The Korean Journal of Ceramics, **3** [1] 13 - 17 (1997)

The Effect of Initial DC Bias Voltage on Highly Oriented Diamond Film Growth on Silicon

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(Received Novermeber 5, 1996)

It is identified that the diamond films grown on bias-treated (100) silicon showed different surface morphologies and film textures according to the initial applied dc bias voltage at the same growth condition. The highly oriented diamond film (HODF) was successfully grown on -200 V bias-treated silicon substrate in which the heteroepitaxial relation of $(100)_{diamond}//(100)_{Si}$ and $[110]_{diamond}//[110]_{Si}$ was identified. On the contrary, the heteroepitaxial relation was considerably disturbed in the samples bias-treated at higher voltages than -200 V. These results indicate that the initial dc bias voltage was a key factor in growing the highly oriented diamond film on (100) silicon substrate. Considering the experimental results, we proposed a new model about heteroepitaxial diamond growth on silicon, in which 9 diamond unit cell are matched with 4 silicon cells and the bond covalency of both atoms is satisfied via the intermediate layer at the interface as well.

Key words : Highly oriented diamond film, DC bias voltage, Heteroepitaxial relation, Intermediate layer

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I. Introduction

In-situ bias-enhanced nucleation (BEN) treatment prior to diamond growth, which was suggested by Yugo *et al.*,[1] is widely utilized to promote the diamond nucleation on silicon substrate. Compared with conventional polishing techniques, the BEN treatment not only increases diamond nucleation density ($\sim 1\times 10^{10}/cm^2$) by two or three orders but also gives less damage to the silicon surface.[2] Recently, several researchers[3-5] deposited the highly oriented diamond films (HODF) on (100) silicon substrate by using this bias treatment. They showed that almost all diamond grains had the heteroepitaxial relation of $(100)_{diamond}//(100)_{Si}$ and $[110]_{diamond}//[110]_{Si}$ even though some discrepancies of a few percent tilt and twist mismatch existed. However, the basic mechanism of heteroepitaxial relation between highly oriented diamond films and silicon is not well understood yet.

This work describes the systematic investigation of dc bias voltage effect on the crystallographic orientation of growing diamond films. Since the applied bias voltage is likely to affect the orientation of diamond nuclei on silicon surface by ion bombardment process, it is expected that this study gives a crucial key to identify the mechanism of diamond heteroepitaxial growth on silicon. Based on the experimental results, a new model about the heteroepitaxial diamond growth on silicon is also proposed.

II. Experimental Procedure

The microwave plasma CVD system (ASTeX1.5 kW HPM/M reactor) was used for BEN treatment and diamond film growth on (100) silicon substrate of 3×3 cm^2 size. The source gases were hydrogen and methane. The substrate was cleaned with acetone in an ultrasonic bath for 10 minutes to remove organic residues on it.

Diamond film deposition consisted of three processing steps that is, i) *in-situ* hydrogen plasma treatment to clean a native oxide on the surface of bare silicon, ii) bias-enhanced nucleation (BEN) treatment in which the negative dc bias was applied through thermocouple sleeve contacting the silicon substrate and varied from -150 to -300 V, and iii) diamond film deposition with a [100] preferred growth condition which was previously established in our system. Their detailed process conditions are summarized in Table 1. The substrate temperature was measured by using the calibrated optical spot thermometer (Minolta TR-630 model).

III. Results

Despite the same growth condition, the deposited films showed remarkably different surface morphologies according to the applied bias voltages as shown in Fig. 1. No continuous film was deposited except the diamond particles of around 15 μm diameter on bias-treated silicon at -150 V (Fig. 1(a)). The density of these diamond particles was approximately $10^{3-4}/cm^2$, which is the same order as that of diamond nuclei on unbiased silicon. Robertson *et al.*[6] suggested that there should be a minimum ion energy to form the subplanted carbon clusters which were responsible for enhancing the diamond nucleation on silicon. It is believed that -150 V was too low to form carbon clusters or to enhance diamond nucleation on silicon substrate. On the other hand, uniform diamond films were deposited on silicon substrate bias-treated at dc voltages higher than -150 V. After 10 hours of deposition, the film thickness was about 3.5 µm.

Almost all the grains of diamond film grown on -200 V bias-treated silicon had flat square surfaces. In addition, they were not only well-aligned with each other but also had a specific orientation relation with respect to silicon substrate. Figure 1(b) shows this highly oriented diamond film. On the contrary, we observed that when the applied dc bias voltage was increased to -250 V and -300 V, diamond grains became misoriented and their surface roughness increased as shown in Fig. 1(c) and (d), respectively.

Table 1. The Detailed Conditions of Three Processing Steps

	In-situ H_2 plasma etching	BEN treatment	diamond film growth
microwave power (watt)	800	800	1000
pressure (torr)	15	15	20
T_{sub} (°C)	700±10	700±10	600±10
CH_4/H_2 ratio (%)	-	5	1
dc bias voltage (volt)	-	-150~-300	-
time (min)	10	10	10 hr

Both conventional x-ray θ-2θ scan diffractometry and pole figure analysis were performed to examine the preferred growth direction of these three diamond films. Figure 2(a) shows θ-2θ scan x-ray diffraction patterns from which we can notice that the smaller the applied dc bias voltage is, the higher (400) peak intensity is. The normalized intensities of four diamond peaks in Fig. 2(a) demonstrated that the diamond film grown on bias-treated silicon at -200 V and -250 V had strong and weak (100) film texture, respectively. On the contrary, the -300 V bias-treated sample did not show any specific film orientation.

Such tendency of film texture change was clearly ascertained by the pole figure analysis of these diamond films. The {111} pole figure of -200 V bias-treated sample is depicted in the left side of Fig. 2(b) in which the four distinct {111} peaks dominated symmetrically. It was also identified that the {111} pole figure of silicon substrate had sharp {111} peaks at the identical positions. This result indicates that the heteroepitaxial relation of $(100)_{diamond}//(100)_{Si}$ and $[110]_{diamond}//[110]_{Si}$ exists between silicon and diamond film.

On the other hand, the {111} pole figure on the right side of Fig. 2(b) indicates that the -250 V bias-treated sample had weak (100) film texture and its crystallographic orientation relation with silicon was considerably disturbed. Finally, the diamond film grown on -300 V bias-treated silicon was proven to have random

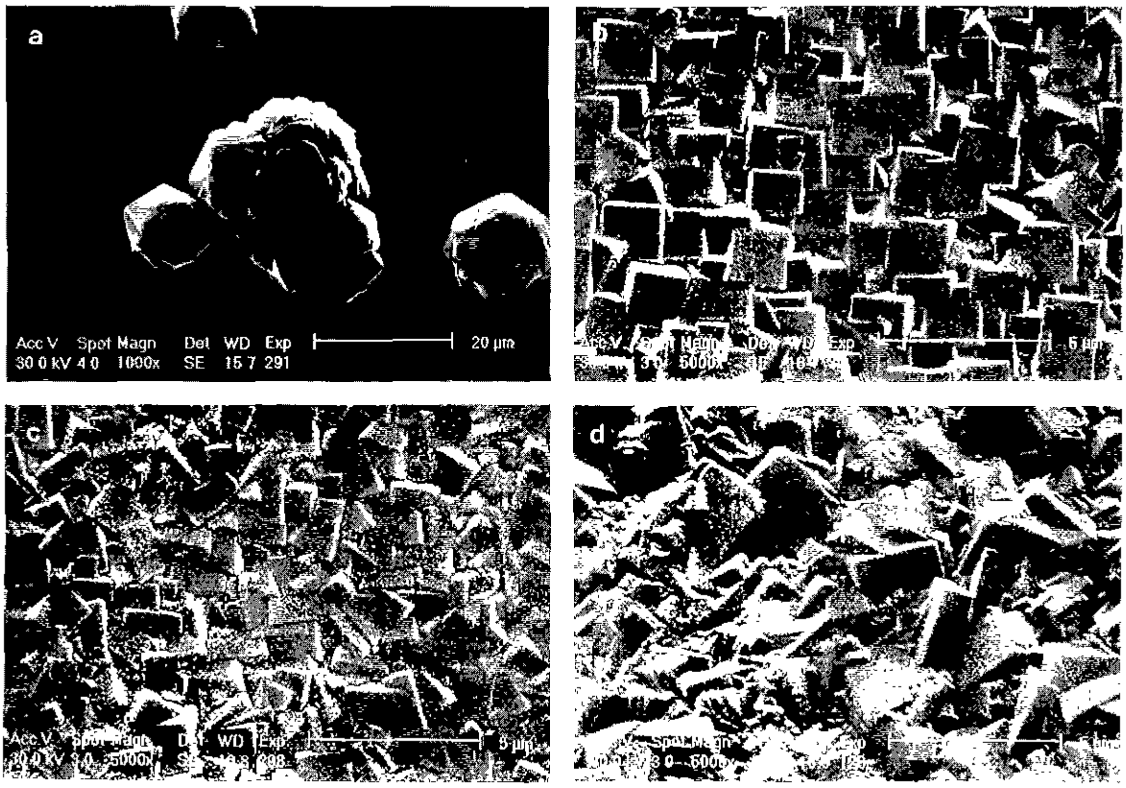
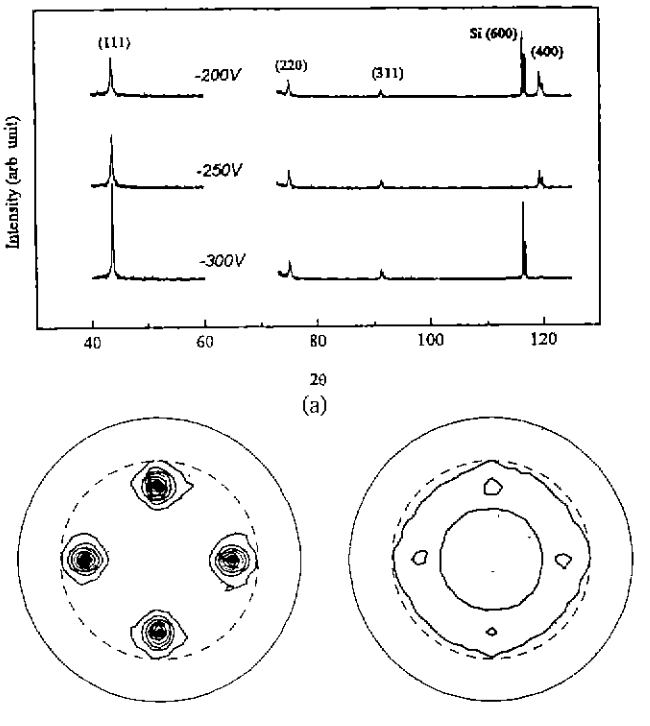


Fig. 1. Surface morphologies of diamond films grown on bias-treated silicons at (a) -150 V (b) -200 V (c) -250 V and (d) -300 V (Note that (a) has the different magnification, ×1000, from others).



-200V (b) -250V

Fig. 2. (a) X-ray diffraction patterns of diamond films grown on bias-treated silicons at -200 V, -250 V and -300 V. (The right-side small peaks of Si (600) and diamond (400) are attributed to Cu k$_{\alpha 2}$ (λ=1.544 Å) x-ray source.) (b) {111} x-ray pole figures of diamond films grown on bias-treated silicons at -200 V and -250 V.

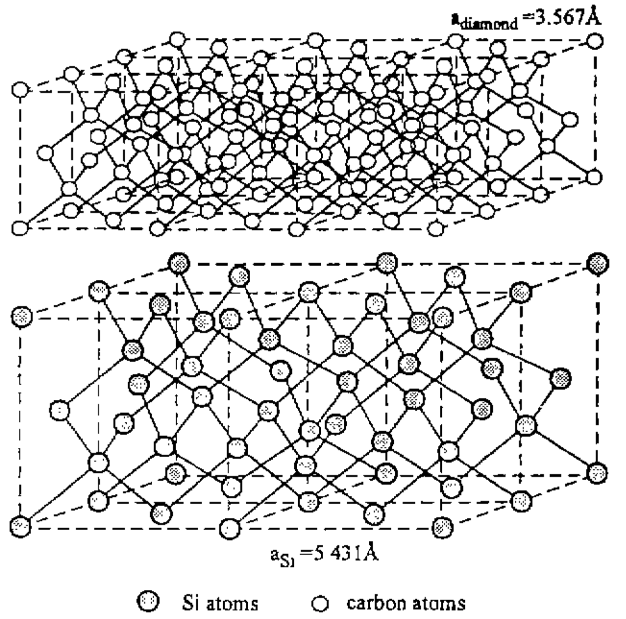


Fig. 3. The lattice matching scheme between 9 diamond unit cells and 4 silicon unit cells.

orientation so that its pole figure cannot be drawn.

From those experimental results that diamond films showed the different surface morphologies and film textures according to the initial applied dc voltages in spite of the same [100] preferred growth condition, we can speculate that the growth mode of diamond films is largely influenced by the diamond nucleation stage.

IV. Discussion

Considering the results of this experiment, we propose the mechanism of heteroepitaxial diamond growth and the effect of dc bias voltage on it.

To begin with, the bias-enhanced diamond nucleation proceeds via two concurrent processes i.e., the ion subplantation process and the surface chemical reaction involving atomic hydrogens. In the ion subplantation, which was suggested by Robertson *et al.*6) from the subplantation experiment of carbonaceous ions, the carbon atoms or carbonaceous ions are subplanted within a few monolayers of silicon substrate. Since this process supplies carbon atoms to silicon surface, the activation barrier for diamond nucleation on silicon can be lowered. Simultaneously, the subplanted carbons might form sp^3 carbon clusters (or diamond clusters) with the aid of atomic hydrogens as well as sp^2 clusters. It is well known in the normal CVD diamond growth that atomic hydrogen promotes the formation of sp^3 carbon clusters by passivating dangling bonds at growing surface and that its related reaction is thermally activated.7) Reinke *et al.*8) claimed that the sp^3 carbon clusters should be diamond nuclei from the experimental result that both the nucleation density of diamond and the concentration of sp^3 clusters had the same dependency on the substrate temperature.

The -200 V bias-treated sample exhibited the heteroepitaxial relation of $(100)_{diamond}//(100)_{Si}$ and $[110]_{diamond}//[110]_{Si}$ with silicon substrate as shown Fig. 1(b) and Fig. 2(b). The diamond film is not likely to have this orientation relation with silicon substrate since the lattice mismatch between them is as much as 52% ($a_{o,Si}$=5.431 Å and $a_{o,diamond}$=3.567 Å). Considered the several unit cells of each lattice, however, it is possible that the diamond lattice maintains the orientation of silicon. As depicted in Fig. 3, the 9 unit cells of diamond can match with the 4 unit cells of silicon, by which the mismatch is reduced to only 1.47% along x or y axis ($3a_{o,diamond}$=10.70 Å and $2a_{o,Si}$=10.86 Å). Actually, Jiang *et al.*9) demonstrated in HRTEM image that there was 3 to 2 correspondence in (111) lattice fringe at diamond/Si interface. This kinds of epitaxial matching is often found in other systems with large lattice mismatch. For example, Vispute *et al.*10) reported the epitaxial Cu/TiN/Si (100) heterostructure by pulsed laser deposition and showed that the 3 lattice constants of Si (a_o=5.43 Å) match with 4 of TiN (a_o=4.24 Å) and the 7 lattice constants of Cu (a_o=3.62 Å) match with 6 of TiN.

Unlike the other metal-related systems, one additional requirement has to be considered to have the het-

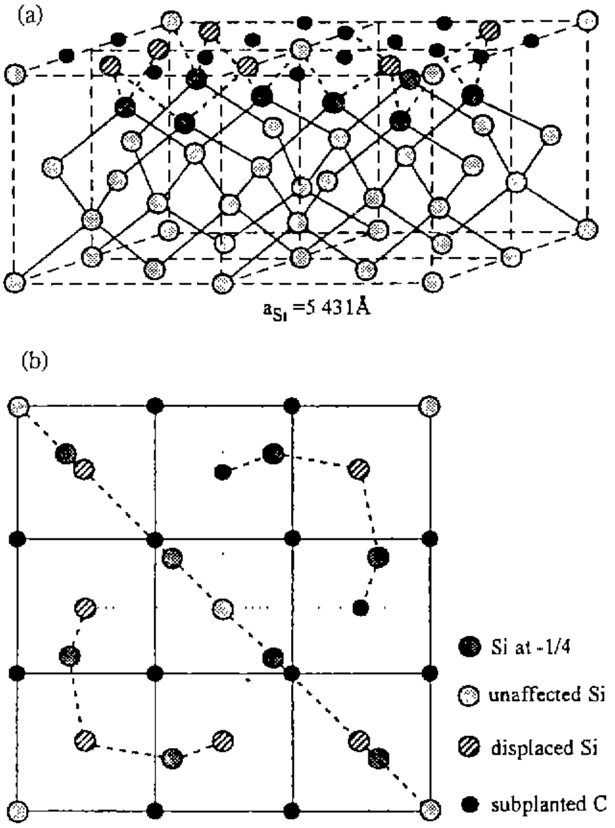


Fig. 4. (a) One possible atomic arrangement of the subplanted carbons, the displaced, and the unaffected silicons on (100) intermediate layer (b) its projection view (The dashed lines indicate the slightly distorted bond between +3/4 height silicons and +1 height atoms).

eroepitaxial relation between diamond and silicon, that is, the bond covalency of carbon and silicon atoms should be satisfied at their interface. It is thought that this requirement can be satisfied by the bombardment of carbonaceous ions during BEN treatment. The accelerating ions with tens of eV cause two phenomena to happen in the top surface of silicon substrate. One is that these ions collide with the surface silicon atoms and then move them away from original sites by momentum transfer. Robertson *et al.*[6] measured the energy distribution of carbonaceous ions striking the substrate during BEN treatment in which the bias voltage was varied from -150 to -350 V and the working pressure and the methane concentrationsv were 15 torr and 2%, respectively. They showed that the carbonaceous ions were accelerated with the average energy of 50 to 120 eV according to the bias voltage. Although this range of ion energy is too low to amorphize the surface of silicon substrate, it is high enough to displace silicon surface atoms with one bonding distance or so. It is known that the required energy to displace silicon atom from its lattice site is around 15 eV.[11] The other one is that, as previously mentioned, the carbon atoms are subplanted into the top layer of silicon lattice.

Due to these two processes, the top surface of silicon substrate becomes composed of three types of atoms i.e., the subplanted carbons, the displaced silicons, and the unaffected silicons. Under the optimum bias voltage, -200 V in this report, the top surface possibly has the diamond (100) lattice. Figure 4(a) depicts one possible example of this intermediate (100) layer having the regular atomic arrangement in which 14 subplanted carbons are designated by small solid circles, 6 displaced silicons by large slashed circles, and 5 unaffected silicons by large shaded circles, respectively. Its (100) projection view is also shown in Fig. 4(b). Such atomic configuration on the surface is satisfactory for the bond covalency requirement without large silicon lattice strain or the severe distortion of silicon tetragonality. Successively, on-coming carbon atoms accumulate on this layer to build the diamond lattice. This proposed mechanism of heteroepitaxial relation between diamond and silicon lattice via the intermediate layer is quite reasonable even though it accompanies with some distortion of silicon tetragonality near the surface as indicated by dashed line in Fig. 4. On the other hand, the bombardment of higher energetic ions in the cases of -250 V and -300 V bias treatment is likely to disrupt the regular arrangement of the atoms on the intermediate layer. Thus, the growing diamond film cannot retain the heteroepitaxial relation with silicon substrate any longer. This is why the heteroepitaxial relation between diamond and silicon became lost as the bias voltage was increased to -300 V, as in this experiment.

V. Conclusions

We observed that the deposited diamond films showed remarkably different surface morphologies and film textures according to the initial applied dc bias voltage despite the same growth condition. The highly oriented diamond film (HODF) was successfully grown on -200 V bias-treated silicon substrate in which the heteroepitaxial relation of $(100)_{diamond}//(100)_{Si}$ and $[110]_{diamond}//[110]_{Si}$ was identified by using both scanning electron microscopy and x-ray pole figure analysis On the contrary, the heteroepitaxial relation was attenuated in the samples bias-treated at higher voltages. These results indicate that the initial dc bias voltage was a critical factor in growing the highly oriented diamond film on (100) silicon substrate.

Considering these experimental results, we proposed a new model about heteroepitaxial diamond growth on silicon. In this model, the diamond lattice matches with silicon by combining its 9 unit cells with 4 silicon unit cells. In addition, the bond covalency of carbon and silicon atoms at the interface is fulfilled via the intermediate layer on top of silicon substrate. Since this layer might have the regular atomic arrangement of the subplanted carbons, the displaced silicons, and the unaffected silicons by ion bombardment process under the optimum dc bias voltage, diamond grains grown on it can maintain the orientation of silicon substrate. The ion bombardment with excess high energy, -250 V or -300 V in this experiment, leads the atomic configuration on the intermediate layer to be randomized so that the orientation relation between silicon and diamond disappears. Further study will be continued to investigate the modified surface structure of silicon substrate after bias treatment and to develop the proposed model of the diamond heteroepitaxial growth on (100) silicon.

Acknowledgment

This research was financially supported by the Korea Science and Engineering Foundation (KOSEF).

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