

Engineering Materials and Processes

Jiyang Fan
Paul K. Chu

Silicon Carbide Nanostructures

Fabrication, Structure, and Properties

Second Edition

 Springer

Engineering Materials and Processes

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Silicon Carbide Nanostructures

Fabrication, Structure, and Properties

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Preface to the Second Edition

It has been 10 years since the publication of the first edition of this monograph, and silicon carbide nanostructures have continued to be a booming field with more and more intriguing and important new developments. We have largely extended the contents of this book to reflect those newest advances as well as some important correlated points that had been missed in the first edition. We try our best to render this second edition still and even more self-contained. It covers the major areas of diverse silicon carbide nanostructures including zero-dimensional nanoparticles and quantum dots, one-dimensional nanowires and nanotubes, two-dimensional graphene-like monolayers and ultrathin silicon carbide, nanoporous structures, nanostructured films, etc. Topics include synthesis and fabrication approaches, microstructures, unique polytypes, various characteristics, and promising applications, emphasizing the strong correlations between structures and properties, which are the permanent pursuing targets of natural science concerning all scale levels and all kinds of materials and structures existing in nature and in the cosmos. The section of point defects and spin dynamics is highly enlarged to reflect the booming advances in this field, especially the explorations of the applications of the SiC point defects in quantum information. More advances concerning impurities and luminescence as well as presolar SiC grains and explorations of their origins are included. In Chap. 4, we discuss more exciting and important advances toward better understanding the basic characteristics of SiC quantum dots. We add more sections involving preliminary applications of SiC nanoparticles. There is now a section in Chap. 5 devoted to the description of more application potential of SiC nanowires such as microwave absorption and thermal management. The section of two-dimensional honeycomb-structured monolayers and ultrathin layers of SiC is highly enlarged in Chap. 6 to reflect the exciting experimental and theoretical breakthroughs in this important field. In Chap. 8, more interesting advances concerning the biological application potential of SiC nanostructures are summarized and discussed.

We express our great gratitude to our tutors (for Jiyang Fan) or colleagues Prof. Xinglong Wu, Prof. Shining Zhu, Prof. Min Xiao, and others for their always guidance, cooperation, and help. Thank the graduate students Dejian Dai, Xiaoxiao Guo, Yuanyuan Li, Nan Zhang, Xuan Ji, Xueli Sun, and others for their contributions to

our explorations of SiC nanostructures. We acknowledge Springer Press, especially senior editor Anthony Doyle, and senior editorial assistant Manju Ramanathan, for their encouragement and patience during the preparation of this book. We also thank our families for their tremendous support without which this book would not have been completed.

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Paul K. Chu

Preface to the First Edition

Although nanostructured silicon carbide is rapidly evolving, the field is still in the infancy stage and full potential of the materials is far from being realized. This book provides the state of the art of the various nanostructures of wide bandgap silicon carbide, including nanoparticles, nanowires, nanotubes, porous structures, nanostructured films, and other complex nanostructures. Topics covered in this book include fabrication methods, polytypes, bulk and surface structures, electronic structures, properties, especially electrical and optical ones, as well as potential applications. The target readership is graduate students and researchers in universities, research institutes, and companies working on SiC and related materials in the fields of materials science, physics, chemistry, electronic engineering, biomedical engineering, and biomedicine.

It is impossible to cover all the aspects of the materials in a single book, and so our intention is to provide an up-to-date review of the relevant results and present a holistic view of this burgeoning field. As a self-contained monograph, Chap. 1 is the brief introduction and Chap. 2 describes the general characteristics of bulk silicon carbide in order to provide necessary and self-contained backgrounds to understand the properties of silicon carbide nanostructures. This chapter emphasizes various unique and core physical characteristics of silicon carbide. It covers bulk crystal structures, introduction of intriguing presolar SiC grains stemming from carbon stars and supernovae, surface reconstruction structures and SiC/SiO₂ interface structures, intrinsic point and extended defects and related photonic and spintronic applications, electronic structures, impurities and luminescence properties, lattice vibration and infrared and Raman characteristics, as well as diverse polytypes and pertinent phase transformations. However, the bulk crystal growth of silicon carbide, general silicon carbide ceramics, and applications of silicon carbide in electric devices are omitted because these fields are far from the topics of this book and too diverse as well as because there are already some excellent books or reviews on these subjects. Chapters 3 and 4 address the porous silicon carbide nanostructures and individual silicon carbide nanoparticles with emphasis on the complex relationship between the structures and luminescence properties and mechanisms. Chapters 5 and 6 describe one-dimensional SiC nanowires and nanotubes as well as two-dimensional SiC

monolayers and ultrathin layers concentrating on the synthesis, intrinsic stacking fault defects, unique properties, and applications. Chapter 7 deals with common silicon carbide nanostructured films focusing on those containing silicon carbide nanocrystals. In Chap. 8, the biological applications of silicon carbide nanostructures are discussed. Topics covered include biomorphic silicon carbide ceramics, biological imaging, and cytotoxicity evaluation.

We express our gratitude to our tutors (for Jiyang Fan) or colleagues, Prof. Xinglong Wu, Prof. Shining Zhu, Prof. Min Xiao, Dr. Teng Qiu, Dr. Gaoshan Huang, Dr. Yimin Yang, Ms. Mengxing Liao, and many others, for their cooperation and help on the studies of silicon carbide nanostructures. We acknowledge Springer Press, especially senior editor Anthony Doyle, and senior editorial assistants Simon Rees, Claire Protherough, Gabriella Anderson, and Sathya Subramaniam, for their encouragement and patience during the preparation of this book. We also thank our families for their tremendous support without which this book would not have been completed.

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Chapter 1

Introduction



The constituents of the earth are simple in that 92 elements, which occur naturally among all existing 118 elements, make up all the materials around us. However, our world is also very complex because almost unlimited types of matters (especially crystals and molecules) can be formed by combining these elements in different spatial arrangements following different symmetries. In this respect, silicon carbide is unique as it has over two hundred crystalline forms and some polytypes of silicon carbide have even been identified from presolar grains in meteorites. Silicon carbide is a family of wide bandgap semiconductors with excellent electric and electronic characteristics that bode well for applications in high-temperature, high-frequency, and high-power electronic devices. Moreover, silicon carbide is a superhard ceramic having a small density as well as superior thermal and mechanical properties. It is environmentally friendly and biocompatible, thus having many potential applications in energy, biomedical engineering, and medicine. Last but not least, both silicon and carbon are extremely abundant on earth and SiC can be produced economically, a big advantage compared to materials composed of noble metals and rare-earth elements.

On the heels of rapid developments of nanoscience and nanotechnology, researchers have been intrigued by the unique properties of fruitful types of silicon carbide nanostructures and their diverse potential applications. Many silicon carbide nanostructures ranging from quasi-zero-dimensional quantum dots to one-dimensional nanowires and nanotubes, to two-dimensional honeycomb-structured monolayers as well as quasi-two-dimensional nanostructured films, have been synthesized and studied. SiC nanostructures possess properties inherent to nanomaterials such as the quantum confinement effect, surface effects, and other size-sensitive characteristics. In addition, nanostructured SiC has unique electronic structures, outstanding electrical and mechanical properties, superior thermal and chemical stability, and favorable biocompatibility and is suitable for applications to microelectronics, nanoelectronics, photonics, energy storage and conversion, and life science.

Researchers began to notice the diversity and potential applications of SiC nanostructures since the 1990s, about the same time when the fabrication and properties of porous Si and Si nanostructures aroused interest. In the early years, researchers were mainly concerned with porous SiC fabricated by electrochemical etching of bulk single-crystalline SiC. Since the invention of solid-state electronic devices, group IV semiconductors have acted as cornerstones of the microelectronics industry which has introduced to modern living the Internet and indispensable electronic gadgets such as personal computers and cell phones. However, in the important application areas involving lighting and display, the roles of group IV semiconductors are rather limited due to their typical indirect bandgaps. As a result, the luminescence arising from the interband transitions of carriers is inefficient compared to direct-bandgap semiconductors such as GaAs. Microscopically, in an ideal indirect-bandgap semiconductor, light absorption or emission occurs via interband transition of an electron, that is, the transition of an electron between two quantum states with different crystal momentum $\hbar k$; in this process, the conservation of energy is readily ensured. However, the small photon momentum cannot ensure conservation of momentum in the transition. Hence, this process typically occurs with absorption or emission of one or a couple of lattice phonons to satisfy conservation of momentum. Such a quantum process involving electrons, photons, and phonons generally has much lower efficiency than the no-phonon electronic transition in a direct-bandgap semiconductor in which only electrons and photons, but no phonons, are involved.

Investigation of a porous Si layer containing nanoparticles reveals that the luminescence efficiency of Si nanoparticles can be improved by several orders of magnitude compared to the bulk materials due to spatial confinement of carriers. In addition, luminescence from porous Si shifts from the near-infrared region of the bulk silicon to the visible regime due to the quantum confinement effect, which predicts that the smaller the quantum dot, the wider is the energy gap. Similar to Si, porous SiC shows visible luminescence with enhanced efficiency. These porous materials are generally fabricated by electrochemical etching of bulk SiC crystals in hydrofluoric acids. However, in most cases, luminescence from porous SiC is characteristic of defect-related luminescence, and hence, light emission is generally attributed to surface defects although the specific defect types are not fully understood.

The nanoparticles and nanowires in porous SiC are not separated but rather they are connected to the SiC substrate and in effect a component of the whole porous SiC crystal. Therefore, their properties are between those of the single crystal and individual nanocrystals. Various types of separate SiC nanocrystals have been fabricated and studied. Gas phase reactions and solution-based chemical reactions can produce SiC nanocrystals, and SiC nanocrystals encapsulated in polymers or other solid matrices have also been produced by techniques such as ion implantation followed by annealing. The luminescence properties of these SiC nanocrystals vary and depend on the fabrication approaches, and as aforementioned, the light emission is generally ascribed to surface defect states. Colloidal SiC nanocrystals suspended in solvents have been prepared by electrochemical or direct chemical etching of SiC bulk crystals followed by ultrasonic treatment. These SiC colloids show intense visible luminescence with tunable peak wavelengths. The light emissions from SiC nanocrystals can

have quantum yields higher than that of bulk materials by several orders of magnitude. The origins of their light emissions are rather complex, combining the interband transition luminescence and surface defect states-correlated luminescence. For the luminescence originating from quantum confinement, the emission band shifts monotonically toward the shorter-wavelength region when the particle size diminishes. On the other hand, there are fruitful surface defects for the compound SiC nanocrystals, and they offer diverse localized quantum states, some of which give rise to distinct colors (blue, green, or even red) of luminescence. Therefore, the intrinsic interband transition luminescence of nonlocalized electrons and surface defects luminescence superimpose and give rise to the detected complex and wideband luminescence. Different colors of light emissions, spanning red, yellow, green, blue, and near-UV, are achievable from SiC crystallites with different sizes and distinct surface structures. Blue and quasi-white light-emitting diodes based on SiC nanocrystals have been demonstrated. Furthermore, silicon carbide has high chemical and thermal stability in comparison with other types of semiconductors. This virtue combined with the color-tunable luminescence enables the use of luminescent SiC nanocrystals in harsh environments. In conjunction with the high surface hydrophilicity, excellent biocompatibility, low density, and high hardness, SiC nanocrystals are very useful in biology and medicine. Additionally, SiC has long been used as filling materials to enhance the mechanical properties of ceramics, and it has been shown that incorporation of SiC nanoparticles into metal nanocomposites can boost the mechanical properties. It has also been found that doping with SiC nanoparticles can substantially enhance the performance of some superconductors.

SiC nanowires have been widely investigated. Several methods have been developed to synthesize such materials, and they involve two main growth mechanisms: vapor–liquid–solid growth with the assistance of metal catalysis and vapor–solid growth without catalysts. Some synthesized SiC nanowires have the SiC/amorphous SiO₂ core/shell structure. Carbon-sheathed SiC nanowires have also been observed but are rare. BN-coated SiC nanowires have been prepared. The synthesized SiC nanowires can be as small as several nanometers or as large as several hundred nanometers in diameter. Their lengths are generally on the order of micrometers, although SiC nanowires with lengths of a few centimeters have also been reported. Besides standard nanowires and nanorods, less common quasi-one-dimensional SiC nanostructures with different morphologies of bamboo, bead, helix, belt, flower, and multileg have also been produced. The SiC nanowires and similar structures often exhibit visible or near-UV luminescence, but the luminescence mechanisms are not well understood. SiC nanowires yield stable field electron emissions with favorable characteristics such as low turn-on fields. Large-scale and highly ordered SiC nanowire arrays have been prepared, and some synthesized SiC nanowires have very sharp ends that are beneficial to field emissions. One-dimensional SiC nanostructures are competent for microwave absorption, thermal management and fire-proofing, and as building blocks of molecular electronic devices. SiC-based coaxial

nanocables such as coaxial SiC/BN nanocables have promising applications in nano-electronic devices. Silicon carbide nanowires having superior mechanical characteristics and electrical conductivity can be utilized to reinforce composite materials or as nanocontacts in harsh environments.

In comparison with SiC nanowires, SiC nanotubes have been less investigated experimentally. They are generally synthesized using carbon nanotube or semiconductor nanowire templates. Most of the synthesized SiC nanotubes are actually not real nanotubes, because the walls of the nanotubes are composed of cubic SiC nanocrystals with different orientations. In other words, they are polycrystalline. However, SiC nanotubes with structures similar to multiwalled carbon nanotubes have been observed. In comparison, there have been many theoretical studies on the structures, electronic structures, and molecular adsorption properties of SiC nanotubes based on first-principles calculations or molecular dynamics simulations. This is understandable because the structures of SiC nanotubes are simpler than that of most of other SiC nanostructures. It consists of fewer atoms than other SiC nanostructures of the same size, and smaller computational power is required. The theoretical results are generally consistent with experimental data. Two-dimensional honeycomb-structured SiC nanosheets similar to graphene have aroused more and more interest in recent years. They have long been widely investigated and predicted by using density functional theory calculations. However, the fabrication of the 2D SiC in laboratories is challenging. Most of the early observed "2D SiC" materials are either ultrasheets composed of 3C-SiC nanoparticles or small fragments with probable honeycomb structures. Very recent advances in this field have enabled experimental fabrication or synthesis of truly honeycomb-structured SiC monolayers. They are indeed stable. But this field is still in infancy, and more developments are expected.

The research history of SiC films is longer than that of SiC nanoparticles and SiC nanowires. However, in the early investigations of SiC films, little attention had been paid to the nanoscale structures of these films due to the limitations in the preparation methods and characterization capability. However, in the last twenty years, researchers have been able to prepare and identify nanostructured SiC films by many methods. Chemical vapor deposition is the most widely used approach to synthesize nanocrystalline SiC films, and ion implantation and high-temperature sputtering have also been adopted to fabricate nanostructured SiC films. Many thin SiC films comprise embedded SiC nanocrystals, and these nanocrystalline SiC films are potentially useful in electronic devices, solar cells, and sensors. Furthermore, many SiC films yield visible light emissions rendering the materials probably suitable for large-area displays.

As biocompatible materials, SiC nanostructures have potential applications in biological imaging. Silicon carbide is an excellent wear-resistant and benign coating on biomedical implants. Porous SiC films with ultrasmall pores are semi-permeable biomaterials. Biomimetic SiC ceramic materials with a wood-like microstructure have been prepared by infiltrating a wood-derived carbon template with silicon or silicon oxide at high temperatures. The biomimetic SiC ceramics coated with bioactive silica show great promise as dental and orthopedic implants with enhanced mechanical and chemical properties.

Theoretical studies play important roles in understanding the structures and properties of various silicon carbide nanostructures. Common approaches include semi-empirical and first-principles calculations as well as molecular dynamics simulations. Many important properties of SiC nanostructures have been theoretically predicted. For example, the energy gap of a SiC quantum dot depends closely on its dimension and surface composition. Calculations show that the difference between cohesive energy and energy gap of different polytypes of SiC quantum dots vanishes gradually as the size diminishes. With decreasing size, the surfaces of the SiC nanocrystals become more important, and in practice, SiC nanoparticles with sizes close to or below one nanometer resemble giant molecules. As a result, the properties of ultrasmall SiC nanoparticles are distinct from those of bulk materials. For example, they may have complex and surface defects-dominated light emissions. Theoretical investigations show that the electronic structures and mechanical properties of SiC nanowires sensitively depend on the nanowire diameter. SiC nanotubes are generally semiconducting and their bandgap may decrease as the tube diameter decreases. This is contrary to the case of SiC nanocrystals. SiC nanotubes may have an indirect or direct bandgap depending on the chirality, and some SiC nanotubes may even be metallic when the surface is terminated by hydrogen atoms.

In this book, the various fabrication and synthesis techniques, diverse properties, and fruitful potential applications of SiC nanostructures are described and discussed. Containing the latest information and knowledge in this fledgling field, it serves as a valuable reference for graduate students and researchers who are interested in these fascinating nanostructures and potential applications galore.