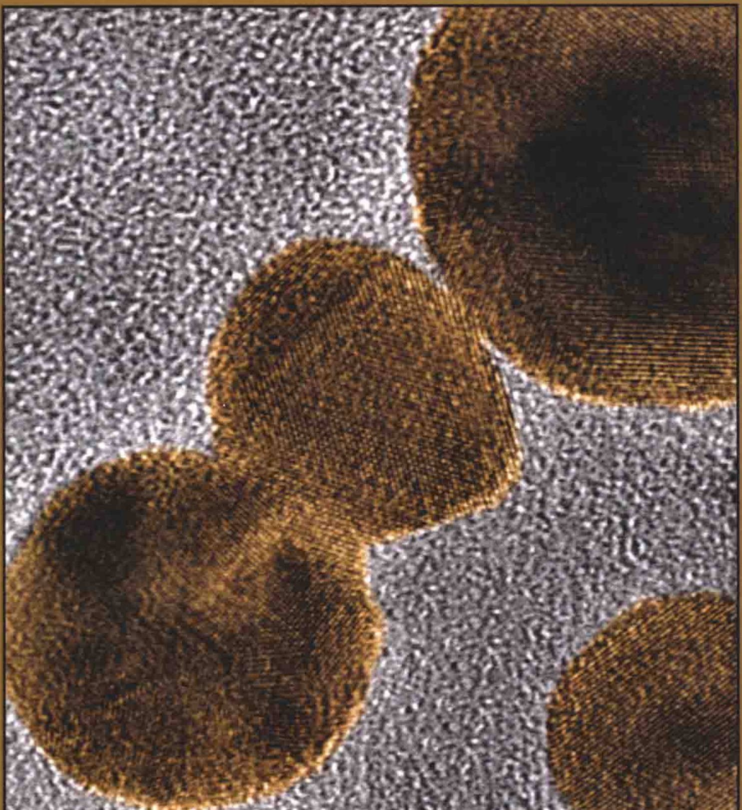
Advances in Materials Science and Engineering

Semiconductor Nanocrystals and Metal Nanoparticles

Physical Properties and Device Applications



Edited by

Tupei Chen • Yang Liu

CRC Press
Taylor & Francis Group

Semiconductor Nanocrystals and Metal Nanoparticles

Physical Properties and Device Applications

Edited by
Tupei Chen • Yang Liu

CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **Informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

Printed on acid-free paper
Version Date: 20160628

International Standard Book Number-13: 978-1-4398-7830-9 (Hardback)

Library of Congress Cataloging-in-Publication Data

Names: Chen, Tupei, editor. | Liu, Yang, 1975 September 12- editor.
Title: Semiconductor nanocrystals and metal nanoparticles : physical properties and device applications / editors, Tupei Chen and Yang Liu.
Description: Boca Raton : Taylor & Francis, a CRC title, part of the Taylor & Francis imprint, a member of the Taylor & Francis Group, the academic division of T&F Informa, plc, [2017] | Series: Advances in materials science and engineering | Includes bibliographical references and index.
Identifiers: LCCN 2016009756 | ISBN 9781439878309 (alk. paper)
Subjects: LCSH: Nanoelectronics--Materials. | Semiconductor nanocrystals. | Semiconductor nanoparticles.
Classification: LCC TK7874.84 .S46 2017 | DDC 621.3815/2--dc23
LC record available at https://lccn.loc.gov/2016009756

Visit the Taylor & Francis Web site at
http://www.taylorandfrancis.com

and the CRC Press Web site at
http://www.crcpress.com

Printed and bound in the United States of America by Publishers Graphics, LLC on sustainably sourced paper.

Semiconductor Nanocrystals and Metal Nanoparticles

Physical Properties and Device Applications

Advances in Materials Science and Engineering

Series Editor

Sam Zhang

Aerospace Materials Handbook, *edited by Sam Zhang and Dongliang Zhao*

Biological and Biomedical Coatings Handbook: Applications, *edited by Sam Zhang*

Biological and Biomedical Coatings Handbook: Processing and Characterization, *edited by Sam Zhang*

Hierarchical Micro/Nanostructured Materials: Fabrication, Properties, and Applications, *Weiping Cai, Guotao Duan, Yue Li*

Hydroxyapatite Coatings for Biomedical Applications, *edited by Sam Zhang*

Nanobiomaterials: Development and Applications, *edited by Dong Kee Yi and Georgia C. Papaefthymiou*

Nanostructured and Advanced Materials for Fuel Cells, *edited by San Ping Jiang and Pei Kang Shen*

Micro- and Macromechanical Properties of Materials, *Yichun Zhou, Li Yang, and Yongli Huang*

Semiconductor Nanocrystals and Metal Nanoparticles: Physical Properties and Device Applications, *edited by Tupei Chen and Yang Liu*

Thin Films and Coatings: Toughening and Toughness Characterization, *edited by Sam Zhang*

Preface

A material particle or cluster having a size in the range of one to several hundreds of nanometers is often referred to as "nanocrystal" or "nanoparticle." *Nanocrystal* is considered as crystalline clusters in either a single crystalline or a polycrystalline arrangement, while *nanoparticle* can represent both crystalline and noncrystalline clusters. Semiconductor nanocrystals with small dimensions are also described as quantum dots. Semiconductor nanocrystals and metal nanoparticles exhibit fascinating behaviors and unique physical properties as a result of quantum size effect. For example, for a semiconductor nanocrystal whose size is smaller than twice the size of its exciton Bohr radius, the excitons are squeezed, leading to quantum confinement. Quantum confinement will modify the electronic and optical properties of the semiconductor nanocrystal, for example, the bandgap of the nanocrystal increases with the decrease of the nanocrystal size. A direct experimental observation of the quantum confinement effect is that different sized quantum dots emit different color light. A good example of the fascinating behaviors of metal nanoparticles is the localized surface plasmon resonance (LSPR) in noble metal (for example, silver and gold) nanoparticles where the conduction electrons oscillate coherently under irradiation by light in the visible and near-infrared regions of the electromagnetic spectrum. The wavelength of excitation of the LSPR shows strong dependence on the size, shape, and dielectric environment of the metal nanoparticles.

Semiconductor nanocrystals and metal nanoparticles are the building blocks of the next generation of electronic, optoelectronic, and photonic devices. For instance, semiconductor quantum dots are particularly significant for optoelectronic/photonic device applications such as photovoltaic devices, light-emitting devices, and photodetector devices due to their tunable absorption spectrum and high extinction coefficient. In electronic applications, semiconductor nanocrystals or metal nanoparticles with sizes smaller than ~5 nm can be used to realize single-electron or few-electron devices (e.g., transistors and memory devices) as such tiny nanostructures exhibit the Coulomb blockade effect at room temperature.

This book examines in detail the physical properties and device applications of semiconductor nanocrystals and metal nanoparticles. It begins by giving a review on the synthesis and characterization of various semiconductor nanocrystals and metal nanoparticles and goes on to discuss in detail their electronic, optical, and electrical properties. Based on the knowledge of the physical properties, the book illustrates some exciting applications in nanoelectronic devices (e.g., memristors, single-electron devices), optoelectronic devices (e.g., UV detectors, quantum dot lasers, solar cells), and other applications (e.g., gas sensors, metallic nanopastes for power electronics packaging).

This book contains 13 chapters. It covers a rapidly developing, interdisciplinary field, and it is also a compilation of some research efforts in the field. It is intended as a reference book for senior undergraduate and graduate students and researchers in microelectronics/nanoelectronics, optoelectronics, photonics, nanoscience and nanotechnology, physics, and materials science.

Tupei Chen
Nanyang Technological University, Singapore
Yang Liu
University of Electronic Science and Technology of China, China

The MathWorks, Inc.
3 Apple Hill Drive
Natick, MA 01760-2098 USA
Tel: 508-647-7000
Fax: 508-647-7001
E-mail: info@mathworks.com
Web: www.mathworks.com

Editors

Tupei Chen received his PhD from the University of Hong Kong, Hong Kong, in 1994. He is currently an associate professor in the School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore. His research areas include electronic and optoelectronic/photonic applications of nanoscale materials, novel memory devices, memristors and applications in artificial neural networks, Si photonics, and metal oxide thin films and applications in flexible/transparent devices. He is the author or coauthor of more than 250 peer-reviewed journal papers, more than 120 conference presentations, and 6 book chapters. He has filed several U.S. patents. He has supervised more than 20 PhD students and over 10 postdoctoral research staff.

Yang Liu received his BSc in microelectronics from Jilin University, China, in 1998 and his PhD from Nanyang Technological University, Singapore, in 2005. From May 2005 to July 2006, he was a research fellow at Nanyang Technological University. In 2006, he was awarded the prestigious Singapore Millennium Foundation Fellowship. In 2008, he joined the School of Microelectronics, University of Electronic Science and Technology, China, as a full professor. He is the author or coauthor of over 120 peer-reviewed journal papers and more than 80 conference papers. He has filed one U.S. patent and more than 30 Chinese patents. His current research includes advanced memory devices and their applications in artificial neural networks, radio frequency integrated circuits (RFICs), photonic/optoelectronic devices, and integrated circuits (ICs).

Contributors

M. Abdullah
Nassiriya Nanotechnology Research Laboratory
Thi-Qar University
Nassiriyah, Iraq

Amin H. Al-Khursan
Nassiriya Nanotechnology Research Laboratory
Thi-Qar University
Nassiriyah, Iraq

A.K. Arof
Centre for Ionics
Department of Physics
Faculty of Science
University of Malaya
Kuala Lumpur, Malaysia

Kit Au
Department of Applied Physics
The Hong Kong Polytechnic University
Kowloon, Hong Kong, People's Republic of China

Denzel Bridges
Department of Mechanical, Aerospace, and Biomedical Engineering
The University of Tennessee, Knoxville
Knoxville, Tennessee

M.H. Buraidah
Centre for Ionics
Department of Physics
Faculty of Science
University of Malaya
Kuala Lumpur, Malaysia

Ngai Yui Chan
Department of Applied Physics
The Hong Kong Polytechnic University
Kowloon, Hong Kong, People's Republic of China

Tupei Chen
School of Electrical and Electronic Engineering
Nanyang Technological University
Singapore, Singapore

Jiyan Dai
Department of Applied Physics
The Hong Kong Polytechnic University
Kowloon, Hong Kong, People's Republic of China

Jacky Even
FOTON Laboratory
National Institute for Applied Sciences
Rennes, France

Zhili Feng
Materials Science and Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee

P. Gangopadhyay
Materials Science Group
Indira Gandhi Centre for Atomic Research
Kalpakkam, Tamil Nadu, India

Zhiming Gao
National Transportation Research Center
Oak Ridge National Laboratory
Knoxville, Tennessee

Spiros Gardelis
Department of Solid State Physics
Faculty of Physics
National and Kapodistrian University of Athens
Athens, Greece

N. Gogurla
Department of Physics
Indian Institute of Technology
Kharagpur, West Bengal, India

Frédéric Grillot
Laboratory for Communication and Processing of Information
Telecom Paris Tech—Université Paris-Saclay
Paris, France

S. Hamad
School of Physics
University of Hyderabad
Hyderabad, Telangana, India

Anming Hu
Department of Mechanical, Aerospace, and Biomedical Engineering
The University of Tennessee, Knoxville
Knoxville, Tennessee

Ning-Cheng Lee
Indium Corporation
Clinton, New York

Helen La Wa Chan
Department of Applied Physics
The Hong Kong Polytechnic University
Kowloon, Hong Kong, People's Republic of China

Ruozhou Li
School of Electronic Science and Engineering
Southeast University
Nanjing, Jiangsu, People's Republic of China

and

Suzhou Key Laboratory of Metal Nano-Optoelectronic Technology
Suzhou Research Institute of Southeast University
Suzhou, Jiangsu, People's Republic of China

Yang Liu
State Key Laboratory of Electronic Thin Films and Integrated Devices
University of Electronic Science and Technology of China
Chengdu, Sichuan, People's Republic of China

Z. Liu
School of Materials and Energy
Guangdong University of Technology
Guangzhou, Guangdong, People's Republic of China

Wing Chong Lo
Department of Applied Physics
The Hong Kong Polytechnic University
Kowloon, Hong Kong, People's Republic of China

Farah T. Mohammed Noori
College of Science
Baghdad University
Baghdad, Iraq

I.M. Noor
Centre for Ionics
Department of Physics
Faculty of Science
University of Malaya
Kuala Lumpur, Malaysia

G. Krishna Podagatlapalli
Advanced Centre of Research in High Energy Materials
University of Hyderabad
Hyderabad, Telangana, India

T. Rakshit
Advanced Technology Development Centre
Indian Institute of Technology
Kharagpur, West Bengal, India

S.K. Ray
Department of Physics
Indian Institute of Technology
Kharagpur, West Bengal, India

Leon M. Tolbert
Department of Electrical Engineering and Computer Science
The University of Tennessee, Knoxville
Knoxville, Tennessee

S. Venugopal Rao
Advanced Centre of Research in High Energy Materials
University of Hyderabad
Hyderabad, Telangana, India

Cheng Wang
School of Information Science and Technology
ShanghaiTech University
Pudong, Shanghai, People's Republic of China

and

FOTON Laboratory
National Institute for Applied Sciences
Rennes, France

Zhiqiang Wang
Department of Electrical Engineering and Computer Science
The University of Tennessee, Knoxville
Knoxville, Tennessee

Zhiyong Wang
Institute of Laser Engineering
Beijing Institute of Technology
Chaoyang, Beijing, People's Republic of China

S.N.F. Yusuf
Centre for Ionics
Department of Physics
Faculty of Science
University of Malaya
Kuala Lumpur, Malaysia

Fan Zhang
Department of Applied Physics
The Hong Kong Polytechnic University
Kowloon, Hong Kong, People's Republic of China

Contents

Preface....................vii
Editors....................ix
Contributors....................xi

Chapter 1 Synthesis and Characterization of Nanocrystals and Nanoparticles....................1
Yang Liu

Chapter 2 Size- and Shape-Controlled ZnO Nanostructures for Multifunctional Devices....................39
S.K. Ray, N. Gogurla, and T. Rakshit

Chapter 3 From Basic Physical Properties of InAs/InP Quantum Dots to State-of-the-Art Lasers for 1.55 μm Optical Communications: An Overview....................95
Jacky Even, Cheng Wang, and Frédéric Grillot

Chapter 4 Optical, Photoluminescence, and Vibrational Spectroscopy of Metal Nanoparticles....................127
P. Gangopadhyay

Chapter 5 Silicon Nanocrystals: Properties and Potential Applications....................191
Spiros Gardelis

Chapter 6 Electronic and Optical Properties of Si and Ge Nanocrystals....................215
Tupei Chen

Chapter 7 Light Emission Properties of Si Nanocrystals Embedded in a Dielectric Matrix....................255
Tupei Chen

Chapter 8 Optical Properties of Semiconductor Nanoparticles in Photoelectrochemical Cells....................283
M.H. Buraidah, S.N.F. Yusuf, I.M. Noor, and A.K. Arof

Chapter 9 Second-Order Nonlinear Susceptibility in Quantum Dot Structures....................307
M. Abdullah, Farah T. Mohammed Noori, and Amin H. Al-Khursan

Chapter 10 Metallic Nanopastes for Power Electronic Packaging....................343
Denzel Bridges, Ruozhou Li, Zhiming Gao, Zhiqiang Wang, Zhiyong Wang, Anming Hu, Zhili Feng, Leon M. Tolbert, and Ning-Cheng Lee

Chapter 11 Applications of Metal Nanoparticles and Nanostructures Fabricated Using Ultrafast Laser Ablation in Liquids........ 367

S. Venugopal Rao, S. Hamad, and G. Krishna Podagatlapalli

Chapter 12 Exploring the $LaAlO_3/SrTiO_3$ Two-Dimensional Electron Gas: From Fundamental to Technical Applications........ 423

Ngai Yui Chan, Fan Zhang, Kit Au, Wing Chong Lo, Helen La Wa Chan, and Jiyan Dai

Chapter 13 Novel Nanoelectronic Device Applications of Nanocrystals and Nanoparticles..... 461

Z. Liu

Index........ 501

1 Synthesis and Characterization of Nanocrystals and Nanoparticles

Yang Liu

CONTENTS

1.1 Introduction 1
1.2 Semiconductor Nanocrystals 2
  1.2.1 Compound Semiconductor Nanocrystals 2
  1.2.2 Elemental Semiconductor Nanocrystals 14
1.3 Metal Nanoparticles 18
1.4 Nanocrystals and Nanoparticles Embedded in a Dielectric Film 23
References 31

1.1 INTRODUCTION

Nanocrystals and nanoparticles are described as clusters having diameters in the range of one to several hundreds of nanometers. A "nanocrystal" is considered as a cluster of crystals, whereas a "nanoparticle" can consist of both crystalline and noncrystalline clusters. The synthesis of nanocrystals/nanoparticles has attracted extensive studies in the past several decades. These materials show size-dependent physical properties that are not shown by their bulk counterparts. For example, a Si nanocrystal shows photoluminescence (PL) and electroluminescence (EL), which cannot be achieved in bulk silicon due to its indirect bandgap. Therefore, precise control during the synthesis of nanocrystals/nanoparticles is of key importance for their applications.

Many techniques are used to synthesize nanocrystals/nanoparticles. Chemical vapor deposition (CVD), physical vapor deposition, ion implantation, sputtering, laser ablation, and spray pyrolysis are all gas-based techniques and have been used successfully for the synthesis of nanocrystals/nanoparticles. They provide the possibility of controlling the nanocrystal/nanoparticle size by adjusting the synthesis parameters such as temperature, pressure, power density, gas flow rate, and so on. Solution-based techniques are of intensive research interest, as they are highly effective in synthesizing nanocrystals/nanoparticles with good size control. Besides, they also have the advantages of low synthesis temperature, flexibility, and low cost. A large variety of methods have been developed to synthesize nanocrystals/nanoparticles, such as reduction, thermal decomposition, and processes with hydrolysis and alcoholysis. At the same time, various techniques have been utilized to characterize the structural and physical properties of nanocrystals/nanoparticles, such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoemission spectroscopy (XPS), X-ray diffraction (XRD), Raman scattering, and so on. In this chapter, we review the methods for synthesizing nanocrystals/nanoparticles. We also discuss the characterization of nanocrystals/nanoparticles using various techniques.

1.2 SEMICONDUCTOR NANOCRYSTALS

1.2.1 Compound Semiconductor Nanocrystals

Compound semiconductor nanocrystals such as CdSe, CdS, GaAs, InAs, and CuCl have been widely investigated. In this section, we discuss the synthesis of compound semiconductor nanocrystals as well as their characterization using various techniques.

Synthesis of II–VI (A2B6) nanocrystals/nanoparticles such as CdS and CdSe is attractive because these materials have potential applications in photosensitive, photovoltaic, optical, and electronic devices. The shape, concentration, and size of the nanocrystals, as well as their size distribution, strongly depends on the synthesis process. CdSe nanoparticles showing quantum size effects was reported in 1993 [1]. Research on nanocrystalline cadmium selenide (CdSe) has been going on for years due to its excellent properties such as light emission, low bandgap (E_g = 1.75 eV), low toxicity, facile surface modification, and thermostability, with applications in light-emitting diodes, solar cells, hydrogen-producing catalysts, and biological imaging [2–15].

Chemical methods are simple, flexible, effective, and low cost to synthesize isolated CdSe nanocrystals, and include solvothermal methods and hydrothermal methods. The solvothermal methods always utilize TOP (tri-*n*-octylphosphine)/TOPO (tri-*n*-octylphosphine oxide), TOP/TOPO/HPA (hexylphosphonic), TOP/TOPO/HDA (hexadecylam), or other reagents to synthesize CdSe nanocrystals [16–23].

The TOP/TOPO method was reported in [16,20] and is illustrated in Figure 1.1. In [16], the synthesis of ZnS-capped CdSe nanocrystals was carried out by using TOP/TOPO with a size of 2.7–3.0 nm. In [20], CdSe nanocrystals were synthesized with a diameter of ~3 nm with TOP/TOPO. The nanocrystals were dried under N_2 flow and dissolved in toluene. Finally, the nanocrystal solution was filtered using a 0.45 mm syringe filter to remove other contaminations from the synthesis process.

The TOP/TOPO/HPA method was used in [17], where $Cd(CH_3)_2$ in heptane and Se/TBP (tri-*n*-butyphosphine) were mixed with TBP and the solution was injected into HPA (hexylphosphonic acid) in TOPO. The size of SeCd nanocrystals could be controlled in the range 5–20 nm by varying the injection volume. The TOP/TOPO/HDA method was reported in [19,21]. In [19], $Cd(CH_3)_2$ and Se/TOP were injected into TOPO and HDA. The size of prepared CdSe nanocrystals was in the range 4.5–5.0 nm. In [21], CdO/SA (stock solution of stearic acid with CdO) was injected into

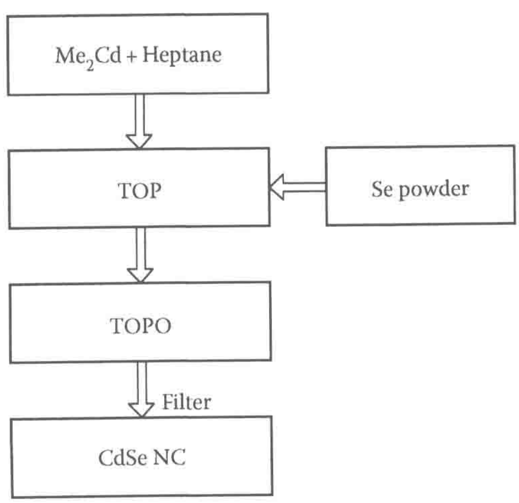


FIGURE 1.1 Process of the TOP/TOPO method.