

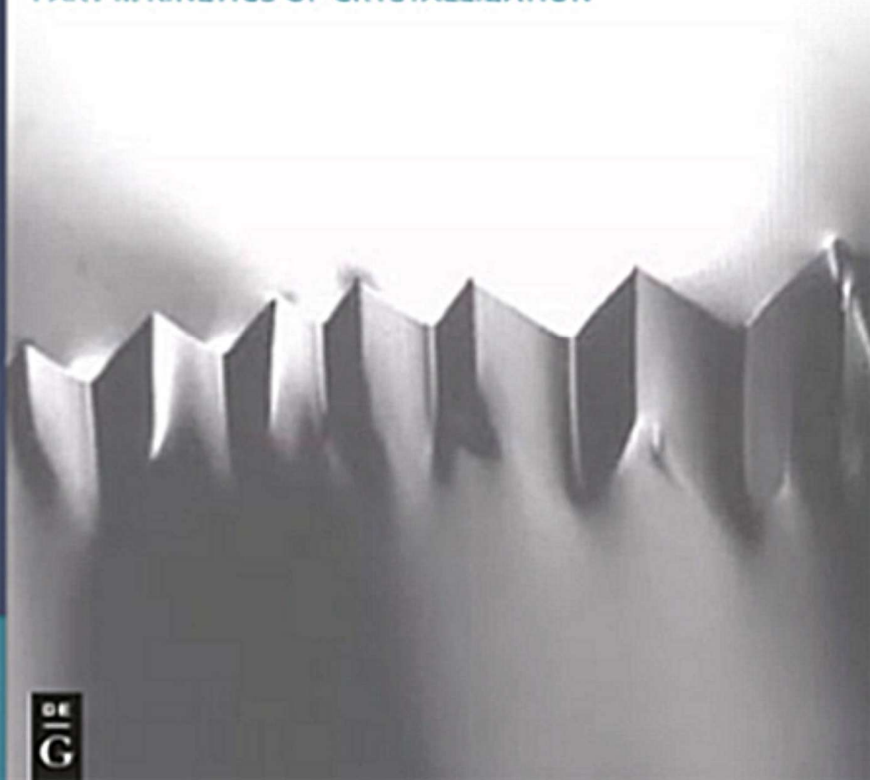
DE GRUYTER

GRADUATE

Peter Rudolph

CRYSTAL GROWTH FUNDAMENTALS

PART II: KINETICS OF CRYSTALLIZATION



Cover image:

Faceted melt-solid interface of a growing antimon crystal in situ observed by a heating system with microscope in the laboratory of **Professor Kozo Fujiwara** at the Institute for Material Science of the Tohoku University in Sendai.

Image area 1.2 mm x 1.0 mm. (*courtesy of Prof. K. Fujiwara*).

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About the author



Peter Rudolph is a professor emeritus of crystallography and crystal growth. He was born in Germany in 1945. He studied and defended his Ph.D. at the Technical University of Lviv (Ukraine). After his long-year stay at the Humboldt University of Berlin and visiting professorship at the Tohoku University in Sendai (Japan), he was employed at Leibniz Institute for Crystal Growth in Berlin. Since 2011 he is active as consultant for crystal growth technology. He acted as lecturer of crystal growth fundamentals in nearly 30 countries. He was a member of the Executive Committee of International Organization of Crystal Growth (2004–2011) and the president of the German Association of Crystal Growth (2010–2011). He was awarded the medal of the German Association of

Crystallography in 1990 and Innovation Prize Berlin-Brandenburg in 2001 and 2008. He is one of the editors of the three-volume *Handbook of Crystal Growth* (Elsevier 2015) and seven other books on crystallization. His professional literature includes over 300 papers and book contributions as well as 35 patent publications. In 2023, he was awarded the Laudise Prize of the International Organization for Crystal Growth for exceptional achievements in the field of crystal growth, particularly with regard to technological solutions.

The present part II deals with the kinetics of crystallization, rather atomic and molecular processes at the nucleation and propagating fluid-solid interfaces. After the atomistic morphology of crystal faces, surface diffusion, nucleation sequences and statistics are introduced the main part of the book deals with models of growing phase boundaries, including diffuse phase transitions, and growth modes of singular (faceted), vicinal (stepped) and atomically rough interfaces. Finally selected step growth instabilities and the kinetics of incorporation of additives (segregation atomistic) are outlined.

However, to control thin film and bulk crystal growth processes as perfectly as possible in addition to thermodynamic and kinetic knowledges, the processes of heat and mass transport, such as temperature distribution, diffusion and convection in fluid phases, must also be mastered, which will be treated in Part III.

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Prologue

The second part of my lecture trilogy on crystal growth fundamentals is now before us. It concerns the kinetics of crystallization – again a fascinating branch permitting us the access to the microscopic, rather, atomistic and molecular processes of the formation and growth of artificial crystals and thin films, which are the core of the over-all high tech in our life.

Let's look again at the sketch of a propagating fluid–solid interface in Fig. P1, already known from Part I. After we have completed the treatment of thermodynamics (I), it is now the turn of kinetics (II) to give us the details of interface nature and incorporation of “building units” (atoms, molecules, and additives) into the growing bulk, nano-, or thin-film crystal. However, before we get started, allow me to give some instructions for using this brochure.

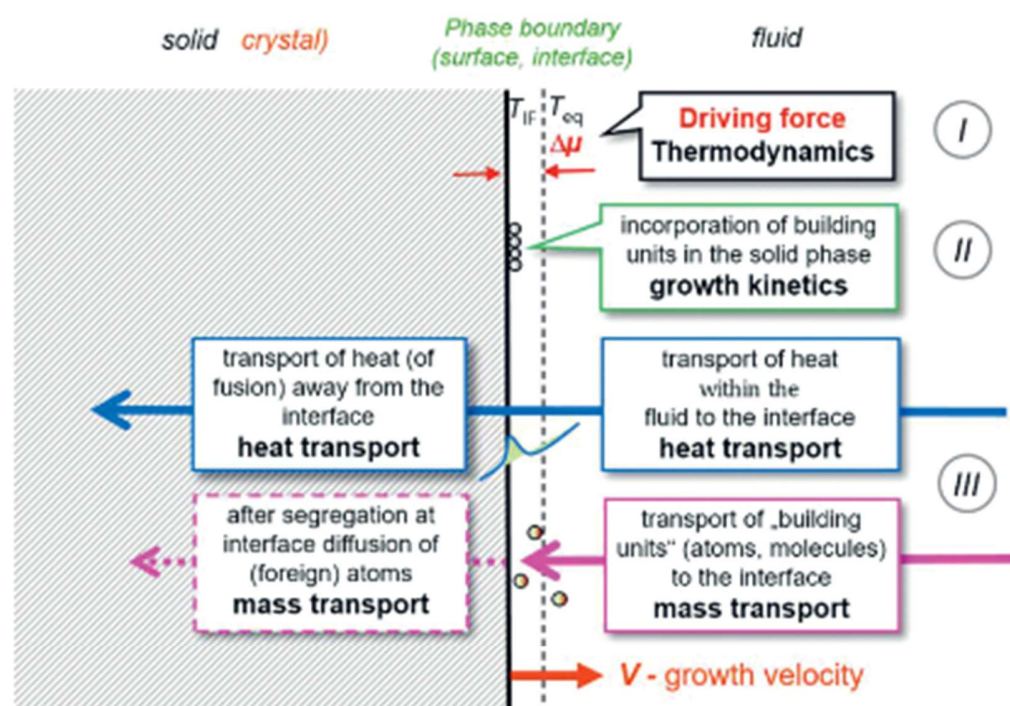


Fig. P.1: Partial processes determining crystal growth: thermodynamic (I), kinetic (II), and transport of heat and mass (III).

This Part II not only follows on directly from Part I, but is actually interwoven with it. In many present passages, reference is made to unconditional relationships to chapters, formulas, and figures in this former part on thermodynamics. It is often advisable to have it with you at the same time in order to obtain conclusive explanations. For instance, the driving force of crystallization was extensively introduced in Part I (see Fig. P1) as essential precondition for the nucleation of the new stable crystalline phase and propagation of the interface within the old instable surrounding fluid

phase. It is, of course, just as much a drive for the desired sequences of kinetic processes, why it is here often mentioned again but under the condition of already detailed knowledge from Part I.

My striving for a relatively simple presentation, comparable to Part I, arises from the problematic aspect of a general lack of knowledge and education about single crystals and crystal growth. Therefore, this trilogy aims first and foremost to contribute to the education of young scientists embarking on a career in crystal, thin film, and nanocrystal research or production, but also to the further training and reference of experienced scientists, engineers, and anyone interested.

One more important point: when I told a former colleague about my idea to write books on crystal growth fundamentals, he said “well, that’s all already known”. I’m sure he was right, but that’s not my point, because I received a decisive such wish from numerous participants of my many lectures which encouraged me to edit a well-compressed and easily comprehensible overview and, above all, with the figures of my slides as they were shown within the lectures. Of course, there are already published excellent books and reviews on crystal growth kinetics. The following are just a few primary examples:

A.A. Chernov, *Modern Crystallography III, Crystal Growth* (Springer, Berlin 1984).

P. Bennema, *Growth and Morphology of Crystals*, in: D.T.J. Hurle (ed.), *Handbook of Crystal Growth*, Vol.1A (Elsevier, North-Holland, Amsterdam 1993).

I.V. Markov, *Crystal Growth for Beginners* (World Scientific Publ. Co., Singapore 2003) 2nd ed. (2008), 3rd ed. (2017);

K.A. Jackson, *Kinetic Processes* (Wiley-VCH, Weinheim 2004); B. Mutaftschiev, *The Atomistic Nature of Crystal Growth* (Springer 2013);

T. Nishinaga, (ed.), *Handbook of Crystal Growth, Second Edition, Fundamentals: Thermodynamics and Kinetics*, Vol. IA (Elsevier, Amsterdam 2015).

As a matter of course, these works are also of basic character for me, and I included numerous keynotes from them. Therefore, they are highly recommended for further in-depth study of the subject matter. On the other hand, I also included own experimental results, which have been achieved together with the former team at the Institute of Crystal Growth in Berlin. For instance, we used the characteristic reduced growth velocity of singular faces in silicon combined with an optimized traveling magnetic field to grow Czochralski crystals with rectangular cross section. Such crystals are applicable for the production of related wafer profiles for solar cells but without material waste which is common for cylindrical crystals. Further, my many years of studies on the melt structuring in II–VI semiconductor compounds are also included. Such behavior, differing markedly from Si and III–V compounds due to the high bond ionicity ratio, leads to preordering and even preorientation before the growing interface. As a result, the seed orientation and regular atom incorporation in the growing crystal are severely impaired. Both are real examples of kinetic processes even at bulk crystal growth.

Of course, kinetics plays a decisive role at epitaxial and nanocrystalline growth. This is considered in this part. Actually, the growth of single-crystalline thin films is based on typical kinetic phenomena to be controlled and even in situ observed, such as “born-to-spread” mechanism and spiral growth on singular faces, step-by-step growth on vicinal faces, and 3D growth on kinetically rough surfaces. Further, the favorable specificity of step-driven bending of threading dislocations occurred. However, all kinetic phenomena are always transferable to bulk growth, especially when facets are presented at the crystallization from the melt but are rather characteristic at the growth from solution and vapor. Thus, the kinetics of crystallization is of overlapping nature. That is why in this book the bulk growth and epitaxial methods are often mentioned side by side but their techniques are not explicitly explained. The knowledge of them is a prerequisite. For those who are not yet sufficiently informed about the growth techniques, the following reviewing works are suggested first:

- J.C. Brice, P. Rudolph, *Crystal Growth in: Ullmanns Encyclopedia of Industrial Chemistry, Sixth, Completely Revised Edition, Vol. 10* (Wiley-VCH, Weinheim 2003);
- P. Rudolph (ed.), *Handbook of Crystal Growth, Second Edition, Bulk Crystal Growth: Basic Techniques, Vol. IIA* (Elsevier, Amsterdam 2015);
- T. Kuech (ed.), *Handbook of Crystal Growth, Second Edition, Thin Films and Epitaxy: Basic Techniques, Vol. IIIA* (Elsevier, Amsterdam 2015); P. Capper (ed.), *P.. Bulk Crystal Growth: Methods and Materials*. (Springer, Heidelberg 2017);
- R.S. Feigelson, *Crystal Growth History: Theory and Melt Growth Processes*, *J. Crystal Growth* 594 (2022) 125800.

Another remarks concern (i) the omitted extra list of symbols. Instead of this under the mathematical equations, they are always explained anew. This is also intentional, as it facilitates the coherent reading and compact study of individual chapters. (ii) The here missing treatment of the phenomenon of morphological instability will be given in Part III due to its close connection with diffusion transport within the boundary layer. (iii) The numeric simulation codes, being of indispensable importance for the knowledge of growth kinetics, are not explained here but their impressive model results are of course sufficiently included. Once more, for those who want to acquire the methodological knowledge, the following exemplary reviews are provided:

- G. Müller, J. Friedrich, *Challenges in modeling of bulk crystal growth*. *J. Crystal Growth* 266 (2004)1.
- J.J. Derby, A. Yeckel, *Modeling of Crystal Growth Processes*, in: G. Müller, J.-J. Metois, P. Rudolph, (eds.), *Crystal Growth – from Fundamentals to Technology* (Elsevier, Amsterdam 2004) pp.143.
- W. Miller, *Simulation of Epitaxial Growth by Means of Density Functional Theory, Kinetic Monte Carlo, and Phase Field Methods*, in: T. Nishinaga, (ed.), *Handbook of Crystal Growth, Second Edition, Fundamentals: Thermodynamics and Kinetics, Vol. IA* (Elsevier, Amsterdam 2015) pp. 521.

Again, 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 coworkers 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 International Organization for Crystal Growth. Their widespread support, critical comments, and recommendations have made an important contribution to the continuous improvement of my lecture level.

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.

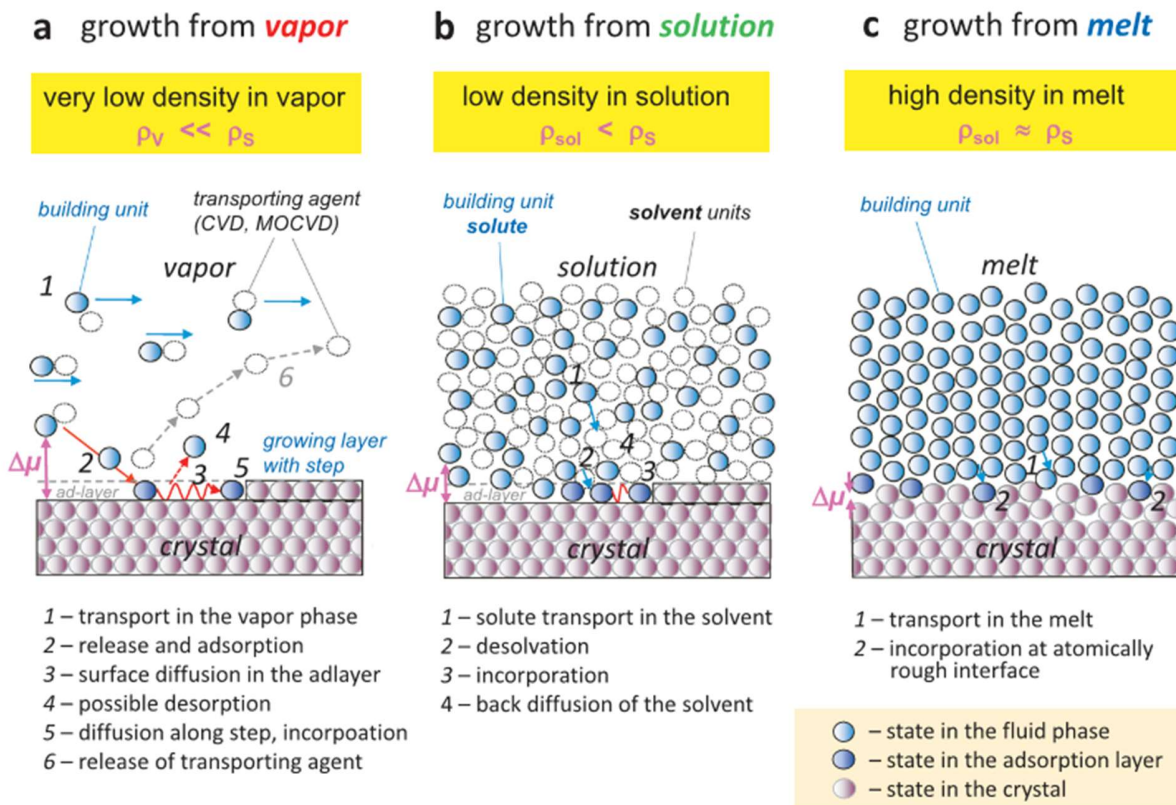


Fig. 1.2: Chronological process events at growing fluid–solid (crystalline) interfaces.