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A geometric model of growth for cubic crystals: Diamond

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ABSTRACT

A mathematical and software implementation of a geometrical model of the morphology of growth in a cubic crystal system, such as diamond, is presented based on the relative growth velocities of four low index crystal planes: {100}, {110}, {111}, and {113}. The model starts from a seed crystal of arbitrary shape bounded by {100}, {110}, {111} and/or {113} planes, or a vicinal (off axis) surface of any of these planes. The model allows for adjustable growth rates, times, and seed crystal sizes. A second implementation of the model nucleates a twinned crystal on a {100} surface and follows the evolution of its morphology. New conditions for the stability of penetration twins on {100} and {111} surfaces in terms of the alpha, beta, and gamma growth parameters are presented.

1. Introduction

Early on in the growth of diamond crystals by chemical vapor deposition (CVD) it was observed that the crystal habit was bounded by the general appearance of several low index planes [1–3]. Four crystal faces with the following Miller indices: {100}, {110}, {111}, {113} were observed under varying growth conditions [4,5]. However, close microscopic examination of these planes often indicated that they were not atomically smooth, but rather displayed steps of various heights. For the purposes of this paper, this 'roughness' which is likely to be important to the local stereochemical modeling of the growth chemistry [6,7], will be ignored in order to focus on a model of the more macroscopic growth features. The macroscopic crystal shape observed most often was cubo-octahedral and was described by a parameter, alpha, which is proportional to the growth velocity of the cube face, {100}, to the octahedral face, {111} [8,9]. Only the slowest growing crystal facets are observed and the relative growth rate of each facet depends on complex factors such as the flux of reactive species to the surface, the surface temperature, and surface structure. Hence, depending on the growth conditions, not all facets will be observed at any given time. In 2006, a morphological growth model which included the possibility of the four observed faces, {100}, {110}, {111}, {113}, was introduced which described the crystal growth morphology in terms of three parameters, alpha, beta, and gamma, defined below [10]. The results of this model, but not the means for computation, have been thoroughly described in multiple subsequent papers [11–15]. The purpose of the present paper is to present a theory behind the implementation of a morphological growth model for diamond (and potentially, other cubic crystals), demonstrate the implementation of the model in readily available software (Wolfram Mathematica), generalize the model to off axis cut surfaces (vicinal) of the initial seed crystal, and to extend the model to demonstrate the morphology of a simple twinned crystal appearing on the {100} face.

Crystal twinning is very commonly observed CVD diamond growth [8,9,16]. Twinning usually occurs on a local {111} plane, and can have the impact of degrading the quality of the material [16–19]. For this reason, the model presented here has been modified to include the nucleation of a twin crystal on the top {100} surface of a seed crystal to show how the morphology of the twin progresses with the alpha, beta, and gamma growth parameters. Conversely, it may be possible to experimentally determine these parameters from the morphology of the twinned crystal in the early stages of growth.

2. Principles of the model

Notation:
3-dimensional vectors are in bold, e.g. $\mathbf{r} = (r_x, r_y, r_z) = (r_1, r_2, r_3)$.
Four-dimensional vectors have an arrow above them, e.g. $\vec{\boldsymbol{r}} = (\boldsymbol{r}, 1)$.
The inner product of two vectors for any number of dimensions is $\langle \boldsymbol{x}, \boldsymbol{y} \rangle = \sum_i x_i y_i$.
The norm of a vector is $\|\boldsymbol{x}\| = \sqrt{\langle \boldsymbol{x}, \boldsymbol{x} \rangle}$.

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2.1. Constructing the polyhedron

The geometric model assumes that there are four directions of growth in the diamond crystal which are normal to the four crystal faces enumerated with the following Miller indices: {100}, {110}, {111}, {113}. Taking all possible permutations and reflections of these vectors, we obtain 50 different growth vectors, collectively denoted as <100>, <110>, <111>, <113>. Each of the vectors is normal to a plane that moves at a constant speed away from the origin (0,0,0) ("the $\boldsymbol{n}$ plane"). For a dimensionless normal vector $\boldsymbol{n}$, call the corresponding speed $V_{\boldsymbol{n}}$ (the velocity vector itself is $V_{\boldsymbol{n}}\hat{\boldsymbol{n}}$, where $\hat{\boldsymbol{n}}$ is the unit vector codirectional with $\boldsymbol{n}$).

The crystal itself is a convex polyhedron $P(t)$, which is the intersection of all the negative half- spaces of the 50 planes (the negative half-space of a uniformly moving n plane at time t is the half-space covered by the plane over the time interval $(-\infty,t)$).

As we will see later, the shape of the crystal depends only on the ratios of the speeds V_{100}, V_{110}, V_{111}, V_{113}, hence the following reduced parameters are introduced:

$$\alpha = \frac{\sqrt{3}V_{100}}{V_{111}},\ \beta = \frac{\sqrt{2}V_{100}}{V_{110}},\ \gamma = \frac{\sqrt{11}V_{100}}{V_{113}}$$

If we introduce a more general and consistent notation of

$$\alpha_n = \frac{\|\boldsymbol{n}\|\, V_{100}}{V_n}$$

then $\alpha = \alpha_{111}$, $\beta = \alpha_{110}$ and $\gamma = \alpha_{113}$, whereas $\alpha_{100} = 1$. Note that V_n is invariant with respect to reflections and permutations of the axes. We shall further refer to α_n as *the growth parameter of the n plane*.

The equation of the $\boldsymbol{n}$ plane at time $\boldsymbol{t}$ is

$$\langle \boldsymbol{r}, \boldsymbol{n}\rangle = d_n l_0 + \|\boldsymbol{n}\|\, V_n t, \quad \boldsymbol{r} \in \mathbb{R}^3$$

where d_n is a dimensionless parameter which controls the initial position of the plane (at $t = 0$) and l_0 is taken to be the initial size of the crystal along the x-axis. In fact, the distance from the origin to the n plane at time $t = 0$ is equal to $\frac{d_n l_0}{\|\boldsymbol{n}\|}$.

It is now natural to introduce dimensionless *normalized Cartesian coordinates* $\hat{\boldsymbol{r}}$, such that

$$\boldsymbol{r} = V_{100} t \hat{\boldsymbol{r}}.$$

Obviously, division by t is not practical in computer calculations, but using dimensionless coordinates makes sense in a theoretical treatment. Then the equation of the $\boldsymbol{n}$ plane $\pi_{\boldsymbol{n}}$ becomes

$$\langle \hat{\boldsymbol{r}}, \boldsymbol{n}\rangle = d_{\boldsymbol{n}} \frac{l_0}{V_{100} t} + \frac{\|\boldsymbol{n}\|\, V_{\boldsymbol{n}}}{V_{100}},$$

which is equivalent to

$$\boldsymbol{\pi_n}: \quad \langle \hat{\boldsymbol{r}}, \boldsymbol{n}\rangle = \frac{2Ld_{\boldsymbol{n}}}{t} + \frac{\|\boldsymbol{n}\|^2}{\alpha_n},$$

where $L = \frac{l_0}{2V_{100}}$.

We see that the set of parameters L, $d_{\boldsymbol{n}}$ and $\alpha_{\boldsymbol{n}}$ completely control the shape of the crystal at all times t, with L being the only parameter with dimensions (L controls the scaling of the time axis and the initial size of the crystal).

Computationally, the easiest way to specify a plane is by providing its normal vector $\boldsymbol{n}$ and the point on that plane closest to the origin, which is the intersection of the plane with the straight line going along $\boldsymbol{n}$. Suppose that this point is

$$\hat{\boldsymbol{r}}_n = \frac{1}{p_{\boldsymbol{n}}}\boldsymbol{n}.$$

Then, from the equation of the plane,

$$p_{\boldsymbol{n}} = \frac{t}{\frac{2Ld_{\boldsymbol{n}}}{\|\boldsymbol{n}\|^2} + \frac{t}{\alpha_{\boldsymbol{n}}}}.$$

Note that, although this formula does not look very simple, these parameters are natural because

$$\lim_{t\to\infty} p_{\boldsymbol{n}} = \alpha_{\boldsymbol{n}}.$$

The numbers $p_{\boldsymbol{n}}$ are the *effective values of the growth parameters* $\alpha_{\boldsymbol{n}}$ at finite times. The same observation proves that the shape of the crystal stabilizes at large times and is determined solely by the parameters α_{110}, α_{111} and α_{113}. Moreover, independent of the initial shape of the crystal, its shape at infinite time is always completely symmetrical (with respect to reflections and permutations of the axes), assuming that growth in all directions is allowed.

Finally, the initial shape of the crystal is determined by the 50 parameters $d_{\boldsymbol{n}}$. When the initial shape of the crystal contains only some of the 50 possible faces, the remaining planes have undefined values of $d_{\boldsymbol{n}}$. From the perspective of crystal growth, it is natural to take such values of $d_{\boldsymbol{n}}$ that the corresponding planes are *tangent* to the initial polyhedron.

Since the slightly more convenient way of specifying a plane is to specify any one of its points, we need a way to calculate $d_{\boldsymbol{n}}$ from that data. Say, we know that the plane $\pi_{\boldsymbol{n}}$ contains a point $\boldsymbol{r} = l_0\, \boldsymbol{v_n}$ at $t = 0$. Then, from the equation of the plane, we have

$$d_{\mathbf{n}} = \langle \boldsymbol{v_n}, \boldsymbol{n}\rangle.$$

The equation of the $\boldsymbol{n}$ plane for $t > 0$ is then

$$\boldsymbol{\pi_n}: \quad \langle \hat{\boldsymbol{r}}, \boldsymbol{n}\rangle = \frac{2L}{t}\langle \boldsymbol{v_n}, \boldsymbol{n}\rangle + \frac{\|\boldsymbol{n}\|^2}{\alpha_{\boldsymbol{n}}},$$

which, when combined with our definition of $p_{\boldsymbol{n}}$, is equivalent to

$$\boldsymbol{\pi_n}: \quad \langle \hat{\boldsymbol{r}}, \boldsymbol{n}\rangle = \frac{\|\boldsymbol{n}\|^2}{p_{\boldsymbol{n}}}.$$

In order to make the equations even simpler, we introduce the following 4-dimensional vectors, as is usually done in computational geometry. Instead of $\hat{\boldsymbol{r}} = (\hat{x}, \hat{y}, \hat{z})$, we take

$$\overrightarrow{\boldsymbol{r}} = (\hat{x}, \hat{y}, \hat{z}, l) = (\boldsymbol{r}, l)$$

and instead of $\boldsymbol{n}$ and $p_{\boldsymbol{n}}$ take

$$\overrightarrow{\boldsymbol{n}} = \left(n_x, n_y, n_z, -\frac{\|\boldsymbol{n}\|^2}{p_n}\right) = \left(\boldsymbol{n}, -\frac{\|\boldsymbol{n}\|^2}{p_n}\right).$$

Then the equation of the n plane is

$$\pi_{\boldsymbol{n}}: \quad \left\langle \overrightarrow{\boldsymbol{r}}, \overrightarrow{\boldsymbol{n}} \right\rangle = 0.$$

Moreover, the negative half-space $P_{\boldsymbol{n}}^-$ is precisely the set of all the points $\overrightarrow{\boldsymbol{r}} = (\hat{\boldsymbol{r}}, l)$ that satisfy the inequality

$$P_{\boldsymbol{n}}^-: \quad \left\langle \overrightarrow{\boldsymbol{r}}, \overrightarrow{\boldsymbol{n}} \right\rangle \leq 0.$$