NanoScience and Technology

For further volumes:
http://www.springer.com/series/3705

The series NanoScience and Technology is focused on the fascinating nano-world, mesoscopic physics, analysis with atomic resolution, nano and quantum-effect devices, nanomechanics and atomic-scale processes. All the basic aspects and technology-oriented developments in this emerging discipline are covered by comprehensive and timely books. The series constitutes a survey of the relevant special topics, which are presented by leading experts in the field. These books will appeal to researchers, engineers, and advanced students.

Vladimir G. Dubrovskii

Nucleation Theory and Growth of Nanostructures

Springer

Vladimir G. Dubrovskii
Saint Petersburg Academic University
Saint Petersburg
Russia

ISSN 1434-4904 ISSN 2197-7127 (electronic)
ISBN 978-3-642-39659-5 ISBN 978-3-642-39660-1 (eBook)
DOI 10.1007/978-3-642-39660-1
Springer Heidelberg New York Dordrecht London

Library of Congress Control Number: 2013945850

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

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. Cirlin. 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