Si interface up to date. In conclusion, our result demonstrates the feasibility of synthesizing epitaxial diamond film directly on Si. The formation of intermediate β-SiC epilayer is unnecessary. The value of the misorientation angle is not unique, and one should make efforts to control it to achieve single-crystal epitaxial diamond film on Si.

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