Twin-step-related growth phenomena of thick diamond film

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Abstract

A thick diamond film prepared by glow discharge plasma assisted chemical vapor deposition (CVD) was investigated by scanning electron microscopy, X-ray diffraction and Raman spectroscopy. The degeneration of the \( \{111\} \) faces into three \( \{110\} \) faces was found to be widespread. Both the \( \{110\} \) and \( \{100\} \) faces grow via a step mechanism, with the steps generally originating from the re-entrant corner formed by twinning. The \( \{100\}\langle111\rangle \) penetration twin on \( \{100\} \) surfaces is discussed in detail. A twin-step growth mechanism of thick diamond film, which explains the formation of cleavage steps on fracture surface, is proposed.

Keywords: Penetration twin; Step; Thick diamond film; Hot cathode glow discharge PACVD

1. Introduction

Diamond, which has various excellent properties, is an attractive material for many potential applications. A number of chemical vapor deposition (CVD) methods have been developed to grow diamond film successfully, and the morphology and the quality of the grown films are very different owing to the different growth conditions used. A careful investigation of the film morphology is essential to obtain a good understanding of the diamond growth mechanism. The macrostructure, such as twins, surface steps and cleavage steps on the fracture surface, may act as a bridge connecting the elementary process and the overall picture of diamond growth.

It is known that microprocesses (twinning on the \( \{111\} \) plane, surface reconstruction and step nucleation) apparently affect the macrostructure. Microprocesses can be controlled by appropriate selection of growth conditions to obtain the desired structure or morphology [1]. Studies using high-resolution electron microscopy (HREM) show that the \( \Sigma = 3 \) twin boundary is the most common defect in diamond films. This defect affects not only the quality but also the morphology and growth process of the diamond film. For example, the \( \Sigma = 3 \) twin with the twin plane parallel to the growth direction could stimulate fast growth [2]. The well-known \( \{100\}\langle111\rangle \) penetration twin (PT), which is often observed, is assumed to originate from the twin plane of microsteps on \( \{111\} \) surfaces [1], and in homoepitaxial diamond films it is associated with step nucleation [3,4]. The possible role of the PT in diamond growth has been discussed by Tamor and Everson [5], but no actual mechanism was proposed. Step nucleation, step anisotropy and step propagation in homoepitaxial CVD diamond films has been studied by Van Enckevort et al. [6]. Steps on \( \{100\} \), \( \{111\} \) and \( \{110\} \) faces are frequently found diamond grown heteroepitaxially [6–8]. Gling and Van Enckevort [9] have explained the influence of surface reconstruction on the lateral orientation of growth steps appearing on the \( \{100\} \) and \( \{111\} \) planes of a diamond-like structure. Cleavage steps on the fracture surface are formed by transgranular fracture resulting from the twin and stack defects in the film [10]. However, the formation process of these cleavage steps has not been discussed.

We have investigated the surface morphology and fracture surface of \( \langle110\rangle \) oriented thick diamond film by scanning electron microscopy (SEM). The \( \{100\}\langle111\rangle \) PT, steps on the \( \{100\} \) surface and the degeneration of the \( \{111\} \) face are discussed in detail. The cleavage steps on the fracture surface are explained by the twin-step growth mechanism.

2. Experimental methods

A thick diamond film was prepared by glow discharge plasma assisted CVD using a mixture of methane and hydrogen on a molybdenum substrate. The diamond structure was confirmed by X-ray diffraction.

3. Results and discussion

A scanning electron micrograph of the surface morphology of the thick diamond film is shown in Fig. 1. The X-ray diffraction (XRD) spectrum and Raman spectrum of the film are shown in Figs. 2 and 3 respectively.

3.1 \{100\}(111) penetration twin and cleavage steps

The ubiquitous triangular defect on the (100) faces was positively identified to be \{100\}(111) PT by Everson et al. [17]. The V-shaped twin which is frequently observed is also confirmed to be \{100\}(111) PT; the V shape is formed by the degeneration of the twin (111) face which will be discussed further in Section 3.3. The PT always appears to initiate growth of a new epitaxial step layer at a higher rate than in defect-free regions in the homoepitaxial growth of diamond [3]. The same phenomenon is more obvious on the thick diamond surface. Fig. 1 shows that the step layers have a nucleation center from which the steps originate and propagate away. The center is obviously related to the re-entrant corner formed by the PT plane and the parent (100) plane. (The PT may be difficult to identify owing to degeneration of the (111) face and overlap of different crystal surfaces). Why is the re-entrant corner appro-
appropriate for promoting step nucleation? A study of the microstructure of the re-entrant corner is necessary, to answer this question.

The (100)(2 x 1) surface reconstruction creates an extra periodic bond chain (PBC), and so contributes to the crystallographic stabilization of this surface. Dimer bonds have to be broken to allow the addition of new atoms [9]. This is why the (100) surface always has a low growth rate and often leads a step growth.

Everson et al. [1] suggest that the PT might begin as a (111) contact twin (Σ = 3 twin) originating on the (111)-like face of a double step on a (100) surface. As the twin grows, a PT appears. When the PT forms, the dimer bonds at the re-entrant corner must be broken by the stronger bond reaction of atom A with atom B or atom C with atoms D and E (Fig. 4(a)). The resultant dangling bonds a and b are the appropriate sites for step nucleation. The nucleation atoms originate from surface diffusion or absorption from the gas phase. The step formed may propagate along either the parent crystal surface or the twin surface depending on the original nucleating structure and the thermal dynamic conditions. It is critical for the mirror plane of the twin to maintain continuous growth. Under certain conditions, the growth of the two crystal surfaces is a competitive process, which will lead to the formation of a step-like internal interface (the grain boundary) deep in the as-grown crystal (Fig. 4(b)). This process is known as the twin-step growth mechanism.

The analysis discussed above is confirmed by an investigation of the fracture surface of the thick diamond film by SEM. Fig. 4(c) is a cross-sectional view of the thick diamond film. A high-magnification view (Fig. 4(d)) reveals that the fracture surface exhibits regular cleavage steps oscillating across the grains. The height (a few hundred nanometers) of the step on the fracture surface is comparable with that on the film surface. This type of cleavage step has not been reported before. Combining the results of the study of surface morphology and the proposed twin-step growth mechanism, we believe that these surfaces are formed by transgranular cleavage [10] along grain boundaries in

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Fig. 4. (a) Structure of the nucleus of a PT viewed along the (110) surface direction common to both crystals. The long broken line indicates the mirror plane of the twin. The short broken lines indicate dimer bonds formed by surface reconstruction. The crosses indicate rupture of dimer bonds. (b) Schematic diagram of the formation process of cleavage steps. Arrows indicate the preferred step nucleation sites. (c) Cross-section of the thick (about 600 μm) diamond film. (d) Scanning electron micrograph of the cleavage steps on the fracture surface.
the crystal and that the cleavage steps are the result of competing growth of the twin and the parent crystal.

3.2. Steps on the {100} surface

By the formation of dimer bonds, \((2 \times 1)\) surface reconstruction makes diamond \{100\} faces behave like the \(F\) face in the CVD growth of diamond [9]. These steps on the reconstructed face create more dangling bonds for lateral growth. The steps on the \{100\} surface are square with closed edges parallel to the \(\langle 100\rangle\) directions (Fig. 1(b)), giving a minimal edge-free energy [9].

The closed edges of the step layers indicate that the crystal growth does not take place by the Burton–Cabrera–Frank [11] mechanism, i.e. it does not proceed by spiral growth using a screw dislocation. As discussed before, the step nucleation center is the re-entrant corner formed by PT.

Because of the competing growth of the twin and the parent crystal, the step nucleation is discrete and leads to multilayer square steps. The similar ‘on-off switching’ of the step nucleation activity in the homoepitaxial growth of diamond [3] may be due to the same process.

When distant from the nucleation center, the step edges gradually become wavy owing to the formation of kinks and surface defects or different propagation rates associated with surface absorption or surface diffusion of growth units. The step face is inclined at an angle that is difficult to measure accurately with the scanning electron microscope (Fig. 1(c)). The microsteps can pile up and form macrosteps that could be observed by SEM.

With lateral growth of step layers on the \(\langle 100\rangle\) surface, a large (90 \(\mu\)m) single crystal (Fig. 5) could be obtained in the thick film. Ravi and Joshi [12], using an oxyacetylene torch at high temperatures, have found evidence for ledge growth and lateral epitaxy of diamond leading to large (100–150 \(\mu\)m) single crystals with \(\langle 100\rangle\) surface orientation. The step growth mechanism in both heteroepitaxial and homoepitaxial diamond may provide a clue for single-crystal growth on non-diamond substrates for practical use.

3.3. Degeneration of \{111\} faces

The \{111\} faces are changed into three crossed planes perpendicular to the adjacent \{100\} faces. They are confirmed to be \{110\} faces by the geometric relationships. Fig. 6 shows a schematic diagram of the division of \{111\} into \{110\} faces, which can be identified on Fig. 1(b).

Kim et al. [13] demonstrated that the roughening of the octahedral faces is a result of degeneration of the \{111\} faces to \{100\} and \{110\} faces, and the resulting competitive growth rates of these two faces. Fig. 1(b) shows that the rough regions only appear at the edges of the \{100\} and \{111\} faces, and the whole \{111\} face has been entirely replaced by crossed \{110\} planes.

The \{110\} faces are not rare and their area is large. Badzian and Badzian [14] found that in the homoepitaxial growth of diamond, the \{110\} face is composed of microfacets with \(\langle 111\rangle\) planes. Zhu et al. [6] observed two-dimensional spiral steps on the \(\langle 110\rangle\) surface. Our results show that \{110\} faces proceed by a step growth mechanism with square step layers and closed edges parallel to \(\langle 110\rangle\) and \(\langle 100\rangle\) directions (Fig. 1(b)). The steps originate from either crossed lines of two \{110\} faces or re-entrant corners formed by twins. Further study of the twins on \{110\} faces is required.

4. Conclusions

Growth phenomena of thick diamond were investigated by SEM and a twin-step growth mechanism of the film was discussed. The results show that (1) the re-entrant corner formed by the penetration twin stimulates step nucleation due to the rupture of dimer bonds on the \(\langle 100\rangle\) surface, (2) cleavage steps on the fracture surface are formed due to the transgranular cleavage along the grain boundary which is formed by twin-step growth, (3) step growth is the main growth characteristic of \(\langle 100\rangle\) and \(\langle 100\rangle\) faces, (4) \{111\} faces degenerate into three \{100\} faces and (5) large single-crystal diamond

![Fig. 5. Large single crystal with \(\langle 100\rangle\) orientation on the surface of the thick diamond film.](image)

![Fig. 6. Schematic diagram of a cubo-octahedron diamond with \{111\} faces degenerated into \{110\} faces [13].](image)
and high-quality thick diamond film can be prepared using the twin-step growth mechanism.

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References