Letter to the Editors

Dissociation of \{1 1 1\} faces into \{1 1 0\} faces in thick diamond films

Haiping Sun*, San Yu, Zhigang Jiang, Dongmei Li, Lin Liu, Zengsun Jin, Guangtian Zou
National Laboratory of Super Hard Materials, Jilin University, Changchun 130 023, People's Republic of China
Received 29 December 1995; accepted 13 November 1996

Abstract

Surface morphology of thick diamond films was investigated using scanning electron microscopy (SEM). The dissociation of \{1 1 1\} faces into \{1 1 0\} faces is positively confirmed by the geometrical consideration of the crystal shapes, such as the V-shaped penetration twins and some other unusual crystal shapes. Growth mechanisms of the diamond \{1 1 1\} and \{1 1 0\} faces are discussed.

PACS: 81.05.Tp; 68.55. a; 61.16.Bg

Keywords: Thick diamond film; Crystal shape; Twin; SEM

Prime Novelty: The dissociation of \{1 1 1\} faces into \{1 1 0\} faces was positively identified in thick diamond films. Some strange crystal shapes are explained by the dissociation of \{1 1 1\} faces and the formation of penetration twin.

Diamond is an attractive material for many applications due to its extreme properties. Diamond films are synthesized successfully by chemical vapor deposition (CVD). The dependence of surface morphology and crystal shapes on the growth conditions is well-known but not fully understood.

Investigation of surface morphology and crystal shapes is an efficient way to understand the growth mechanism.

The typical shape of diamond crystals is cubo-octahedron. Usually, the \{1 0 0\} faces are smooth and the \{1 1 1\} faces are rough. The growth feature of \{1 1 1\} faces is always an interesting topic. Kim et al. [1] believed that the roughness of \{1 1 1\} faces arises from the competing growth of \{1 0 0\} and \{1 1 0\} faces, and the \{1 1 0\} faces separate the \{1 1 1\} faces into three \{1 1 0\} faces. Keiji and Noriko [2] found that the growth of \{1 1 1\} faces is multi-nucleation, and the \{1 1 1\} faces consist of many small triangles and triangular pits, and the \{1 1 0\} faces frequently appear at the edges of the...
{111} surface. Because scanning electron microscopy (SEM) images do not provide direct information for indexing crystal planes, it seems unacceptable to say that the faces that appeared on {111} faces must be {110} faces. In fact, the planes composing the hopper-shaped (111) face found by Mehta et al. [3] are indexed to be of the families of {221} and {331} faces via quantitative measurement using atomic force microscopy (AFM). Up to now, there is no quantitative identification of the dissociation of {111} faces into {110} faces.

In this work, surface morphology of thick diamond film which was synthesized by glow-discharge plasma-assisted chemical vapor deposition (CVD) [4] was investigated by SEM (HITACHI X-650 and H-8110 scanning attachment for HITACHI 8100 TEM). The dissociation of {111} faces into three {110} faces was positively identified by the geometrical consideration of the crystal shapes.

An SEM image of the surface morphology of the thick diamond film is shown in Fig. 1a. All the growth planes are covered by macrosteps. The ⟨110⟩ direction seems to be the preferred growth direction of the crystals. The crystal shape is similar to a section of the normal cubo-octahedron that has six square ⟨100⟩ faces and eight triangular ⟨111⟩ faces. The difference comes from the ⟨111⟩ faces that change from triangular shape to a concave shape, and the growth of the ⟨111⟩ faces is, in fact, replaced by the growth of other faces. In our case, as observed in Fig. 2a and illustrated schematically in Fig. 2b and in Fig. 3a, the ⟨111⟩ faces dissociate into ⟨110⟩ faces.

The ubiquitous triangular defect, as indicated by arrows labeled ‘t’ in Fig. 1a, on ⟨100⟩ faces of vapor-grown diamond was positively identified to be an ⟨100⟩⟨111⟩ penetration twin by Everson et al. [5] using scanning tunneling microscopy (STM) and AFM. The penetration twins appear as sections of cubo-octahedra oriented with ⟨221⟩ direction parallel to the crystal’s ⟨100⟩ surface normal. When the dissociation of ⟨111⟩ faces happened to the twin ⟨111⟩ face (all the crystal planes of the penetration twins are labeled with a superscript apostrophe in this paper), a V-shaped penetration twin is formed, as illustrated in Fig. 3a. When the twin grows under certain conditions, the twin will almost bury the parent plane. In one case, the twin ⟨101⟩ face will connect with the parent ⟨110⟩ face and finally the two faces will develop into one plane (see Fig. 1b and Fig. 3a), and in another case, the twin ⟨010⟩ face and the parent ⟨110⟩ face will develop into one plane (see Fig. 1c and Fig. 3a). These kinds of developments of crystal shapes happened in the thick diamond films and the unusual crystal shapes could be observed in the SEM image, as indicated by arrows labeled ‘a’ and ‘b’, respectively, in Fig. 1a and illustrated schematically in Fig. 1b and Fig. 1c. It will be proved that these phenomena could not appear unless the ⟨111⟩ faces of both parent crystal and penetration twin dissociate into ⟨110⟩ faces.

As illustrated in Fig. 3a, the appearance of the ⟨100⟩⟨111⟩ penetration twin is equivalent to a 60° rotation of the section of the cubo-octahedron about a ⟨111⟩ direction emerging from the ⟨100⟩ face. The twin ⟨111⟩ is parallel to the parent ⟨111⟩ and, with a 60° rotation about ⟨111⟩, ⟨100⟩ will be parallel to ⟨100⟩. Fig. 3b is a vector diagram in which A (111), B (101) and C (110) are the normal vectors of parent (111), (101) and (110) faces, respectively. The relationships of the three vectors are given by: A B = 0, A C = 0 and γ = arccos(B/C) = 60°. With a 60 rotation about A, vector B will be parallel to C. Now it is safe to say that the twin ⟨101⟩ is parallel to C. Thus, it is possible for the twin ⟨101⟩ face and the parent ⟨110⟩ face to grow into one plane indicated by an arrow labeled ‘a’ in Fig. 1a and illustrated schematically by shadow in Fig. 1b. Any other kind of dissociation of ⟨111⟩ faces will not result in the same geometrical relationship. In the same way we could prove that, with a 60 rotation about A, vector D (010) will be parallel to either the twin D' (010) direction or the parent E ⟨110⟩ direction (see Fig. 3a). Then the twin ⟨010⟩ face and the parent ⟨110⟩ face may have a chance to grow into one plane indicated by an arrow labeled ‘b’ in Fig. 1a and illustrated schematically by shadow in Fig. 1c.

Some other unusual morphology, as indicated by an arrow labeled ‘c’ in Fig. 1a, may be formed due to the growth of penetration twin and the dissociation of ⟨111⟩ faces. The growth of ⟨100⟩⟨111⟩ penetration twin and the dissociation of ⟨111⟩
Fig. 1. Surface morphology of the synthesized thick diamond film is shown in (a). Label 't' indicates the penetration twin. Label 'a', 'b' and 'c' indicate the unusual crystal shapes that resulted from the growth of penetration twin and the dissociation of \{111\} faces into \{110\} faces. Schematic drawings of the crystal shapes labeled 'a' and 'b' in (a) are shown in (b) and (c), respectively, in which the twin face and the parent face grow into one plane indicated by shadow.

The growth habit of \{111\} faces is always an interesting topic. Different growth mechanisms were proposed and the reasons given for the appearance of the \{110\} faces at the edges of \{111\} faces are rather different. Kim et al. [1] explained...
the appearance of {110} faces by the competing growth of {110} and {100} faces and then the dominant growth of {110} faces at the crystal edges. Keiji et al. [2] thought that the inhomogeneity of the effective carbon concentration on the {111} surface may be the reason for the appearance of the {110} faces. When the growth of the center of the {111} faces is delayed due to the lower carbon concentration, the {110} faces will appear. The first explanation was not ever positively confirmed by
experimental results, and the second explanation did not explain why is it that the \{110\} faces and not other faces are necessary to appear. In fact, other planes, such as the \{221\} and \{331\} faces, may also appear to form the hopper-shaped \{111\} faces [3].

Gas-surface interactions are complex chemical-dynamic processes that enable the growth of diamond by CVD under metastable conditions [6] and determine the properties of the deposited films. These surface interactions have not been fully understood. Under different growth conditions, the growth mechanisms of the diamond faces may be different.

Drawing from the results discussed above, we conclude that under certain conditions, the growth of \{111\} faces is an evolution process in which, as described by Keiji et al. [2], the \{111\} faces will evolve from smooth surfaces at nucleation stage to rough surfaces and to a concave shape. But the growth mechanism of \{111\} may not always be a multi-nucleation process [2] and the concave shape of \{111\} faces may not always be formed by \{110\} faces [3]. Probably, the dissociation of \{111\} faces is a crystal-scale related growth habit. Our results show that, first, when the crystals grow large enough, under our experimental conditions, the dissociation of \{111\} faces into \{110\} faces occur and the competing growth of \{110\} and \{100\} faces, as supposed by Kim et al. [1], only happens at the edge regions, as shown in Fig. 1a and Fig. 2a. Second, the appearance of \{110\} faces is not rare and the growth of \{111\} faces is, in fact, replaced by the growth of \{110\} faces, which means that the \{110\} faces are dominant faces on the thick diamond film surface. Third, the \{110\} faces grow via macrosteps that originate from the reentrant corner, as seen in Fig. 1a and Fig. 2a. The properties of the macrosteps on \{110\} faces are similar to that on the \{111\} faces. The growth properties of the steps on \{100\} faces in thick diamond films are discussed elsewhere [4].

References