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GRADUATE

*Peter Rudolph*

# CRYSTAL GROWTH FUNDAMENTALS

PART I: THERMODYNAMICS OF CRYSTALLIZATION



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# **Crystal Growth Fundamentals**

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Part I: Thermodynamics of Crystallization

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## Prologue

Crystal growth is a fascinating field that is more and more needed in almost all walks of life. Unfortunately, this fact is hardly known. Why? On the one hand, this task is typically associated with the production of artificial gemstones only (often, when I introduced myself to previously unknown persons, I was asked whether I am able to produce a diamond or even a “crystal vase”). Indeed, meanwhile relatively small but perfect diamond crystals can be grown. However, they are nowhere near as interesting for the gemstone trade as they are for high-power microelectronics. Substrates made of single crystalline diamond show highest thermal conductivity, enabling an enormous dissipation of process heat. And so we have already reached one of the most important application fields of artificial crystals (the “crystal vase” made from glass and, thus, nothing to do with crystal growth we quickly put aside). Nanocrystals, high-quality epitaxial thin films, and bulk crystals are of high importance for micro- and optoelectronics, photonics, computing, communications, energy saving and storage, radiation generation and detection, medicine, biotechnology, homeland security, and so on.

On the other hand, crystals are usually not recognizable on the exterior of a technical equipment or device. Mostly, they are small-sized centerpieces of a device or the basic slice of a circuit or in a process machine entirely covered by protective casing and conductors. For instance, today each automobile, computer, cell phone, CT scanner, or tool for laser operations is equipped with devices made of various crystalline pieces. A large charge from them is directly visible as a light-emitting pixel display. Rarely are bigger make of a crystal in the form of quite large silicon wafers to be seen, as in solar cells. Or, who knows right away that the huge lenses with a diameter of 300 mm in lithography systems of ultra-short wavelengths (so-called waver steppers) are made from  $\text{CaF}_2$  single crystals?

However, the most problematic aspect of the general lack of knowledge about single crystals and crystal growth proves to be the absence of education and inadequate media presentation. Usually, artificial monocrystals are treated as of secondary importance within the framework of physics, chemistry, and materials science. Mostly, their crystallographic and growth principles as well as broad applications are outlined in introduction only. Obviously, this has to do with the fact that the mastery of crystallization and epitaxial processes on highest level as possible requires a profound interdisciplinary knowledge that combines physics, chemistry, mathematics, crystallography, materials science, electronics, automation, engineering, and so on. Nowadays elementary and special knowledge of biology and medicine also belong to it. These facts upgrade the wide field of crystal growth to a challenging quasi-self-contained interdisciplinary branch of science.

Unfortunately, the current level of related academic education does not meet this challenge. Even during the last decades, training in this field is decreasing. Looking back on the international situation at the turn of the century, compared with today, many more academic departments and research laboratories dealt with the fundamentals, ex-

periments, and technology developments of crystal growth. At present, there are only two autarkic institutes for crystal growth in Berlin (Germany) and Kharkiv (Ukraine). Of course, additionally, numerous excellent institutes of materials science with partial orientation on crystal exist, as in the USA, Japan, China, Switzerland, South Korea, Singapore, and India. However, where and how the young academics having a special knowledge for their needed crystal growth research are educated? I would like to remind the readers that until the German reunification in two self-dependent departments of crystallography at the universities of Berlin and Leipzig were trained “Diploma Crystallographers” with comprehensive knowledge on crystal growth and analysis. In addition to the basic courses of physics, chemistry, and crystallography, the students attended profound lectures on thermodynamics and kinetics of phase transition, crystal growth fundamentals and technologies, defects, and crystal applications. I by myself lectured for many decades in Berlin such disciplines and supervised numerous PhD students on crystal growth. Unfortunately, such goal-oriented education no longer exists. After one of my popular scientific lectures on crystal growth and application in 2011 in a high school, one of the enthusiastic pupils asked me “where can I study this fantastic subject?”. Sadly, my answer was “nowhere. . .”. Today, as anywhere in the world, a young scientist who is assigned a task on growth and analysis of a new crystal material, nanocrystal or epitaxial layer must familiarize themselves in a time-consuming independent study via textbooks and internet data, however, without any seminar-style discussions and practical trainings. Fortunately, there are some occasionally organized international and national schools on crystal growth providing over a period of about 1-week fundamental lectures. Over the years, the high interest and visitor volume at such training courses are the evidence that the demand of specialists contradicts the actual situation of missing academic education yet. Therefore, it is also clear why according to the statistics and scores of publication databases even reviews and editions on crystal growth and defect formations show exceptionally high read rates.

How did it come to such contradictory situations? First, there is a widespread tendency that the fundamentals and technological means of crystallization phenomena and their control are more or less already solved. Of course, over more than a half century of the development of crystal growth technology, most of the important mechanisms have become well understood. But that is not to say that all new challenges and arising problems are already mastered. For instance, although we understand fully the conditions under which morphological growth instabilities occur, it is still not possible to obtain the detailed parameters that permit the production of large, homogeneous alloy (mixed) single crystals consisting of two more components that would be invaluable as tailored substrates. For its future mastery, the crystallization process must be combined with newly developed automation programs. Further, twinning remains a serious limiter of yield in the growth of single crystals with low stacking fault energy. It seems to be due to the appearance of facets but we do not exactly understand the decisional origin yet. Then, the optimum growth conditions of high-quality large-sized GaN crystals, being extraordinary important for optoelectronics and future high-power devi-

ces, are not yet mastered. Also, the production of reproducible CdTe single crystals as radiation detectors for medical diagnostics by computer tomography needs still the minimization of diverse growing-in defect phenomena. The many other examples include growth of functional materials for electromechanical energy harvesting, monocrystals for high-efficiency hydrogen storage, periodically structured crystals for photonics, and perfect monocrystalline lenses for laser-excited fusion energy. Many further arguments can be extended to the branches of nanocrystals and epitaxial thin films too.

Another reason of the current public drop in activity levels in crystal growth study and education is due to the high-tech and strategic character of single crystals and advanced thin-film configurations. Meanwhile, there are only few remaining highly developed industrial producers with market leaderships which are increasing isolate itself, and thus excluded from the public sphere with the aim to ensure the dominating role of international competition. Actually, the number of speakers from industry at conferences of crystal growth is significantly reducing. As a result, numerous development problems, especially of technological character, do not make their way to the outside but are developing further in own R&D laboratories without access for public academic researchers. In part, this is understandable. However, it does not solve the question of where these companies draw their highly qualified new employees? Is it really sufficient to transmit the working knowledge behind the closed doors only? Taking, for example, the scientific penetration of current related patent publications (now the almost only allowed communication type of the industry), the precision of which leaves often much to be desired.

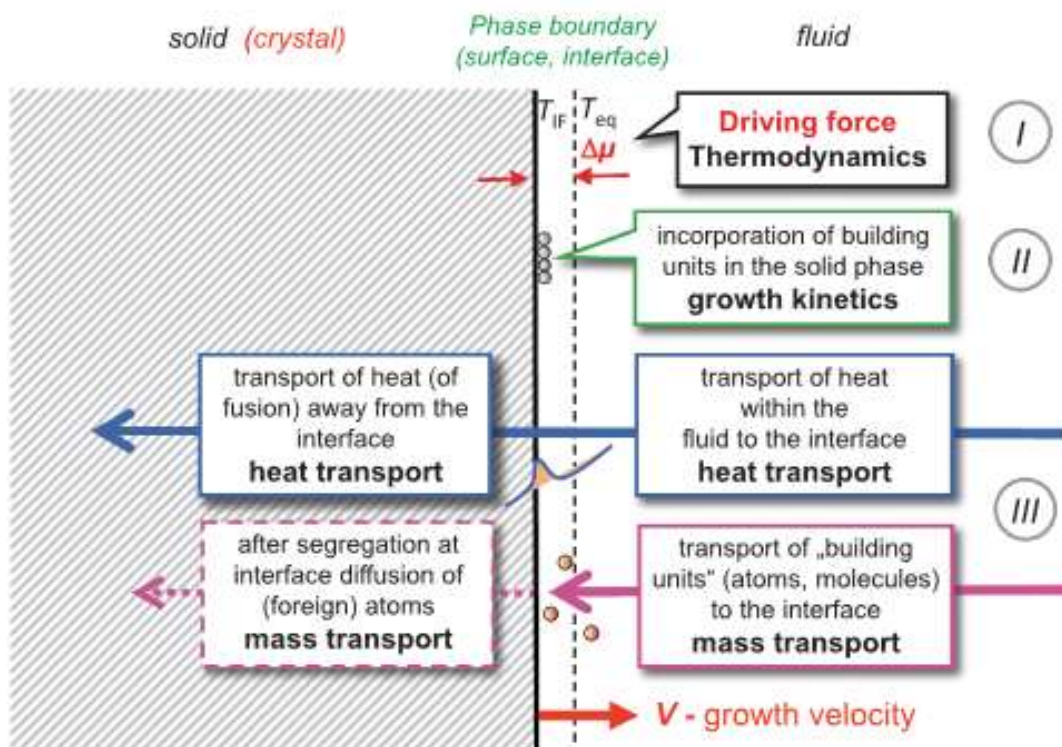
Finally, until now the crystal growth community has hardly any financial and political supporters. Despite the long-standing efforts of the International Organization of Crystal Growth (IOCG) and numerous related national associations, the general attention is decreasing among the governments. In recent years, numerous institutes and laboratories specified on crystal growth and even some national crystal growth communities have disbanded. The common opinion is that the mission and necessity of crystal growth can be settled by the firmly established areas of physics, chemistry, and materials science. However, until now this succeeded only to a limited extent.

Whatever the development, it is my deep intention to contribute to maintaining and reinforcing the knowledge of fundamentals of crystal growth even to the worldwide young researchers. Therefore, I publish now my related lectures that I hold over 20 years at the Humboldt University in Berlin and subsequently in many universities, institutes, and companies in about 30 countries. Moreover, I was teacher of 7 international summer schools of the IOCG and about 20 crystal growth courses of the International Union on Crystallography (IUCr) and diverse national communities. Now is the time to commit my lecture texts and slides to publish. Of course, during all of this time of my knowledge transfer I was always tried to keep abreast with the latest state of development and to bring the present book to the current state of the art.

I would like to emphasize that there is already a wide collection of excellent reviews and textbooks on crystal growth fundamentals. Most of them I studied as base

material for my lectures and refer to them at the end of my lecture parts. I recommend emphatically using these papers and books for in-depth knowledge. However, in my opinion, a coherent textbook series of introductory character on fundamentals of crystal growth and defect control even for newcomers and further training is still missing. Of course, the outstanding three volumes are Elsevier's *Handbook of Crystal Growth* of first edition (1994) and second edition (2015), and Springer's *Handbook of Crystal Growth* (2010). Though the numerous chapters of these editions have been written by various authors of different scientific levels requiring in many cases high expertise, numerous redundancies are unavoidable. In comparison, it is intended that the overall image of the present lecture collection is coherent and particularly suitable for beginners. No detailed presentations of higher mathematics are provided (some special important derivations are given in gray backing Spec boxes). As a special feature, figures are prepared in the graphical form identically with my lecture slides often combining sketches and images with the general formulas. They also contain the corresponding authors and literature references for further studies.

The starting slide is shown in Fig. P.1. It shows a sketched *crystallization front*, also named *solid–fluid interface*, propagating with normal *growth velocity*  $v$ . thermodynamically,  $v$  depends on the *driving force of crystallization*  $\Delta\mu$  being the potential difference between the phases, here proportional to the difference between the equilibrium temperature ( $T_{\text{eq}}$ ) and undercooled value ( $T_{\text{IF}}$ ) at the interface. However, be-



**Fig. P.1:** Partial processes determining crystal growth: thermodynamic (I), kinetic (II), and transport of heat and mass (III).

cause the thermodynamics is not able to impart the crystallization processes at the growing interface in microscopic details, the branch of *kinetics* becomes involved. It shows the various interface nature from atomistic view and its growth mode as a function of its atomically smoothness and roughness as well as of the presence of defects and foreign atoms. Finally, each crystallization requires temperature and concentration (pressure) *gradients*. This is due to the necessary control of the transport of heat, especially the generated heat of fusion away from the interface. Additionally, the transport of crystal *building units* (atoms, molecules, and dopants) toward the growing interface is required. At the same time, undesired foreign atoms (impurities) should be repulsed at the growing interface as effectively as possible. As can be seen, the crystal growth processes prove to be varied and versatile, which requires a comprehensive study. It can be stated that the *fundamentals of crystal growth* are based on three factors:

- (i) *thermodynamics* (of phase transition),
- (ii) *kinetics* (of crystallization processes), and
- (iii) *transport* (of heat and mass).

This is summarized in Fig. P.2.

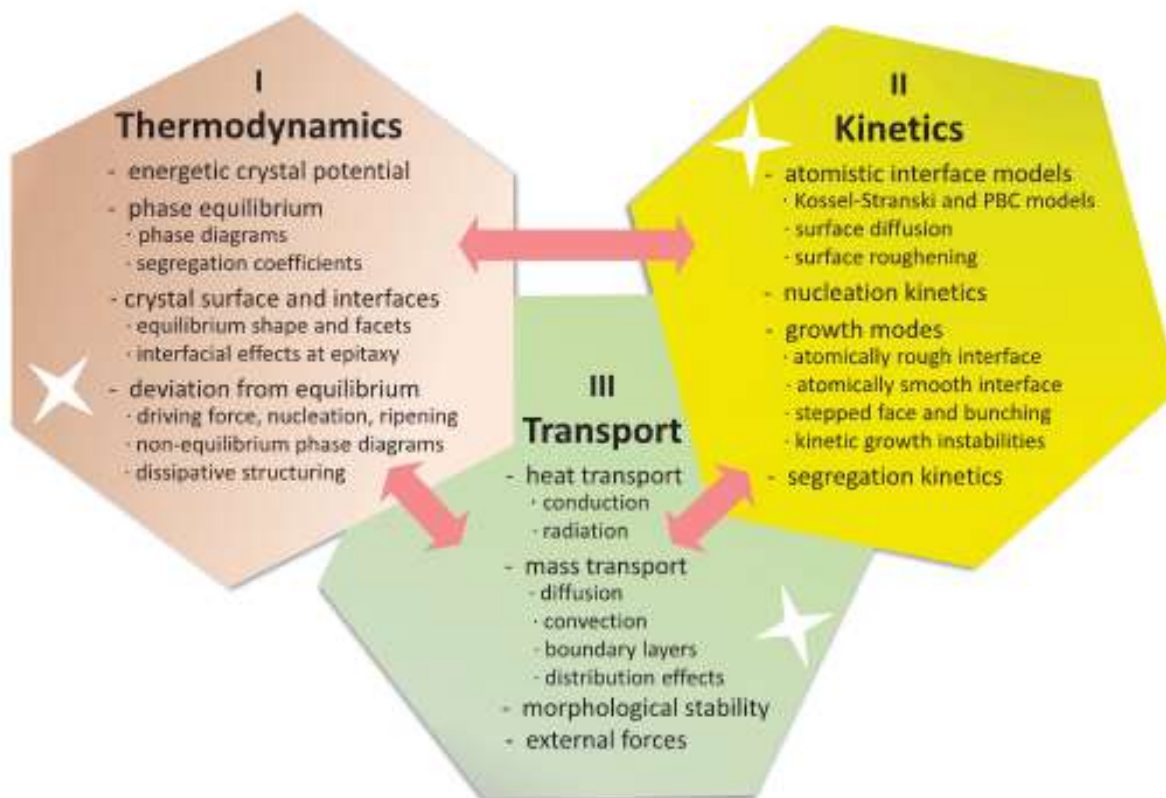


Fig. P.2: Three pillars of fundamentals of crystal growth.

Some decisional topics of each field to be treated by the following lectures are added. Of course, all three basics are closely interrelated. Nevertheless, their individual treatment has proven to be the best and most logical for teaching effectiveness. In a fourth lecture part, the origins of

(iv) *crystal defect* formations and their mastery are planned to add. Their exact understanding is only possible on the basis of the three crystal growth fundamentals (i)–(iii).

My lecture parts correspond to this chronology.

I am very grateful to all previous national and international students for their participation and interest in discussions in my lectures. I also have to thank all my former research co-workers and teaching colleagues at the universities and institutes where I was employed as well as numerous members of the German Association of Crystal Growth and IOCG. Their widespread support, critical comments, and recommendations have made an important contribution to the continuous improvement of my lecture level. I would particularly like to mention two scientists who shaped my own professional training in the field of crystal growth fundamentals essentially. On the one hand, this is Dr. Lars Ickert, who introduced me by his excellent lectures into the fundamentals of phase transition, nucleation, and epitaxy as I started to work at the Department of Crystallography, of the Humboldt University, as young postdoc. On the other hand, this is Prof. Alexander A. Chernov who fascinated me with his fabulous training course on crystal growth fundamentals during the former international summer school on crystal growth in Varna (Bulgaria). Also his comprehensive chapter on crystal growth in Springer's *Modern Crystallography III* (1984) provided me the first overall overview of this enthusiastic scientific field.

It is a great pleasure for me to thank the Walter de Gruyter GmbH for enabling the publishing of my long-lived lecture courses on fundamentals of crystal growth in book form and, particularly, for including my lecture slides as figures in original design. My special thanks go to the Senior Acquisitions Editor Physical Sciences Kristin Berber-Nerlinger, the Editor Ute Skambraks, and the Senior Project Manager Kowsalya Perumal for the excellent cooperation, consultancy and their great effort with the print preparation of text, formulas and reproductions.

*Peter Rudolph*  
Schönefeld, May 2025