IN SITU DIRECT OBSERVATION OF A CRYSTAL SURFACE AND ITS SURROUNDINGS

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Abstract. Direct observation of growth layers with mono-molecular height on crystals growing in aqueous solution phases became possible in situ by improving microscopies and crystal growth systems. This high resolution direct observation method was successfully applied to the growth and dissolution of CdI₂ and Ba(NO₃)₂ crystals in order to investigate some problems on the crystal growth mechanisms which had not been solved yet. Schlieren method and Mach-Zehnder interferometry were later coupled to the system with the intention of visualizing the transport phenomena of a solute towards the crystal surfaces. Although this method was originally planned to the growth of crystals at a room temperature, it was later extended to the growth in melts or solutions at an elevated temperature as high as 1800 K, by employing a high temperature growth cell which was specially made for this purpose. It was concluded that hydrodynamics around growing crystals play considerably important roles on the growth kinetics. It was also concluded that the clustering of molecules might take place at least very adjacent to the surface of Ba(NO₃)₂ in an aqueous solution. This clustering forms a high density layer with large refractivity at relatively high supersaturation, which would initiate the secondary nucleation in the surrounding solutions by applying fluid shear to the crystal.

1. Introduction

Since crystal growth proceeds at the crystal-liquid interface, if a direct observation of both crystal surface and its surroundings could be realized in situ, it would give us wider informations on the crystal growth mechanism. Although there have been a number of in situ observations on moving steps¹⁻⁹ even before the birth of the BCF theory,¹⁰ these observations were aimed either to demonstrate spiral steps with relatively large thickness by selecting a suitable crystal for surface observation, or to verify a proposed theoretical growth model such as the BCF theory by measuring the
dependence of step velocities on supersaturation and so on. It, however, has become clearer through careful observations of crystal surfaces\textsuperscript{[1]–[3]} or kinetical measurements of growth rate of crystals\textsuperscript{[4,5]} that the actual crystal growth process especially in solution phases is not so simple as has been supposed so far and no single experimental method would be suitable to verify each proposed growth model.

Tsuchamoto\textsuperscript{[6]} considerably improved the method of in situ observation of crystal surfaces for kinetical experiments by applying modern optical technologies and enabled us to observe "live" mono-molecular growth steps in an aqueous solution both by transmission microscopy and by reflection microscopy.\textsuperscript{[7]} Since this high resolution in situ observation was performed in well controlled growth conditions and recently coupled with Schlieren method or Mach-Zehnder interferometry, crystal growth mechanisms became possible to be investigated by means of several independent in situ methods.

The method was recently developed further to the high temperature in situ observation,\textsuperscript{[18]–[20]} so that one can investigate the growth of crystals even from high temperature melts or solutions at 1800 K. This method was first applied to silicate crystals\textsuperscript{[18]–[20]} in order to investigate natural crystallization. Van Enckevort\textsuperscript{[21]} recently applied principally the same method to the investigation of the growth of Bismut Germanate (Bi\textsubscript{4}Ge\textsubscript{3}O\textsubscript{12}), which got large attention as a scintillator crystal in the fields of medical science and high energy physics, and obtained numbers of interesting phenomena on the metastable phases by coupling the ex situ infrared absorption measurement. This indicates the wider applicability of the in situ observation not only in fundamental sciences but also in industrial technologies.

The present paper will summarize some of the recent results which have been obtained in the laboratory of the present author by using these high resolution in situ observation methods.

2. Experimental

2.1 Optical system
2.1.1. Surface observation

The key point for the success of the in situ observation of mono-molecular growth steps can be attributed to the elimination of optical aberration described in ref. (17). Although there have been several works\textsuperscript{[1]–[9]} on the in situ observation of growth steps in aqueous solution phases, these works were limited to low magnifications when the steps were very thin. As is well known, the optical aberrations sharply increase if the thickness of the glass plates or the solution in the optical path increases. This is because conventional microscopes are made assuming that there is no substance between the objective surface and the objective lens. So some of the important observations were performed using the aberration-free lenses which were
specially manufactured for the present in situ observations for reflection microscopy.\textsuperscript{17)} The importance for reducing the optical aberration is shown in Fig. 1, as an example. Here a differential interference contrast microscope after Nomarski\textsuperscript{22)} was employed, in which growth layers with 15 Å step height of SiC were nearly invisible by ordinary microscopy when a water layer with 3.3 mm thick covered the crystal surface. However these thin steps were clearly visible in situ by the aberration-free microscopy.

The principle of the in situ observation of growth steps is shown in Fig. 2, in which the section of the growth steps is illustrated. Due to the height difference of the growth steps a phase difference of a light beam passing through the crystal arises. Unfortunately the phase difference of the light is

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image.png}
\caption{Effect of optical aberrations upon the contrast of differential interference contrast microscopy, 15 Å steps of a SiC crystal (arrow), (a) with the aberration-free lens and (b) with a conventional lens.}
\end{figure}
invisible for our eyes, which has to be converted to visible intensity differences either by phase contrast microscopy\(^{23}\) or by differential interference contrast microscopy.\(^{22}\) If the crystal is platy and clearly transparent without large inclusions, this type of transmission microscopy can be employed. Otherwise reflection microscopy is recommended.

2.1.2. **Step height**

Experiments had been started with the aim of improving images of growth steps on a crystal growing in an aqueous solution. Out of varieties of crystals CdI\(_2\) was selected for the first experiment because of its platy form being suitable for surface observation. It was later that the other crystals such as NaCl and Ba(NO\(_3\))\(_2\) were also investigated. In Fig. 3 spiral steps of CdI\(_2\) starting from the outcrop of a dislocation is shown. One can discern a dislocation connected to the spiral centre, as indicated by an arrow. Since the visibility of steps was remarkably improved in the present in situ observation, the height of very thin steps could be measured in situ by means of internal interferometry\(^{23}\) using a monochromatic light.

The normal growth rate of the crystal was sometimes measured by measuring the velocity of the displacement of the interference fringes. Since these fringes appeared only when the crystal was very perfect, growth rate was
measured also by ordinary focusing method. If necessary, the step height was measured ex situ by conventional multiple beam interferometry after Tolansky,\textsuperscript{24,25} after the crystal was taken out from the solution followed by silvering the surface to increase the reflectivity of the surface.\textsuperscript{12,26} The minimal step height being measured so far during in situ observation was 14 Å, which corresponds to the mono-molecular step height of CdI\textsubscript{2}. Although much thinner steps can be seen on a TV screen, the measurement of the step height in situ was unsuccessful. Taking a photographic image from the TV screen was also impossible because of the rapid movement of these steps.

2.1.3. Visualization of the mass transfer around a growing crystal

Schlieren method or Mach-Zehnder interferometry was employed for this purpose. The former method was applied for the qualitative observation and the latter method was applied for the quantitative measurements of the gradient of refractive index, which is proportional to the concentration gradient, of the solution near the crystal. Lenses with 8 cm in diameter (focal length, $f=80$ cm) were used for both systems. A He–Ne laser (5 mW) and a halogen lamp (100 W) were respectively employed for the interferometry and the Schlieren system. The schematic system is shown in Fig. 4.

2.2 Video system

High speed and high resolution black and white TV cameras were employed for the detailed surface observations. The CCD black and white TV cameras, Sony, were mainly employed for recording Schlieren images and interference fringes obtained by Mach-Zehnder interferometry. All the video images were recorded into video tape recorders, Sony U-matic, though some
Fig. 4. System for the visualization of the mass transfer process around a crystal.
image processing$^{16-20}$ was applied before the recording, in order to increase the sharpness and the contrast of the images. The image processor is not a digital system$^{16}$ at this moment but a real time analogue system,$^{17-20}$ which is mainly due to the high speed of this processing.

2.3 Growth system for aqueous solution growth

Depending upon the purposes several types of growth cells were employed. Flow systems$^{16}$ and stagnant solution systems with stirrers were respectively employed for kinetic measurements being coupled with the observations of crystal surfaces and the observation of a convection around a growing or a dissolving crystal. In every case the growth system was placed in a thermostated room with the temperature stability of less than 0.5$^\circ$ C and thus the temperature stability of the solution in the growth cell became much less than 1/100$^\circ$ C. The temperature was measured by digital thermometers, Takara, with beat type thermistors.

In order to carry out experiments on the effect of the solution velocity upon the growth rate and the hydrodynamics around a growing crystal, the speed of the solution flow were varied from $\sim$0 to $\sim$20 cm/s by changing the voltage of the solution pump, which was roughly measured by measuring the movement of the smallest air bubbles in the solution by light scattering.

2.4 High temperature in situ observation

So far the growth system for in situ observation was described for the crystal growth in an aqueous solution. However it would be more useful for wider fields of interests, if such an in situ observation with high quality images could be performed at an elevated temperature above 1500$^\circ$ C. This is because most of industrially important crystals such as semiconductors or natural crystals are grown at high temperatures.

In situ observations of growth or melting processes of crystals in high temperature solutions have been almost impossible until recent years, or even when it was performed, the image was rather poor.$^{27}$ However such a high temperature in situ method was recently developed considerably, Fig. 5, which enabled us to visualize not only the growth process of a crystal, Fig. 6 but also the growth steps of a crystal.$^{18-20}$ This became possible mainly by the improvement of the growth method, optical systems and a heating system.

This high temperature in situ observation has then been developed further and five different growth cells have already been made in our laboratory. Materials used for these systems were mainly silicates in our laboratory$^{18-20}$ because of the importance in natural crystallization. We have been investigating metastable nucleation and growth of silicate crystals in relation to the change of the interfacial energy between the crystal and the solution.$^{20}$ GaAs is also planned to be investigated in situ as a next step.
Fig. 5. High temperature in situ observation system.
3. Observation and the Discussions

3.1 Influence of the solution velocity on the surface

Before the kinetical measurement of the growth step, the influence of the solution flow velocity on the surface morphologies of crystals were investigated. This was mainly performed using CdI$_2$, the brief summary of which is as follows. When the solution flow velocity is large enough, the surface pattern becomes simpler and simpler as the growth proceeds, because thinner steps in between thick steps advance more rapidly followed by catching up with the next thicker steps. Consequently the surface becomes covered with relatively thick steps of nearly the same height. When the solution is stagnant, the surface, on the contrary, becomes more complex. This is because all the steps
of different height and of different origins advance at the same rate. The same result was obtained for dissolution process as well. So desirable steps could be selected to some extent by changing the flow velocity. Of course changing the supersaturation is another important factor.

So far it has been assumed that, if the solution velocity is large enough, the surface supersaturation on a crystal is very close to the bulk supersaturation and thus only surface kinetics play a dominant role. Although the necessary solution velocity for achieving the surface kinetic regime varies depending upon the viscosities and other physical properties of the solution, it has usually been assumed in our laboratory that the solution velocity \(>10\) cm/s is enough for the growth in an aqueous solution. This is based upon the data which was obtained by measuring the step velocities of CdI\(_2\) vs solution velocity,\(^{16}\) more exact data of which were obtained using Ba(NO\(_3\))\(_2\).\(^{28}\) In Fig. 7 the dependence of the step velocity upon the solution velocity which is expressed as the electric voltage for the solution pump is shown. One can see that the step velocity becomes unchanged above \(~10\) cm/sec, though the solution velocity actually increased when judged from the movement of tiny air bubbles in the solution. So the growth in this regime is regarded not to be controlled by volume diffusion but by surface kinetics.

![Graph showing step velocity vs solution velocity](image)

**Fig. 7.** Step velocity vs solution velocity, which is expressed by the voltage of the solution pump.
Experiments were thus performed in the two growth regimes. One is the
growth in a nearly stagnant solution and the other was in a rapidly running
solution.

3.2 An old problem on the growth rate vs supersaturation

Our newly developed in situ observation methods were employed to
reinvestigate an old problem on the crystal growth rate of K–Alum. The data
in Fig. 8 at lower supersaturation was obtained by Bennema\(^{29}\) and at higher
 supersaturation by Botsaris-Denk,\(^{30}\) showing two different mechanisms
being involved. Recent measurements by employing a modern weighing
method also showed the same results.\(^{31}\) Since Bennema concluded that the
BCF spiral growth was operative at his growth region, another mechanism
such as a two-dimensional nucleation mechanism might be expected at higher
 supersaturation.\(^{30,32}\) However beautiful spiral hillocks\(^{33}\) were observed in
both supersaturation ranges.\(^{34}\) This is not only for K–Alum but a very similar
result was obtained for Ba(NO\(_3\)_\(_2\)) in our laboratory.\(^{12,35}\) So the investigation
on this problem was performed using this crystal.

In order to investigate whether this unusual change of the growth rate at
around 1% of supersaturation is attributed to the unusual change of step
velocity or not, the velocity of isolated steps, \(>100\ \text{Å}\) high, was measured in
situ by differential interference contrast microscopy,\(^{22}\) where the velocity of
the solution flow around the crystal was \(\sim 15\ \text{cm/s}\). As shown in Fig. 9, the
step velocity suddenly increased at around 1% of the supersaturation, leading
to the appearance of a kink in the step velocity vs supersaturation, though the

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**Fig. 8.** Growth rate vs supersaturation of K–Alum, where a kink point appears
showing two different mechanisms being involved.
absolute supersaturation at which the kink appears varied depending, probably, upon the height of steps. The same tendency was obtained during the dissolution process as well, Fig. 9.

The advance rate of very thin spiral steps with the height of less than 50 Å were also measured in order to check whether this abrupt increase of the step velocity was only for isolated steps or not. In Fig. 10 a spiral hillock used for the investigation is shown. The TV image is increased in its sharpness and the contrast by means of analogue real time image processing by taking the deriverty of the lateral intensity of the video signal prior to the recording into a video tape recorder. This procedure results in the comparable image contrast as obtained by in situ observations,\(^{(17), (35)}\) though the lateral resolution on the TV screen is still poorer. In Fig. 11 the relation between the spiral step velocity and the bulk supersaturation is shown. One will again notice the sharp increase of the step velocity at \(\sim 1\%\) of supersaturation.

These two measurements both for isolated steps and for spiral steps clearly confirm that the abrupt change of the step velocities cause the abrupt change of the normal growth rate at \(\sim 1\%\) of supersaturation, because in both cases the critical supersaturation is almost the same being about 1\%.
Fig. 10. Spiral steps, ~30 Å height, of Ba(NO$_3$)$_2$, (a) by in situ observation and (b) by ex situ observation.

Fig. 11. Spiral step velocity vs supersaturation.
We therefore investigated the surrounding solutions around a growing crystal if the change of the supersaturation at around 1% of supersaturation would lead to the abrupt change on the concentration gradient or the convections.

3.3 Surroundings around a growing crystal

3.3.1 Influence of the bulk supersaturation on the mass transfer

Although there are several possibilities for visualizing the concentration gradient and the convection phenomena around a growing or dissolving crystal in aqueous solutions,\textsuperscript{36}–\textsuperscript{42} we employed Schlieren method and Mach-Zehnder interferometry. The former method has an advantage in picturing out images of the concentration gradient qualitatively. The latter method has the advantage in the quantitative in situ measurement of the concentration gradient using the interference fringes. This method can detect a very small change of the refractive index of the solution of the order of $10^{-7}$ and thus more sensitive than the others.

There have been many attempts to measure the concentration gradient around a growing crystal in an aqueous solution in order to investigate the phenomenological growth mechanism of crystals or the stability of a crystal shape.\textsuperscript{38}–\textsuperscript{46} Visualizing the convection phenomena around a growing or dissolving crystal is another approach\textsuperscript{36}–\textsuperscript{37}, in which the discussion is based upon hydrodynamics of the solution. However these observations have been performed in relatively high supersaturations compared with the kinetical experiments on crystal growth rates. This is because Schlieren method or interferometry is so sensitive for the slight change of refractive index along the optical path that the design of the growth cell in which a crystal is placed in a solution has to be simplified as much as possible. This results in relatively rough control of the solution temperature and thus makes it impossible to keep the supersaturation very low. So even exact crystal growth rates were not measured in most cases. What we are interested in is the possible change of crystal growth, being associated with the change of concentration gradient and the convective phenomena around a growing crystal at low supersaturations.

In Fig. 12 a Schliéren image is shown taken by Onuma\textsuperscript{28} during the growth of a crystal in a stagnant solution. A clear diffusion layer with the thickness of 400 $\mu$m can be seen as a white boundary. The change in thickness on increasing the supersaturation of the solution was measured, Fig. 13. Here a critical supersaturation at $1\textendash;2\%$ is noticed, above which no further increase in thickness can be seen. It is also noticed that the thickness widely scatters at $1\textendash;2\%$ of supersaturation.

In order to investigate this change of the thickness of the diffusion layer, a further detailed observation was performed both by Schlieren method and by Mach-Zehnder interferometry. The result from a crystal with the diameter of
Fig. 12. A diffusion boundary layer observed by Schlieren method.

≈1 mm is summarized in Fig. 14, in which the thickness of the solution above the surface is more than 3 mm and thus several times more than the thickness of the observed diffusion layer. The seed crystal was surrounded by (111) faces and attached to the tip of a glass rod. The top face was kept horizontally for the surface observation by means of reflection type Nomarski interference contrast microscopy. When the supersaturation is less than 0.5%, only a diffusion boundary layer could be discerned, Fig. 12. On increasing the supersaturation, a convection plume starts to develop, Fig. 14(a). The critical supersaturation varied depending on the experiments but was typically 0.5–1%. In this regime the plume was very unstable and the development is intermittent. As the supersaturation increased further, typically above 5%, the convection plume went upwards in a very stable manner, Fig. 14(b). So it can be concluded that the large scatter of the thickness of the diffusion boundary layer at around 1% is attributed to the development of the unstable convection.

It may be important to note that the large scatter in the thickness of the
diffusion layer leads to the large deviation of the growth rate at 1–2% of supersaturation. One of the examples is shown in Table 1, in which one can clearly see that the deviation of the growth rate at low and high supersaturations becomes much smaller than the deviation at medium supersaturation, though the temperature control was equally accurate, <1/100°C. It might be interesting to speculate that this large deviation of the growth rate would result in the periodic growth zoning in a crystal even at very constant bulk supersaturation. Since the distribution of impurities into the crystal depends on the growth rate of a crystal, the concentration of impurities would also become periodic.

3.3.2. Development of a convection plum

It is important to check whether this observation is in agreement with the theory in hydrodynamics. As a model the following situation will be discussed. A diffusion boundary with the thickness of 300 µm is present horizontally on top of a crystal face and there is a concentration gradient vertically, namely, there is a difference of solute concentration between the bottom and the top of the diffusion layer. The top face is assumed to be large enough as a simplification.

Since the Raighly number, \( Ra \), is given by

\[
Ra = \frac{g(d\rho/dC)(C_0 - C_{sat})L^3}{D\eta},
\]

the Raighly number in the diffusion layer at 0.5% of supersaturation becomes
Fig. 14. Change of a convection plum on increasing the supersaturation, $\sigma$. (a) an unstable and intermittent convection plum at $\sigma \sim 2\%$ and (b) a stable plum at $\sigma \sim 7\%$. 
TABLE 1. A large scatter of the average normal growth rates at medium supersaturations, 
Ba(NO3)2):

<table>
<thead>
<tr>
<th>Bulk supersaturation (%)</th>
<th>Average growth rate (10^-6 mm/s)</th>
<th>Dev. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>5.27</td>
<td>8.54</td>
</tr>
<tr>
<td>1.14</td>
<td>3.27</td>
<td>23.2</td>
</tr>
<tr>
<td>2.40</td>
<td>5.90</td>
<td>43.9</td>
</tr>
<tr>
<td>3.52</td>
<td>7.32</td>
<td>12.8</td>
</tr>
<tr>
<td>5.20</td>
<td>13.9</td>
<td>14.4</td>
</tr>
<tr>
<td>7.42</td>
<td>24.7</td>
<td>14.9</td>
</tr>
<tr>
<td>9.90</td>
<td>25.1</td>
<td>13.1</td>
</tr>
</tbody>
</table>

~2700, if the following reasonable values are used. The gravitational constant 
\(g = 980 \text{ cm}^2/\text{s}\), the variation of solution density with solute concentration 
\(dp/dc = 0.2\), the thickness of the diffusion layer \(L = 0.03 \text{ cm}\), the viscosity of the 
solution \(\eta = 1 \times 10^{-2} \text{ poise}\), the diffusion constant \(D = 1 \times 10^{-5} \text{ cm}^2/\text{s}\) and the 
difference of the concentration \(C_0 - C_{sat} = 0.05\) at the supersaturation of 0.5%. 
If the Rayleigh number exceeds a critical value, 1700, a convection is 
theoretically known to become stable. Therefore the calculated and the 
measured value agree reasonably well, if we consider the \(Ra = 1700\) is for a 
rigid situation.

It may be important to note that only 0.5% of supersaturation is enough 
for the development of a convection in a diffusion layer due to the 
concentration gradient. There have been many attempts to suppress the 
convection by decreasing the thickness of the growth cell or giving a 
temperature gradient vertically, by which thermal convections might be 
suppressed. However the convection due to the growth or the dissolution of a 
crystal in a solution system cannot be suppressed as long as the thickness of the 
growth cell is larger than that of the diffusion boundary layer.

One of the experimental results may support this conclusion. Simon\(^{47}\) 
measured the growth rate of a crystal in a very thin growth cell with the 
intention of suppressing the possible convections. However he concluded that 
even in that case the growth rate was at least two times larger than the 
expected value being calculated by a diffusion controlled model. They 
therefore concluded that another transport mechanism such as a flow or 
convection had to be taken into account for the interpretation of the growth 
rate.

So far the discussion was made for the stagnant solution system. 
However a convection plume also develops even in a running solution above 10 
\(\text{cm/s}\). Of course the convection plume does not go upwards but flows sideways 
along the flown direction of the running solution. It was generally observed
that a convection starts to develop when the supersaturation is more than 1%,
though this critical value cannot be interpreted by such a simple hydro-
dynamics as for the stagnant system.

Since we here again obtained the critical supersaturation, \(\sim 1\%\), we may
conclude that the abrupt change of the growth rate at \(\sim 1\%\) of supersaturation
is attributed to the development of convection flows around a crystal though
the critical supersaturation varies depending upon the crystal size or the
position to some extent. Therefore the growth below this critical supersatura-
tion is interpreted to be controlled by the volume diffusion and above this
supersaturation by surface kinetics.

3.4 Possible origin of secondary nucleus

Although several mechanisms have been postulated on the origin of the
secondary nucleus,\(^{49-54}\) the effect of fluid shear, among others, has not been
well clarified yet.

An important phenomenon due to fluid shear was for the first time
observed through the present in situ observations. When the diffusion layer
around a crystal growing at \(\sim 7\%\) of supersaturation was observed carefully, a
strange layer with the thickness of \(<100 \, \mu m\) could be observed adjacent to the
crystal surface, Fig. 15(a). The refractive index of the layer is very close to that
of the crystal and far different from that of the solution when judged from the
change of the contrast. So the density of the layer is much higher than that of
the solution and very close to that of the crystal. Here the layer is called a high
density layer. This layer behaved like a fluid because the layer became wavy
when the crystal was rotated slightly. The high density layer was invisible
when the supersaturation was less than \(\sim 7\%\).

When the high density layer was blown away into the surrounding
solution by a forced flow using a stirrer in a cylindrical growth cell, Fig. 15(b),
a large numbers of secondary nucleus were detected by Schlieren method, Fig.
15(c). Since this phenomenon could rarely be seen when no seed crystal was
used, a systematic work was done. The result is shown in Fig. 16. Here the
incubation time until visible nucleus could be detected by laser scattering
using He–Ne laser after the stirring was applied to the system is plotted against
the degree of supersaturation. Below the supersaturation of \(\sim 7\%\) there is no
difference whether or not a seed crystal is present in the solution. However
above 7\%, the difference becomes clear. A large reduction of the incubation
was measured. Considering this measurement and the observation of the high
density layer at \(>7\%\) of supersaturation, we might conclude that the high
density layer is responsible for the formation of secondary nucleus and that
the layer possibly consists of embryo-like clusters.

Maiwa et al.\(^{35}\) observed helical dislocations only when a Ba(NO\(_3\)_2
crystal was grown above 5\% of supersaturation in an aqueous solution. Since
the movement of vacancies or interstitials is required for the formation of
Fig. 15. High density layer being responsible for the secondary nucleation of Ba(NO$_3$)$_2$. (a) a high density layer, $H$, with large refractive index and diffusion boundary layer, $D$, observed by Schlieren method on top of the (111) face, $C$. (b) Applying a forced convection flow so as to flow away the high density layer to the surrounding solution with a magnetic stirrer and (c) numbers of secondary nucleus, $N$, in the solution.
helical dislocations and this situation cannot usually be achieved at room temperature, this high density layer might also be responsible for the formation of the helical dislocations by supplying numbers of vacancies or interstitials to the crystal surface.

The author would like to express his thanks to K. Onuma, H. Nakamura and K. Maiwa for their experiments. He is indebted to Professor P. Bennema and W. Van Enckevort for their discussion on the growth mechanism of crystals and Professor N. Kobayashi for his discussion on hydrodynamics. Thanks are also due to Professor I. Sunagawa for his supporting discussion and the critical reading of the present manuscript. This work is financially supported by a Grant-in-Aid for Fundamental Researches from the Japan Ministry of Education and is technically supported by Olympus Optical Co., Japan.

REFERENCES

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(13) For instance,


(34) Tsukamoto, unpublished.


In situ Direct Observation of a Crystal Surface and Its Surroundings


DISCUSSION

Chernov

What was the step height region where the ν(h) dependence has been observed?

A: The minimal step height we could measure was 14 Å for CdI₂ but much thinner steps are visible in situ. The step height of Ba(NO₃)₂ also varies depending on growth conditions. We usually use the growth steps for such measurements with around 30 Å step height because it is easy to get good optical contrast and they behave similarly as much thinner steps.

Bennema

I found from rate versus supersaturation experiments for potash alum for γ<σ<10⁻² a linear curve going through the origin and for σ≥10⁻² deviating points. This was later repeated. I had to assume the following things (i) a spiral growth mechanism operates (ii) there seems to be a conflict between the linear law and the parabolic BCF law and the only way to solve this problem is to assume that a group of spirals located on a grain boundary show cooperation leading to a linear curve. (This follows from the BCF theory). (iii) The deviating points are due to a decomposition of a group of cooperating spirals.
The idea of spiral growth was confirmed by van Enkevort who really saw spirals. (See thesis van Enkevort) and by your work. The change from linear to deviating points now seems to be caused by a change in the hydrodynamic regime.

How do we now explain the linear law for \( \gamma \leq \sigma \leq 10^{-2} \)?

A: First of all I am not interesting in the lineality at smaller supersaturation but the sudden change of growth rate at about 1% of supersaturation. In my opinion before discussing the lineality it is necessary to check whether the experimental scatters at low supersaturation is due to the effect of, say, impurities or other effects, such as the competition of several growth spirals. It is not always that the same number of spirals is active during the whole period of the growth rate measurements, which usually takes at least several hours by weighing method as you applied. If you would therefore measure the growth rate of a single spiral in a short time, you might obtain a beautiful parabolic relation.

Chernov

Was the growth regime kinetical or diffusional?

A: According to the currently accepted criterion, our experiments were carried out in kinetical regime. This can be seen in the experimental result in which we measured the step velocity vs. relative velocity of the solution. In our growth experiment growth rate measurements were carried out when the step velocity did not change by increasing the relative solution velocity. However I doubt whether or not this currently accepted criterion is true, because even in that regime there is no dependence of the step velocity upon the height of the step, namely all steps advance at the same rate, though the step heights are different. On increasing the solution velocity further, these thinner steps advance much faster than the thicker layers as can be expected for the growth in kinetical regimes. So I think our experiment was carried out still in the diffusional regime, though the solution velocity was as high as \( > 15 \text{ cm/s} \).

Hallett

The role of applied electric field in ice growth from the vapor is to change step velocity by a large amount. This can be interpreted in terms of a locally induced flow. It would be of interest to apply an electric field during solution growth and examine its influence on step growth. Can you do this in your experiment?

A: We have not applied the electric field to the growth of aqueous solution grown crystals but the lead crystals grown from solution for the electric crystallization, which has not been published yet. Since the experimental set up is not so much different as this, it is possible to do such an experiment as you asked. The more interesting experiment, I think, is to
apply the magnetic field to the aqueous solution system. Since the electrical field easily changes the chemical potential of the solution and thus changes the thermodynamics. However the change of thermodynamics by applying the magnetic field as large as 2000 Gaus must be negligible, though we observed a large reduction of the growth rate both for NaCl and KDP but not for Ba(NO₃)₂.

Aquilano
When considering the Bennema and Botseris curves on K–Alum crystals, we must remember that their curves concern one crystal form only of the crystal. If the sudden change over from linear (I) to the linear (II) laws is due to hydrodynamics, this change should be present (more or less at the same σ values) on all crystal forms. We measured (R, σ) curves of six different forms of the same crystal simultaneously and we observed the “sudden increase” on 4 out of six forms. I think that convection can help the sudden growth increase but I presume, according to my experiments, that the first reason is “kinetic change over”.

A: Whether a convection plume appears or not due to the concentration gradient near the surface depends largely upon the viscosity, the concentration gradient, the thickness of the diffusion layer and even the shape or the position of the crystal. It is therefore not so easy to say whether all your crystals were growing in the same growth condition in the sense of hydrodynamics.

Yakovlev
There is some concentration distribution between crystal surface and bulk solution. Therefore there is a similar reflective index distribution. Namely did you observe this by interferometer? Why the boundary between diffusion layer and bulk solution is so sharp in this case?

A: The concentration distribution between the crystal surface and the bulk solution appears as the diffusion layer which you saw in our slides, if you would employ Schlieren method or Mach Zehender interferometry. The reason why the boundary is so sharp in our photographs is simple. We used a high contrast film or increased the contrast of the video image by image processor.

Coriell
Is it possible to measure interface supersaturation from your data and then plot velocity vs interface supersaturation?

A: Yes, it is possible. This is one of the reasons why we had started this kind of experiments. As you know, almost all experiments on the growth rate measurements are carried out assuming that the surface concentration is proportional to or the same as the bulk supersaturation, if the stirring of
the solution is enough and therefore the relative solution velocity is high enough. However who can say the stirring is enough in your experiment as answered to the question by Bennema? This was my old question. During the course of our experiments I started to think about the movement of the environment itself, which has been neglected in most of the interpretation of the growth rate measurements of crystals. If there is a movement of the surrounding solution due to, say, hydrodynamical reasons just near the surface, the measurement of the concentration near the surface will not help to interpret the growth rate of a crystal because the rate equation due to diffusion in the sense of Nernst is no more valid.