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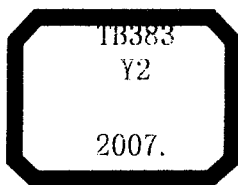
# Self-Organized Nanoscale Materials

## 自组织纳米材料

Motonari Adachi    D. J. Lockwood



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## 国外物理名著(影印版)系列序言

对于国内的物理学工作者和青年学生来讲,研读国外优秀的物理学著作是系统掌握物理学知识的一个重要手段。但是,在国内并不能及时、方便地买到国外的图书,且国外图书不菲的价格往往令国内的读者却步,因此,把国外的优秀物理原著引进到国内,让国内的读者能够方便地以较低的价格购买是一项意义深远的工作,将有助于国内物理学工作者和青年学生掌握国际物理学的前沿知识,进而推动我国物理学科科研和教学的发展。

为了满足国内读者对国外优秀物理学著作的需求,科学出版社启动了引进国外优秀著作的工作,出版社的这一举措得到了国内物理学界的积极响应和支持,很快成立了专家委员会,开展了选题的推荐和筛选工作,在出版社初选的书单基础上确定了第一批引进的项目,这些图书几乎涉及了近代物理学的所有领域,既有阐述学科基本理论的经典名著,也有反映某一学科专题前沿的专著。在选择图书时,专家委员会遵循了以下原则:基础理论方面的图书强调“经典”,选择了那些经得起时间检验、对物理学的发展产生重要影响、现在还不“过时”的著作(如:狄拉克的《量子力学原理》)。反映物理学某一领域进展的著作强调“前沿”和“热点”,根据国内物理学研究发展的实际情况,选择了能够体现相关学科最新进展,对有关方向的科研人员和研究生有重要参考价值的图书。这些图书都是最新版的,多数图书都是2000年以后出版的,还有相当一部分是2006年出版的新书。因此,这套丛书具有权威性、前瞻性和应用性强的特点。由于国外出版社的要求,科学出版社对部分图书进行了少量的翻译和注释(主要是目录标题和练习题),但这并不会影响图书“原汁原味”的感觉,可能还会方便国内读者的阅读和理解。

“他山之石,可以攻玉”,希望这套丛书的出版能够为国内物理学工作者和青年学生的工作和学习提供参考,也希望国内更多专家参与到这一工作中来,推荐更多的好书。



中国科学院院士  
中国物理学会理事长  
2007年3月20日

# Preface

Novel system performance through nanostructuring has been recognized in many branches of science in the latter half of the 20th century. In computer science, the computational efficiency has improved by nearly four orders of magnitude in 30 years, using energy consumed per operation as a metric. To achieve further advances will require the reduction in size of electronic devices to the scale of molecules; that is, a totally different type of computational machinery is required: molecular electronics. The requirement for inventing a new technology paradigm has created research opportunities for scientists in a very wide range of disciplines.

Nature uses molecular self-assemblies composed of surfactant molecules in biomineralization to construct nanostructures regulated at the atomic scale. Advances in synthetic molecular biology have resulted in highly efficient biological systems, which perform elegant energy and mass conversions using hierarchical assemblies of microstructures, again regulated at the atomic scale (e.g., the structure of the photosynthetic reaction center of a purple bacterium and the structure and reaction mechanism of enzymes).

In order to realize the tremendous potential of nanostructure science and technology, the extremely important challenges are how to exploit synthetic methods for structures regulated at the atomic scale and to construct materials across the hierarchy of length scales from the atomic to mesoscopic and/or to macroscopic scale.

This book comprises a survey of different approaches to the synthesis of nanoscale materials and the hierarchical assemblies produced from them, which have been prepared using self-organized mechanisms via chemical and bio-inspired methods. These methods have two principal advantages. First, nanoscale materials can be synthesized under mild conditions. For example, the layer-by-layer adsorption method in the liquid phase can accumulate different layers consecutively at room temperature just like the multilayer formation by molecular beam deposition at high temperature. The prime advantage of mild conditions such as room-temperature formation is essential for the utilization of biomaterials and is also recommended from an environmental point of view. Second, synthesis using self-organized mechanisms can make nanosize materials at the

scale of Avogadro's number. For comparison, it is very difficult to make nanosize materials at the scale of Avogadro's number by fabrication methods using an individual atom or molecule, such as manipulating atoms or molecules with the atomic force microscope (AFM) tip. Thermal, chemical, and structural stabilization of the nanostructured materials and removal of defects are other challenges still for the future.

The growth and properties of semiconductor quantum dots have been studied extensively in the last decade. These novel nanostructures offer interesting prospects for the development of new electronic or optoelectronic devices. In particular, if the size, shape, and positioning of those structures can be controlled, they become very attractive for applications in areas such as telecommunication wavelength integrated photodetectors, tunable light sources, and single-photon light sources. In Chapter 1, "Self-Assembled  $\text{Si}_{1-x}\text{Ge}_x$  Dots and Islands," Jean-Marc Baribeau, Nelson L. Rowell, and David J. Lockwood review progress in our understanding of  $\text{Si}_{1-x}\text{Ge}_x$  island growth on (001) Si. The evolution of the island morphology with  $\text{Si}_{1-x}\text{Ge}_x$  coverage is particularly complex and understanding it has led to a better knowledge of strained heterosystems. The chapter summarizes the effect of various growth parameters or postgrowth treatments on the shape of the  $\text{Si}_{1-x}\text{Ge}_x$  islands, their composition and strain distribution, their spatial distribution, and their vertical correlation in multilayer stacks. The vibrational properties of these  $\text{Si}_{1-x}\text{Ge}_x$  nanostructures are presented along with a detailed review of their optical properties, which are of key importance in device applications. The self-organization of the  $\text{Si}_{1-x}\text{Ge}_x$  islands is a feature of special significance if they are to become building blocks of novel devices. Various approaches that have been used to engineer  $\text{Si}_{1-x}\text{Ge}_x$  islands and, in particular, to control their size and spatial distribution are described. Recent progress in the use of  $\text{Si}_{1-x}\text{Ge}_x$  island superlattices as fast telecommunication infrared photodetectors is detailed.

One of the most active trends in modern materials chemistry is the development of synthetic methods to obtain size- and shape-controlled inorganic nanocrystals. The shape and size of inorganic nanocrystals determine their widely varying electrical and optical properties. As reported in Chapter 2, "Synthesis of Titania Nanocrystals: Application for Dye-Sensitized Solar Cells" by Motonari Adachi, Yusuke Murata, Fumin Wang, and Jinting Jiu, titania nanocrystals, which have a large surface area with controlled surface structure and high electron transport properties, are important for producing high-efficiency dye-sensitized solar cells (DSCs). DSCs have significant potential as a low-cost alternative to conventional *p-n* junction solar cells. Morphological control and high crystallinity are key properties needed in titanium oxide materials for such cells. A promising way to increase the efficiency of titanium oxide DSCs is to improve the properties of the semiconductor electrode using a network structure of single-crystalline anatase nanowires instead of a porous titania film composed of nanosize particles. In this chapter, the formation of a network structure of single-crystalline  $\text{TiO}_2$  nanowires by an "oriented attachment" mechanism is presented in detail. Methods are given for the morphological control of anatase nanocrystals using dodecanediamine as a surfactant, and the formation mechanism is discussed together with the synthesis

of nanosheets of quasi-anatase phase. Finally, the application of a  $\text{TiO}_2$  network of single-crystalline anatase nanowires in DSCs is considered.

Nanosized building blocks with low dimensionality such as nanowires, nanorods, nanotubes, and nanosheets have emerged as technically important systems, which provide fundamental scientific opportunities for investigating the influence of size and dimensionality on their optical, magnetic, and electronic properties as well as potential components for nanodevices. In Chapter 3, "Soft Synthesis of Inorganic Nanorods, Nanowires, and Nanotubes" by Shu-Hong Yu and Yi-Tai Qian, the latest developments on new mild soft-solution-based strategies for the fabrication of low-dimensional nanocrystals are reviewed. Examples of such approaches are the hydrothermal/solvothermal process, the solution-liquid-solid mechanism, capping agent/surfactant-assisted synthesis, the bio-inspired approach, and the oriented attachment growth mechanism. Current developments show that soft-solution synthesis provides alternative strategies for the rational synthesis of a variety of low-dimensional nanorods, nanowires, nanosheets, and nanotubes with a controllable size, shape, length scale, and structural complexity. This new growth mechanism could offer an additional tool to design advanced materials with anisotropic material properties and could be used for the synthesis of more complex crystalline three-dimensional structures.

Porous inorganic materials such as zeolites and zeolitelike crystalline molecular sieves are of great interest due to their range of commercial applications in traditional areas such as catalysis, adsorption/separation, and ion exchange and the more specialized fields of MRI contrast agents and blood-clotting agents. The term *zeolite* refers to the specific class of aluminosilicate molecular sieves, although the term is frequently used more loosely to describe compounds other than aluminosilicates that have frameworks similar to known zeolites. Here, in Chapter 4, "Assembly of Zeolites and Crystalline Molecular Sieves" by Jennifer L. Anthony and Mark E. Davis, various aspects of the assembly processes for synthesizing zeolites and other crystalline molecular sieves are overviewed. Topics covered include the thermodynamics and kinetics of the crystallization process, the possible self-assembly mechanisms in the crystallization, and the roles that the various components of the synthesis play in determining the ultimate structure that is formed. The importance of understanding how zeolites and zeolitelike molecular sieves are assembled from a molecular/atomic point of view is emphasized and the knowledge gained is applied to designing a chiral molecular sieve.

As discussed in Chapter 5, "Molecular Imprinting by the Surface Sol-Gel Process" by Seung-Woo Lee and Toyoki Kunitake, molecular imprinting is a fairly representative method of template synthesis and it has been recognized as a means for preparing specific binding sites for given molecules in appropriate matrices. In this approach, the shape and functionality of organic molecules as the template are transcribed onto microporous materials. The configuration of the functional groups in the template can be fixed within the matrix. In comparison with the more conventional sol-gel procedures, the characteristics of the surface sol-gel process, which was developed as a means for preparation of ultrathin metal oxide films, are presented. This process gives rise to oxide gel films of nanosize thickness, and

applications. We expect it to attract a broad community of researchers in physics, chemistry, biology, engineering, and materials science and hope that established scientists and technologists as well as graduate students will find much relevant and interesting information contained between these covers. The extensive references appearing at the end of each chapter are also valuable resources in themselves. In the preparation of this book, we have had the opportunity to see how far this field has developed, but we are sure that much exciting work lies ahead of us still in this field!

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# 1

## Self-Assembled $\text{Si}_{1-x}\text{Ge}_x$ Dots and Islands

JEAN-MARC BARIBEAU,<sup>†</sup> NELSON L. ROWELL,<sup>‡</sup>  
AND DAVID J. LOCKWOOD<sup>†</sup>

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### 1.1. Introduction

The growth and properties of semiconductor quantum dots have been studied extensively in the last decade. These novel nanostructures offer interesting prospects for the development of new electronic or optoelectronic devices. In particular, if the size, shape, and positioning of those structures can be controlled, they become very attractive for applications such telecommunication wavelength-integrated photodetectors or tunable or single-photon light sources.

$\text{Si}_{1-x}\text{Ge}_x$  is a prototypical system of self-organization of nanostructures in semiconductor heteroepitaxy. Despite the 4.18% lattice mismatch between Si and Ge, it is possible to grow  $\text{Si}_{1-x}\text{Ge}_x$  alloys pseudomorphically on Si. This misfit causes the deformation of the alloy lattice to conform to the substrate lattice constant in the plane of growth. This leads to a tetragonal distortion in the deposited film that persists up to a critical thickness<sup>1-3</sup> beyond which deformation can no longer be elastically accommodated and relaxation of the lattice occurs through the generation of misfit dislocations. When deposited on (001) Si, Ge and  $\text{Si}_{1-x}\text{Ge}_x$  alloys can also undergo a transition from planar two-dimensional growth at small thickness to a three-dimensional island structure at higher coverage.<sup>4,5</sup> The development of a three-dimensional morphology is an alternative to the generation of dislocations as a means to minimize the energy of the heterosystem.<sup>6,7</sup>

In the last decade, considerable work has been done on the growth and characterization of  $\text{Si}_{1-x}\text{Ge}_x$  islands and dots.<sup>8-11</sup> In this chapter, we review progress in our understanding of  $\text{Si}_{1-x}\text{Ge}_x$  island growth on (001) Si. In particular, we discuss the evolution of the island morphology with  $\text{Si}_{1-x}\text{Ge}_x$  coverage, which is particularly complex and has led to a better understanding of strained heterosystems. We look at the effect of various growth parameters or postgrowth treatments on the shape of the islands. We also review recent progress in the determination of the composition and strain distribution of  $\text{Si}_{1-x}\text{Ge}_x$  islands. The spatial distribution of the islands and their vertical correlation in multilayer stacks is also described. We also discuss the vibrational properties of these  $\text{Si}_{1-x}\text{Ge}_x$  nanostructures and present a detailed review of their optical properties that are of key importance in device applications. The self-organization of the  $\text{Si}_{1-x}\text{Ge}_x$  islands is a feature of special

importance if they are to become building blocks of novel devices. We describe various approaches that have been examined to engineer  $\text{Si}_{1-x}\text{Ge}_x$  islands and, in particular, control their size and spatial distribution. Finally, we briefly review recent progress in the use of  $\text{Si}_{1-x}\text{Ge}_x$  island superlattices as fast telecommunication infrared photodetectors and for other applications.

## 1.2. $\text{Si}_{1-x}\text{Ge}_x$ Island Growth

### 1.2.1. *Growth Modes in Heteroepitaxy*

Based on considerations from thermodynamics, epitaxy of dissimilar materials can proceed according to three different growth modes.<sup>12</sup> The system will evolve into a specific morphology in order to minimize energy. Planar growth, commonly referred to as the Frank–van der Merwe mode,<sup>12</sup> is predicted if the sum of the surface free energy of the epitaxial film and the free energy of the epitaxial layer/substrate interface is smaller than the original substrate surface free energy. In other words, under those conditions the deposited film wets the substrate. The opposite case leads to three-dimensional growth or the Volmer–Weber mode, as it is energetically favorable that the original surface remains exposed, that is, the film does not wet the substrate. In an intermediate case, known as the Stranski–Krastanow mode,<sup>13</sup> growth initially proceeds layer by layer to wet the surface and then undergoes a transition to three-dimensional morphology as the surface free energy evolves. The different situations are illustrated in Figs. 1.1a–1.1c. Because epitaxy is most often carried out under nonequilibrium conditions, kinetics may dictate the exact growth morphology, and deviations from the simple thermodynamic description often arise.

A further complication in the description of heteroepitaxy arises if there exists a mismatch between the lattice constants of the substrate and the film. In general, epitaxy of dissimilar materials with a large lattice misfit will not be possible, because the deposited atoms are not in registry with the host lattice. However, if the mismatch is sufficiently small, defect-free growth can proceed through strained-layer epitaxy.<sup>15</sup> In this case, strain builds up in the film to accommodate the lattice mismatch with the substrate. Eventually, the associated stress in the crystal cannot be maintained and is relieved by the formation of interface or misfit dislocations. If growth is carried out close to equilibrium conditions (high temperature, low growth rate), morphological changes may be another pathway available for the relief of strain. It may be energetically favorable for the surface atoms of a planar film to diffuse sideways and form three-dimensional structures if this results in a reduction of the stress energy larger than the gain in surface free energy. This is illustrated schematically in Fig. 1.1d. Although the minimization of surface energy favors nucleation at sites that share the most atomic bonds (site 2), this results in increased strain energy as the lattice is distorted to conform both to the host lattice and the adjacent atom. It may then become energetically favorable for the incoming atoms to nucleate on isolated sites (site 1) or even on top of adsorbed atoms (site 3), which

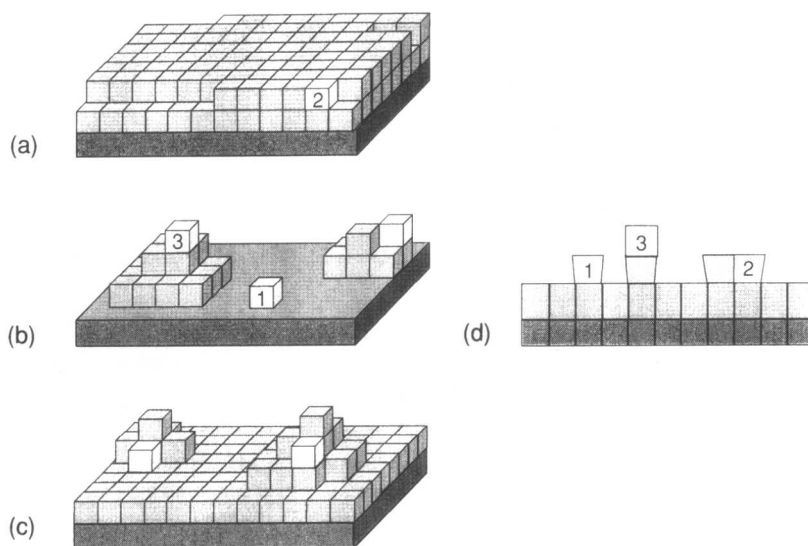


FIGURE 1.1. Schematic illustration of the three growth modes in heteroepitaxy: (a) Frank-van der Merwe, (b) Volmer-Weber, and (c) Stranski-Krastanow. Lighter blocks represent preferred nucleation sites in each case. (d) Schematic illustration of stress-driven morphological evolution. (After Ref. 14.)

while increasing the surface energy, reduce the strain energy. In such circumstance, the roughness of the surface will increase with continuous film growth, leading to the formation of three-dimensional islands. These strain-induced morphological instabilities may result in a complex evolution of three-dimensional islands on the surface with coverage, as their shape evolves to minimize energy.

The development of strained-layer epitaxy in the early 1980s<sup>16,17</sup> has revolutionized solid-state electronics by enabling band-gap engineering of semiconductors. The synthesis of defect-free semiconductor heterostructures and multiple quantum wells has led to the development of novel devices. Avoiding strain relaxation by limiting the thickness of heterostructures and maintaining two-dimensional morphology were key requirements in the fabrication of most devices. In the last decade, however, the morphological instabilities of strained systems that were first seen as undesirable (see Fig. 1.2) have attracted considerable interest. Heteroepitaxy in the regime of growth instability is an attractive way to synthesize novel structures at the nanometer scale without resorting to lithographic techniques. By optimizing growth parameters, it is also possible to fabricate semiconductor nanostructures with well-controlled physical properties. Furthermore, those nanostructures can exhibit high size uniformity or form ordered arrays on a substrate. This tendency for semiconductor islands to self-organize is very attractive for the conception of novel quantum devices. The  $\text{Si}_{1-x}\text{Ge}_x/(001)$  Si heterostructures are prototypical examples of such self-assembled islanding systems. In the following