Heteroepitaxial diamond film formed on Si(001) wafer*

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Single-crystal diamond films that are necessary for electronic device applications have only been grown homoepitaxially on diamond substrates. Although the heteroepitaxial growth of single-crystal diamond films is still a challenge for today's scientists, it is the most hopeful way to success. There is some evidence that diamond can be grown epitaxially on μm-sized cubic boron nitride (c-BN) crystals[1,2]. However, Si is the most hopeful material for heteroepitaxial growth. The high lattice mismatch between silicon and diamond (the lattice parameter of Si is $a=0.543$ nm; the surface energy of Si (111) plane is 1.5 $J\cdot m^{-2}$ while the lattice parameter of diamond is $a=0.356$ nm; the surface energy of diamond is 6 $J\cdot m^{-2}$) has caused considerable controversy about the possible heteroepitaxial diamond growth on silicon substrates. Therefore, pretreatment of the substrate is commonly applied to obtaining diamond films on Si wafer. Textured diamond growth on β-SiC and the growth of oriented diamond films a few μm thick on silicon substrates have been obtained using bias-enhanced nucleation of diamond on silicon. Based on the experimental results mentioned above, Stoner *et al.* came to a conclusion that any observed local epitaxy of diamond on the Si substrate is most likely a result of limited diamond epitaxial growth on the interfacial β-SiC layer[3−5]. However, in this paper we submit the direct evidence of heteroepitaxial diamond directly formed on a mirror-polished silicon wafer observed by the high-resolution cross-sectional transmission electron microscopy (HREM). There is an angle of about 7.3° between Si (100) and D(100) heteroepitaxial crystalline planes. This is a rather encouraging finding and deserves careful theoretical and experimental attention.

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1 Experimental methods

In this work a mirror-polished n-type silicon {001} wafer was used as substrate. The sample had been cleaved into a 2 cm × 1 cm square along its crystal lines and cleaned with a typical chemical cleaning process before loading. The diamond film was deposited on Si(100) substrate in a typical hot filament chemical vapor deposition (HF-CVD) device which is similar to that used by Chu *et al.*[6] and the premixed mixtures of CH_4+H_2 were fed into the chamber. The experimental parameters of growth process are as follows: gas flow H_2/CH_4 sccm (the standard cubic centimeter per minute) was 100/1.6; pressure, 2—3 kPa; the distance from tungsten filament to substrate, 8 mm; filament temperature, 2 000 ℃; substrate temperature held at 800 ℃ that was measured by a thermocouple (PtRh) spotwelded to a Ta tab on the side of the support fixture; the growth time was 4 h and the total thickness about 500 nm. The pretreatment process: the DC bias voltage was −40 V and the treatment time 1 h.

For the HREM analysis, the diamond film was cleaned by an ultrasonic wave bath and the cross-sectional specimens were cut along the {110} planes of the Si substrate. Cross-sectional pieces were cut perpendicularly to the interfaces with a low-speed diamond saw. Disk of 0.5 mm thickness was cut from the slabs and thinned by mechanical grinding until the thickness was 30— 40 μm. Then it was further thinned by argon ion beam, milled and perforated at 5— 6 kV with an LBS-1 ion thinner to produce the final HREM samples. By virtue of its extremely fine spatial resolution and ability to elicit crystallographic information from small areas, HREM reveals the details of the morphology that are not apparent for other techniques. The HREM observation was carried out using a JEOL-2010 electron microscope with a point resolution of 0.19 nm.

2 Experimental results and discussion

As indicated by HREM image as shown in fig. 1, it is clear that the diamond film was grown directly from the Si substrate without any intermediate layer in this area, where about 90 rows of diamond (D) atoms on the D(100) plane have an epitaxial relationship with 60 rows of Si atoms on the Si(100) plane (there are about 40 rows of D atoms on 25 rows of Si atoms in the area without amorphous layer). The dislocations and deformations of the D atoms on the interface can be seen. Between Si(100) and D(100) there is an angle of about 7.3°. From the lattice spacings of these planes, the lattice constant of cubic diamond was determined to be 0.356 nm.

An amorphous layer was also found in the specimen. However, compared with other work[7] (the thickness of amorphous layers is about 5— 10 nm), the thickness of the amorphous layer is thinner (about 1 nm) and changes continuously in the image area(see fig. 1). So it is doubtful whether this amorphous layer was formed in the

specimen preparation process, especially in the perforation step. As the atoms bonded on the interface are weaker than those in perfect cystal, they are much easier to be amorphous by ion bombardment. The observation result of twinning near interface also supports this point.

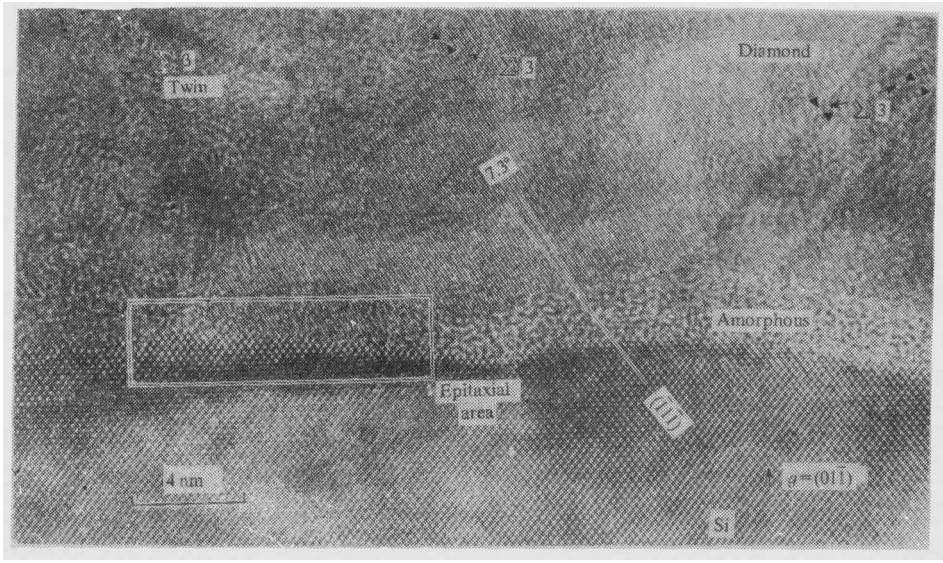

Fig. 1. Lattic image of the heteroepitaxial diamond formed on Si(100) wafer (specimen observed in a ⟨110⟩ direction).

In this sample the intermediate layer has been analysed along the interface of the sample. A lot of twinning was observated. A very interesting and important phenomenon is that all the twinnings observed on the interface or near interface area belong to the same type (the coherent twin boundaries of type $\Sigma = 3$ (first-order twins)).

Compared with a typical HF-CVD, the only difference in our synthesis process is the pretreatment of Si substrate. Experimental result shows that the hinder of diamond directly formed on Si substrates have been overcame by the negative DC biasing pretreatment. The effects of the biasing pretreatment on Si and SiC substrates have been clearly discussed by Stoner and Glass[7]: An amorphous oxide seems to have deleterious effects on heteroepitaxial nucleation and the growth of diamond. The attempts to remove fully the oxide from Si wafers without biasing were proved unsuccessful, thus suggesting that earlier failures to achieve heteroepitaxial of diamond on SiC may have been in part due to the inability to remove the surface oxide. There are experiment results showing that the biasing pretreatment on Si promotes nucleation on silicon by the formation of an interfacial carbide layer covered with a very thin (0.5— 1 nm) nondiamond carbon film, removes oxide and suppresses oxide formation on the surface.

From our result the formation of SiC layer is not a necessary condition for the diamond heteroepitaxial nucleation on Si substrates. The key factor to obtain

heteroepitaxial diamond on Si is the pretreatment condition that minimizes the surface damage while still can clean the Si surface (e. g. remove the surface oxide) and keeps the surface clean during synthetic process.

3 Summary

The first direct evidence of heteroepitaxial diamond formed directly on a mirror-polished silicon wafer has been obtained by high-resolution cross-sectional transmission electron microscopy. The film was synthesized by an improved HF-CVD process involving pretreatment and growth. It was found that there was an about 7.3° angle between Si(100) and D(100) heteroepitaxial planes. The same type of twinnings (the coherent twin boundaries of type $\Sigma=3$) exist on and near the interface. From discussion, biasing pretreatment was believed to have effects of surface cleaning, which is a very important step for heteroepitaxial nucleation on a mirror-polished silicon wafer. In this work a heteroepitaxial diamond film with twinning and microtwinning crystals was obtained. Although not a perfect single crystal, it is helpful to a better understanding of the fundamental mechanisms of diamond synthesis.

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