

Pressure Dependence of Growth Mode of HFCVD Diamond

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Abstract

Polycrystalline diamond films with surface morphologies of {100} and {111} facets were synthesized using hot filament assisted chemical vapor deposition (HFCVD) from a methane–hydrogen gas mixture. It is found that under the HFCVD conditions, metastable equilibrated growth of diamond crystal can be controlled by changing parameters. In the present case, the manner of the growth is obviously dependent upon ambient pressure, i.e. at higher pressure, diamond {100} is the favorable growth surface, whereas {111} is the favorable growth surface at lower pressure. This oriented growth of CVD diamond is discussed in terms of as-grown surface free energy (AGSFE) which is a function of surface structure and surface reactions. The results illuminate the development of oriented growth of HFCVD diamond by controlling growth conditions.

Keywords: Diamond; CVD; Crystal growth; Morphology

1. Introduction

Various morphologies and crystallographic orientations of CVD diamond crystals with different parameters are known [1–8]. Recently, highly oriented vapor-deposited diamonds have been reported [9–12]. It is usually believed that the surface planes are generally characterised by low indexes such as {100}, {111}, etc., and that the shape of a particular crystal is dependent on how it has grown [13]. In general, it was concluded by Yarb. and Messier [14] that equilibrated growth results in {111} faces as the growing surface, because the <111> directions are the slowest growth directions. As the deposition condition moves away from equilibrium, {100} cube faces appear initially, resulting in a mixture of growth faces and generally a more complex growth morphology. Further movement away from equilibrium can lead to a dominant {100} cube morphology in the later stages of growth evolution, unless the {110} faces become energetically favorable [14]. However, the equilibrium conditions were not defined.

There is little understanding of the CVD diamond steady-state surface structures and surface reactions during growth [15], but these can be expected to depend on deposition conditions. Most investigations in this area have employed gas concentration and temperatures of both filament and substrate. For example, Kobashi et al. [7] report {111} faceting at CH₄ concentration of

less than 0.4% and {100} faceting at CH₄ concentration between 0.5 and 1.2%. But their results are in contrast to those of Spitsyn et al. [3] who reported {100} faceting at a lower methane concentration. Table 1 shows the effect of substrate temperature (T_s), filament temperature (T_f) and methane concentration on morphologies of CVD diamond from several researchers. Unfortunately, some of these results are contradictory and have not been completely understood.

If all the preparation–morphology relations were understood, it would be possible to design diamond morphology for specific applications while, conversely, understanding the growth history of a film by examining its internal morphological evolution [14]. In this article, it is reported that CVD diamond has oriented growth tendencies under different ambient pressures.

2. Experimental details

The diamond films were grown on 10 × 15 mm² n-type Si(111) in a stainless steel chamber which has a base pressure of around 10⁻⁷ Torr maintained by a turbo pump. The Si substrate was scratched with diamond powders and was then cleaned with alcohol in an ultrasonic bath for 15 min. The chamber was pumped down to 6 × 10⁻³ Torr prior to hydrogen introduction. The ratio of hydrogen flow rates to methane in sccm

Table 1
Morphologies of CVD diamond under different growth conditions

Ref.	Method	Substrate and pretreatment	Conditions for {111} morphology	Conditions for {100} morphology
1	MWCVD	Si	700 °C(T_s)	1000 °C(T_s)
2	MWCVD	Si(100) scratched with diamond powder	2000 °C(T_r)	2100 °C(T_r)
3	MWCVD	Si, Mo, W	800 °C(T_s)	1000 °C(T_s)
4	MWCVD	Si(100) scratched with diamond powder	1050 °C(T_s)	950 °C(T_s)
5	MWCVD	Si(111) scratched with diamond powder	0.3% CH ₄	1.0–2.0% CH ₄
6	MWCVD	Si	0.5% CH ₄	2–4% CH ₄
1	MWCVD	Si	2% CH ₄	0.2% CH ₄
7	MWCVD	Si	0.3% CH ₄	0.8–1.2% CH ₄

was controlled carefully at 100:0.5. The mixing gases are introduced into the chamber flowing past a tungsten filament. The temperatures of the tungsten filament and of the substrate measured by an optical pyrometer and a K-type thermocouple were set at 2000 and 800 °C, respectively. In this experiment the pressures were set at 5 and 20 Torr respectively to investigate pressure effects on diamond growth. The surface morphologies of the growing surface were observed with SEM.

3. Results and discussion

The surface morphologies from the sample grown at 20 Torr for 20 h, shown in Fig. 1(a), consist of pure four-fold {100} facets. It is observed that the smooth flat {100} surface lay in different directions with no hillocks on the {100} facets. Fig. 1(b) shows the surface morphology of the sample grown at 5 Torr for 20 h. Almost all crystals have three-fold {111} facets. Many more hillocks are observed on the original {111} surfaces compared to the {100} surfaces. These surface morphologies indicate that the {100} surface is the more favorable growing surface under lower pressure, whereas the {111} is the more favorable surface under higher pressure.

The growth shape is an overall result of the growth process and contains a great deal of information on growth phenomena. It is well known that the eventual shape of the crystal depends on the growth rates in various directions and that a crystal is surrounded by those faces that are growing most slowly. Spitsyn et al. [3] described how the relative growth rate in the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions determines crystal shape. A parameter, Γ , was first defined by Spitsyn et al. [3] as the ratio of growth rate in the $\langle 100 \rangle$ to that of the $\langle 111 \rangle$ directions, i.e. $\Gamma = V_{100}/V_{111}$. In general, for Γ near $\sqrt{3}$, growth in $\langle 100 \rangle$ direction is fastest, with the result that growing surfaces are {111} and the isolated crystal is nearly octahedral. For Γ near $1/\sqrt{3}$, growth in $\langle 111 \rangle$ is fastest, with the result that growing surfaces are {100} and the isolated crystal almost cubic [2].

However, a major problem with Spitsyn's mode is

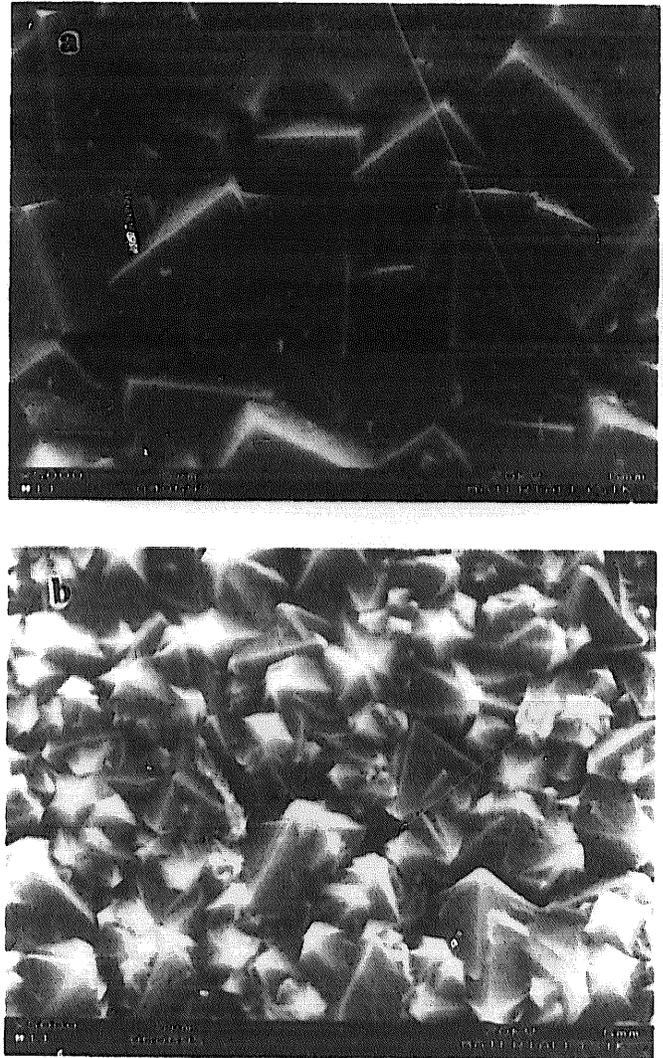


Fig. 1. (a) A typical {100} morphology of CVD diamond which is grown under 20 Torr and 0.5% CH₄ in hydrogen for 20 h; (b) a typical {111} morphology of CVD diamond which is grown under 5 Torr and 0.5% CH₄ in hydrogen for 20 h.

that there are no theoretical nor experimental reasons for defining Γ as a ratio of growth rates [16]. In fact it can be demonstrated geometrically that Γ should be a ratio of the distances from the Wulff point to surfaces $\{hkl\}$, i.e. $\Gamma = d_{100}/d_{111}$, where d_{100} and d_{111} denote the

distances from surfaces {100} and {111}, respectively. The distances d_{hkl} result essentially from different growth rates of corresponding {hkl} faces. Fig. 2 gives schematically the influence of Γ on morphology. The {100} face on the cubo-octahedron disappears by its rapid growth in the corresponding $\langle 100 \rangle$ direction, i.e. by $d'_{100}/d'_{111} > \sqrt{3}$. Obviously, the final growth morphology, octahedron, corresponds to $d_{100}/d_{111} = \sqrt{3}$.

In order to determine the relationship of d_{hkl} to diamond morphology, it is considered that the shape of a diamond crystal changes from cubo-octahedron to octahedron (Fig. 3). Let the length of the edge of the {100} faces be x and the length of the edge of the octahedron be a . The distances from the Wulff point to surfaces {100} and {111} are, respectively, $d_{100} = OP$ and $d_{111} = OR$. Geometrically it is readily obtained that $OR = OS/\sqrt{3} = (\sqrt{2}/2)a/\sqrt{3} = a/\sqrt{6}$, i.e. $d_{111} = a/\sqrt{6}$; $OP = OS - PS = (a-x)\sqrt{2}/2$, i.e. $d_{100} = (a-x)/\sqrt{2}$, therefore

$$\Gamma = \frac{d_{100}}{d_{111}} = \frac{(a-x)\sqrt{3}}{a} \quad (1)$$

For $x=0$, $\Gamma = \sqrt{3}$, then the growth shape is an octahedron. For $x=a/2$, $\Gamma = \sqrt{3}/2$, is the condition for a cubo-octahedron.

On the other hand, if γ_{100} and γ_{111} denote the

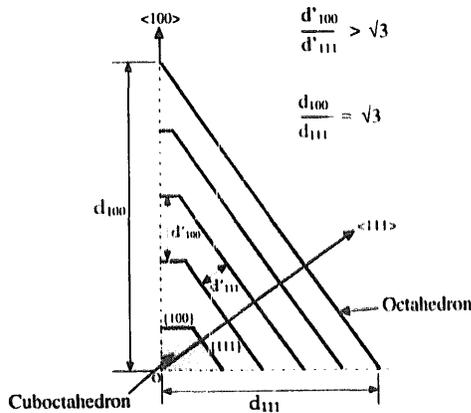


Fig. 2. Section through a crystal growing on planes {100} and {111}. The {100} face disappears by its rapid growth in the corresponding $\langle 100 \rangle$ direction. During growth, $d'_{100}/d'_{111} > \sqrt{3}$. The final growth morphology, an octahedron, corresponds to $d_{100}/d_{111} = \sqrt{3}$.

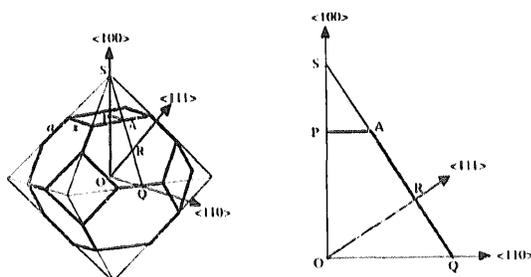


Fig. 3. The shape change from octahedron to cubo-octahedron.

surface free energies per unit area for {100} and {111} respectively, the total surface free energy of the cubo-octahedron in Fig. 3 is $\gamma = 6x^2\gamma_{100} + 2\sqrt{3}(a^2 - 3x^2)\gamma_{111}$. The volume of the crystal is $V = \sqrt{2}/3 (a^3 - 3x^3)$. For continuous growth of an equilibrated crystal, the condition is that

$$\frac{\partial \gamma / \partial a}{\partial V / \partial a} = \frac{\partial \gamma / \partial x}{\partial V / \partial x}, \text{ i.e. } \frac{4\sqrt{3}a\gamma_{111}}{\sqrt{2}a^2} = \frac{12x\gamma_{100} - 12\sqrt{3}x\gamma_{111}}{-3\sqrt{2}x^2} \quad (2)$$

whence

$$r = \frac{\gamma_{100}}{\gamma_{111}} = \frac{(a-x)\sqrt{3}}{a} \quad (3)$$

For $x=0$, $r = \sqrt{3}$ is the condition for an octahedron, whereas $x=a/2$, $r = \sqrt{3}/2$, is the condition for a cubo-octahedron.

Considering changes between cubo-octahedron and cube, a similar calculation is carried out and the expressions are obtained as follows:

$$\Gamma = \frac{d_{100}}{d_{111}} = \frac{b\sqrt{3}}{3b-2y} \quad (4)$$

and

$$r = \frac{\gamma_{100}}{\gamma_{111}} = \frac{b\sqrt{3}}{3b-2y} \quad (5)$$

where b is the edge length of the original cube and y is the length needed to create a {111} face on each corner. For $y=0$, $\Gamma = 1/\sqrt{3}$ and $r = 1/\sqrt{3}$ the growth shape is a cube. For $y=b/2$, $\Gamma = \sqrt{3}/2$ and $r = \sqrt{3}/2$ the conditions are for a cubo-octahedron.

Comparing Eqs. (1) and (3) as well as Eqs. (4) and (5), a demonstration of the Wulff theorem for the low index surfaces of {100} and {111} is obtained:

$$\frac{d_{100}}{d_{111}} = \frac{\gamma_{100}}{\gamma_{111}} \quad (6)$$

It states that the distance from Wulff point to a certain surface, which may be considered as the thickness of layer deposited on that face [17], is directly proportional to its surface free energy per unit area. The surface free energy plays an important role in determining the morphology of the crystal. Generally, for $r \geq \sqrt{3}$ the octahedron should result and if $r \geq 1/\sqrt{3}$, then the cube. For values in between, the intermediate shapes should be formed: truncated octahedron for $2/\sqrt{3} < r < \sqrt{3}$, the cubo-octahedron for $r = 2/\sqrt{3}$ and truncated cube for $1/\sqrt{3} < r < 2/\sqrt{3}$.

In the case of strongly covalently bonded materials, the surface free energy is simply equal to the energy per unit area of surface associated with breaking bonds that would connect the crystal to that occupying the other

half of space [18]. The surface free energy of diamond is therefore given by [19]

$$\gamma_{hkl} = \frac{h}{(h^2 + k^2 + l^2)^{1/2}} \frac{3E^0}{8d_0^2} \quad (7)$$

where E^0 and d_0 denote, respectively, the energy and the length of the C–C bond in diamond. It is obvious that the ratio between surface free energies of {100} and {111} surfaces, $\gamma_{100}/\gamma_{111}$, equals $\sqrt{3}$, implying that the equilibrium shape of diamond should be an octahedron which displays the {111} surface [20].

However, in the case of diamond growth, the surface free energy must be different from the ideal one. Wells [17] points out that during the growth process, the surface free energy is a function not only of the atomic structure of the surface but also of all interactions between surface atoms and foreign atoms which may be present. This surface free energy is called as-grown surface free energy (AGSFE). Based on the Wulff theorem, it is reasonable to expect that diamond growth morphology may be determined by the AGSFE, depending on both the surface configuration and the surface reactions that provide the diamond growth. Obviously, it is very difficult to determine AGSFE quantitatively because the surface reactions may vary with growth environment, depending on the as-grown surface state and the parameters of temperature, pressure and composition.

In the present case, the AGSFE of diamond during the CVD process may depend on ambient pressure. It is evident that the ratio of the AGSFE, $\gamma_{100}/\gamma_{111}$, is changed from $\sqrt{3}$ to $1/\sqrt{3}$ when the pressure decreases from 20 to 5 Torr. It implies that the {111} surface grows fast under a pressure of 20 Torr and the {100} surface grows fast under a pressure of 5 Torr.

4. Conclusion

Different morphologies of HFCVD diamond are obtained with two ambient pressures. Under lower pressure, 5 Torr, {111} is the surface morphology. Otherwise under higher pressure, 20 Torr, {100} is the surface morphology. This phenomenon may be understood as a result of the influence of the pressure on AGSFE.

Under higher pressure, the ratio of the AGSFE between the diamond {100} and {111} is increased to around $\sqrt{3}$, resulting in the {111} growing surface, whereas under the lower pressure, the ratio is decreased to around $1/\sqrt{3}$, resulting in the {100} growing surface.

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