Chapter 1

Introduction

1.1. Introduction

Nanotechnology is a technology that deals with small structures or small-sized materials. The typical dimension spans from subnanometer to several hundred nanometers. A nanometer (nm) is one billionth of a meter, or 10^{-9} m. Figure 1.1 gives a partial list of zero-dimensional nanostructures with their typical ranges of dimensions.[1,2] One nanometer is approximately the length equivalent to ten hydrogen or five silicon atoms aligned in a line. Small features permit more functionality in a given space, but nanotechnology is not only a simple continuation of miniaturization from micron meter scale down to nanometer scale. Materials in the micrometer scale mostly exhibit physical properties the same as that of bulk form; however, materials in the nanometer scale may exhibit physical properties distinctively different from that of bulk. Material in this size range exhibits some remarkable specific properties; a transition from atoms or molecules to bulk form takes place in this size range. For example, crystals in the nanometer scale have a low melting point (the difference can be as large as 1000°C) and reduced lattice constants, since the number of surface atoms or ions becomes a significant fraction of the total number of atoms or ions and the surface energy plays a significant role in the thermal stability. Crystal structures stable at elevated temperatures are stable only at much lower temperatures in nanometer sizes, so ferroelectrics and ferromagnetics may lose their ferroelectricity and ferromagnetism when the materials are shrunk to the nanometer scale. Bulk semiconductors become insulators when the characteristic dimension is sufficiently small (in a couple of nanometers). Although bulk gold does not exhibit catalysis properties, Au nanocrystal demonstrates to be an excellent low temperature catalyst.

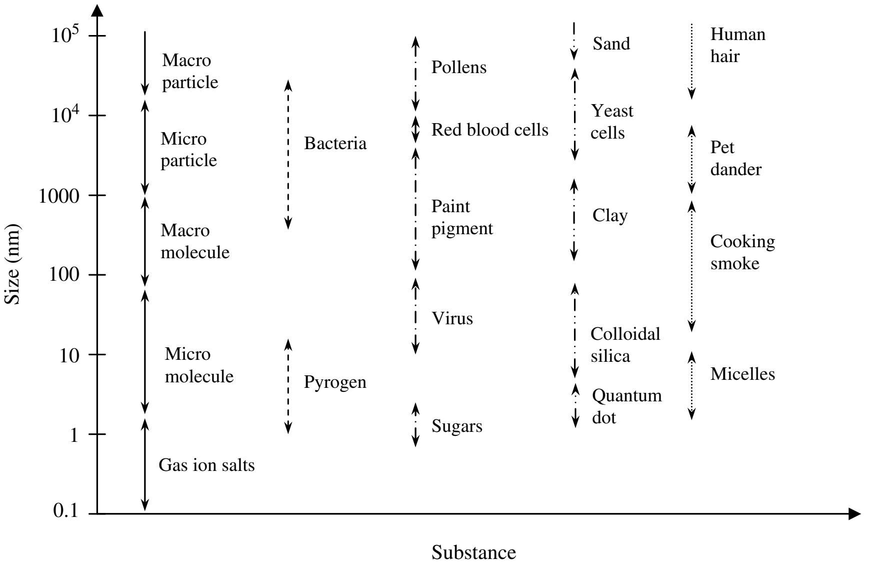

Figure 1.1. Examples of zero-dimensional nanostructures or nanomaterials with their typical ranges of dimension.

Currently there are a lot of different opinions about what is nanotechnology. For example, some people consider the study of microstructures of materials using electron microscopy and the growth and characterization of thin films as nanotechnology. Other people consider a bottom-up approach in materials synthesis and fabrication, such as self-assembly or biomineralization to form hierarchical structures like abalone shell is nanotechnology. Drug delivery, e.g., putting drug inside carbon nanotubes, is considered as nanotechnology. Microelectromechanical systems (MEMS) and lab-on-a-chip are considered as nanotechnology. More futuristic or science fiction-like opinions are that nanotechnology means something very ambitious and startlingly new, such as miniature submarines in the bloodstream, smart self-replication nanorobots monitoring our body, space elevators made of nanotubes and the colonization of space. There are many more other definitions that people working in nanotechnology use to define the field. These definitions are true to certain specific research fields, but none of them covers the full spectrum of nanotechnology. The many diverse definitions of nanotechnology reflect the fact that nanotechnology covers a broad spectrum of the research field and requires true interdisciplinary and multidisciplinary efforts.

In general, nanotechnology can be understood as a technology of design, fabrication, and applications of nanostructures and nanomaterials. Nanotechnology also includes fundamental understanding of physical properties and phenomena of nanomaterials and nanostructures. Study on the fundamental relationships between physical properties and phenomena and material dimensions in the nanometer scale, is also referred to as nanoscience. In the United States, nanotechnology has been defined as being "concerned with materials and systems whose structures and components exhibit novel and significantly improved physical, chemical and biological properties, phenomena and processes due to their nanoscale size".[3]

In order to explore novel physical properties and phenomena and realize potential applications of nanostructures and nanomaterials, the ability to fabricate and process nanomaterials and nanostructures is the first corner stone in nanotechnology. Nanostructured materials are those with at least one dimension falling in nanometer scale, and include nanoparticles (including quantum dots, when exhibiting quantum effects), nanorods and nanowires, thin films, and bulk materials made of nanoscale building blocks or consisted of nanoscale structures. Many technologies have been explored to fabricate nanostructures and nanomaterials. These technical approaches can be grouped in several ways. One way is to group them according to the growth media:

(1) Vapor phase growth, including laser reaction pyrolysis for nanoparticle synthesis and atomic layer deposition (ALD) for thin film deposition
(2) Liquid phase growth, including colloidal processing for the formation of nanoparticles and self-assembly of monolayers
(3) Solid phase formation, including phase segregation to make metallic particles in glass matrix and two-photon-induced polymerization for the fabrication of three-dimensional photonic crystals
(4) Hybrid growth, including vapor–liquid–solid (VLS) growth of nanowires.

Another way is to group the techniques according to the form of products:

(1) Nanoparticles by means of colloidal processing, flame combustion, and phase segregation
(2) Nanorods or nanowires by template-based electroplating, solution–liquid–solid growth (SLS), and spontaneous anisotropic growth
(3) Thin films by molecular beam epitaxy (MBE) and atomic layer deposition (ALD)
(4) Nanostructured bulk materials, for example photonic bandgap crystals by self-assembly of nanosized particles.

There are many other ways to group different fabrication and processing techniques such as top-down and bottom-up approaches, spontaneous and forced processes. Top-down is in general an extension of lithography. The concept and practice of a bottom-up approach in material science and chemistry is not new either. Synthesis of large polymer molecules is a typical bottom-up approach, in which individual building blocks (monomers) are assembled to a large molecule or polymerized into bulk material. Crystal growth is another bottom-up approach, where growth species either atoms, or ions, or molecules orderly assemble into desired crystal structure on the growth surface.

1.2. Emergence of Nanotechnology

Nanotechnology is new, but research on nanometer scale is not new at all. The study of biological systems and the engineering of many materials such as colloidal dispersions, metallic quantum dots, and catalysts have been in the nanometer regime for centuries. For example, Chinese is known to use Au nanoparticles as an inorganic dye to introduce red color into their ceramic porcelains more than thousand years ago.[4,5] Use of colloidal gold has a long history, though a comprehensive study on the preparation and properties of colloidal gold was first published in the middle of the 19th century.[6] Colloidal dispersion of gold prepared by Faraday in 1857[7] was stable for almost a century before being destroyed during World War II.[6] Medical applications of colloidal gold present another example. Colloidal gold was, and is still, used for treatment of arthritis. A number of diseases were diagnosed by the interaction of colloidal gold with spinal fluids obtained from the patient.[8] What has changed recently is an explosion in our ability to image, engineer, and manipulate systems in the nanometer scale. What is really new about nanotechnology is the combination of our ability to see and manipulate matter on the nanoscale and our understanding of atomic scale interactions.

Although study on materials in the nanometer scale can be traced back for centuries, the current fever of nanotechnology is driven at least partly by the ever shrinking of devices in the semiconductor industry and supported by the availability of characterization and manipulation techniques in the nanometer level. The continued decrease in device dimensions has followed the well-known Moore's law predicted in 1965 and illustrated in Fig. 1.2.[9] The figure shows that the dimension of a device halves approximately every eighteen months and today's transistors have fallen well in the nanometer range. Figure 1.3 shows the original centimeter scale contact transistor made by Bardeen, Brattain, and Shockley on 23 December 1947 at AT&T Bell Lab.[10] Figure 1.4 shows an electronic device that is based on a single Au nanoparticle bridging two molecular monolayers for electrical studies.[11] Many scientists are currently working on molecular and nanoscaled electronics, which are

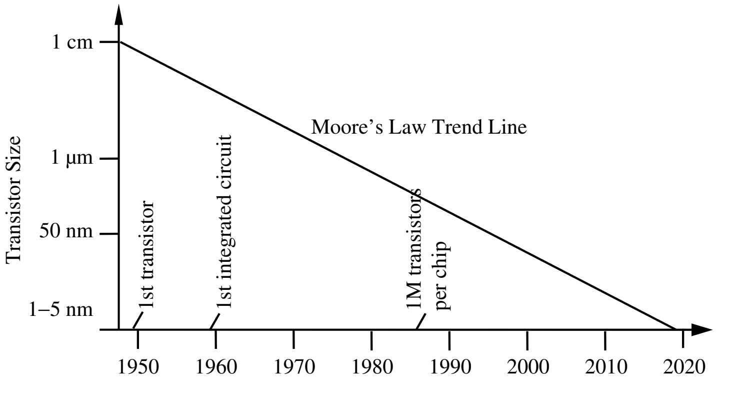

Figure 1.2. "Moore's Law" plot of transistor size versus year. The trend line illustrates the fact that the transistor size has decreased by a factor of two every 18 months since 1950.

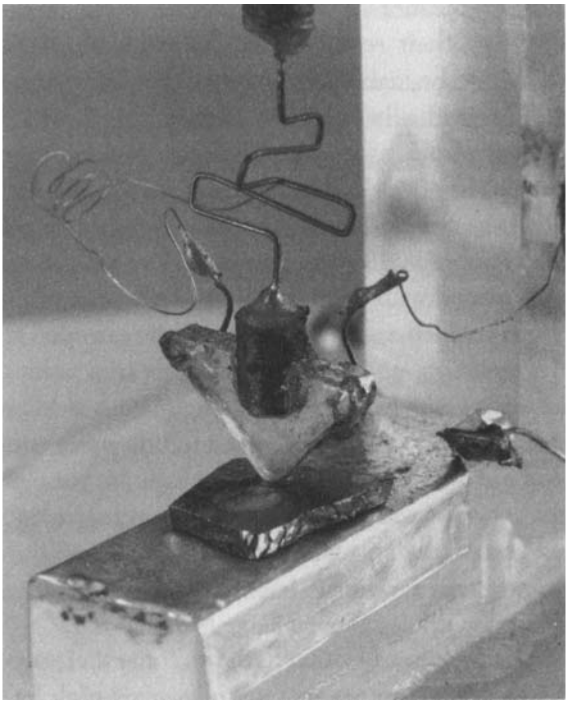

Figure 1.3. The original contact transistor made by Bardeen, Brattain, and Shockley on 23 December 1947 at AT&T Bell Lab. [M. Riordan and L. Hoddeson, *Crystal Fire*, W.W. Norton and Company, New York, 1997.]

constructed using single molecules or molecular monolayers.[12–14] Although the current devices operate far below fundamental limits imposed by thermodynamics and quantum mechanics,[15] a number of challenges in transistor design have already arisen from materials limitations and device physics.[16] For example, the off-currents in a metal oxide semiconductor field-effect transistor (MOSFET) increase exponentially with device scaling. Power dissipation and overheating of chips have also become a serious issue in further reduction of device sizes. The continued size shrinkage of transistors will sooner or later meet with the limitations of the materials' fundamentals. For example, the widening of the bandgap of semiconductors occurs when the size of the materials reaches de Broglie's wavelength.

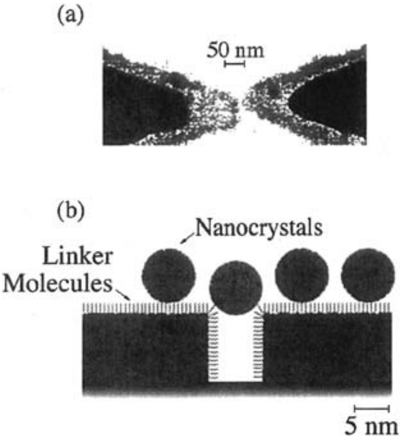

Figure 1.4. (a) Field emission SEM image of an Au lead-structure before the nanocrystals are introduced. The light gray region is formed by the angle evaporation, and is ~10 nm thick. The darker region is from a normal angle evaporation and is ~70 nm thick. (b) Schematic cross-section of nanocrystals bound via a bifunctional linker molecule to the leads. Transport between the leads occurs through the mottled nanocrystal bridging the gap. [D.L. Klein, P.L. McEuen, J.E. Bowen Katari, R. Roth, and A.P. Alivisatos, *Appl. Phys. Lett.* **68**, 2574 (1996).]

Miniaturization is not necessarily limited to semiconductor-based electronics, though simple miniaturization already brings us significant excitement.[17] Promising applications of nanotechnology in the practice of medicine, often referred to as nanomedicine, have attracted a lot of attention and become a fast growing field. One of the attractive applications in nanomedicine is the creation of nanoscale devices for improved therapy and diagnostics. Such nanoscale devices are known as nanorobots or more simply as nanobots.[18] These nanobots have the potential to serve as vehicles for delivery of therapeutic agents, detectors or guardians against early disease and perhaps repair of metabolic or genetic defects. Studies in nanotechnology are not limited to miniaturization of devices. Materials in nanometer scale may exhibit unique physical properties and have been explored for various applications. For example, gold nanoparticles have found many potential applications using its surface chemistry and uniform size. Au nanoparticles can function as carrier vehicles to accommodate multiple functionalities through attaching various functional organic molecules or biocomponents.[19] Bandgap-engineered quantum devices, such as lasers and heterojunction bipolar transistors, have been developed with unusual electronic transport and optical effects.[20] The discovery of synthetic materials, such as carbon fullerenes,[21] carbon nanotubes,[22] and ordered mesoporous materials,[23] has further fueled the research in nanotechnology and nanomaterials.

The invention and development of scanning tunneling microscopy (STM) in the early 1980's[24] and subsequently other scanning probe microscopy (SPM) such as atomic force microscopy (AFM)[25] have opened up new possibilities for the characterization, measurement, and manipulation of nanostructures and nanomaterials. Combining with other well-developed characterization and measurement techniques such as transmission electron microscopy (TEM), it is possible to study and manipulate the nanostructures and nanomaterials in great detail and often down to the atomic level. Nanotechnology is already all around us if you know where to look.[26] Nanotechnology is not new; it is the combination of existing technologies with our newly found ability to observe and manipulate at the atomic scale that makes nanotechnology so compelling from scientific, business and political viewpoints.

1.3. Bottom-Up and Top-Down Approaches

Obviously there are two approaches to the synthesis of nanomaterials and the fabrication of nanostructures: top-down and bottom-up. Attrition or milling is a typical top-down method in making nanoparticles, whereas the colloidal dispersion is a good example of bottom-up approach in the synthesis of nanoparticles. Lithography may be considered as a hybrid approach, since the growth of thin films is bottom-up whereas etching is top-down, while nanolithography and nanomanipulation are commonly a bottom-up approach. Both approaches play very important roles in modern industry and most likely in nanotechnology as well. There are advantages and disadvantages in both approaches.

Among others, the biggest problem with top-down approach is the imperfection of the surface structure. It is well-known that the conventional top-down techniques such as lithography can cause significant crystallographic damage to the processed patterns,[27] and additional defects may be introduced even during the etching steps.[28] For example, nanowires made by lithography is not smooth and may contain a lot of impurities and structural defects on surface. Such imperfections would have a significant impact on physical properties and surface chemistry of nanostructures and nanomaterials, since the surface over volume ratio in nanostructures and nanomaterials is very large. The surface imperfection would result in a reduced conductivity due to inelastic surface scattering, which in turn would lead to the generation of excessive heat and thus impose extra challenges to the device design and fabrication. Regardless of the surface imperfections and other defects that top-down approaches may introduce, they will continue to play an important role in the synthesis and fabrication of nanostructures and nanomaterials.

Bottom-up approach is often emphasized in nanotechnology literature, though bottom-up is nothing new in materials synthesis. Typical material synthesis is to build things atom-by-atom on a very large scale and has been in industrial use for over a century. Examples include the production of salt and nitrate in chemical industry, the growth of single crystals and deposition of films in electronic industry. For most materials, there is no difference in the physical properties of materials regardless of the synthesis routes, provided that chemical composition, crystallinity, and microstructure of the material in question are identical. Of course, different synthesis and processing approaches often result in appreciable differences in chemical composition, crystallinity, and microstructure of the material due to kinetic reasons. Consequently, the material exhibits different physical properties.

Bottom-up approach refers to the approach to build a material up from the bottom: atom-by-atom, molecular-by-molecular, or cluster-by-cluster. In organic chemistry and/or polymer science, we know polymers are synthesized by connecting individual monomers together. In crystal growth, growth species, such as atoms, ions, and molecules, after impinging onto the growth surface, assemble into crystal structure one after another. Although the bottom-up approach is nothing new, it plays an important role in the fabrication and processing of nanostructures and nanomaterials. There are several reasons for this. When structures fall into a nanometer scale, there is little choice for a top-down approach. All the tools we have possessed are too big to deal with such tiny subjects.

Bottom-up approach also promises a better chance to obtain nanostructures with less defects, more homogeneous chemical composition, and better short and long range ordering. This is because the bottom-up approach is driven mainly by the reduction of Gibbs free energy, so that such produced nanostructures and nanomaterials are in a state closer to a thermodynamic equilibrium state. On the contrary, top-down approach most likely introduces internal stress, in addition to surface defects and contaminations.

Figure 1.5 shows a miniature "The Thinker" fabricated by a technique called two-photon polymerization.[29] Figure 1.6 shows a "molecular person", consisting of 14 carbon monoxide molecules arranged on a metal surface fabricated and imaged by scanning tunneling microscopy.[30] These two figures show what the current technology or nanotechnology is capable of, and new capability is being developed and the existing techniques are being further improved pushing the current limit to further smaller size.

1.4. Challenges in Nanotechnology

Although many fundamentals have long been established in different fields such as in physics, chemistry, materials science, and device science and technology, and many researches on nanotechnology have been based on these established fundamentals and technologies, researchers in nanotechnology face many new challenges that are unique to nanostructures and nanomaterials. Challenges in nanotechnology include the integration of nanostructures and nanomaterials into or with macroscopic systems that can interface with people.

Challenges include the building and demonstration of novel tools to study at the nanometer level what is being manifested at the macrolevel. The small size and complexity of nanoscale structures make the development of new measurement technologies more challenging than ever. New measurement techniques need to be developed at the nanometer-scale and may require new innovations in metrological technology. Measurements of physical properties of nanomaterials require extremely sensitive instrumentation, while the noise level must be kept very low. Although material properties such as electrical conductivity, dielectric constant, tensile strength, are independent of dimensions and weight of the material in

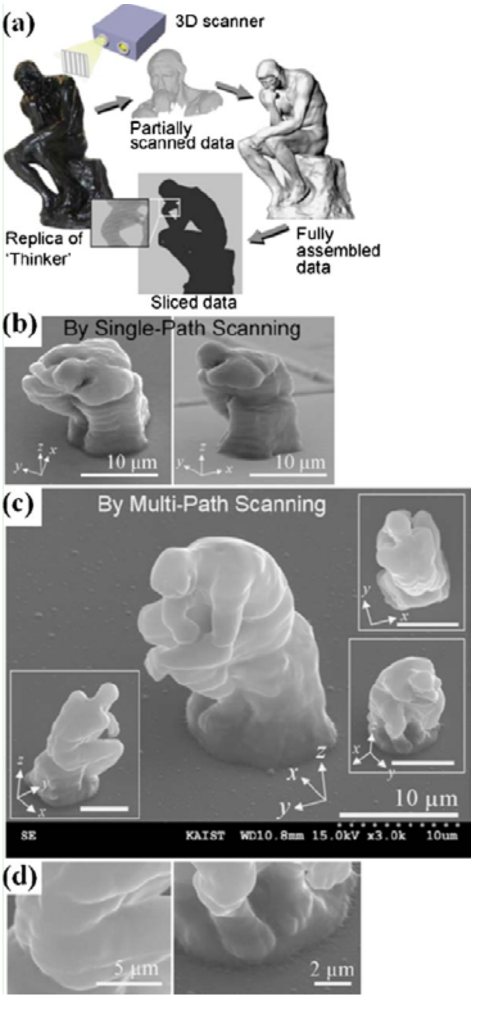

Figure 1.5. (a) Procedures of creation of CAD data using a 3D scanner based on white-light interferometer: original replica of "The Thinker", partially scanned 3D points data, fully assembled STL data, and 2D sliced data using a homemade program (the inset of sliced data is partially magnified data). The total number of layers is 667 layers. (b) SEM images of failed "micro-Thinker" (by single-path scanning method) due to the flow and surface tension of a developing material. (c) SEM images of reproduced micro-Thinker by double-scanning path. The insets are the same micro-Thinker with various view angles, and the scale bars are 10 μm. (d) Partially magnified images of micro-Thinker: skins displaying muscles, two feet, and toes can be found. [Dong-Yol Yang, Sang Hu Park, Tae Woo Lim, Hong-Jin Kong, Shin Wook Yi, Hyun Kwan Yang, and Kwang-Sup Lee, *Appl. Phys. Lett.* **90**, 013113 (2007).]

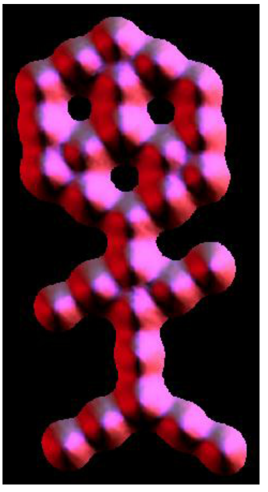

Figure 1.6. A molecular person consisting of 14 carbon monoxide molecules arranged on a metal surface fabricated and imaged by scanning tunneling microscopy. [P. Zeppenfeld and D. M. Eigler, *New Scientist* **129**, 20 (23 February 1991) and http://www.almaden.ibm.com/vis/stm/atomo.html.]

question, in practice, system properties are measured experimentally. For example, electrical conductance, capacitance, and tensile stress are measured and used to calculate electrical conductivity, dielectric constant, and tensile strength. As the dimensions of materials shrink from centimeter or millimeter scale to nanometer scale, the system properties would change accordingly, and mostly decrease with the reducing dimensions of the sample materials. Such a decrease can be easily as much as six orders of magnitude as sample size reduces from centimeter to nanometer scale.

Other challenges arise in the nanometer scale, but are not found in the macrolevel. For example, doping in semiconductors has been a very well-established process. However, random doping fluctuations become extremely important at nanometer scale, since the fluctuation of doping concentration would be no longer tolerable in the nanometer scale. With a typical doping concentration of $10^{18}/cm^3$, there will be just one dopant atom in a device of $10 \times 10 \times 10\ nm^3$ in size. Any distribution fluctuation of dopants will result in a totally different functionality of device in such a size range. Making the situation further complicated is the location of the dopant atoms. Surface atom would certainly behave differently from the centered atom. The challenge will be not only to achieve reproducible and uniform distribution of dopant atoms in the nanometer scale, but also to precisely control the location of dopant atoms. To meet such a challenge, the ability to monitor and manipulate the material processing in the atomic level is crucial. Furthermore, doping itself also imposes another challenge in nanotechnology, since the self-purification of nanomaterials makes doping very difficult.

For the fabrication and processing of nanomaterials and nanostructures, the following challenges must be met:

(1) Overcome the huge surface energy, a result of enormous surface area or large surface to volume ratio
(2) Ensure all nanomaterials with desired size, uniform size distribution, morphology, crystallinity, chemical composition, and microstructure, that altogether result in desired physical properties, and
(3) Prevent nanomaterials and nanostructures from coarsening through either Ostwald ripening or agglomeration as time evolutes.

1.5. Scope of the Book

The aim of this book is to summarize the fundamentals and technical approaches in synthesis, fabrication, and processing of nanostructures and nanomaterials so as to provide the readers with a systematic and coherent picture of the field. Therefore, this book would serve as a general introduction to people just entering the field and for experts seeking for information in other subfields. It has been the intention of the authors that this book is intended to be tutorial and not a comprehensive review. The research on nanotechnology is evolving and expanding very rapidly. That makes it impossible for a book to cover all the aspects of the nanotechnology field. Furthermore, this book has been primarily focused on inorganic materials, although, efforts have been made to include the relevant organic materials such as self-assembled monolayers and Langmuir–Blodgett films as part of Chapter 5. Of course, in the synthesis, fabrication, and processing of nanostructures and nanomaterials, organic materials often play an indispensable role, such as surfactants in the synthesis of ordered mesoporous materials, and capping polymers in the synthesis of monodispersed nanoparticles.

In the synthesis, fabrication, and processing of nanostructures and nanomaterials, one of the great challenges is to deal with the large surface to volume ratio and the resulting surface energy. Therefore, the entire chapter, Chapter 2, has been devoted to the discussion on the physical chemistry of solid surface prior to introducing various synthesis techniques for various nanostructures and nanomaterials. A good understanding of the surface properties of solids is essential for the understanding of the fabrication and process of nanostructure materials.

Chapter 3 is focused on the synthesis and processing of zero-dimensional nanostructures including nanoparticles and heteroepitaxial core–shell structures. In this chapter, the fundamentals of homogeneous and heterogeneous nucleation as well as the continued growth immediately following the initial nucleation will be discussed in detail. Particular attention will be paid to the fundamentals for the control of particle size, size distribution, and chemical composition. Various methods for the synthesis for nanoparticles and core–shell structures are reviewed.

The formation of one-dimensional nanostructures is the subject of Chapter 4. One-dimensional nanostructures include nanorods, nanowires, and nanotubules. In this chapter, we discussed spontaneous anisotropic growth, catalyst-induced anisotropic growth such as vapor–liquid–solid growth, template-based synthesis, electrospinning, and nanolithography. Essential fundamentals are discussed first, prior to the discussion of the details of various techniques used in the synthesis of one-dimensional nanostructures.

Chapter 5 is on the formation of two-dimensional structure, i.e., thin films. Since there are relatively abundant information on the deposition of thin (less than 100 nm) and thick (above 100 nm) films, the discussion in this chapter has been kept as brief as possible. The focus has been mainly on the less extensively covered subjects on conventional thin film books: atomic layer deposition and self-assembled monolayers. These two techniques are extremely important in making very thin films, and are capable of making films less than 1 nm in thickness.

Chapter 6 discusses the synthesis of various special nanomaterials. The coverage in this chapter is somewhat different from other chapters. Here we also included some brief introduction to those special nanomaterials. Carbon fullerenes and nanotubes have been discussed first with a brief introduction to what are carbon fullerenes and nanotubes including their crystal structure and some physical properties. Mesoporous materials were discussed second. In this section, three types of mesoporous materials were included, ordered mesoporous materials with surfactant templating, random structured mesoporous materials, and zeolites. Other special nanomaterials discussed in this chapter include the core–shell structures, organic–inorganic hybrid materials, inverse opals. Bioinduced nanomaterials have been discussed lastly in this chapter.

In Chapter 7, various physical techniques for the fabrication of nanostructures are discussed. A variety of lithography methods using light, electron beams, focused ion beams, neutral atoms and X-rays were discussed first. Nanomanipulation and nanolithography were discussed with a brief introduction of scanning tunneling microscopy (STM) and atomic force microscopy (AFM) first. Then soft lithography for the fabrication of nanostructures was discussed.

Chapter 8 is the characterization and properties of nanomaterials. Most commonly used structural and chemical characterization methods have been reviewed in the beginning. The structural characterization methods include X-ray diffraction (XRD) and small angle X-ray scattering (SAXS), scanning and transmission electron microscopy (SEM/TEM), and various scanning probe microscopy (SPM) with emphasis on STM and AFM. Chemical characterization methods include electron spectroscopy, ion spectroscopy, and optical spectroscopy. Physical properties of nanomaterials include melting points, lattice constants, mechanical properties, optical properties, electrical conduction, ferroelectrics and dielectrics, and superparamagnetism.

Chapter 9 gives some examples of applications of nanostructures and nanomaterials. Examples include nanoscale and molecular electronics, catalysis of gold nanocrystals, nanobots, nanoparticles as biomolecular probes, bandgap-engineered quantum devices, nanomechanics, carbon nanotube emitters, photoelectrochemical cells, lithium-ion rechargeable batteries, hydrogen storage, thermoelectrics, environmental applications, and photonic crystals and plasmon devices.

References

1. *Microscopy and Histology Catalog*, Polysciences, Warrington, PA 1993–1994.

2. N. Itoh, in *Functional Thin Films and Functional Materials: New Concepts and Technologies*, ed. D.L. Shi, Tsinghua University Press and Springer-Verlag, Berlin, p. 1, 2003.
3. *National Nanotechnology Initiative 2000 Leading to the Next Industrial Revolution*, A Report by the Interagency Working Group on Nanoscience, Engineering and Technology (Washington DC: Committee on Technology, National Science and Technology Council), http://www/nano.gov.
4. J. Ayers, in *Ceramics of the World: From 4000 BC to the Present*, eds. L. Camusso and S. Bortone, Abrams, New York, p. 284, 1992.
5. H. Zhao and Y. Ning, *Gold Bull.* **33**, 103 (2000).
6. J. Turkevich, *Gold Bull.* **18**, 86 (1985).
7. M. Faraday, *Phil. Trans*. **147**, 145 (1857).
8. J. Turkevich, *Gold Bull.* **18**, 86 (1985).
9. B.E. Deal, *Interface* **6**, 18 (1976).
10. M. Riordan and L. Hoddeson, *Crystal Fire*, W.W. Norton and Company, New York, 1997.
11. D.L. Klein, P.L. McEuen, J.E. Bowen Katari, R. Roth, and A.P. Alivisatos, *Appl. Phys. Lett.* **68**, 2574 (1996).
12. M.A. Reed, C. Zhou, C.J. Muller, T.P. Burgin, and J.M. Tour, *Science* **278**, 252 (1997).
13. R. F. Service, *Science* **293**, 782 (2001).
14. J.H. Schön, H. Meng, and Z. Bao, *Science* **294**, 2138 (2001).
15. J.D. Meindl, Q. Chen, and J.A. Davis, *Science* **293**, 2044 (2001).
16. M. Lundstrom, *Science* **299**, 210 (2003).
17. R.P. Feynman, *J. Microelectromech. Syst.* **1**, 1 (1992).
18. C.A. Haberzettl, *Nanotechnology* **13**, R9 (2002).
19. D.L. Feldheim and C.D. Keating, *Chem. Soc. Rev.* **27**, 1 (1998).
20. F. Capasso, *Science* **235**, 172 (1987).
21. W. Krastchmer, L.D. Lamb, K. Fostiropoulos, and D.R. Huffman, *Nature* **347**, 354 (1990).
22. S. Iijima, *Nature* **354**, 56 (1991).
23. C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartulli, and J.S. Beck, *Nature* **359**, 710 (1992).
24. G. Binnig, H. Rohrer, C. Gerber, and E. Weibel, *Phys. Rev. Lett.* **49**, 57 (1982).
25. G. Binnig, C.F. Quate, and Ch. Gerber, *Phys. Rev. Lett.* **56**, 930 (1986).

26. T. Harper, *Nanotechnology* **14**, 1 (2003).
27. B. Das, S. Subramanium, and M.R. Melloch, *Semicond. Sci. Technol.* **8**, 1347 (1993).
28. C. Vieu, F. Carcenac, A. Pepin, Y. Chen, M. Mejias, L. Lebib, L. Manin Ferlazzo, L. Couraud, and H. Launois, *Appl. Surf. Sci.* **164**, 111 (2000).
29. Dong-Yol Yang, Sang Hu Park, Tae Woo Lim, Hong-Jin Kong, Shin Wook Yi, Hyun Kwan Yang, and Kwang-Sup Lee, *Appl. Phys. Lett.* **90**, 013113 (2007).
30. P. Zeppenfeld and D. M. Eigler, *New Scientist* **129**, 20 (23 February 1991) and http://www.almaden.ibm.com/vis/stm/atomo.html.