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加工、表征与应用

Semiconductor Nanostructures for Optoelectronic Devices

Processing, Characterization and Applications

Gyu-Chul Yi

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《纳米科学与技术》丛书序

在新兴前沿领域的快速发展过程中，及时整理、归纳、出版前沿科学的系统性专著，一直是发达国家在国家层面上推动科学与技术发展的重要手段，是一个国家保持科学技术的领先权和引领作用的重要策略之一。

科学技术的发展和应用，离不开知识的传播：我们从事科学研究，得到了"数据"（论文），这只是"信息"。将相关的大量信息进行整理、分析，使之形成体系并付诸实践，才变成"知识"。信息和知识如果不能交流，就没有用处，所以需要"传播"（出版），这样才能被更多的人"应用"，被更有效地应用，被更准确地应用，知识才能产生更大的社会效益，国家才能在越来越高的水平上发展。所以，数据→信息→知识→传播→应用→效益→发展，这是科学技术推动社会发展的基本流程。其中，知识的传播，无疑具有桥梁的作用。

整个 20 世纪，我国在及时地编辑、归纳、出版各个领域的科学技术前沿的系列专著方面，已经大大地落后于科技发达国家，其中的原因有许多，我认为更主要的是缘于科学文化的习惯不同：中国科学家不习惯去花时间整理和梳理自己所从事的研究领域的知识，将其变成具有系统性的知识结构。所以，很多学科领域的第一本原创性"教科书"，大都来自欧美国家。当然，真正优秀的著作不仅需要花费时间和精力，更重要的是要有自己的学术思想以及对这个学科领域充分把握和高度概括的学术能力。

纳米科技已经成为 21 世纪前沿科学技术的代表领域之一，其对经济和社会发展所产生的潜在影响，已经成为全球关注的焦点。国际纯粹与应用化学联合会（IUPAC）会刊在 2006 年 12 月评论："现在的发达国家如果不发展纳米科技，今后必将沦为第三世界发展中国家。"因此，世界各国，尤其是科技强国，都将发展纳米科技作为国家战略。

兴起于 20 世纪后期的纳米科技，给我国提供了与科技发达国家同步发展的良好机遇。目前，各国政府都在加大力度出版纳米科技领域的教材、专著以及科普读物。在我国，纳米科技领域尚没有一套能够系统、科学地展现纳米科学技术各个方面前沿进展的系统性专著。因此，国家纳米科学中心与科学出版社共同发起并组织出版《纳米科学与技术》，力求体现本领域出版读物的科学性、准确性和系统性，全面科学地阐述纳米科学技术前沿、基础和应用。本套丛书的出版以高质量、科学性、准确性、系统性、实用性为目标，将涵盖纳米科学技术的所有领域，全面介绍国内外纳米科学技术发展的前沿知识；并长期组织专家撰写、编辑出版下去，为我国

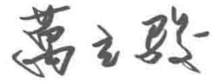
表面分子组装》，是对相关工作的归纳总结。

多年来，本人的研究组开展固体表面分子组装研究，不但发展表面组装方法，还一直试图找到分子结构-固体种类-组装结构间的关系，也不放过发现组装结构中重要现象的机会并阐明原因，意欲探索表面分子组装规律，利用分子组装实现表面功能化。书中在介绍固体表面的结构特点和 STM 技术等表面分子组装基础知识之后，顺序介绍了简单烷烃/烷烃衍生物分子的组装结构、复杂配合物分子的组装、主客体组装以及功能化组装等，随后介绍结构转化研究、手性结构研究、电化学环境下的组装和相变化，最后是可能的表面功能化，内容安排尽量承上启下、先易后难且逻辑相关。

借此机会，我要感谢我研究组的研究生们，他们倾心科学，随我多年耕耘于固体表面分子组装研究领域，努力工作，夜以继日，他们终学有所成，也留下了丰富的科研结果。陈婷、严会娟、殷雅侠、陈庆、张旭、崔博、管翠中、郑轻娜等还参与了书稿内容整理、文献核对等工作。感谢科学出版社杨震、张淑晓和刘冉诸位编辑的悉心指导，感谢国家出版基金对本书的出版资助。感谢国家自然科学基金委员会、科技部和中国科学院，多年来，我的研究工作一直得到他们的支持，本书中的研究内容大多是在他们的资助下获得的科研成果。

还要感谢我的妻子姜红，她不厌其烦地整理我写下的零散片段，帮助打字输入我的手写书稿，保存相关资料，愿本书的出版给她带去一份快乐！

分子组装研究历史已久，内容丰富，且时有挑战课题出现，也有轰动性和里程碑性成果问世。限于水平和时间，书中不妥之处在所难免，恳请各位前辈和同行不吝赐教。出版本书意在抛砖引玉，以诱导、鼓励更多的科技工作者，尤其是青年科技工作者加入该研究行列，发展新技术，探索规律，攻坚克难；同时，发现新问题和解决新问题，推动分子组装研究不断发展。



Preface

The goal in nanotechnology is to make high-performance nanodevices. For nanodevice fabrications, novel *bottom-up* approach, fabricating devices and systems by hierarchical assembly or controlled growth of nanoscale materials, has attracted tremendous interest. Because this bottom-up method allows single-crystalline nanostructure growth on a variety of substrates, the bottom-up method has been used to prepare high-quality nanomaterials even on amorphous glass, plastic, and graphene substrates. In the bottom-up approach, one-dimensional (1D) semiconductor nanostructures, including nanorods, nanowires, nanobelts, and nanotubes, are vital components for fabricating optoelectronic and photonic nanodevices. In particular, 1D semiconductor nanostructures such as nanowires, nanorods, and nanotubes open up significant opportunities for the fabrication of high-performance optoelectronic nanodevice. For the fabrication of high-efficiency optoelectronic devices including light-emitting diodes (LEDs) and solar cells, 1D heteroepitaxial nanostructures with well-defined crystalline interfaces must be essential building blocks since embedding quantum structures in individual nanostructures would enable novel physical properties such as quantum confinement to be exploited, such as the continuous tuning of spectral wavelength by varying the well thickness. Sophisticated optoelectronic nanodevices can be readily fabricated by composition and doping controls of semiconductor nanostructures. Furthermore, nanodevices based on vertically ordered 1D nanostructures permit extremely small size and ultrahigh density. Here, this book introduces the current status of semiconductor nanostructures for optoelectronic devices and outlines the processing and characterizations of semiconductor nanostructures and their optoelectronic device applications.

In Chaps. 1–6, current research activities related to the synthesis of 1D semiconductor nanostructures by various growth methods and their optoelectronic device applications are reviewed. Chapter 1 provides an overview of vapor–liquid–solid growth process, which has widely been employed for preparation of semiconductor nanowires. Using this technique, Si, Ge, GaAs, InP, GaP, ZnO, and GaN nanowires have been synthesized and several nanodevices including p–n junction semiconductor nanowire LEDs and solar cells have been fabricated. In Chaps. 2 and 3, catalyst-free metal-organic vapor phase epitaxy to prepare high purity semiconductor nanostructures is introduced. Here, the processes to control positions, conductivities, and compositions of nanostructures for fabricating coaxial nanostructure LEDs are also described. Chapter 4 describes synthesis methods and characteristics of AlN nanostructures for UV optoelectronic device applications. Chapter 5 reviews the research progress on the controlled synthesis of a wide variety of nanowire heterostructures such as branched heterostructures, which includes solution phase and template-based methods. Meanwhile, the semiconductor nanostructures can be hybridized with graphene, which has recently been attracting much attention as a novel nanomaterial system for flexible optoelectronic devices as details are described in Chap. 6.

In Chaps. 7 and 8, structural and optical characterizations of semiconductor nanomaterials and nanostructures are reviewed. Chapter 7 introduces research on structural properties of ZnO and GaN nanostructures using X-ray absorption fine structure. As described in Chap. 8, optical properties of semiconductor nanostructures were investigated using luminescence characterization techniques, which are nondestructive, nonintrusive, and sensitive to the presence of defects or impurities in nanomaterials.

The last three chapters describe nanodevice applications of 1D semiconductor nanostructures. In Chap. 9, lasing characteristics of single and assembled nanowires are reviewed. Chapter 10 introduces near-field optical evaluation and the use of nanorod quantum structures for nanophotonic devices such as a nanophotonic gate. Finally, Chap. 11 presents the overview of nanowire solar cell studies, and integration strategies for practical device applications.

This book entitled "Semiconductor Nanostructures for Optoelectronic Devices – Processing, Characterization and Applications" is being introduced to review the recent works in the field of 1D nanomaterials and their optoelectronic device applications. Each chapter is written by leading scientists in the relevant field. Thus, I hope that high-quality scientific and technical information is provided to students, scientists, and engineers who are, and will be, engaged in fabrications of semiconductor nanostructures and their optoelectronic device applications.

I extend my acknowledgment to Dr. Claus Ascheron of Springer-Verlag for his guidance and suggestions.

Seoul
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Gyu-Chul Yi

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Contents

Chapter 1
Vapor–Liquid–Solid Growth of Semiconductor Nanowires

Heon-Jin Choi

Abstract Nanowires make possible to manipulate light in novel methods and thus are promising materials for advanced optoelectronics. To exploit the potential, the growth behavior has to be controlled since it dominates the physical and chemical states and, in turn, the optical properties of nanowires. In this chapter, the vapor–liquid–solid (VLS) mechanism for the growth and modulation of nanowires was discussed. The chapter first reviewed the fundamental aspects of the VLS mechanism. Then the state of the art of the growth and modulation of nanowires for optoelectronics were discussed from the point of view of the critical issues pertaining to this mechanism. Some examples of optoelectronic devices that had been fabricated based on the VLS mechanism were also reviewed in an effort to cover the cutting edge technology in this area. Lastly, a summary and several different perspectives on the VLS mechanism were presented.

1.1 Introduction

Nanowires are hair-like, one-dimensional (1D) nanomaterials with diameters in the sub-one hundred nanometer scale and lengths ranging from several hundreds of nm to as high as a few cm. Owing to their nanoscale dimensions in the radial direction, they have size confinement effects that give them novel physical properties as compared to bulk materials. Their one-dimensional geometry on the nanometer scale provides an extremely high surface area with a nanoscale radius of curvature and great mechanical flexibility with near theoretical strength. These properties are advantageous in many chemical and mechanical applications. The geometry also

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provides anisotropic properties that should be interesting from the point of view of nanomaterials science and engineering. Their length, reaching as high as the cm scale, makes them easy to manipulate for device fabrication.

Nanowires are promising materials for advanced optoelectronics. In addition to the unique aspects of their physical, chemical, and mechanical properties, the size of these materials is comparable to visible light in wavelength from 400 to 650 nm. This implies that nanowires can be used to handle light on a nanometer scale and thus can be used as building blocks for advanced optoelectronics. Indeed, novel methods of the manipulation of light with nanowires, including nanoscale Fabry–Perrot mode stimulated emission, wave guiding of photons, random lasing action, highly efficient luminescence, and extremely sensitive photodetection, have recently been demonstrated. The concept of many advanced nanowire-based optoelectronic devices including light-emitting diodes (LEDs), lasers, optical sensors, photo diodes, and photovoltaic cells have also been demonstrated.

The physical and chemical states of nanowires dominate their optical properties. The length and diameter of nanowires as well as their alignment affect the emission and absorption properties. The composition, impurity, or doping level, defect concentration, crystal structure, growth direction, and nature of the facets are also critical to the emission and/or stimulated emission and absorption. It should be noted that these physical and chemical states are closely related to the growth of nanowires. Therefore, one must fully understand the growth behavior of nanowires and develop rational, reliable growth processes to exploit the potential of nanowires in optoelectronics.

Nanowires are a result of anisotropic, 1D crystal growth on a nanometer scale. Therefore, the key issue related to the growth of nanowires is how to induce 1D crystal growth in a controlled manner. Regarding this, many approaches have been studied, including the use of the metal-catalyst-assisted vapor–liquid–solid (VLS) mechanism, the vapor–solid (VS) mechanism, and the template-assisted (TA) mechanism. Among these, the VLS mechanism is the most widely used owing to its simplicity and versatility when applied in many semiconductor systems.

This chapter reviews the growth of semiconductor nanowires by the VLS mechanism in the area of optoelectronics. As mentioned earlier, the growth process is critical to the physical and chemical state of nanowires and thus their optical properties. Therefore, a review of the growth process may be helpful so as to facilitate the preparation of superior nanowires for optoelectronics. This chapter focuses on the VLS mechanism. This may, however, limit our viewpoint regarding the growth of nanowires, as other mechanisms are also available. However, the VLS mechanism is a mainstay at present. Therefore, it may be sufficient to review the state of the art of this area. This chapter seeks to explain the understanding of what the VLS mechanism is as well as the manner in which better nanowires can be grown for optoelectronics. Accordingly, the chapter first reviews the fundamental aspects of the VLS mechanism. The growth of nanowires and a number of critical issues pertaining to VLS mechanism follow. Some examples of optoelectronic devices that have been fabricated based on the VLS mechanism are also reviewed in an effort