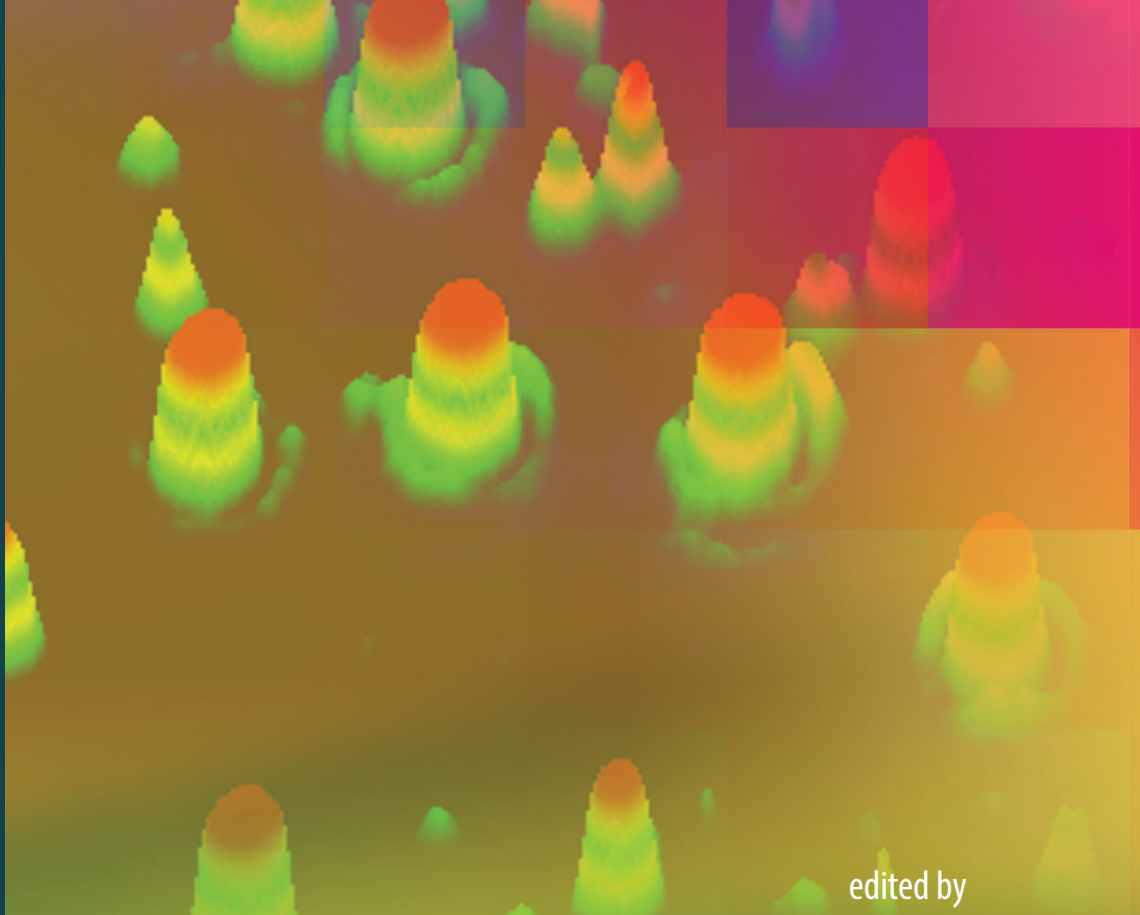

edited by
Christian von Borczyskowski
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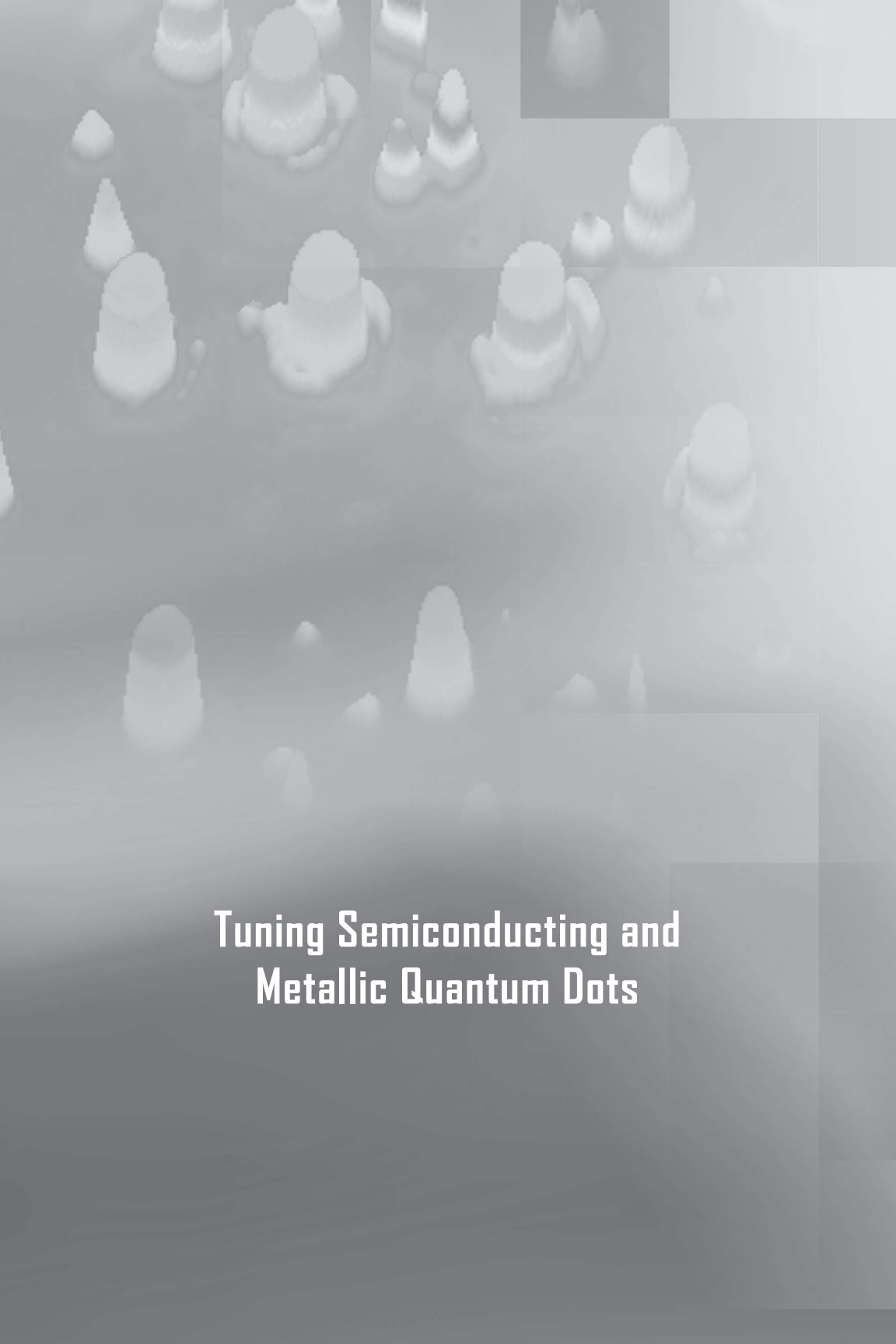
Spectroscopy and Dynamics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For Sabine and Tamara

Contents

Preface

During the last few decades, nanomaterials have become an intensively growing field of interest, with respect to both applications and fundamental science. These materials, especially from semiconductors and metals, are equally important for applications such as nanoelectronics, sensoric applications, and life sciences. Nowadays, this field can be characterized by several material classes, including the related preparation or manufacturing processes. According to the widely varying features of these materials, scientific approaches in analyzing, understanding, and modeling are inherently interdisciplinary and cover a still growing range of physical, chemical, and biological disciplines. Common to many of these materials is the fact that their properties depend on the dimensions in the nanometer range: size matters! According to the extremely small size, a large surface-to-volume ratio is an inherent property of all these materials. This opens access to both surface and core features. However, this perspective is not merely a linear superposition of the respective properties but constitutes completely new ones. Naturally, interfaces play a central role. Though this is a central aspect of nanomaterials, a detailed understanding and control of inherent properties of surfaces and interfaces, such as structure–function relationships, has to be investigated with respect to the specific class or even subclass of nanomaterials.

Moreover, in an analogy to quantum well structures, dimensions can be further downsized to quantum dots from semiconductors or metals. At a critical dimension, bulk properties (such as optical ones) deviate from those of the bulk and become size dependent. This results in considerably changed features intermediate between both the original solid and its constituting atoms (or molecules). In this respect (optical) properties can be tuned by the dimension of the (nano)material.

In this book, we will concentrate on the optical properties of colloidal semiconductor quantum dots and to some extent also those of metal particles. Since there is already a considerable number of publications reviewing the size dependence of optical properties

of such nanomaterials, we prefer to concentrate on interfaces or surfaces and the perspectives of tuning of the related electronic energies and dynamics.

The experimental approach is based on static and dynamic optical spectroscopy, both on ensembles of quantum dots and on single ones. The latter approach is extremely sensitive and opens a wide field for detailed understanding and sensoric applications in material and life sciences. This has been recently acknowledged by the 2014 Nobel Prize in Chemistry awarded to E. Betzig, S. Hell, and W. E. Moerner for the invention and implementation of super-resolution optical microscopy.

Experimental reports in this book, some of them even unpublished, are based on results obtained in our groups during the last 10 years and especially include luminescence intermittency (blinking dynamics) in single quantum dots. The latter is a fascinating phenomen, often observed but far from being understood at a microscopic level.

The book is organized in the following way: We have virtually divided it into two parts: "Electronic States of Quantum Dots" (Chapters 1–3) and "Single Quantum Dots" (Chapters 4–6). Each part starts with an introductory chapter followed by several case studies in separate chapters. The introductory parts summarize relevant basic aspects of the related subjects and are to a certain extent a kind of review without being exhaustive in the respect. Correspondingly, the bibliography at the end of each chapter contains some leading papers, recent reviews, and books in which the readers may find some additional specific references relevant to their subjects of interest.

In "Electronic States of Quantum Dots," we report on several not yet reported spectroscopic features of CdSe excitons or trap states and related temperature-dependent exciton–phonon coupling. Both subjects pay special attention to the influence of the heterogeneous interfaces, including organic ligands on colloidal quantum dots.

The chapters in "Single Quantum Dots," besides a basic introduction to the related optical properties and detection schemes, concentrate on a review of experiments on single metal (Ag) nanoclusters. The central part is the tuning of photoluminescence intermittency (blinking) and spectral diffusion of CdSe quantum dots with special emphasis on interface-related effects. We present a new model for blinking processes.

Altogether, we aim with this book for a thorough understanding of subtle effects of interfaces and surfaces, which noticeably tune optical properties with respect to both optical energies and (interfacial) dynamics. We feel that we contribute to a deeper understanding of these to a large extent heterogeneous nanostructures. We make as often as possible use of a combination of experiments on ensemble and single nanostructures, an approach which has so far not been intensively used in literature. In the end our contributions might in the case of blinking processes be useful for either suppressing such effects for highly sensitive sensoric applications or even controling blinking for applications in stochastically based super-resolution microscopy.

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Eduard Zenkevich
Minsk, Belarus
September 2016

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All results from our groups in Chemnitz and Minsk have been obtained by graduate students, PhD students, and postdocs. We appreciate all the work which they have contributed to the development of this field during the last 10 years.

The book contains many results which have not yet been published: Ines Trenkmann (parts of Chapter 6), Cornelius Krasselt and Clemens Göhler (parts of Chapters 4 and 6), and Stefan Krause (parts of Chapter 5).

Writing a book like this would not have been possible without many fruitful discussions and help in writing and layout. Especially, we would like to mention Danny Kowerko (experimental part of Chapter 4), Frank Cichos and Michel Orrit (modified version of blinking models in Chapter 4), and Clemens Göhler, Thomas Blaudeck, and Cornelius Krasselt for figure preparations. Stefan Krause prepared the graph of Ag nanoparticles on the cover page, which is gratefully acknowledged.

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Quantum dot spectroscopy is based on for over more than 25 years on a stimulating and fruitful cooperation between research groups from Minsk (Zenkevich) and Chemnitz (von Borczyskowski). The scientific and personal exchange was strongly supported over these years by the Volkswagen-Foundation, INTAS, DAAD, and especially within the framework of the DFG Research Unit FOR 877.