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Vladimir G. Dubrovskii

Nucleation Theory and Growth of Nanostructures

 Springer

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*Dedicated to the memory of my father,
Professor German V. Dubrovskii*

Preface

Nucleation theory provides a powerful tool for growth modeling of a variety of objects: from liquid droplets to thin solid films and biological structures. Theoretical approaches based on nucleation theory apply whenever the particles, or “nuclei,” of a new phase emerge spontaneously in a metastable surrounding of an old phase. Typical examples include water condensation from supersaturated vapors and growth of vapor-deposited surface islands. In most cases, nuclei of interest consist of at least several tens of atoms and are terminated by distinct boundaries with a metastable phase. Such systems can be well described within the frame of the classical approach involving macroscopic approximations for the formation energy and a kinetic equation for time-dependent distribution of nuclei over sizes, coupled with the material balance. With the known thermodynamics of a particular system and at the given growth conditions, classical nucleation theory allows for a detailed modeling in terms of size distribution. Perhaps the most important result of this approach in the Zeldovich nucleation rate, showing how many stable nuclei would emerge per unit time in a given system at the known supersaturation.

Nucleation theory has been proved very practical, capable of answering (qualitatively as well as quantitatively) important technological questions such as: what happens to the size distribution if the growth temperature is raised or the influx is terminated? Consequently, many excellent reviews and books have been published devoted to nucleation theory and applications. So, the question arises: why this new book on nucleation theory might be useful? Of course, it is the readers who will decide. The main intention in this work, which makes it rather different from others, was to link the two subjects that I have been studying for many years: analytical research in general nucleation theory and growth modeling of semiconductor nanostructures obtained by modern epitaxy techniques.

The general topic was my “first love” in the 1980s, when I was a student at the Department of Statistical Physics of St. Petersburg State University under the supervision of Professors F. M. Kuni and A. P. Grinin. Later on, I started my own research in the growth kinetics of thin films, largely inspired by the excellent works of S. A. Kukushkin and A. V. Osipov, who applied nucleation theory for surface islands. The subject of semiconductor nanostructures attracted my attention much later, at the beginning of the 2000s, after I entered Zh. I. Alferov Laboratory of Physics of Semiconductor Heterostructures at Ioffe Institute and

then have been working at St. Petersburg Academic University. It turned out that nucleation theory in open systems helps to substantially extend our knowledge about the growth behavior and properties of sophisticated semiconductor nanostructures such as quantum dots and nanowires. In this research, I was supported by my Ioffe teachers and friends, R. A. Suris, V. M. Ustinov, and G. E. Cirilin. Many studies have been performed together with my former pupil N. V. Sibirev. I would like to express my sincere thanks to all these people for their help in different aspects of my work. Over time, my own group has grown into a theoretical laboratory dealing mainly with nucleation theory and its applications in physics of nanostructures. With other groups in our city also continuing their research, St. Petersburg can be truly called “the nucleation city,” a nice place to work in this field.

However, our research would not be possible without external collaboration both in nanostructure growth theory and modeling experimental data from other groups. Here, I would like to thank my main collaborators, namely, F. Glas and J. C. Harmand from LPN CNRS (France) for a long and fruitful joint work on semiconductor nanowires, and C. J. Chang-Hasnain from UC Berkeley (USA) for collaboration in the field of III–V nanowires and nanoneedles. Other colleagues include P. Pareige (University of Rouen, France) and B. Grandidier (IEMN Lille, France) who invited me to work on Si and Ge nanowires, E. Gil (University of Clermont-Ferrand, France) on hydride vapor phase epitaxy of nanostructures, H. Riechert (PDI Berlin, Germany) on self-induced GaN nanowires, D. Bimberg (TU Berlin, Germany) on InAs quantum dots, D. Zeze (Durham University, UK) on applications, and X. Ren (BUPT, China) on III–V nanowires. Especially, it was Frank Glas who not only made an outstanding contribution to the entire field of nanostructure modeling (which I use extensively throughout the book) but has also stimulated my own research by fruitful discussions over many years. Of course, I was also influenced by other theorists with whom I have not had a chance of working together, particularly J. Tersoff, D. Kashchiev and J. Johansson. I am grateful to many colleagues and friends for inviting me for short stays with their groups, providing me with new data and a little more “free time” to work.

The content of the book, defined by the general subject and the topics of my own research over the last 20 years, is the following. [Chapter 1](#) presents a systematic introduction to classical nucleation theory. It is written in such a way that the readers who are looking for only a brief preview of the subject can skip after this chapter. Nevertheless, the introduction contains original material: theoretical considerations of the droplet stability in unusual configurations and some exact solutions to the discrete rate equations. The main goal of the chapter is to formulate and justify the macroscopic approach, the basic kinetic equations, the stationary state, and the Zeldovich nucleation rate. [Chapter 2](#) is the most mathematized part of the book. Here, I consider in detail different stages of the entire nucleation–condensation process (usually in open systems), separated from each other due to a timescale hierarchy. A special emphasis is given to the double-exponential distribution shape at the nucleation stage. After that, the regular growth stage, the Ostwald ripening and the direct coalescence stages are studied,

based on the continuum theory. At the end of the chapter, I present some exactly solvable cases of discrete rate equations for irreversible growth, with interesting mathematics and applications. In [Chap. 2](#), the main ideas of this work are formulated in the general case, showing how the morphology of emerging nanoparticles can be tuned by technologically controlled conditions such as temperature and flux.

[Chapter 3](#) is devoted to self-induced nanoislands of three types: the Stranski–Krastanow semiconductor quantum dots, III–V nanoneedles on lattice mismatched substrates and metal islands on insulators. Here, the exposition becomes friendlier for non-theorists. I start the analysis with a general description of the Stranski–Krastanow growth and consider the driving force: elastic relaxation on free side facets. General theory is then applied for growth modeling of different nanostructures and formulating the kinetically controlled knobs to tune the resulting morphology. Theoretical predictions are compared with many experimental data (which is also the case in the foregoing chapters), making the whole composition of easier access for a more general audience.

Almost half of the book is devoted to modeling of semiconductor nanowires. In [Chap. 4](#), the “vapor–liquid–solid” growth method of nanowire synthesis is considered catalyzed by metal particles. The chapter starts with a physical introduction explaining the essentials of this method. After that, I present the advanced growth modeling of “vapor–liquid–solid” nanowires. This includes the size-dependent limitations on the growth rate, the mononuclear growth, the diffusion-induced contributions, and the two-dimensional nucleation at the liquid–solid interface or at the triple phase line. In many cases, general theory can be reduced to simple models for complex growth phenomena such as nonlinear growth effects and self-consistency between the material transport and the nucleation-mediated nanowire elongation. I consider in detail the length-time, length-radius and other important theoretical dependences in comparison with relevant experimental data.

[Chapter 5](#) concerns more specific aspects of nanowire modeling: elastic relaxation and plastic deformation in nanowires on lattice mismatched substrates, nanowire shapes, doping, self-catalyzed growth, self-induced GaN nanowires on silicon substrates and cooperative growth effects. Here, the conventional nucleation theory is considerably modified in many respects. In particular, one of the most interesting features of nucleation in confined volumes of catalyst droplets is a self-regulatory oscillatory behavior of supersaturation. This feature originates from a special type of timescale hierarchy where nucleation and growth becomes much faster than the refill stage, and has an interesting impact on nucleation statistics and the morphology of nanowires. In [Chap. 6](#), I consider polytypism of III–V nanowires, a surprising effect which appears to be closely related to peculiarities of nucleation during the vapor–liquid–solid growth. Crystal structures of III–V materials are carefully described, along with relevant data on the bulk energy differences and surface energies of relevant nanowire sidewalls. This part goes far beyond the nucleation topic, but is absolutely necessary for modeling. After that, I describe theoretical approaches that allow us to understand and control crystal structures in different nanowires. At the end, while considering the Ga-catalyzed

formation of GaAs nanowires and their zincblende structure, I return to the very beginning of the book and further develop a model of the wetting growth mode of nanowire growth.

Each chapter begins with a brief introduction describing its subject and structure. I use the numbering of mathematical expressions and figures of the (x,y) type, where x is the chapter number and y is the number of this formula within the chapter, for example, (4.35) is formula No. 35 of Chap. 4. I have tried to make the book self-consistent so that the reader could find all the necessary material in the text, which should be convenient for students. However, some parts are explained only briefly, with the reference list containing almost 600 citations. Not many acronyms are used in the text (so that nanowire remains nanowire but not NW) due to my personal dislike of acronyms.

I sincerely hope that this work and my modest contribution to growth modeling of nanostructures will attract more researches, especially young scientists, to this rapidly growing field in the future.

Finally, I wish to thank Springer Edition and in particular Executive Editor in Physics, Claus Ascheron, for inviting me to write this book.

Saint Petersburg

Vladimir G. Dubrovskii

Contents

1	Fundamentals of Nucleation Theory	1
1.1	Thermodynamics of Phase Transition	4
1.2	Scenarios of Phase Transition	11
1.3	Laplacian Pressure and Gibbs–Thomson Effect	15
1.4	Contact Angle	18
1.5	Formation Energy	24
1.6	Adsorption and Thin Films	30
1.7	Growth Rates	38
1.8	Rate Equations of Nucleation Theory	43
1.9	Exact Solutions	47
1.10	Continuum Approximation	55
1.11	Stationary State	57
1.12	Stages of Nucleation-Condensation Process	64
2	Theoretical Description of Condensation Stages	75
2.1	Transformation to Invariant Size	77
2.2	Nucleation Stage	81
2.3	Nucleation Modes	88
2.4	Green Function at the Growth Stage	95
2.5	Absence of Fluctuation-Induced Spreading at the Nucleation Stage	100
2.6	Time Evolution of Size Spectrum	101
2.7	Asymptotic Growth Stage	112
2.8	Ostwald Ripening	115
2.9	Tailoring the Size Distribution	122
2.10	Kolmogorov–Johnson–Mehl–Avrami Model	129
2.11	Three-Dimensional Thin Films	133
2.12	Growth Rate of a Crystal Facet of Arbitrary Size	138
2.13	Irreversible Growth	143
2.14	Formation of Peptide Chains	156
2.15	Open Irreversible Systems	161
3	Self-Induced Islands in Lattice Mismatched Systems	167
3.1	Size Quantization in Semiconductor Nanostructures	170

3.2	Stranski-Krastanow Growth	178
3.3	Elastic Relaxation in Nanostructures	190
3.4	Growth Scenarios and Preferred Aspect Ratio	197
3.5	Formation Energy of Stranski-Krastanow Islands	207
3.6	Nucleation Stage and Critical Thickness	213
3.7	Growth of Stranski-Krastanow Islands	219
3.8	Modeling of Size Distribution	223
3.9	Role of Surface Steps	225
3.10	Subcritical Quantum Dots	228
3.11	Kinetically Controlled Engineering of Quantum Dot Ensembles	231
3.12	Theory and Experiment: InAs/GaAs System	235
3.13	Theory and Experiment: Ge/Si System	243
3.14	III–V Nanoneedles and Nanopillars	249
3.15	Growth Kinetics of GaAs Nanoneedles	260
3.16	Growth Properties of Co Nanoislands on $\text{CaF}_2/\text{Si}(111)$	265
4	Vapor–Liquid–Solid Growth of Nanowires	275
4.1	Vapor–Liquid–Solid Growth Mechanism	277
4.2	Alternative Growth Mechanisms	298
4.3	Role of Size-Dependent Effects	304
4.4	Role of Surface Energies	310
4.5	Triple Phase Line Nucleation	315
4.6	Non-planar Growth Interfaces	318
4.7	Adsorption-Induced Growth	323
4.8	Diffusion-Induced Growth	332
4.9	Simplified Growth Equations	342
4.10	Self-Consistent Growth Models	347
4.11	Length—Radius Dependences	355
4.12	Temperature Conditions for the VLS Growth	369
4.13	Growth Chronology of a Single InPAs Nanowire	379
4.14	Non-linear Effects in Nanowire Growth	384
4.15	Narrowing the Length Distribution of Ge Nanowires	390
5	Special Topics of Nanowire Growth and Morphology	397
5.1	Axial Nanowire Heterostructures	399
5.2	Nanowires on Lattice Mismatched Substrates	403
5.3	Core-Shell Nanowire Heterostructures	410
5.4	Cylinder-to-Cone Shape Modification	416
5.5	Growth Modeling of CdTe Nanowires	427
5.6	Nucleation Statistics	430
5.7	Self-Regulated Pulsed Nucleation in Catalyzed Nanowires	435
5.8	Boron Distribution in Si Nanowire	442
5.9	Ga-catalyzed GaAs Nanowires	448

5.10	Self-Induced GaN Nanowires	456
5.11	Nucleation of GaN Nanowires	463
5.12	Scaling Growth Kinetics	471
5.13	Vertical Growth Rate of GaN Nanowires	476
5.14	Cooperative Effects in Nanowire Growth	482
5.14.1	Shadow Effect	483
5.14.2	Re-emission Assisted Growth of InSb-InAs Nanowires	488
5.15	Chemical Potentials for Au-assisted VLS Growth of III-V Nanowires	493
6	Crystal Structure of III–V Nanowires	499
6.1	Crystal Structures of III–V Materials	501
6.2	Experimental Observations of Polytypism	509
6.3	Surface Energies of Nanowire Sidewalls	515
6.4	Equilibrium Radius of Zincblende-Wurtzite Transition	523
6.5	Kinetic Theory of Wurtzite Phase Formation	526
6.6	Further Development of Kinetic Approach	532
6.7	Kinetic Radius of Structural Transition	538
6.8	Crystal Phase Engineering	541
6.9	Benefits of High Growth Rate	553
6.10	Zincblende Structure of Ga-catalyzed GaAs Nanowires	559
6.11	Wetting Mode of VLS Growth	563
6.12	Wurtzite Structure of III–V Nanoneedles	568
	References	573
	Index	591