The Korean Journal of Ceramics, **3** [3] 155 - 158 (1997)

Three-dimensional TEM Characterization of Highly Oriented Diamond Films on a (100) Silicon Substrate

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(Received November 5, 1996)

Highly oriented diamond films were deposited on a (100) silicon substrate by bias enhanced nucleation technique. Both plan-view and cross-section TEM were applied to study the nucleation and growth mechanism of diamond grains. Randomly oriented polycrystalline diamond grains with internal microtwins were observed at the nucleation stage while defect free regions were retained at the growth stage and were apparently related with the epitaxy of diamond films From our experimental results, the nucleation and texture formation mechanism of diamond films is discussed.

Key words : Highly oriented diamand films, Bias enhanced nucleation. TEM

I. Introduction

Highly oriented diamond films have been extensively studied due to its extraordinary thermal and electronic properties. Great progress has been made in epitaxy of diamond films on silicon in the past few years. Recently, Stoner *et al.*[1] and Jiang *et al.*[2] synthesized [100] oriented diamond films on Si substrate by biasenhanced MPCVD. Various microstructural studies on oriented diamond films have been reported to understand the mechanisms which are responsible for the oriented growth on silicon. Wolter *et al.*,[3] Schaller *et al.*[4] and Maeda *et al.*[5] have reported the presence of β-SiC interlayer between the film and the substrate. They have speculated that the texture is due to SiC which has been epitaxially formed on silicon. On the other hand, Lin *et al.*[6] and Chen *et al.*[7] have reported the evidence of direct epitaxy between the diamond film and the silicon substrate synthesized by HFCVD.

In the present study we have employed transmission electron microscopy (TEM) and scanning electron microscopy (SEM) to study three-dimensional microstructures of epitaxial diamond films.

II. Experimental Procedure

Epitaxial diamond films were deposited on single crystal (001) silicon substrates by plasma-assisted CVD which has been discussed in detail elsewhere.[8] Nucleation was induced by applying a DC bias of -200V to the substrate. The experimental condition in each step is given in Table 1.

Plan-view and cross-section TEM specimens were prpared by a standard technique of polishing and dimpling followed by ion milling. Plan-view TEM specimens were prepared by a precisely controlled back-thinning technique to reveal the microstructures near the silicon/diamond interfacial area and film surface area as a function of film thicknesses. However, cross-section TEM sample preparation was not successful since a glued layer formed between film and substrate due to its poor adhesion. TEM observations were carried out in a Philips. EM400 microscope operated at 120 kV. The surface morphology of the films was examined by an AMRAY 1400 SEM.

III. Results

Highly oriented diamond films were sucessfully grown by the MPCVD technique. Figure 1 shows the SEM surface image of a 10 μm thick film. The film surface shows well-developed (001) diamond surface with crystallite size of $0.6\times0.6\ \mu m^2$. A large percentage of the crystal edges are aligned parallel to one another which are approximately parallel to the [110] direction of the silicon substrate.

TEM micrographs in Fig. 2 show the plan-view microstructure of the specimen near the diamond/silicon interface. In Fig. 2(a), the dark area shows the overlapped image of diamond grains and silicon substrate. An overlapped diffraction pattern of (100) single crystal silicon and polycrystalline diamond grains is shown in Fig. 2(b).

Table 1. Deposition Conditions in Each Step

	Nucleation stage	Growth stage
M. W. power (W)	700	700
Gas concentration	4% CH_4-H_2	2% CH_4-H_2
Pressure (Torr)	20	90
Temperature (°C)	600	970
Time	25 min.	4 hrs.

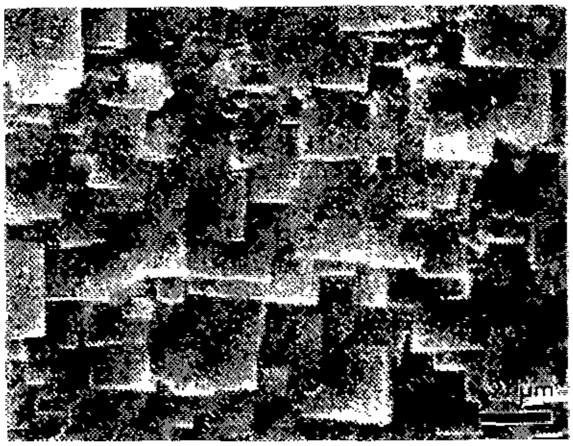

Fig. 1. SEM micrograph of a highly oriented diamond film showing the alignment of the diamond grains.

From these figures, it is apparent that diamond film is composed of randomly oriented polycrystalline grains with an average grain size about 0.2 μm. There seems to be no macroscopic scale interlayer like a β-SiC between the film and substrate within this specimen. However, the cross-section TEM micrograph in Fig. 3 clearly shows that some continuous interlayer with a thickness of 10 nm exists between the film and substrate as indicated by arrow. This layer can be crystalline β-SiC or amorphous C layer as reported elsewhere. High resolution electron microscopy will be applied to identify this phase in the near future. A closer examination at higher magnification shows that the diamond grains contain

Fig. 3. Cross-section TEM micrograph showing continuous interlayer (dark contrast) between silicon substrate and diamond grains.

several sets of microtwins as shown in Fig. 4(a). The micrographs clearly reveal that at least two different sets of twins exist and the angle between different twin planes is about 72°. Figure 4(b) shows the diffraction pattern obtained from these microtwins. There are a large number of forbidden reflections due to double diffraction generated at the twin-matrix boundaries. Each {111} plane acts as a twin plane and the streaks lie in a direction normal to the twin planes. In some areas, separations between the grains are evident as shown in Fig. 3(a). The separation was continuous along the boundaries. There seems to be no distinct phase in this gap, but there is some possibility of an amorphous phase.

Figure 5 shows a plan-view TEM micrograph near the middle of the film layer. The distance from the film/substrate interface of this area is about 1 μm. Well-defined rectangular-type defect free regions were formed with highly defected boundary areas in every grain. The amount of separation gap was much less as compared with the previous sample. There seems to be some orientation relationship among these defect free regions.

Figure 6 shows plan-view TEM micrographs near the

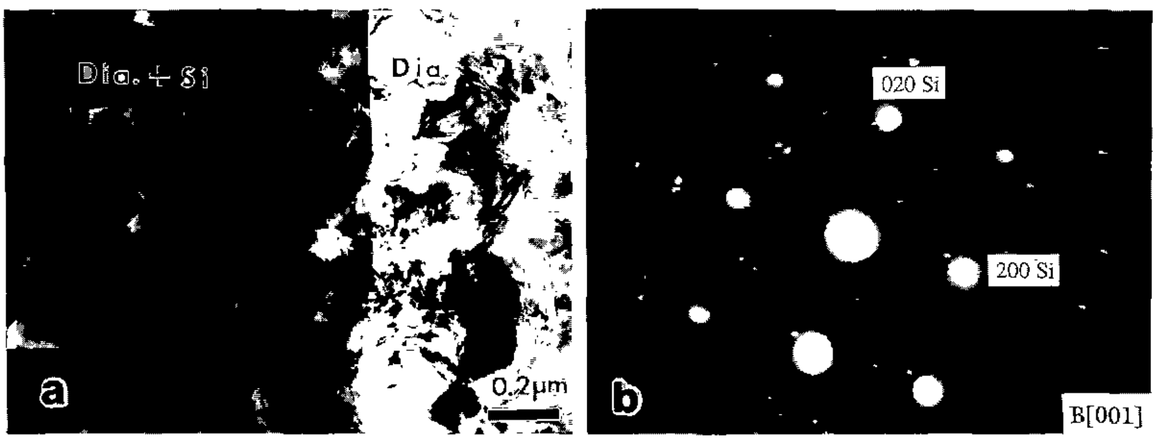

Fig. 2. (a) Plan-view TEM micrograph of a diamond film showing the overlapped area of diamond grains and silicon substrate. (b) Diffraction pattern from the overlapped area.

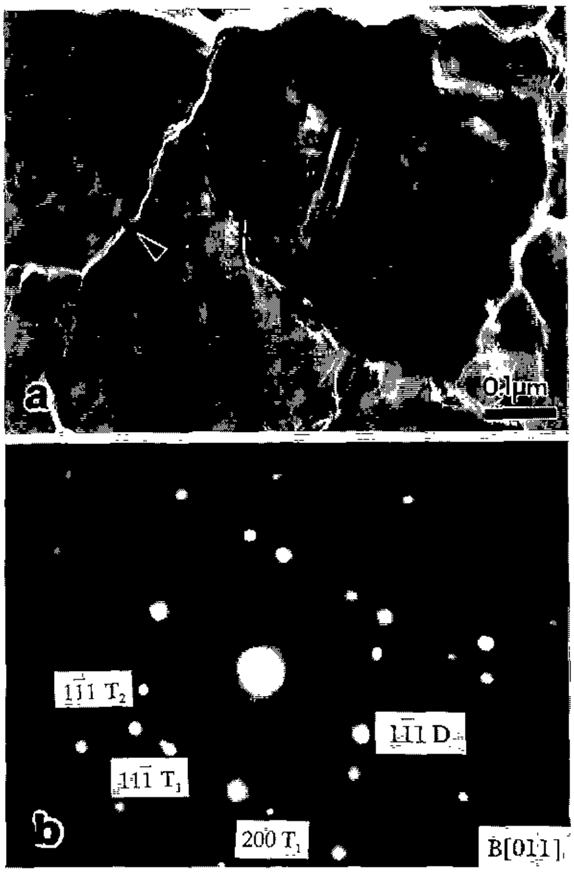

Fig. 4. (a) Plan-view TEM micrograph of a diamond film showing internal twins and separation between the grains. (b) Diffraction pattern from the internal twins (D: diamond, T: twin).

Fig. 5. Plan-view TEM micrograph showing well-defined defect free regions and highly defected boundaries.

highly oriented film surface area. Well-aligned diamond grains are shown in this figure with a representative [001] zone axis diffraction pattern from grain A. Nearly all of the boundaries are parallel to the [110] direction and contain a high density of dislocations. Fig. 6(b) is a weak beam dark field image showing the individual dislocations at the boundary. The misorientation was measur-

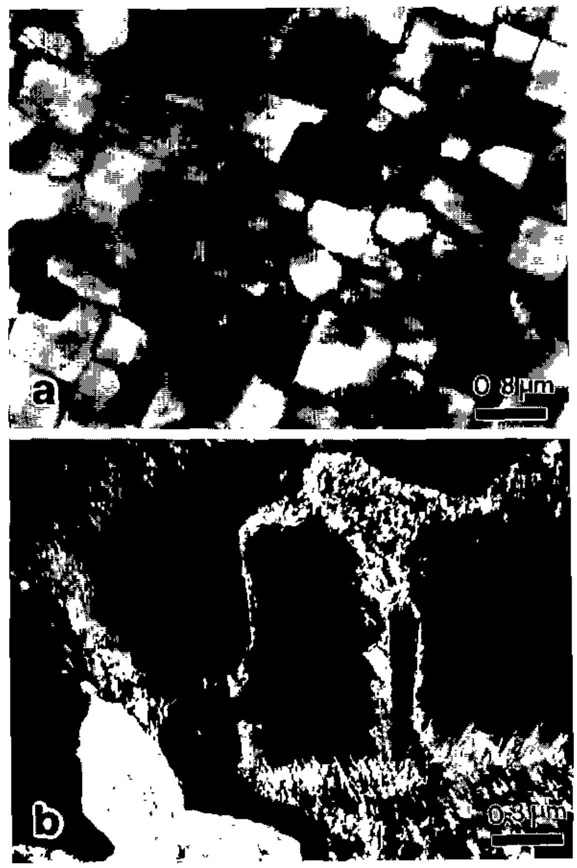

Fig. 6. Plan-view TEM micrographs showing (a) highly oriented diamond grains and (b) boundary dislocations.

ed from several grains by diffraction technique. The largest misorientation between different grains was estimated to be less than 10°.

IV. Discussion

It has been an established theory that epitaxial SiC formed during the carburization and/or biasing step plays an important role in highly oriented diamond films. A portion of overgrown diamond nuclei, which have a specific orientation relationship with SiC, dominate the texture of the films.

In the present study it has been identified that diamond grains formed during nucleation stage, do not have any orientation relationship. Some interlayer between diamond and silicon was identified in cross-section TEM. It is possible that this layer is a C-containing amorphous phase because the continuous crystalline SiC layer has not been reported. Even if this is a crystalline phase, it is obvious that this phase has no specific orientation relationship with the diamond nuclei.

This experimental result supports the theory of Evolutionary selection rule.[9] The film texture is determined by growth condition, i.e. $\alpha=(\upsilon_{100}/\upsilon_{111})\sqrt{3}$, according to this theory. Morever, Tamor *et al.*[10] have reported that the growth of twin followed this selection rule very well. In our experiment it is evident that microtwins in diamond nuclei disappear when the diamond grains have some orientation relationship. This reult suggests that the grain rotation through twinning can be related with texture. It is possible to form (100) texture by overgrown twins whose (100) plane is parallel to the film surface. The separation gaps between grains observed in the early stage of nucleation can make the grain rotation much easier. The misorientation between grains can be further decreased by intergranular misfit dislocations as the diamond film developes to grow.

V. Conclusions

Highly oriented diamond films have been synthesized by bias-enhanced MPCVD technique. At the nucleation stage non-epitaxial diamond grains formed with internal microtwins. As the diamond grains grew, rectangular-shaped defect free regions formed with high density defect regions at boundary areas. At the later stage of growth these defect free regions were well aligned to develop highly oriented films. We suggest that Evolutionary selection rule can be a main controlling factor to dominate the epitaxy. Grain rotation by twinning and misfit dislocations can be a cause of the (100) texture.

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