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H-plasma-annealed and homoepitaxially grown diamond (001) surface structure studied with reflection high-energy electron diffraction

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Diamond (001) surfaces have been studied using reflection high-energy electron diffraction after annealing in H plasma and after homoepitaxial growth of diamond films. These surfaces show the transition from double-domain to nearly single-domain structures with misorientation angles toward ⟨110⟩, which is dependent upon temperature. When surfaces are close to the single-domain structure, type-*A* terraces dominate the H-plasma-annealed surfaces and type-*B* terraces are the major domain of the as-grown film surfaces. We infer that the step formation energies increase in the order of D_A, S_A+S_B, and D_B on the surfaces annealed in H plasma, and in the order of D_B, S_A+S_B, and D_A on the as-grown film surfaces.

In the epitaxial growth of thin films, controlling surface structures is of great importance because it determines the surface morphologies and eventually the physical properties of films. Observations of macrosteps,[1–5] growth hillocks,[1,3–9] dimer row extension,[10–12] etc., on (001) homoepitaxial diamond films grown by chemical vapor deposition (CVD) indicate that steps play a crucial role in the homoepitaxial growth of diamond films. Recently, Tsuno *et al.*[13] have reported that a nearly single-domain (*S*-domain) surface with double-layer (DL) steps is developed when growth occurs by step flow. Our previous papers[4,5] have also shown that step-flow growth proceeds with the surface close to the *S*-domain structure, while hillock or random growth occurs with the double-domain (*D*-domain) structure on the diamond (001) surface. Several factors such as the misorientation angles of substrates, methane concentrations, and substrate temperatures have been known to affect the surface structure and morphologies.[4,5,13] Little has been reported in the literature, however, on the domain or step structures of diamond (001) although they are of great consequence for understanding the growth mechanisms of CVD diamond films.

In this paper we studied diamond (001) surfaces annealed in H plasma and homoepitaxially grown diamond (001) film surfaces using reflection high-energy electron diffraction (RHEED). It was observed that the surface structure changed in terms of domain and step structures with surface misorientation angles and temperatures.

Synthetic Ib-type single-crystal diamond substrates of Sumitomo Electric were used for this study. Misorientation angles of mirror-polished substrate surfaces were determined with respect to the (001) plane by x-ray diffraction. The measurement results are given in Table I. H-plasma annealing and diamond growth were carried out in a microwave plasma-assisted CVD system. The H-plasma annealing was performed at the substrate temperatures of 875–1200 °C with a gas pressure of 80–150 Torr and a flow rate of 100 SCCM H_2 (SCCM denotes cubic centimeter per minute at STP). Growth experiments were carried out at 875 and 1200 °C with 0.5% CH_4 in H_2 at 80 Torr and 100 SCCM. The substrate temperatures were measured by optical pyrometry. For RHEED experiments, we used a conventional transmission electron microscope (Phillips 420T). RHEED patterns were taken in the [100] azimuth with the accelerating voltage of 40 kV and with the glancing angles of 1°–4°.

On the reconstructed diamond (001) surface, the 2×1 (type-*A*) and 1×2 (type-*B*) terraces where dimer rows are parallel and perpendicular to the lower step edges, respectively,[14] generate diffraction spots alternately along the half-order Laue ring ($L_{1/2}$) in a RHEED pattern with the [100] azimuth. Thus, one can know which series of half-order spots originate from 2×1 or 1×2 terraces by analyzing a geometry of a sample setup. The RHEED intensity of a half-order spot from the domain whose unit cell is defined by two lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ and which is composed of $M\cdot N$ unit cells may be expressed by[15]

$$I\propto|F|^2\frac{\sin^2[\frac{1}{2}M\mathbf{a}_1\cdot(\mathbf{k}-\mathbf{k}_0)]}{\sin^2[\frac{1}{2}\mathbf{a}_1\cdot(\mathbf{k}-\mathbf{k}_0)]}\frac{\sin^2[\frac{1}{2}N\mathbf{a}_2\cdot(\mathbf{k}-\mathbf{k}_0)]}{\sin^2[\frac{1}{2}\mathbf{a}_2\cdot(\mathbf{k}-\mathbf{k}_0)]},$$

where F, $\mathbf{k}_0$, and $\mathbf{k}$ are the structure factor of the unit cell, incident wave, and scattered wave vectors, respectively. Using the theory of diffraction from a plane grating,[16] the maximum intensity of the half-order spot may be written by

$$I_{\max}\propto|F|^2(M\cdot N)^2.$$

We can assume that the structure factors for 2×1 and 1×2 terraces are equivalent because these two types of terraces are identical except for the 90° rotation of bonding geometry.[17] Therefore, the intensities of ij and ji half-order spots are considered to be simply proportional to the squares of the areas of the 2×1 and 1×2 domains, respectively. This study investigated the domain structures of diamond (001) by comparing the intensities of two series of the half-order spots.

Figure 1 shows RHEED patterns of the 0.1° and 3.5° off surfaces annealed at 875, 1000, and 1200 °C in H plasma. The 0.1° off surface exhibits, for all temperatures investigated, the symmetrical intensity distribution of the half-order spots. On the other hand, the 3.5° off surface shows, at 875 and 1000 °C, that the type-*A* half-order spots (indicated by arrowheads) have much stronger intensities than the type-*B* half-order spots (see Ref. 5 for indexing of RHEED spots).

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TABLE I. Surface misorientation angles of (001) diamond substrates toward the [110] and $[1\bar{1}0]$ direction measured from x-ray diffraction.

Substrates	Misorientation toward [110]	Misorientation toward $[1\bar{1}0]$	Total misorientation angles	Deviation of nominal misorientation directions from $[1\bar{1}0]$
0.1° off	0.1°	0.1°	0.1°	45.0°
3.5° off	0.2°	3.5°	3.5°	3.3°
11.0° off	7.0°	8.5°	11.0°	39.2°
3.1° off	0.8°	3.0°	3.1°	14.9°

At 1000 °C, however, intensity difference between the type-*A* and type-*B* is reduced as compared to that of 875 °C. Contrarily, at 1200 °C, the 3.5° off surface exhibits no alternate intensity variation of RHEED spots along $L_{1/2}$.

In conclusion, upon annealing in H plasma, the 3.5° off surface is close to the *S*-domain structure at 875 and 1000 °C, on which the type-*A* terraces are wider than the type-*B* terraces. On the 3.5° off surface at 1200 °C and on the 0.1° off surface at 875–1200 °C, however, the areas of the type-*A* and type-*B* terraces are almost equal (i.e., *D*-domain structure). The surface 11.0° tilted toward approximately [100] was also studied. This surface showed the *D*-domain structure at the same temperature range.

Figure 2 shows RHEED patterns of films grown on the 0.1° and 3.5° off substrates at 1200 °C. On the 0.1° off film surface, the intensities of type-*A* and type-*B* half-order spots do not change alternately. On the contrary, the 3.5° off film surface reveals that the type-*B* half-order spots (marked by arrowheads) are far brighter than the type-*A* spots. Thus, when grown at 1200 °C with 0.5% CH_4, the 0.1° off film shows the *D*-domain surfaces while the 3.5° off film has the surface close to the type-*B* *S*-domain structure. It is worth noting that the 3.5° off surface exhibiting the *D*-domain structure in H plasma at 1200 °C transforms to the surface close to the *S*-domain structure during growth at 1200 °C. The as-grown 11.0° off film revealed the *D*-domain surface structure.

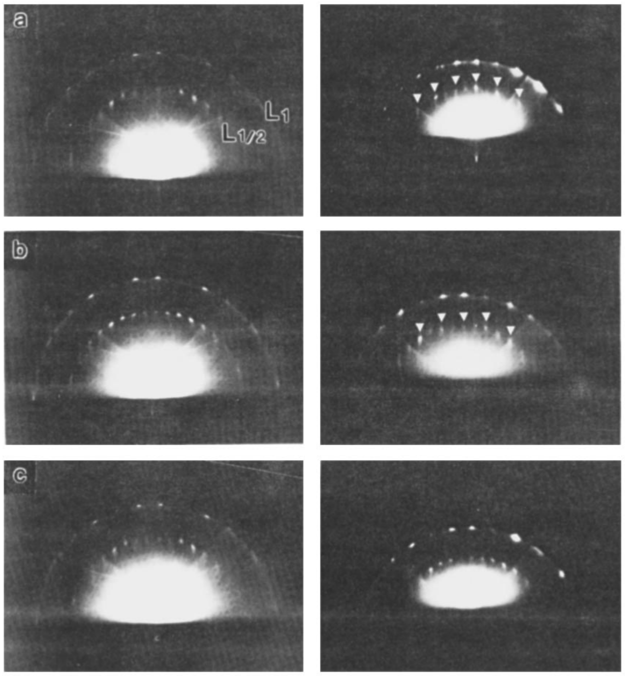

FIG. 1. RHEED patterns of diamond (001) surfaces annealed in H plasma at (a) 875 and (b) 1000 °C for 30 min, and (c) 1200 °C for 10 min. The left and right patterns are taken from the 0.1° and 3.5° off substrates, respectively. $L_{1/2}$ and L_1 in (a) denote the half-order and first-order Laue rings, respectively, and arrowheads in (a) and (b) indicate the type-*A* 2×1 half-order spots.

The surface structure was investigated in sequence after preannealing of a substrate in H plasma, homoepitaxial growth, and postannealing of the as-grown layer in H plasma at 875 °C. RHEED patterns of the 3.1° off surface taken after each step are given in Fig. 3. After preannealing in H plasma, the intensity of type-*A* spots is stronger than that of type-*B* spots along $L_{1/2}$. However, homoepitaxial growth at 875 °C makes the type-*B* half-order spots brighter. The as-grown sample was treated again in H plasma. The postannealing converts the type-*B* terrace dominant surface to the type-*A* terrace dominant surface. The 3.1° off surface preannealed and postannealed in H plasma or homoepitaxially grown is close to the *S*-domain structure under the above conditions. But it should be noted that the type-*A* terraces dominate the H-plasma annealed surface while the type-*B* terraces are the major domain of the as-grown film surface.

Not much is known about the diamond (001) surface structure. Thus it is useful to begin our discussion by briefly summarizing the reports on the Si(001) surface since it has been intensively studied recently. One expects similarities

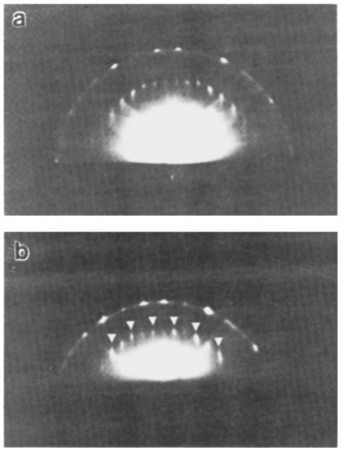

FIG. 2. RHEED patterns of (001) homoepitaxial diamond films grown for 30 min at 1200 °C, 0.5% CH_4 on (a) 0.1° off and (b) 3.5° off substrates. The type-*B* 1×2 half-order spots in (b) are marked by arrowheads.

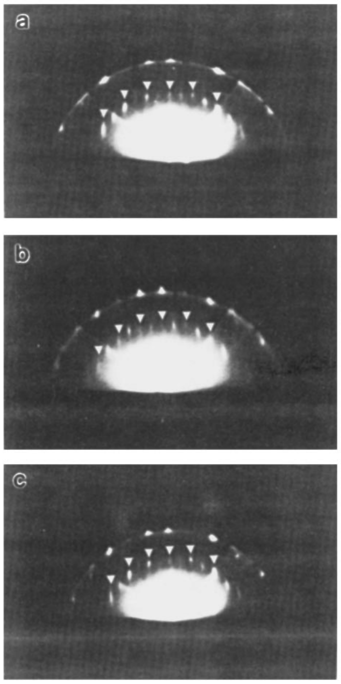

FIG. 3. RHEED patterns of diamond (001) surfaces (a) preannealed in H plasma for 10 min, (b) grown for 30 min with 0.5% CH_4 in H_2, and (c) postannealed in H plasma for 5 min at 875 °C. Arrowheads indicate the type-*A* half-order spots.

between Si and diamond surfaces because both not only possess the same bulk crystal structure but also reveal the dimer-type 2×1 reconstruction on the (001) surface. But there would be also differences due to different bonding energies, as well as to different growth processes such as molecular-beam epitaxy (MBE) for Si and CVD for diamond.

On clean Si(001), there are two types of single-layer (SL) and DL steps, labeled in the following by S_A, S_B, D_A, and D_B.[14] Type-*A* and type-*B* steps are parallel and perpendicular to the dimer rows in the upper terraces, respectively. On Si(001), even if S_A steps have the lowest formation energy, D_B steps are energetically more favorable than alternating S_A+S_B steps on the surfaces tilted toward [110] or $[1\bar{1}0]$. D_A steps are significantly higher in energy than D_B or S_A+S_B steps.[14]

To figure out the equilibrium surface structure, Alerhand *et al.*[18] and Poon *et al.*[19] have pointed out that surface strain relaxation and thermal roughening of steps should be considered as well as step formation energies. The dimerized reconstruction induces anisotropic surface stresses on terraces: tensile and compressive stresses along and across the dimerization direction, respectively.[20,21] On a SL-stepped surface, anisotropic surface stresses cancel each other across the step edges, but this relaxation does not occur on a DL-stepped surface because it comprises the same type of terraces. Thus, the surface strain relaxation lowers the energy of a SL-stepped surface. Thermal effect also reduces the free energy of a SL-stepped surface due to an increase in the configuration entropy associated with ragging of S_B step edges, in contrast to rather straight S_A step edges. Recent work elaborated by Tong and Bennet[22] and Pehlke and Tersoff[23] has shown that the transition from SL- to DL-stepped surfaces gradually occurs with the misorientation angles. As the misorientation angles increase, the areas of type-*B* and type-*A* terraces continuously increase and decrease, respectively, while only SL steps occur. Above approximately 1.5°, alternating S_A+S_B steps start to collapse into D_B steps. The content of D_B steps monotonically increases until only DL steps exist above 4°–5°.

When diamond (001) is close to the *S*-domain structure, the type-*A* half-order spots are stronger than the type-*B* spots after annealing in H plasma and vice versa after homoepitaxial growth. This implies that the terraces producing the brighter half-order spots are wider than the other type of terraces. Unequal areas of type-*A* and type-*B* terraces can be accompanied by either unequal spacing of S_A and S_B steps on a SL-stepped surface or the presence of DL steps together with SL steps. We believe that our 3.5° and 3.1° off surfaces close to the *S*-domain structure comprise DL steps mixed with SL steps. Our assumption regarding the existence of DL steps on these surfaces is supported by the observations of Tsuno *et al.*[13] and Kuang *et al.*[24] The former have reported for the as-grown 4.3° off surface that low-energy electron diffraction (LEED) reveals far brighter intensities in one series of half-order spots and then scanning tunneling microscope (STM) images show mostly D_B steps. Kuang *et al.*[24] have recently observed using STM that D_A steps locally coexist with SL steps on the 1.5° off diamond (001) surface annealed in H plasma, although LEED exhibits the *D*-domain surface structure. Our 3.1° and 3.5° off surfaces close to the *S*-domain structure may lie in the middle of transition between SL- and DL-stepped surfaces.

When a surface is misoriented above the critical angle along [110] or $[1\bar{1}0]$, a DL-stepped surface is more stable than a SL-stepped surface. If kinks are present, however, SL and DL steps can coexist.[25–27] In our case kinks are forcibly introduced because for the substrates used in this study the tilting directions are deviated from the exact [110] or $[1\bar{1}0]$ (refer to Table I). If D_A steps occur on annealed diamond (001), D_B steps would be created locally along kinks. But if D_B steps are higher in energy than alternating S_A+S_B steps, D_B steps split into S_A+S_B steps, then D_A steps and S_A+S_B steps would be present along step edges and at kinked regions, respectively, on the annealed surface. The fact that alternating SL steps have lower formation energy than D_B steps is supported by the observation of the *D*-domain structure on the surface 11.0° tilted toward approximately [100]. Otherwise, the 11.0° off surface would produce a nearly *S*-domain RHEED pattern. The same explanation is applicable for the as-grown surfaces on which D_B steps have a lower energy than S_A+S_B, and D_A steps have the highest energy. Conclusively, the step formation energies increase in the order of D_A, S_A+S_B, and D_B types on the H-plasma annealed surfaces and in the order of D_B, S_A+S_B, and D_A types on the as-grown surfaces.

As shown in Fig. 1, the 0.1° off diamond surface annealed at 875 °C indicates the *D*-domain structure, but the 3.5° off surface annealed at the same temperature is close to the *S*-domain structure. This indicates that the transition from SL- to DL-stepped surfaces occurs with the misorientation angles as it does on Si(001). Besides, temperature affects this transition. In Fig. 1, the 3.5° off surface annealed at 875 °C shows strong type-*A* half-order spots and faint type-B spots, but the intensity difference is reduced at 1000 °C, and finally, no variation is observed at 1200 °C for this surface. Thus, it appears that the misorientation angles of transition between SL- and DL-stepped surfaces become larger at higher temperatures.

DL steps occurring on Si(001) annealed in ultrahigh vacuum (UHV) or grown by MBE are always of type D_B. Our RHEED results indicate, however, that D_A steps can exist on annealed diamond (001). Recently, D_A steps were observed on H-plasma annealed diamond (001) by Kuang *et al.*[24] We address here the question of why D_A steps can be stable on annealed diamond (001). There are hardly any impurity atoms to satisfy dangling bonds of nonbonded edge atoms on Si(001) during annealing in UHV or MBE growth. On Si(001), therefore, edge atoms of D_B, S_B, and D_A steps are rebonded to lower terrace atoms by forming dimerlike bonds.[14,26] With the rebonded step structures on Si(001), the formation energies increase in the order of S_A, D_B, S_B, and D_A steps.[14]

However, the environment of CVD for diamond is quite different not only during annealing in H plasma but also while growing in hydrocarbon plasma. The H plasma produces plenty of H atoms to form H-terminated diamond (001) surface with monohydride structure.[28] Since H atoms satisfy dangling bonds, rebonding of edge atoms would not occur. H termination of edge atoms appears to change the relative step formation energies so that D_A steps are more stable than D_B or S_A+S_B steps. The environment during CVD diamond growth in hydrocarbon plasma is more complicated because there are hydrocarbon radicals as well as H atoms. It is thought that diamond growth occurs at step edges by adsorption of hydrocarbon radicals with a subsequent abstraction of H atoms. The fact that the relative stabilities of steps during growth are different from those of steps during annealing in H plasma indicates that hydrocarbon precursors are adsorbed on step edges and change step structures and, consequently, the relative step formation energies during growth.

In summary, RHEED has been used to study diamond (001) surfaces annealed in H plasma and as-grown diamond films. The surface annealed in H plasma shows the transition from the D-domain structure to the nearly S-domain structure with increasing misorientation angles. This transition is temperature dependent. The as-grown films have shown the D-domain structure on the well-oriented surface (0.1°) and the surface close to the S-domain structure on the misoriented surface (3.5°). When the surface is close to the S-domain structure, type-A terraces dominate the H-plasma annealed surface while type-B terraces are the major domain of the as-grown film surface. It is considered that the step formation energies increase in the order of D_A, S_A+S_B, and D_B on the surfaces annealed in H plasma and in the order of D_B, S_A+S_B, and D_A on the as-grown films.

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