ANALYSES OF STRIATED FACES AND HABIT CHANGE OF POLAR CRYSTALS: APPLICATION OF AN EXTENDED PBC METHOD

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Abstract. Severe contradictions still exist between the theoretical morphology deduced by the PBC method and the observed morphology, if not only external morphology but also surface microtopography of crystal faces are taken into consideration. Representative examples are well developed faces yet exhibiting only striations, and development of polar faces on non-centro symmetric crystals. By extending the original PBC method to include varying surface diffusibility model, these problems were analyzed. It was demonstrated that depending on growth conditions which may have relations with the sizes of growth unit, morphological characteristics may change.

1. Introduction

The PBC method (HARTMAN and PERDOK1) is based on an assumption that the growth unit is atomic or ionic entities, since it considers only interatomic bondings. It predicts the “structural morphology” of a crystal, which in principle does not relate to thermodynamic parameters. Although the structural morphology deduced from the PBC analysis often shows a close similarity with the observed growth morphology, there still are, in many cases, severe controversies, if not only external morphology, but also surface microtopography are taken into consideration. Well developed habit-controlling faces often exhibit only striations, and not step patterns, which makes a contradiction to the theoretical expectation. Scalenoahedral faces of calcite serve as a representative example. Development of polar faces is another example.

If growth unit is changed, the morphology should be not the same as that deduced based on atomic entities. It is the purpose of this paper to analyze how morphology of a crystal will be modified when growth unit is changed,
and to see whether hitherto unexplained phenomena, like well developed striated faces or development of polar faces, could be understood or not. In other words, the PBC method is extended by introducing a concept of larger growth unit.

By changing the size of growth units, we may relate the morphology of a crystal to the growth parameters since the growth units may vary depending on the growth conditions. Namely, we try to deduce growth morphology, not structural morphology, by introducing larger growth units.

The basic assumptions in the proposed extended PBC method are as follows:

1. Growth units change their mean size depending on growth conditions, and the sizes are more or less uniform under a given growth condition (Fig. 1). Sub critical size is assumed for them.

2. Depending on the size of growth unit, the thickness of a slice is varied.

3. The thickness of a slice must be varied with discrete values \((n/m d_{hkl}, n, m; \text{ integer})\).

In the analysis based on this extended PBC method,\(^3\) we shall pay our attention to the problems of striated faces and polar crystals, since severe contradictions between theory and experiment is seen in these two problems.

2. Striated Faces

Parallel straight lines appearing on crystal faces are called "striations". Most crystals exhibit striations on some faces. Striations usually appear as a set of parallel straight lines, in one crystallographic direction on a face. In classic textbook of mineralogy or crystallography, they are considered as due to oscillatory combination of a set of faces.

![Diagram of number vs size of growth units for various growth conditions.](image)

**Fig. 1.** Diagram of number vs size of growth units for various growth conditions.
According to Sunagawa's classification, three types may be distinguished among crystal faces on which only striations are seen:

Type 1. Vicinal faces. These are high index $S$ faces and develop small. They appear as profiles consisting of piled-up steps developing on the neighboring $F$ face.

Type 2. An $S$ face on the PBC analysis, yet develops large to control the habit. $\{hkil\}$ faces of calcite are a representative example, and exhibit only striations under any growth conditions.

Type 3. An $F$ face on the PBC analysis, and exhibit either striations or step patterns depending on growth conditions.

Type 4. Striations due to elongated growth layers. $\{100\}$ faces of pyrite exhibit such striations. This is an $F$ face.

There is no controversy between theory and experiment as to Type 1 and Type 4 striations. However, as to the surface characteristics of Type 2 and Type 3, we have to find appropriate explanation. In what follows we shall pay our attention to Type 2 and 3 striations.

In analyzing the origin of striations, two approaches were adopted. The first one is directly deduced from the Assumption 2. Namely, slice to be considered can vary according to growth conditions. If a slice is halved, an $F$ face in the original PBC analysis transforms to an $S$ face on which only striations will appear. In Fig. 2, this is schematically shown for two possible cases. We call this method a “Variable slice method (V-method)”.

The other approach is based on the analysis of anisotropy of surface diffusibility of adatoms. This is in principle applicable to ionic or partly ionic crystals. In this method growth units are assumed to be ionic. Since this method corresponds to the treatment using smallest growth units in V-method, this can be applied only for crystals grown under low supersaturation condition. We call this method “Surface diffusion anisotropy method (S-method)”.

When the surface diffusion is the rate determining process, surface diffusibility depending on the orientations causes anisotropic advancement of growth layers. In this method striations are understood as an elongated growth layer.

In this case, the anisotropy of surface diffusibility would become more effective at lower temperature, because the mobility of ions diminishes. Thus, in this method temperature plays a more important role than supersaturation in relation to the appearance of striations. In general, striations will appear when a crystal grows at lower temperature range.

On the other hand, in the V-method, hypothetical growth units can vary their sizes depending on the supersaturations. Thus the thickness of a slice can vary depending on supersaturations. In this method the supersaturation plays a more important role. Since we may assume that the size of growth unit decreases as supersaturation diminishes, $F$-faces will transform to $S$-face as
decreasing supersaturation, leading to the appearance of striations. The direction of striations are parallel to the direction of stronger PBC. In other words, chain energies have strong anisotropy within a crystal face, i.e., there is a direction in which the chain energy is greater than the other directions. This leads to the appearance of striations. According to the V-method, striations would be exaggerated under lower supersaturation. Under high supersaturation striations will not appear.

In actual cases, both effects i.e. anisotropy in surface diffusibility and that due to the change of growth units, may play a co-operative role in creating striations on crystal faces. In Fig. 3, this is schematically shown. Striations will not appear under higher supersaturation and higher temperature range, whereas they will appear under lower supersaturation and lower temperature range. This prediction qualitatively agrees with the general tendency that natural crystals show striations more frequently than artificial crystals. Figures 4 and 5 show summaries of observations on striations on quartz and pyrite, respectively, showing well agreement with the prediction in Fig. 3. In
what follows, we shall apply the two methods to quartz and pyrite crystals, and see how striations develop.

2.1 Quartz

Striations parallel to the horizontal axis are commonly observed on \{10\overline{1}0\} faces of natural quartz crystals, whereas \{10\overline{1}1\}, \{01\overline{1}1\} always exhibit triangular or circular step patterns. On the contrary, synthetic quartz crystals grown from NaOH or KOH solutions show eccentric growth spirals, not striations, on the \{10\overline{1}0\} faces, when they are grown from alkali solution. In general, circular step patterns are seen on \{10\overline{1}0\} and \{01\overline{1}1\} faces of synthetic quartz crystals. Recently, it has been reported by Hosaka and Taki that synthetic quartz crystals also exhibit striations on prism face, when they are grown from KCl or NaCl solution. Therefore, the surface microtopographs of \{10\overline{1}0\} faces vary from the one showing step patterns to another showing only striations depending on the growth conditions.

Quartz has three independent PBC's, [00.1], [01.1], [10.0], which
Fig. 3. Schematic morphodrom for striations in relation to supersaturation ($\sigma$) and temperature ($T$).

Fig. 4. Summary of observations of striations of [10\overline{1}0] faces on quartz crystals. They are arranged so as to correspond to the growth conditions $\sigma$ and $T$.\textsuperscript{5-7}
construct the three $F$-forms, \{10\overline{1}0\}, \{10\overline{1}1\} and \{01\overline{1}1\}.\textsuperscript{5}

2.1.1. \textit{V-method (broken bond model)}

Prismatic face (1100) is composed of three PBC's [00.1](2.47), [11.0](0.68) and [11.1](2.50), where in parentheses “minimum thickness” $d_{hkl}$ which is the minimum thickness to construct the corresponding PBC, are also shown. Figure 5 shows a projection parallel to [11.0]. Bonds forming PBC's are also shown. For (1100) face, the unit thickness of identical face is $d_{1100}=4.25$ Å. By broken bond method $E_{\text{att}}(1100)=2$ bonds/unit. According to the V-method, a half slice taken for calculating surface energy will be identical (or nearly identical) for each half. The two half slices, 1/2 A and 1/2 B are also shown. Their unit thickness is $d_{1100}/2=2.125$ Å. The surface energy of each slice is the same, $E_A^{R}=E_B^{R}=2$ bonds/unit. Since the exposure of silicon atom which may lead to unsatisfied bond should be avoided, we shall introduce the following limitation when a slice is chosen “Choose a slice with which the surface always possesses oxygens”. Figure 6 shows slices chosen in this manner. The PBC [11.0] which has $d_{\text{min}}=0.68$ Å, can run through a slice 1/2 A. On the other hand [00.1] PBC has $d_{\text{min}}=2.47$ Å, so it can run through neither 1/2 A slice nor 1/2 B slice. [11.1] PBC has $d_{\text{min}}=2.25$ Å. [11.1] can not run through 1/2 slices. Thus

\textbf{Fig. 5.} Summary of observations of striations on pyrite crystals. They are arranged according to their growth conditions.\textsuperscript{9-12}
if half slices are taken, [11.0] PBC becomes the only effective PBC within this face. In Fig. 6 s-s' shows the surface of slice 1/2 B indicating that it does not contain PBC. Thus possible site where a new SiO₂ molecule is incorporated to the block belonging to the 1/2 A (hatched area) are A, B, ..., and F. The site E or F has two bonds to the crystal but the other sites have only one. This implies that the growth will take place more rapidly in [11.0] direction than [00.1] direction, which will result in a strong anisotropy. The (1010) face will thus show striations.

Major rhombohedral r {0111} face contains three PBC's [10.1], [01.1] and [11.1]. These PBC's have the same $d_{\text{min}} = 0.9$ Å, and they are all equivalent for the V-method. The slice $d_{0111}$ cannot be halved. Consequently this face will exhibit equidirectional surface microtopograph and will show no striation under any growth conditions.

Minor rhombohedral z {1011} face contains three PBC's [10.0], [01.1] and [11.1]. They have the same $d_{\text{min}} = 1.4$ Å within this face. Thus similarly as (0111), this face will show no striations.

2.1.2. V-method (point charge model)

In this treatment Sr⁺⁺ and O⁻⁻ are assumed. The chain energies of each PBC together with the values of their half slices are tabulated in Table 1. For
TABLE 1. Chain energies in each direction on a quartz by point charge model which are calculated by CHAIN[2].

<table>
<thead>
<tr>
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<th>full</th>
<th>1/2 A</th>
<th>1/2 B</th>
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<tbody>
<tr>
<td>{0110}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[00.1]</td>
<td>59.27</td>
<td>36.35</td>
<td>16.57 (e^2/Å)</td>
</tr>
<tr>
<td>[11.0]</td>
<td>57.00</td>
<td>38.44</td>
<td>16.65</td>
</tr>
<tr>
<td>[10.1]</td>
<td>56.34</td>
<td>35.23</td>
<td>16.11</td>
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<tr>
<td>{0111}</td>
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<td></td>
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<tr>
<td>[10.0]</td>
<td>56.65</td>
<td>29.74</td>
<td>11.89</td>
</tr>
<tr>
<td>[11.1]</td>
<td>56.98</td>
<td>31.08</td>
<td>12.82</td>
</tr>
<tr>
<td>[01.1]</td>
<td>56.70</td>
<td>31.10</td>
<td>12.90</td>
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<td>{0111}</td>
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<tr>
<td>[10.0]</td>
<td>56.90</td>
<td>35.10</td>
<td>11.63</td>
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<tr>
<td>[11.1]</td>
<td>57.73</td>
<td>35.01</td>
<td>11.89</td>
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<tr>
<td>[01.1]</td>
<td>57.73</td>
<td>35.91</td>
<td>11.89</td>
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</table>

(1010) face, $E_{ch}$ [00.1] is slightly higher than the other chains. This may correspond to the elongation along [00.1] of prism face. But in the half slice A and B, there is not much difference in chain energies of the three PBC's. This leads to expect that the surface microtopograph will be elongated along [11.0] if a slice is halved. In the case of major and minor rhombohedral faces, [10.0] chain is slightly weaker than the other chains. This may correspond to the morphology of isosceles triangular growth pyramid.

2.1.3. S-method

For prismatic faces, as shown in Fig. 7, a projection along [12.0] the

![Diagram](image-url)

Fig. 7. A projection normal to (1010). Closed circles are Si^{4+} ions and open circles are O^{2-} ions.
surface of (10\overline{1}0) can be divided into regions of positive ions extending in the [10.0] direction and alternative similar regions of negative ions. Such arrangement of ions on the surface leads to the following difference of surface diffusibility

$$D_{[00.1]} < D_{[10.0]}.$$

where $D_{[uvw]}$ is the surface diffusibility along the direction $[uvw]$. On this face if growth is controlled by surface diffusion, growth layers are expected to elongate along [10.0]. On the $z$ face, it is evident that there is no such directions. No dependence of surface diffusibility on orientations is expected for this face. Growth layers will advance following the symmetry of the face. On the $r$ face the situation is the same as for the $z$ face. This face has no direction to cause a difference of surface diffusibility. From the aforementioned point of view, only [10\overline{1}0] face is expected to show striations, when crystals grow under low supersaturation condition.

Consequently striations on the $m$ {10\overline{1}0} face, which are elongated growth layers, can be explained by both the V-method and S-method. In both methods, striations are expected to occur when a crystal grows under low supersaturation. This probably explains why synthetic quartz growth from alkaline solutions does not show striations, whereas striations develop in KCl or NaCl solution, where growth rate is much slower than alkaline solution, suggesting much lower effective supersaturation.

2.2 Pyrite

It is well known that {100} and {210} faces of most pyrite crystals exhibits striations parallel to [001]. It is also known that a few pyrite crystals show striations perpendicular to [001], i.e. parallel to [120] on their {210} faces. The striations of the former type on {210} faces are called "positive striations", and the latter type "negative striation",\textsuperscript{9} (Fig. 8). Recently pyrite crystals have been synthesized by various methods.\textsuperscript{10-13} The observations on natural and synthetic pyrite crystals are summarized in Fig. 5.

![Fig. 8](image_url)

**Fig. 8.** Schematic figure to show positive (left, //[001]) and negative striations (right, //[120]) on {210} of pyrite (after Endo and Sunagawa\textsuperscript{9}).
2.2.1. \textit{V-method (broken bond model)}

The (010) face is composed of [100], [001], [101], [10\overline{1}] (1.23); [102], [10\overline{2}] (3.30); [201], [20\overline{1}] (2.70) PBC’s.\textsuperscript{14} For (010) face, slice \(d_{010}\) must be halved to \(d_{020}\) by the extinction rule. Further halving is impossible. Although only [100], [001] and [101] PBC’s will be effective if \(d_{020} = 2.70\, \text{Å}\) is taken, the face (010) still remains as an \(F\)-face and there are no directions in which PBC’s become stronger than the other directions. Therefore the surface features of this face should be square.

The (210) face is composed of [001] (0.55); [\overline{1} 20], [121], [\overline{1}2\overline{1}] (1.59) PBC’s. When a half slice \(1/2\, d_{210}\) is taken, only [001] PBC becomes effective, which implies that the face transforms from an \(F\)-face to an \(S\)-face which should exhibit striations in [001] direction.

The (111) face is constructed by [\overline{1}10](2.41); [\overline{1}1\overline{2}](1.70) and equivalent PBC’s. It is evident when \(1/2\, d_{111}\) slices are taken, there are no effective PBC’s in this face. The face becomes a \(K\)-face.

2.2.2. \textit{V-method (point charge model)}

From a crystal chemical point of view, this model may not be applicable, since the bond type of pyrite is almost covalent. However we shall apply this model as representing an extreme case. Table 2 summarizes the chain energy of each face. These values lead to the following relations.

\{100\}; \(E_{cb}[010] > E_{cb}[001]\) for any case.

This face would exhibit elongated growth layers along [010] direction. This contradicts with the observations.

\{210\}; In full slice, both directions have almost similar chain energies. But in \(1/2\) A slice, \(E_{cb}[120] > E_{cb}[001]\). This would correspond to the negative striations.

\{111\}; Both directions have almost same chain energies in any case.

2.2.3 \textit{S-method}

\{100\}; In both [100] and [010] directions, cations and anions are arranged in narrow regions with the same sign, respectively. But [010] direction is parallel to the potential valley or ridge, thus an ion can diffuse easier in this

\begin{table}
\caption{Chain energies in each direction on a pyrite.}
\begin{tabular}{|c|c|c|c|}
\hline
 & Full & 1/2 A & 1/2 B (e\textsuperscript{2}/Å) \\
\hline
{100} & & & \\
[001] & -3.781 & -0.846 & -1.064 \\
[010] & -5.169 & -1.283 & -1.686 \\
\hline
{210} & & & \\
[001] & -9.952 & -1.950 & -5.849 \\
\hline
\end{tabular}
\end{table}
direction. On the other hand, [100] direction is vertical to the potential valley or ridge, thus an ion has to overcome the potential barrier to diffuse along this direction.

{210}; It is evident that in [\bar{1}20] direction, cations and anions are arranged in rows, respectively. On the other hand, in [001] direction, such a linear arrangement is not seen. It follows from this that [\bar{1}20] direction is the easiest diffusion direction on the (210) face. Growth layers are expected to elongate along this direction.

{111}; There is no particular direction along which ions can diffuse easier.

2.3 Summary on striations

The results of applications of the two methods to actual examples may be summarized as follows;

Quartz; Both methods predict striations to occur on the prism faces but not on rhombohedral faces, and that striations will be more exaggerated when crystals grow under either lower temperature or lower supersaturation. This is consistent with the observations on natural, NaOH, KOH grown and NaCl, KCl grown synthetic quartz crystals. From the difference between NaOH, KOH solution and NaCl, KCl solution it is conjectured that supersaturation plays a more important role than temperature.

Pyrite; Elongated growth layer observed on {100} are explained by S-method. On {210}, V-method leads to [001] positive striations and S-method leads to [\bar{1}20] negative striations. It follows from this that the negative striations will appear under lower supersaturation condition than for positive striations.

3. Polar Crystals

The polar development of faces in non-centrosymmetric crystals cannot be understood on the basis of the original PBC method alone, since for the two polar faces PBC’s are exactly the same. Monier and Kern\(^{(15,16)}\) investigated the morphology of polar crystals grown from the vapor phase, and Hartman\(^{(17)}\) discussed the morphology of sphalerite on the basis of polarization energy. His conclusion was that (\overline{1}1\overline{1}) face should develop larger than (111), which supported Monier and Kern’s observation. On the contrary Komatsu and Sunagawa\(^{(18)}\) reported that (111) face are larger than (\overline{1}1\overline{1}) faces for natural sphalerite. As mentioned here, there is a severe conflict between theory and observations. We shall apply the extended PBC method to this problem. The analytical method is directly deduced from the assumption 1.

3.1 Analytical method

AB crystal will be considered as a representative example. Coordination
number of each atom is four. When the crystal grows from a dispersed phase, it may be assumed that there are many types of possible combinations of A and B atoms in the surroundings near the crystal surface which may act as hypothetical growth units. As important possible combinations, we assume \(AB, AB_2, AB_3, AB_4, A_2B, A_3B, A_4B\) and independent atoms of A and B. We shall denote the probability of existence of these groups as \(p_1, p_2, p_3, p_4, p_{-2}, p_{-3}, p_{-4}\) and \(p_0\), respectively. \(p_i\) denotes the probability of existence of the group which consist of an A atom and \(i\) B atoms \((AB_i)\) (Fig. 9). When \(i\) is equal to zero, each atom exists as an isolated individual \((A, B)\). If \(i\) is less than zero, \(-i\) is the number of A atoms bonded to a B atom \((A_iB)\). Naturally, \(p_1 = p_{-1}\). The total value of probabilities must be a unity;

\[
\sum_{i=-4}^{4} p_i - p_1 = 1.
\]

It is reasonable to assume that \(p_i\) is a function which depends mainly on growth temperatures \(T\) in absolute and \(f\), relative concentration of B (when B is a volatile component \(f\) corresponds to the partial pressure or fugacity), i.e.

\[ p_i \equiv p(T, f). \]

Now if we assume a constant \(f\), we may expect that as increasing temperatures, proportion of independent atoms as compared to those forming groups will increase, since their mobility increases. On the contrary at lower temperatures atoms will have a tendency to form groups. If a constant \(T\)

![Diagram](image)

**Fig. 9.** Growth unit of \((A, B), (AB), (AB_2), (AB_3),\) and \((AB_4)\) are shown. Closed circles are A atoms and open circles are B atoms.
is assumed, we may expect surplus B atoms for higher f.

We may therefore summarize;

for constant f high $T$ $p_0 \gg p_{1-4}$
low $T$ $p_4 \gg p_{1-4}$ or $p_{4-4} \gg p_{1-4}$
for constant $T$ high $f$ $p_4 \gg p_{1-4}$
low $f$ $p_{4-4} \gg p_{1-4}$.

PBC analysis will be made on an assumption that there can be growth unit of not only isolated atoms but also atomic groups near the growing interface.

Although there can be many combinations, we assume the combinations $(A_4B)$, $(A, B)$ $(AB_4)$ as extremes and other combinations will be regarded as derivations from these. Attachment energy or surface energy will be calculated for each extreme case. Thus attachment energies and surface energies vary depending on the states of hypothetical growth units. Then these energetic values are assumed in the linear relationship with the values of the extreme cases. Note here, only the case of $p_0 = 1$ corresponds to the analysis by the original PBC method.

3.2 Application to representative crystals

3.2.1. Sphalerite type structures

The space group is $F43m$. Each Zn atom is surrounded by four S atoms and each S atoms by four Zn atoms. In this structure, there is only one kind of “strong bond”, Zn–S bond. The bonding energy of a Zn–S bond is taken as a unit “E”. In the following treatment only a relative value of energy will be used, since it is not necessary to consider the absolute value of the E.

Figure 10 shows a [110] projection of sphalerite structure. Solid circles represent Zn atoms and open circles S atoms. When $p_0 = 1$, both (111) and (111) surfaces cut one Zn–S bond per unit area since only isolated atoms were taken into consideration for energy calculation. Accordingly, surface energies are the same for both (111) and (111) surfaces. In the case of $p_4 = 1$, ZnS$_4$ tetrahedrons should be taken into consideration at the independent unit in energy calculations. In this case, (111) slice cuts three bond on (111) surface, but only one bond on (111) surface. So both the attachment energy and the surface energy of (111) surface are larger than those of (111) surface, which leads to a larger development of (111). On the contrary, in the case of $p_{4-4} = 1$, independent units becomes Zn$_2$S tetrahedron. As shown in Fig. 10 numbers of broken bond by (111) slice are just in a reversed form of $p_4 = 1$.

Similarly, attachment energies and surface energies can be calculated for all $F$-faces for different growth units. $F$-faces of sphalerite are {111}, {111}, {220}, {002}.[17,19]

Figure 11 is a schematic diagram to show changes in attachment energies
Fig. 10. Projection of the sphalerite structure along [110]. Closed circles are Zn atoms and open circles are S atoms. ZnS units are also shown by dotted lines and hatched area.
Fig. 11. Schematic diagram of relationship between $E_{\text{att}}$ and growth unit. At $0, p_0=1$ and at $-1, p_{-4}=1$.

dependning on growth units. The vertical axis shows the attachment energy and horizontal axis the growth units, as expressed in the form described earlier. Since faces with low attachment energy can develop larger, we may expect the following relations. When $p_0 \approx 1$, $\{111\}$ and $\{\overline{1}1\}$ will develop nearly equally, resulting in an octahedral habit. When $p_4 \approx 1$, $\{\overline{1}1\}$ will develop larger and $\{111\}$ will diminish. When $p_{-4} \approx 1$, $\{111\}$ will develop larger and $\{\overline{1}1\}$ will become much smaller. Assuming a constant temperature $T$, the horizontal axis of Fig. 11 corresponds to $f$, i.e. sulphur fugacity (for sphalerite). Figure 11 indicates that sphalerite crystal will become octahedral consisting of equally developed $\{111\}$ and $\{\overline{1}1\}$ for low $f_s$, whereas tetrahedral habit with only $\{111\}$ is expected for high $f_s$. On this basis, commonly observed habit $\{111\} \succ \{\overline{1}1\}$ for natural sphalerite reported by Komatu and Sunagawa\textsuperscript{17} may be explained. When $p_{-4}=1$, the attachment energy of $\{111\}$ is smaller than that of
\{\overline{111}\} which will result in the habit \{111\} > \{\overline{111}\}. This indicates that the natural sphalerite should have been grown under low temperature and low sulphur fugacity conditions. In contrast to this, the observations reported by MONIER and KERN,\textsuperscript{15} i.e. general tendency of \{111\} < \{\overline{111}\}, may be explained by that their observations were made principally on synthetic crystals which grew under higher temperature and sulphur fugacity.

For GaAs which has the same sphalerite structure, it is reasonable to expect a similar relation between attachment energies and growth units as above, though the absolute values may be different.

Figure 12 shows the anisotropy of growth rates of GaAs reported by SHAW.\textsuperscript{20} The results may be explained if his experiment is assumed to have been made under the condition indicated by the stout arrow in Fig. 11.

![Polar diagram of GaAs deposition rate versus crystallographic orientation](image)

Fig. 12. Polar diagram of GaAs deposition rate versus crystallographic orientation (after SHAW\textsuperscript{20}).

### 3.2.2. Wurtzite type structure

The number of broken bond cut by (10\overline{1}0) slice changes from 2 bonds to 4 bonds as going from $p_0 = 1$ to $p_4 = 1$. Similarly as described above, attachment energies can be calculated for all possible $F$-faces, \{0002\}, \{000\overline{2}\}, \{10\overline{1}0\}, \{10\overline{1}1\} for $p_0 = 1$ and $p_4 = 1$. Figure 13 is a schematic diagram showing the change of attachment energies. Polarity is not evidently seen at $p_4 = 0$ but becomes evident at $p_4 = 1$. 
NEWKIRK and SMITH\textsuperscript{21)} synthesized BeO crystals by flux method and showed that the habit changes depending on temperature and the amount of MoO$_3$ in the flux. They prepared a morphodrom of BeO crystals in relation to temperature and the amount of MoO$_3$ in the flux (Fig. 14), in which “prism” crystal has well developed \{10\overline{1}0\}, \{10\overline{1}1\}, (000\overline{1}) and small (0001), “pyramid” and “platy” crystals have well developed \{10\overline{1}1\}, (000\overline{1}) faces associated by small (0001) faces.

If it is safe to assume that the increase in the amount of MoO$_3$ in the flux proportionally corresponds to the increase of oxygen fugacity, the
morphodrom may be accounted for as follows based on the present analysis; At $T=1400^\circ$C.

This condition corresponds to $p_4$, because temperature is high and $f$ is small, where it is expected as seen in Fig. 14 that both (0001) and (000$\bar{1}$) will develop nearly equally, resulting in platy crystal.

At $T=1300^\circ$C

With the same value of $f$, the decrease of $T$ leads to the increase of $p_4$. Then the difference of attachment energy between (0001) and (000$\bar{1}$) becomes larger, which leads to the increase of growth rate of (0001). Then plate will be thickened. As going to the right of this morphodrom, the difference in the attachment energies between (0001) and (000$\bar{1}$) will become larger according to the increase of $p_4$, which results in larger development of (000$\bar{1}$) face than (0001).

At $T=1200^\circ$C

As $T$ decreases, $p_4$ will increase and eventually (0001) will disappear.

3.3 Summary

In the original PBC method, only atomic or ionic entities are taken as growth unit in the analysis. Thus the morphology deduced is the idealized or
abstracted one, and has no relation with growth parameters. It can be used as a standard, but cannot give a prediction on habit changes depending on growth conditions. We introduced hypothetical growth units and extended PBC method. This extension leads to a prediction on habit changes depending on growth parameters, since the size of growth units can be related to growth parameters.

In the new method, it is broadly assumed that attachment energy changes linearly with changes of growth units. This may not be true in reality. The attachment energy changes discontinuously at $p_4=0$. However, such a discontinuity is difficult to imagine to occur in nature, where more or less gradual change, though this may not be linear, is expected.

In spite of these rather vague assumptions, the present method can give more or less a satisfactory explanation to the morphology of polar crystals in relation to $T$ and $f$. Naturally, it is expected that the polarization energy which is not considered in this method, may also affect simultaneously the morphology of polar crystals. But the polarization energy may not vary depending on the change of growth conditions as was discussed in the previous theories.\textsuperscript{17,22}

REFERENCES


