

Epitaxy of diamond on Si(100) and surface-roughening-induced crystal misorientation

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In a recent paper [Phys. Rev. Lett. **84**, 3658 (2000)] a direct diamond epitaxy on the silicon substrate is demonstrated not only at the interface formed during the growth process but also at the nucleation sites. Small (001) terraces with dimensions of several atomic distances at the site of nucleation are observed due to the roughening of silicon surface and lead to the grain misorientation. To further improve the understanding of the subject the microstructure and interfaces in diamond films on silicon substrates grown in the stages of the bias-enhanced nucleation (BEN) and the initial crystal growth were studied by means of atomic force microscopy, scanning electron microscopy, and high-resolution transmission electron microscopy. It is showed that the roughness of the wafer starts to increase from the beginning of the BEN and the renucleation on existing crystallites induced by the ion bombardment leading to the loss of epitaxy.

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I. INTRODUCTION

In the past decade, a rapidly growing interest in diamond technology, due to its huge application potential in different fields, has been aroused.¹⁻⁴ While diamond films have been synthesized routinely since 1982, it only became possible about 10 years later to grow large area heteroepitaxially oriented diamond films on silicon substrate which is the basic material for today's microelectronics.^{5,6} This important progress towards a technical application has stimulated further interest in studies on details of the deposition processes and the structural properties. In spite of much significant experimental progress made in the intensive research and development in the past few years,⁷ the synthesis of single crystalline diamond films still remains a great challenge for physicists and materials scientists.

The crucial difficulty in depositing a single crystal film of diamond is the so far observed crystallographic orientation deviation of individual diamond grains with respect to the silicon substrate and thus small-angle grain boundaries. The highly [001]-oriented films, which are prepared via a bias-enhanced nucleation process (BEN), consist of columnar grains with a limited lateral size of several micrometers.⁸ Between these diamond grains an orientation deviation of up to several degrees exists, which is accommodated by the formation of small-angle grain boundaries. Recent investigations have shown that these boundaries consist of arrays of dislocations and are free of amorphous layer.⁹ A high density of crystal defects, mainly consisting of micro-twins and stacking faults, is found in the near-grain-boundary regions.⁸

To realize the deposition of single crystalline films the barrier of the lattice misorientation of the individual diamond grains must be reduced or eliminated. Grain coalescence from diamond nuclei with very small tilting during the formation of large crystals was observed recently which sheds light on the growth of single-crystalline diamond films.¹⁰ However, the grain coalescence is realized by introduction of a disclination and is only possible for the grains with a small grain misorientation ($<2^\circ$) and small grain size due to the lowering of the formation energy of the disclinations.¹¹

For further reducing the crystal misorientation knowledge about the basic mechanism and its relations to the local structure status of the substrate surface and to the conditions for nucleation of the diamond crystals must be improved. To improve our understanding about the origin of the crystal misorientation and to control the epitaxial nucleation process more effectively we present here, after our previous letter,¹ an extended surface and interface investigation with significant additional materials. In the first part, the BEN process were investigated by bias current measurements and atomic force microscopy (AFM) showing that the roughness of the wafer starts to increase from the beginning of the BEN. In the second part, we monitored the initial growth process and show the re-nucleation induced by the ion bombardment leading to the loss of epitaxy.

II. EXPERIMENT

Diamond-on-silicon samples were prepared by microwave plasma chemical vapor deposition (MWCVD) using the well-known two-step process.⁷ In the first step, heterogeneous nucleation of [001]-oriented diamond crystallites was achieved *in situ* on a 2-inch *n*-type (001) silicon wafer by applying a negative bias potential to the substrate (BEN). The second step is an established diamond growth process without biasing the substrate. The experimental parameters are given in Table I and more details have been published in previous papers.^{7,8}

TABLE I. Preparation conditions of the samples.

| Process step | Nucleation | Growth |
|----------------------------------------|------------|---------|
| H ₂ concentration (vol. %) | 97 | 94 |
| CH ₄ concentration (vol. %) | 3 | 5 |
| CO ₂ concentration (vol. %) | | 1 |
| Gas pressure (mbar) | 20 | 43 |
| Substrate temperature (°C) | 850 | 730–780 |
| Bias voltage (V) | –150 | |
| Power (W) | 850 | 1500 |

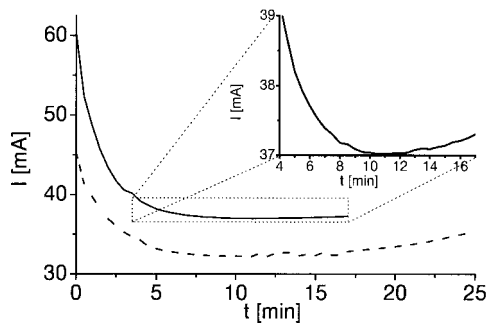


FIG. 1. Bias currents vs biasing time of two samples interrupted after 17 and 25 min deposition.

The bias current was measured with a Voltcraft M-4650B multimeter. The current was measured every 15 sec with a resolution of 0.01 mA. The morphology, the crystallographic orientation and the grain boundary of the substrates and films were analyzed by field emission scanning electron microscopy (SEM, JEOL 6300F, operated at 3 kV), by transmission electron microscopy (TEM), and atomic force microscopy (AFM).

All the AFM measurements were performed using a commercial instrument (Park Scientific Instruments), operating in air. Pyramidal Si_3N_4 tips with a typical radius of curvature of 50 nm were used.

The interfaces between diamond films and silicon (001) were investigated using the $[110]$ oriented cross-section specimens by means of HRTEM. The specimens were prepared using standard procedures of mechanically grinding and dimpling, and final Ar^+ -ion milling at 5 keV and at a low angle of incidence of about 10° . The investigations were carried out on a JEOL 4000EX electron microscope, operated at 400 kV.

III. RESULTS AND DISCUSSION

A. Monitoring of the incubation step in a bias-enhanced nucleation process

The nucleation process was monitored by bias current measurements and afterwards with AFM. A series of samples was prepared in a microwave process with different process interruptions.

After the bias voltage is switched on the bias current drops to a minimum and then rises continuously. The minimum is very shallow. The current changes versus time was not exactly reproducible, but for all experiments they showed the similar behavior. Figure 1 shows the bias current as function of BEN time in two experiment processes, which were stopped after 17 and 25 min, respectively.

AFM images of nucleated samples show that no stable nuclei are formed until the local bias current minimum is reached, although the roughness of the samples increases. Figure 2 shows $2 \times 2 \mu\text{m}^2$ AFM images taken from samples after 4, 7, 13, 19, 22, and 25 min BEN process, respectively, on silicon (001). From the atomic force micrographs of the samples prepared with process time less than 13 min no diamond islands can be found [Figs. 2(a) and 2(b)]. For a deposition time of 13 min [Fig. 2(c)] diamond islands of several

tens nanometers in height were formed, which is much higher than the peak value of the surface roughness of silicon substrate which is normally saturated after 20 min time at micro-scale. The islands shown in the Figs. 2(c)–2(f) are stable, as confirmed by the further diamond growth. Once the islands are formed they grow fast and their size and density increase with the deposition time and the amount of material deposited. After 25 min deposition [Fig. 2(f)] the silicon surface was fully covered with the islands.

The fact that the diamond nuclei are not formed for deposition time less than 13 min was interpreted partly in terms of carbon diffusion into the silicon substrate which controls the steady-state carbon supersaturation at the surface during deposition.¹² Silicon substrates can absorb carbon into the bulk by forming carbide and thereby delay the diamond nucleation. It was showed^{12,13} that the surface steps and surface defects should serve as the nucleation site. Therefore the surface modification needed for nucleation could be the reason for the induction time.

Figure 3 shows an increase with the BEN time of the surface root mean square (r.m.s.) roughness of the uncovered areas of silicon surface evaluated from the AFM images. The r.m.s. roughness of a bare silicon wafer is 0.4 \AA . After 4 min of BEN the r.m.s. roughness is 2 \AA and after 7 min of BEN 8.6 \AA . In both cases the slope of the bias current is still negative. AFM images of samples, which were kept in the nucleation stage as long as the bias current started to rise again, revealed stable diamond nuclei. As the nuclei are formed the r.m.s. roughness value of the whole sample surface increases rapidly with their number for r.m.s. = 17.4 \AA at a density of $0.5 \text{ nuclei per } \mu\text{m}^2$ to r.m.s. = 121 \AA at a density of $30 \text{ nuclei per } \mu\text{m}^2$. In the first case the bias current increased by 0.3 mA from the local minimum before the BEN was aborted and in the later 1.65 mA . The r.m.s. roughness of a uncovered Si surface depends on the BEN time and reaches a maximum value of approximately 20 \AA (Fig. 3) before the surface is fully covered.

Two steps are identified in the BEN process from the AFM observation. In the first one the silicon surface became rough before stable nuclei were created. The lateral peak-valley distance of the roughened silicon surface is in the range of up to 100 nm and the peak height only several nanometers (please note the scaling difference of the images in Fig. 2). This surface roughening is caused by an inhomogeneous surface etching process. It is widely accepted that the silicon substrate can be etched by both H^+ ions and atomic hydrogen in a hydrogen plasma. The inhomogeneous etching is the result of a complicated combination of the crystal anisotropy, the local fluctuation of the plasma energy density and the surface contamination, most likely due to the deposition of hydrocarbon species. The drop of bias current after switching on the bias voltage is, however, possibly caused by the simultaneous addition of methane gas leading to a change in the plasma chemistry at the surface and cannot be related to the roughening of the silicon surface. Nevertheless the drop of bias current indicates a decreased plasma intensity at the sample surface, because less electrons are accelerated from the sample surface into the plasma. In a second step stable diamond nuclei starts to form. As diamond

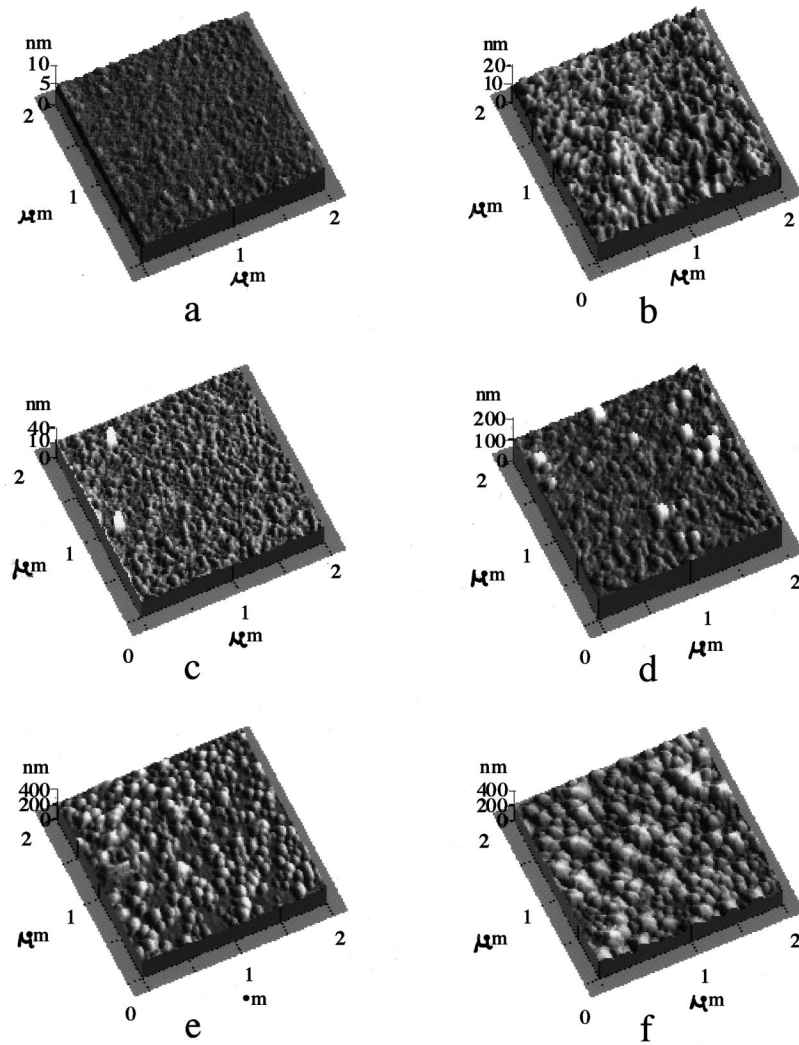


FIG. 2. $2 \times 2 \mu\text{m}^2$ micrographs of atomic force microscopy showing the surface morphologies after (a) 4 min, (b) 7 min, (c) 13 min, (d) 19 min, (e) 22 min, and (f) 25 min bias enhanced nucleation time.

has a very high secondary electron emission the bias current starts to rise. Because more electrons are accelerated into the plasma, it becomes more intensive. After nucleation the diamond crystallites grow rapidly larger leading to the fast increase in the surface roughness shown in Fig. 3.

From our results we believe that the induction time of diamond nucleation is due to an incubation process for the formation of stable diamond nuclei. The adsorption of hydrocarbon species onto the silicon substrate is a very frequent process. The peak density of the roughened silicon surface shown in Fig. 2 corresponds to the site number of the hydrocarbon deposition which is also in a similar range of the highest observed nucleation density of diamond in our microwave plasma process ($5 \times 10^{10} \text{ cm}^{-2}$).¹² However, all the adsorbed hydrocarbon species, which have a “mask” effect and prevent the local surface etching leading to the roughening, cannot reach the critical size to become the stable nuclei. Therefore in most experiments, the nucleation density of diamond crystallites is lower than this limitation. As has been shown in Ref. 1 the local surface roughening process is also responsible for the crystal misorientation.

As it will be discussed in the following section, a precise control of the BEN process which limits the renucleation is necessary for obtaining an epitaxial film. To control the BEN by the bias current is a good way, but is also complicated

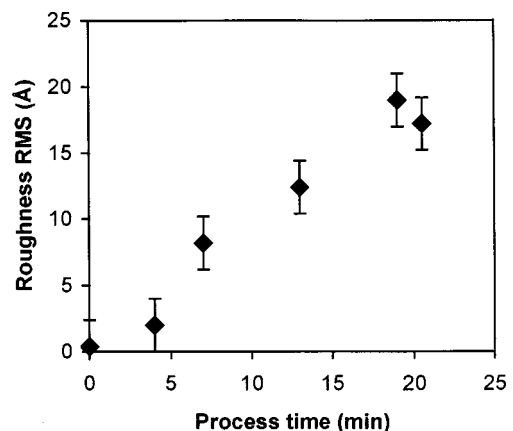


FIG. 3. Surface roughness (r.m.s.) vs process time.

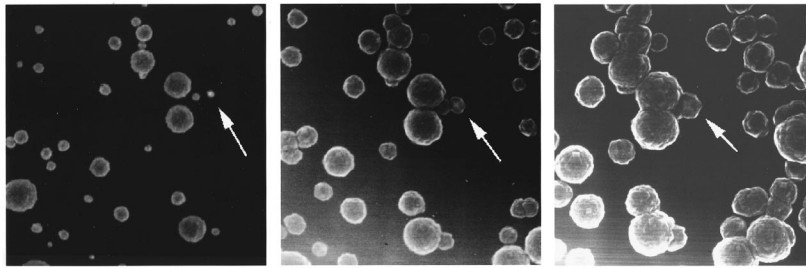


FIG. 4. SEM images of the sample after 20, 60, and 80 min deposition time (left to right).

since the bias current is a function of many parameters. Beside the process pressure and the process power the bias current is a function of all surfaces in contact with the plasma including the walls of the inner chamber, the substrate itself and the parts of the substrate table which is not covered by the substrate. All these surfaces are altered during the BEN. But as the plasma shows its highest density in the middle of the chamber right over the substrate, its surface is altered most and should have the largest influence on the change of the bias current during the nucleation.

B. Monitoring of the initial growth and the renucleation process

As is shown in the previous section, a certain period of time is necessary for the initiation of nucleation. From investigation of reflection-high-energy-electron diffraction (RHEED) (Ref. 13) it is suggested that the diamond nuclei formed at the beginning of the nucleation stage are well oriented. As the nucleation time increases, the nuclei increase dramatically in density up to $5 \times 10^{10} \text{ cm}^{-2}$ and most of them are randomly oriented. Schreck *et al.*¹⁴ studied the processing space for epitaxial nucleation by x-ray measurements and found a very narrow time window for optimal crystal alignment. These results confirm the importance of precisely controlling the nucleation process for epitaxial growth. The reason for the decrease of well-oriented nuclei with forwarding ion bombardment during BEN was believed mainly due to the secondary nucleation on the existing diamond islands. To confirm this prediction the initial growth process of the diamond nuclei were monitored in 20 min steps after BEN process. A patterned sample enables herewith certain nuclei to be found after every growth step under the SEM. Figure 4 shows an area of the sample after 20, 60, and 80 min deposition time (left to right). A well-oriented nucleus indicated by an white arrow is clearly seen. This crystallite was extremely small after the nucleation step. Large nuclei, in contrast, show a loss of their good orientation. An comparison with other positions of the same sample shows no oriented large nucleus. This confirms the prediction that only the nuclei, which are formed just before the BEN process is stopped, have a good orientation. These nuclei are not suffered from the continuous ion bombardment after nucleation.

This mechanism suggested for the loss of good orientation is more clearly demonstrated in Fig. 5. We see crystallites grown on three nuclei with different sizes after nucleation. The left crystallite was grown on a large nucleus. It is a

polycrystalline cauliflowerlike island with statistically oriented facets in overall directions. The middle crystallite shows a loss of good orientation due to a secondary nucleation. The right-hand picture is taken from a monocrystalline crystallite which is grown from a small nucleus and it shows a perfect orientation. The fact that well-oriented crystallites are only grown from small, not bombarded nuclei and the random islands grown from large, bombarded nuclei reveal the negative influence of the ion bombardment on formed nuclei. Under a well-controlled nucleation step, nearly all crystallites are epitaxially oriented and can grow without secondary nucleation.¹³ Upon the established growth technique the conventional growth step can easily be controlled without crystal twinning.

The results of cross-sectional TEM investigation further support the mechanism revealed from the SEM results. Figure 6 shows a cross-sectional TEM image of an interface region between a diamond grain and silicon substrate. A hillock of silicon substrate is clearly seen at the central region of the interface. The top of this hillock should, as discussed in previous paper,¹ represent the nucleation site as indicated by the large white arrow. On top of the hillock a strongly distorted structure can be observed. Crystal twinning of the nucleus was shown to originate within 5 nm from the nucleation site. Three start points of the crystal twins are indicated by small white arrows. All the three start points (small arrows) of the crystal twinning can be reached by the growing surface from the nucleation site (large arrow) within 2 min and the crystal twinning is therefore introduced during the BEN process due to the ion bombardment-induced re-

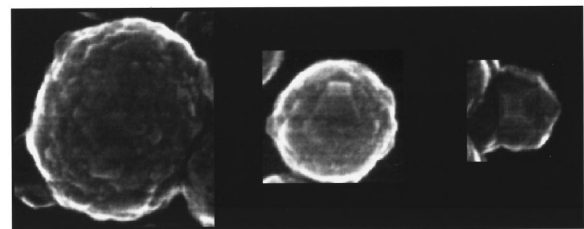


FIG. 5. The loss of good orientation for large nucleus due to the ion bombardment after the nucleation process. The picture shows crystallites deposited for 80 min on nuclei of different sizes after nucleation. Left is a very large island with facets in all directions. In the middle picture a relatively large crystallite is grown on the nucleus with a limited secondary nucleation. Right is an oriented crystallite growing from a nucleus formed before stopping the BEN process.

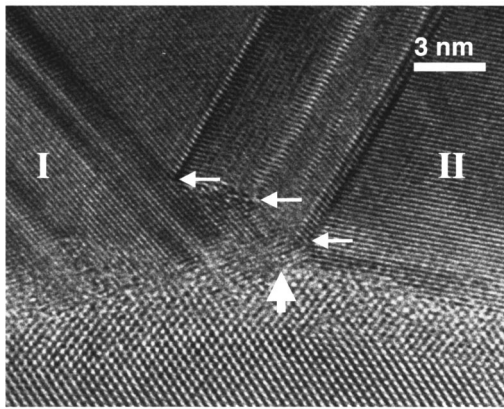


FIG. 6. High resolution lattice image of a diamond nucleus with twin formation.

nucleation. The short growth step in our experiment was performed under strictly controlled conditions and the twin formation is inhibited.

In addition, crystal tilting around the $[110]$ crystal axis of about 10° for the left hand side part of the grain (region I of Fig. 6) and about 45° for the right hand part can be observed. After the suggested model in Ref. 1, the misorientation of the left side part should be a consequence of the rough silicon surface and the small area connection of diamond nucleus with silicon substrate. From Fig. 6 it is obvious that the

nucleus was formed on a slightly damaged and atomically rough silicon surface. According to our model shown in Ref. 1, crystal tilting can only be overcome if the diamond nucleation starts from a relatively large, clean and perfect areas of the silicon surface. The large orientation difference between the right side and the substrate is clearly a result of crystal twinning.

IV. SUMMARIES AND CONCLUSIONS

In summary, crystal misorientation in heteroepitaxial diamond films already occurs in the nucleation stage. The major reason for the misorientation is the very limited area of the (001) facets due to the substrate surface roughening induced by hydrogen plasma etching. The area of these small (001) facets is not large enough for the diamond nucleus to adjust the initial tilt. Minimization of the roughness of the substrate surface is necessary for the reduction of crystal tilt.

High quality heteroepitaxial diamond films can only be deposited by precisely controlling the BEN process. Our experiments show that the bias current control is an effective method to control the nucleation process. If the nucleation process is stopped in time after the bias current just begins to increase, well-oriented films can be grown.

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