Direct Local Epitaxy of Diamond on Si(100) and Surface-Roughening-Induced Crystal Misorientation

X. Jiang

Fraunhofer-Institut für Schicht- und Oberflächentechnik, Bienroder Weg 54E, D-38108 Braunschweig, Germany

C. L. Jia

Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

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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. The small (001) terraces with dimensions of several atomic distances at the site of nucleation are formed due to the roughening of silicon surface and lead to the grain misorientation. A model is presented which attempts to explain the initial stages of diamond growth. Predictions are made for methods of improving the nucleation of epitaxial diamond crystallites.

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In the past decade, growth of metastable diamond has been developed by means of low-pressure chemical vapor deposition. Concurrently, due to its huge application potential in electronics, a rapidly growing interest in diamond technology has been aroused [1–3].

While diamond films have been synthesized routinely since 1982, it only became possible about ten years later to grow large area heteroepitaxially oriented diamond films on the most important silicon substrate [4,5]. 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 progress made in the intensive research and development in the past few years [6], 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 lack of knowledge on the orientation deviation of individual diamond grains and its relations to the local structure status of the substrate surface and to the conditions for nucleation of the diamond crystals. 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 [7]. 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 [8]. A high density of crystal defects, mainly consisting of microtwins and stacking faults, is found in the near-grain-boundary regions [7].

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 [9]. However, the grain coalescence is believed to be possible only for the grains with a small misorientation ($<2°$).

In this work we demonstrate the direct nucleation of diamond on silicon by means of high-resolution transmission electron microscopy (HRTEM). The deviation of the grain orientation is for the first time related to the surface status of the silicon substrate at the nucleation sites. On the basis of the experimental investigation a model for the crystal misorientation is suggested and discussed.

Diamond-on-silicon samples were prepared by microwave plasma chemical vapor deposition (MWCVD) using the well-known two-step process [6]. 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 have been published in previous papers [6,7].

The interface structure between a heteroepitaxial diamond and silicon with a perfectly epitaxial orientation was revealed by HRTEM in 1995 [10]. A high-resolution lattice image of the interface is shown in Fig. 1. The cubic-to-cubic orientation relationship between diamond and silicon, i.e., $(001)_{\text{diamond}} \parallel (001)_{\text{silicon}}$ and $[110]_{\text{diamond}} \parallel [110]_{\text{silicon}}$, is clearly demonstrated. No secondary phases like β-SiC, graphite, and amorphous carbon can be recognized in the interface area. Regarding the image at a glancing angle along the two sets of {111} planes, it becomes obvious that the large lattice mismatch between silicon ($a_{\text{Si}} = 0.543$ nm) and diamond ($a_{\text{D}} = 0.357$ nm) is accommodated by the introduction of a 3:2 registry (with 1.5% mismatch) for the diamond lattice with respect to that of silicon. Following the lattice fringes from Si, across the interface, to the diamond we find that every third lattice plane of diamond terminates at the interface as denoted by arrows.

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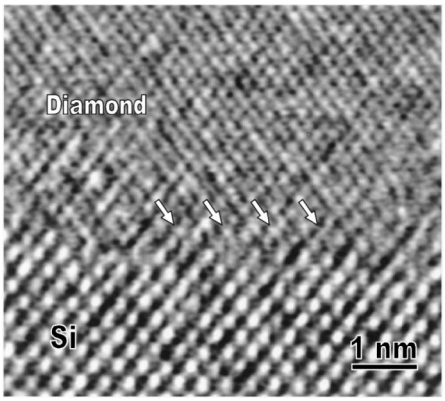

FIG. 1. A lattice image of the interface between diamond and silicon. The micrograph was taken along the [110]-zone axis of diamond and silicon crystals.

The lattice image shown in Fig. 1 provides us with strong evidence that diamond crystals can be epitaxially grown directly on silicon in spite of the large lattice misfit. A thin epitaxial intermediate layer is unnecessary for the epitaxy. This important conclusion has, however, been queried in recent years due to the fact that different interface configurations have been observed in different laboratories. In early studies, the diamond films with random orientation were nucleated by scratching the substrates with diamond seed crystals, and it was found that diamond was grown on Si through a β-SiC intermedium layer [11]. This β-SiC layer was also frequently found after the diamond nucleation stage by means of BEN [12,13]. Considering the large lattice mismatch the formation of a β-SiC intermedium layer seems to be reasonable since the misfit between diamond and β-SiC, $\delta = (a_{\beta\text{-SiC}} - a_{\mathrm{D}})/a_{\mathrm{D}} = 22\%$ is much smaller than that between diamond and silicon, $\delta = (a_{\mathrm{Si}} - a_{\mathrm{D}})/a_{\mathrm{D}} = 52\%$. From this point of view and the available experimental findings it is even believed [12] that the diamond nuclei were formed only on a β-SiC layer. The observed direct contact of epitaxial diamond to silicon would be considered as a result of an extended growth of diamond nuclei on a β-SiC layer to the surrounding area where the β-SiC layer was etched away. The interface structure formed at the nucleation stage might be different from that formed during the extended growth process.

In order to investigate the interfaces located both at the nucleus sites and in the surrounding area, cross-sectional specimens for HRTEM investigation were prepared from the diamond film wafers after a very short growth process of only a few min. Figure 2(a) shows a cross-sectional image of a diamond grain with a lateral grain size of about 120 nm. At the central region of the interface a hillock of silicon substrate is clearly seen, as denoted by an arrow, with a lateral size of only 10 nm. {111} twinning occurs in this grain and the majority of lamellae start on the sides of the hillock. Considering the widely accepted phenomenon that the silicon substrate can be etched during the nucleation and growth processes this hillock should be the place under the protection of the early formed diamond or silicon carbides. Therefore the top of this hillock must be the nucleation site of diamond.

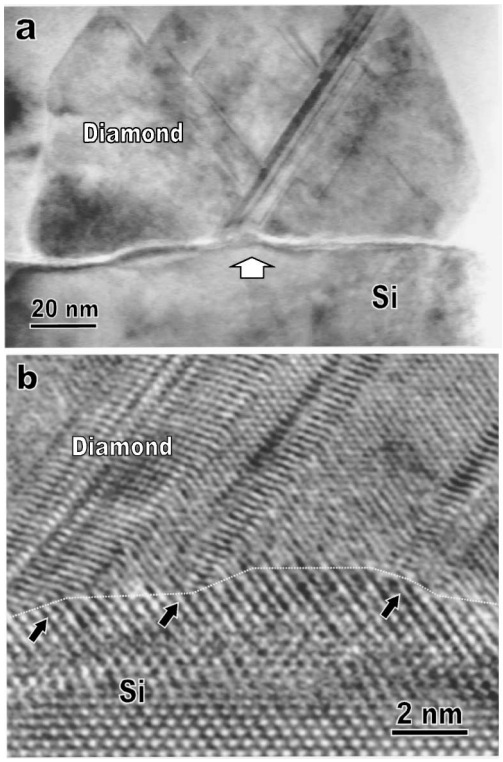

FIG. 2. (a) A low magnification [110] image of a diamond grain. An arrow shows a hillock at the central part of the interface. The majority of twins occur near the hillock. (b) Enlargement of the hillock area in (a). A dotted line traces the facet morphology of the hillock. Three arrows mark the facet edges on the sides of the hillock, where the {111} lamellae start.

Figure 2(b) shows the enlarged lattice image of the hillock area in Fig. 2(a). A direct bonding of the diamond lattice with silicon substrate is evident at the top of the hillock. No β-SiC can be recognized. It is additionally seen that the top of the hillock is faceted. The dotted line traces the morphology of the hillock. A contrast irregularity of the hillock region can be seen which is due to a local lattice strain or a local thickness difference of the TEM sample. An interesting point is that twin lamellae clearly start at the facet edges on the sides of the hillock denoted by arrows and run into the grain. From this lattice image 1° clockwise tilt can be measured with respect to the silicon substrate. Numerous experiments on the diamond nucleation showed that, if the BEN process is performed at moderate bias voltage and growth temperature and the incubation time is short, diamond can nucleate directly on Si substrate, instead of the formation of a β-SiC or an amorphous carbon layer [14].

It was found that one of the most important factors influencing the orientation of the crystalline nuclei is surface roughness of the silicon substrate. Figure 3 shows a lattice

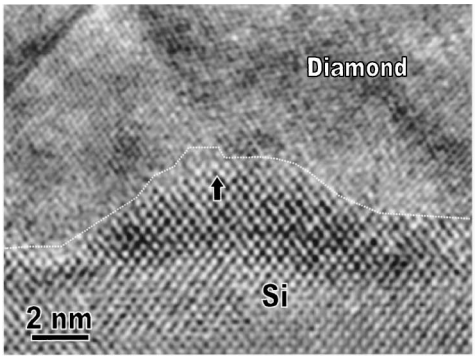

FIG. 3. [110] lattice image of a diamond grain with a tilt angle of about 6° around the [110] axis, showing a small (001) facet on top of the hillock. An arrow denotes a facet edge which induces a twin boundary.

image of a diamond grain misoriented with respect to the cubic-to-cubic relation. The HRTEM lattice image shows again a hillock at the central region of the grain/substrate interface. The top (001) facet of the hillock has a dimension of several $(1\bar{1}0)$ atomic planes only. The diamond grain in this image has a deviation of 6° from the ideal orientation by a rotation around the common (silicon and diamond) $[1\bar{1}0]$ zone axis. Note that a twin boundary is seen once again to start at a facet edge marked by an arrow. With respect to the grain orientation, a better situation is evident for the diamond grain in Fig. 2(b) than in Fig. 3. The good orientation of the diamond grain can be attributed to a relatively flat morphology of the hillock on the substrate. In addition, we observe a flat interface between the well-oriented grain and silicon substrate displayed in Fig. 1. From the above results it is evident that the misorientation of the diamond grains on (001) silicon is closely related to the appearance and status of the hillocks on substrate where diamond grains directly contact the silicon. This indicates that diamond nucleation occurred on the top of these hillocks.

These observations provide us with strong evidence that crystal tilting is related to structural distortion of the substrate surface and thus to the concomitant local strain. In order to understand the origin and nature of the experimentally observed diamond grain tilting, the three-dimensional nucleation and growth processes were studied in a step-by-step manner by means of the molecular orbital PM3 calculation [15,16], which is based on the MNDO semiempirical Hamiltonian of Hartree-Fock theory. A cluster model composed of more than one hundred silicon atoms with a hydrogen-saturated boundary was selected to simulate a rough silicon (001) substrate involving a silicon island on the surface. At the initial state of diamond nucleation, an adsorbed CH_2 may be bonded with and bridge two surface Si atoms, while two hydrocarbon or a single C-C species may form a heptagon with the neighboring surface Si atoms, as schematically shown in Fig. 4(a). According to the PM3 calculation, the Si-C and C-C bond lengths tend to be close to those in β-SiC and in diamond,

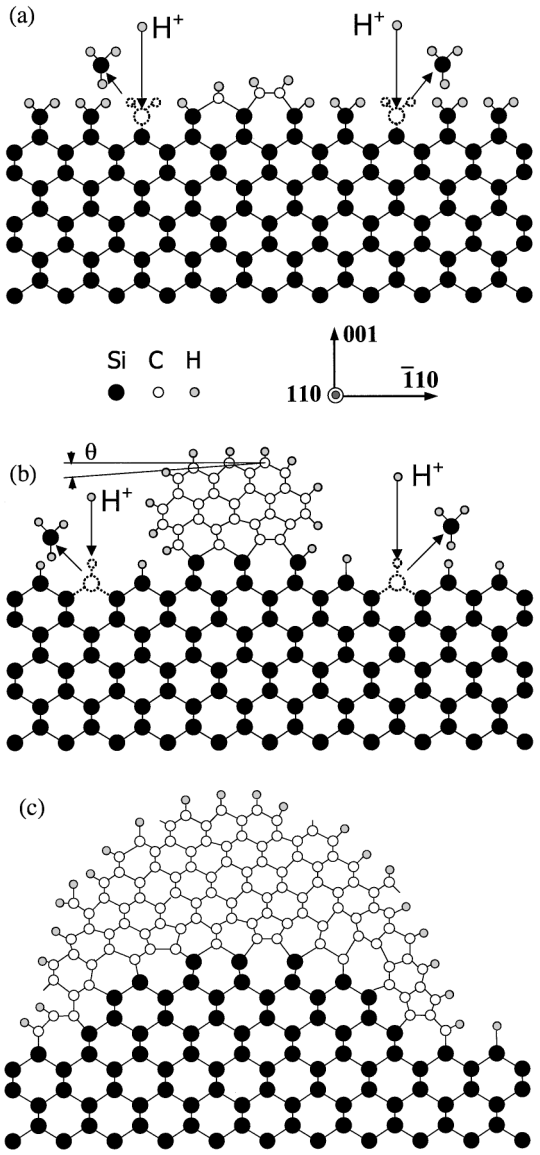

FIG. 4. Schematic sketches illustrating the sequence of formation of the surface hillock and diamond nucleus. (a) The initially deposited carbon configuration and H^+ ion etching on the silicon (001) surface, (b) further etching of the silicon surface and formation of tilted diamond nucleus, and (c) further growth of the nucleus and formation of the surface hillock due to etching.

respectively, due to structural relaxation. However, the carbon-related bond angles may deviate appreciably from the tetrahedral value (109.47°) because of internal strain. As a result, the carbon atoms are not located on the same plane parallel to the silicon surface. By overcoming the deviation in the tetrahedral bonding orientation, deposition may continue towards formation of a diamond embryo. At the interface between the diamond embryo and silicon, an interfacial dislocation will appear accompanying the formation of a pentagon/heptagon bonding configuration, as shown in Fig. 4(b). The formation of such a diamond embryo actually partially compensates the bond tilt created during the deposition of the first

carbon layer. Because of the limited contact area between the diamond embryo and the Si(001) terrace, on the other hand, the crystal tilt will remain and the structure mismatch will be accommodated during crystal growth by varying the number of the terminating {111} planes at the interface (pentagon/heptagon bonding configurations) [10]. This is schematically demonstrated in Fig. 4(c).

Our model shows that the crystal tilt is already introduced at the initial clustering stage and can interpret the HRTEM result in Fig. 3 quite well. However, if the pentagon/heptagon unit is positioned symmetrically in the diamond embryo, the local lattice strain which is presently considered to be the driving force of the tilt will be balanced in a symmetrical way. On the other hand, if such a diamond embryo is formed in a sufficiently large area of (001) terrace, the initial tilt should be significantly reduced or eliminated by a homogeneous distribution of the pentagon/heptagon unit. The fact that a relatively flat top of the hillock in Fig. 2 leads to a better orientation ($\theta = 1°$) of the diamond grain corroborates the theoretical model. In practice, the deposition conditions in the nucleation stage should be chosen in such a way that the nucleation rate is as high as possible and the etching effect of the plasma is as small as possible in order to obtain a well-oriented diamond film on silicon substrate.

In summary, a direct diamond epitaxy on the silicon substrate was demonstrated not only at the interface formed during the growth process but also at the nucleation sites. According to the HRTEM investigation of the interfaces and PM3 modeling of the diamond nucleation on silicon, crystal misorientation in 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 by forming homogeneously distributed pentagon/heptagon units. In addition, the experimental investigation reveals that the facet edges located on the sides of the hillock favor the occurrence of {111} twinning. Minimization of the roughness of the substrate surface is not only necessary for the reduction of crystal tilt, but also for the decrease of the twin density.

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