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Review

In-situ observation of crystal growth and the mechanism

Katsuo Tsukamoto [a,b,*]

[a] Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita 565-0871, Japan
[b] Graduate School of Science, Tohoku University, Aramaki Aoba, Sendai, 980-8578, Japan

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Abstract

The spatial and time resolution in the measurements of growth rates and the observation of surface morphologies and the associated transport phenomena reflecting their growth mechanism have been developed because advanced microscopes and interferometers have attained nano-scale resolution. The first part covers the historical background how in-situ observation of crystal growth at molecular-level by optical and other scanning methods had been developed for understanding of crystal growth by measuring crystal growth rates and by observing surface nano-topographies, such as growth steps and spiral hillocks, with the same vertical resolutions comparable to that of the scanning probe microscopic techniques. The potential of recently developed interferometric techniques, such as Phase-Shift Interferometry (PSI) is then reviewed with the principle of the optics. Capability of measuring growth rates of crystals as low as 10^{-5} nm/s (1 μm/year) is introduced. Second part of the article emphasizes basic interferometric technique for the understanding of crystal growth mechanism by measuring growth rate *vs* supersaturation. Utilization of these techniques not only in fundamental crystal growth fields but also in environmental sciences, space sciences and crystallization in microgravity would briefly be introduced. At the end, we select a few examples how growth mechanism was analyzed based on these kinetic measurements.

Keywords: in situ observation; crystal growth; spiral growth; interferometer; AFM; microscope

1. Introduction

There is a growing interest in understanding growth kinetics, and variations in surface morphologies and the related properties of a crystal growing from various environments. It has been experimentally, as well as theoretically, established that growth history and defect structure of the growing crystal are intricately linked with its time-dependent shape and surface topography along with the associated transport phenomena. These parameters, in conjunction with interfacial solution temperature and the level of supersaturation govern finally the growth rates and the resultant surface and external morphology of the growing crystal. Therefore, in order to ensure the growth of crystals, it is important to get these precise parameters, namely "*in situ*" observation/measuring during the growth process at the best possible spatial and time resolution. Optical visualization techniques are thus useful for online real-time monitoring of the growth process and understanding the crystal growth mechanism directly.

1.1. Verification of spiral theory: surface observations vs *growth rate measurements*

Frank [1] suggested a possibility that growth of crystals at low supersaturation could take place at the emergent points of dislocations of the crystal so that any real crystal should have a number of dislocations with a screw component, terminating on the surface. When the growth takes place on these exposed "molecular terraces," the

* Tel.: +81 22 7956661; fax: +81 22 7956661.
E-mail address: ktsuka@m.tohoku.ac.jp.

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edges of these layers develop into spiral patterns centered on the dislocation. Thanks to the development of phase-sensitive optical microscopes, numerous spiral steps had been observed on SiC [2], diamond [3], natural hematite crystals [4,5], verifying the applicability of the spiral theory to the growth from vapor, hydrothermal or melt phases. However, observation of spirals on aqueous solution grown crystals was not successful because of degradation of the surface due to a remaining solution layer on top of the surface. Therefore, the spiral growth mechanism of aqueous solution grown crystals had not been verified except a few cases by surface observation method immediately after that.

Before the observation of spirals on aqueous solution crystals, Bennema [6–8] noticed the importance of the relation between growth rates of crystals with the supersaturation of solution. For that experiment, he developed a fine weighing method to measure the growth rate of solution grown from extremely small supersaturation, as reviewed in the next section.

The spiral growth of aqueous solution crystals was later confirmed by an optical observation of spirals steps on the surface of NaCl and KCl crystals [9–11], as shown in Fig. 1. In such crystals that are largely dissolved in an aqueous solution, the separation of the crystal from solution is difficult, leading to degradation of the surface after the crystal was taken out from the solution. This degradation effect is also called to be "shut-off effect." Evidences showing spiral growth have been obtained on KDP [12], ADP [13] and protein crystals by optics [14,15]. Since these observations were not in-situ methods, the effect of the "shut-off" on the surface patterns due to the degradation of the surface had to be discussed seriously and also there is no time information involved in the patterns. These difficulties led to the recent development of in-situ observation of crystal growth. In those days, these spirals of transparent crystals were observed by coating the crystal faces with a thin film of silver of reflectivity nearly 90% in order to reduce the reflection from inside of the crystal. This technique has been used until in-situ observation methods and confocal techniques have developed recently.

Numerous growth spirals were observed on the faces of carborundum, SiC [2,16] and measured with the aid of phase-contrast microscopy and multiple-beam interferometry [17]. The surfaces were observed not only for the verification of the spiral growth theory but also for the characterization of differences in their arrangement and polytypes, namely, uniquely distinguished layers in the unit cell and their origins. In recent years, varieties of studies [18] have been done on the relation between the growth mechanism and the perfection of crystals, for instance, hollow tube-free crystals to improve the quality of SiC crystals.

1.2. Growth rate versus supersaturation measurement

Bennema [6–8] measured the growth rate of K-Alum and $NaClO_3$ crystals from aqueous solution as a function of supersaturation. He pointed out the importance of the relation to verify the spiral growth mechanism for growth from solution, as shown in Fig. 2, for which experiment he developed a fine weighing method to measure the growth rate of solution grown from extremely small supersaturation, as shown in Fig. 3. He concluded that the BCF spiral theory that had been developed for crystal growth from vapor could also be applied to the growth

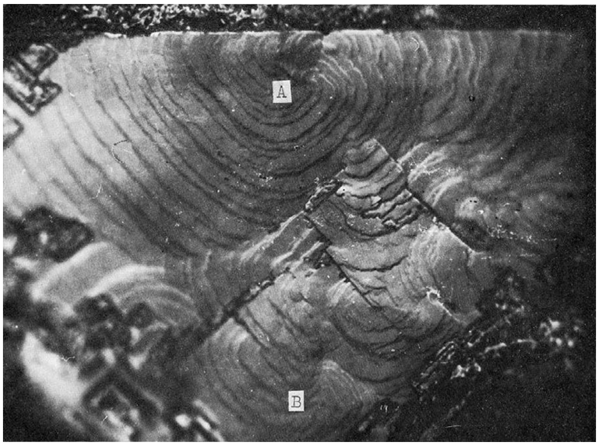

Fig. 1. Composited spiral steps from solution-grown KCl crystal, *ex situ* observation by differential interference contrast microscopy. A and B are the spiral centers. Note the mosaicity of a crystal.

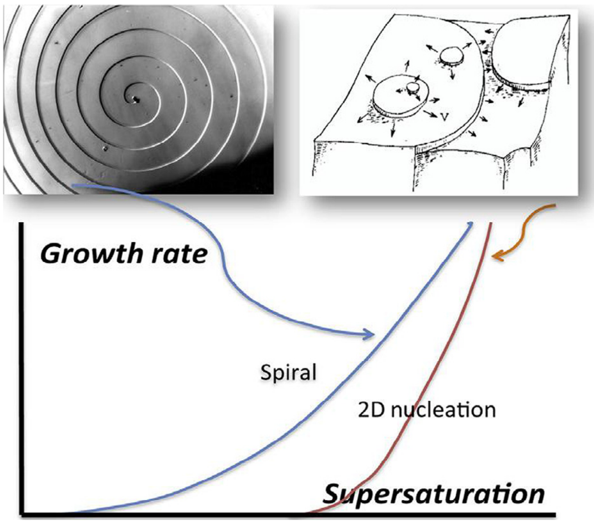

Fig. 2. Idealized growth rate vs supersaturation relationship that depends on growth mechanism. Spiral: spiral growth; 2D nucleation: 2D nucleation growth.