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Silicon Carbide

From Materials Science to Nanotechnology
and Microelectronics

Edited by Mariana Amorim Fraga



Silicon Carbide - From Materials Science to Nanotechnology and Microelectronics

Edited by Mariana Amorim Fraga

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Aims and Scope of the Series

Materials science has always occupied an extremely high position in the human development process. As we explore the oceans of stars, various industries have put forward more stringent requirements for the performance of materials, forcing us to pay more and more attention to the development of new materials. At the same time, the formation of a data-driven scientific paradigm is dramatically shortening the development cycle of new materials. The huge data generated by synergistically combining theories, high-throughput experiments, high-throughput computation, and artificial intelligence is greatly contributing to our ability to utilize materials science to solve real-world problems. The three topics of this book series - Metals and Nonmetals; Composite Materials; and Surface Science - will address important areas of advancement in materials science. There will be a range of interesting works published under these topics.

Meet the Series Editor



Prof. Chonghe Li received his Ph.D. from the Chinese Academy of Sciences in 1995. From 1995 to 2000, he worked as a researcher at the Shanghai Institute of Metallurgy, Chinese Academy of Sciences, where he also served as director of the research laboratory. In 2000, he was appointed Professor at the Institute of High-Performance Computing in Singapore, where he worked on computation and simulation in materials science until 2004. Since then, he has been a professor at the School of Materials Science and Engineering, Shanghai University, China, as well as the director of the Shanghai Specialty Casting Engineering and Technology Research Center. Prof. Li's research focuses on titanium alloys, titanium-aluminum single crystals, intermetallic compounds, theoretical calculations, alloy design, and special refractory materials. His broad scientific expertise is well recognized by the scientific community around the world. He is a member of the editorial board of the journal *Metals*. As an author, he has published more than 200 peer-reviewed papers, 2 books, and over 40 patents.

Meet the Volume Editor



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Preface

The continuous evolution of advanced semiconductor materials has driven innovations in nanotechnology, microelectronics, and energy conversion. Among these materials, silicon carbide (SiC) has emerged as a strategic platform enabling new device architectures and functionalities. This edited volume, *Silicon Carbide – From Materials Science to Nanotechnology and Microelectronics*, brings together recent developments from fundamental materials research to emerging applications. The book aims to provide an overview and perspective for researchers, students, and professionals working in materials science, electrical engineering, and related fields.

The first section of the volume, titled “Fundamentals, Materials, and Processing”, explores both fundamental aspects and technological advances in SiC. Chapter 1, *Introductory Chapter: Silicon Carbide at the Forefront of Materials Innovation and Device Integration*, provides an overview of the evolution of SiC research and its central role in enabling next-generation electronic and energy systems. Chapter 2, *Nanomaterials and Nanoelectronics: Synthesis, Properties, and Applications for Nanotechnology*, discusses the synthesis routes and functional properties of various nanomaterials, including SiC-based nanostructures, highlighting their relevance in nanoscale electronics and device miniaturization. Chapter 3, *Silicon Carbide Thin Films: Innovations in Property, Process, and Applications*, examines advances in SiC thin-film deposition and processing, emphasizing their importance for device integration. Chapter 4, *Electrical Properties in Heavily Al-Doped 4H-SiC by Hall-Effect Measurement*, presents key aspects of the characterization of doped SiC and its impact on electronic transport. Chapter 5, *Rapid Thinning in SiC Wafering: Innovations and Impacts on the Value Chain*, explores wafer processing technologies that are critical to scaling and cost-effective device manufacturing.

The second section, “Applications and Emerging Technologies”, focuses on state-of-the-art applications and future perspectives. Chapter 6, *Fluorescent Silicon Carbide Quantum Dots*, reviews the unique properties of SiC quantum dots and their potential applications in optoelectronics. Chapter 7, *Silicon Carbide in Photoelectrochemical Water Splitting: Advances, Applications, and Future Horizons*, highlights the role of SiC in energy conversion and sustainable technologies, particularly in photocatalysis and clean energy production.

Together, these chapters illustrate the interdisciplinary nature of silicon carbide research and its relevance to multiple technological domains, from basic materials science to industrial-scale applications. The contributors to this volume are internationally recognized experts who provide in-depth and up-to-date perspectives on both the scientific and technological fronts.

I want to express my sincere gratitude to all chapter authors for their commitment and contributions, as well as to the reviewers for their valuable feedback. I also thank

the editorial team for their support throughout the preparation of this volume. Their efforts have been essential in ensuring the quality and coherence of the final work.

I hope that this book will serve as both an accessible reference and an inspiration for researchers, engineers, and students interested in the rapidly evolving field of silicon carbide science and technology.

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Section 1

Fundamentals, Materials, and Processing

Introductory Chapter: Silicon Carbide at the Forefront of Materials Innovation and Device Integration

Mariana Amorim Fraga

1. Silicon carbide: An outstanding material with expanding horizons

In recent years, there has been growing academic and industrial interest in multifunctional materials that can be applied in energy systems, electronics, biomedicine, and emerging technologies. Silicon carbide (SiC) has long been recognized as a wide bandgap semiconductor with remarkable properties, including high thermal conductivity, chemical inertness, and superior breakdown electric field [1]. Originally studied and developed for high-power and high-temperature electronics, SiC has evolved into a promising material across diverse fields, including quantum technologies, biosensing, and renewable energy systems [1, 2].

The current status in SiC research and development (R&D) arises from a convergence of technological demands: the push toward more efficient energy systems [1], the need for materials resistant to extreme environments [3], the expansion of silicon-compatible platforms, and the miniaturization of devices for high-temperature, high-voltage, and high-power applications [4]. These factors have driven innovation not only in the synthesis and processing of SiC but also in its integration into novel device architectures.

What sets SiC apart is its tunability. From bulk single crystals to nanoscale films and quantum dots, the material offers a range of structural and electronic characteristics that can be engineered to suit specific applications. At the nanoscale, SiC exhibits unique behaviors, such as size-tunable fluorescence and enhanced charge carrier mobility, that open new possibilities in optoelectronics, photonics, and biomedical sensing [5]. Furthermore, SiC has been used in biomedical applications due to its biocompatibility and chemical inertness. SiC has been integrated into implantable medical devices, neural interfaces, and in vivo chemical sensors, expanding its impact into bioelectronics [2]. Moreover, SiC has been shown to be an excellent option both as a bulk substrate and as a thin film for the development of MEMS (Micro-Electro-Mechanical Systems) sensors [6].

A promising application of SiC lies in the field of electric vehicles (EVs) [1]. Due to its high breakdown voltage, thermal stability, and fast switching capability, SiC enables the development of more compact, efficient, and reliable power electronics, such as inverters and onboard chargers [7]. These components are essential for improving the overall energy efficiency and performance of EVs, leading to increased

driving range, reduced cooling requirements, and lighter systems. As the EV market continues to grow, SiC-based devices are expected to play a central role in advancing next-generation electric mobility [1, 7].

Beyond electric mobility, SiC is finding growing use in several emerging technological domains. In aerospace and space technologies, SiC-based electronics are valued for their exceptional radiation, mechanical stress, and extreme temperature resistance, making them ideal for satellites, deep-space probes, and avionics in harsh environments [1]. In the field of renewable energy, SiC devices enable more efficient power conversion in photovoltaic inverters, hybrid energy systems, and battery platforms, contributing to the advancement of smart grid infrastructure [8].

Another interesting application of SiC is as substrate for gallium nitride (GaN) growth [9]. In high-frequency communications, GaN on SiC has allowed the development of compact, high-efficiency power amplifiers for next-generation 5G and 6G wireless networks, as well as automotive and defense radar systems.

2. Advances in synthesis, processing, characterization, and examples of applications

Recent developments in SiC wafering, epitaxial growth, and doping techniques have significantly enhanced material quality and enabled unprecedented control over its electrical and optical properties [10, 11]. For instance, aluminum doping in 4H-SiC has shown promise for tailoring conductivity in power electronic devices, enabling the development of more compact and efficient transistors, diodes, and integrated circuits [12]. At the same time, innovations in rapid wafer thinning—through techniques such as grinding, chemical-mechanical polishing (CMP), and plasma etching—are reshaping fabrication workflows and improving cost-efficiency across the semiconductor value chain [11]. These advances are particularly relevant for high-power and high-voltage applications, where thermal management and device scaling are critical [13].

Thin-film technologies, particularly those involving SiC, have benefited from deposition techniques such as atomic layer deposition (ALD), chemical vapor deposition (CVD), and physical vapor deposition (PVD) [14]. These methods allow the fabrication of conformal thin films with well-controlled composition and low-defect densities, which are crucial for applications requiring surface uniformity, high aspect-ratio coverage, and chemical stability.

SiC thin films have been successfully integrated into flexible electronics [15]. Moreover, their use in MEMS devices continues to expand, with demonstrated applications in inertial sensors, resonators, and BioMEMS platforms, benefiting from the material's mechanical strength, corrosion resistance, and compatibility with silicon-based processing [6].

Advances in nanoscale characterization techniques have further accelerated the development of high-performance SiC-based devices. Hall-effect measurements, scanning capacitance microscopy (SCM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) are now routinely employed to assess doping profiles, defect densities, grain boundaries, and carrier mobility at nanometer resolution [16]. These tools provide critical feedback for optimizing synthesis and post-processing conditions, directly influencing device reliability and performance.

One particularly promising material are the SiC quantum dots. Their non-toxic nature, photostability, and compatibility with biological systems position them as

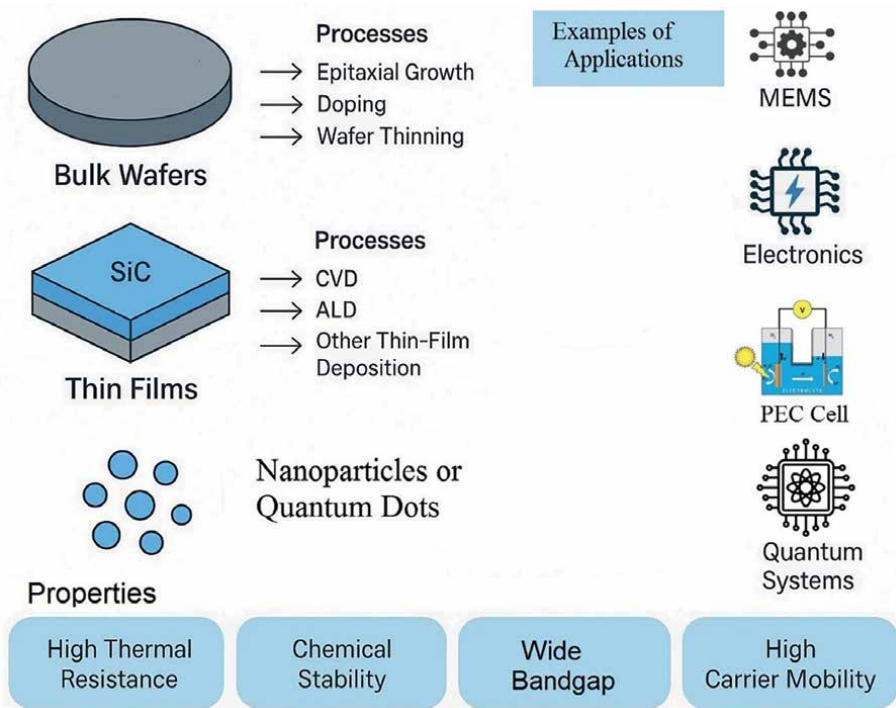


Figure 1.
 Overview of silicon carbide, its structural forms, associated synthesis processes, and potential applications.

strong candidates for bioimaging and theranostics, where safe and stable contrast agents are essential [17]. Meanwhile, in the field of clean energy, SiC-based photoelectrodes are gaining attention for their potential in photoelectrochemical (PEC) water splitting, offering robust, efficient, and scalable alternatives to traditional materials used for hydrogen generation [18].

Several application innovations have also emerged from SiC material and process advances. In power electronics, vertical SiC MOSFETs and Schottky diodes with low on-resistance and high breakdown voltages are already in commercial use, improving efficiency in electric vehicle powertrains and renewable energy inverters [19]. In quantum technologies, isotopically pure or vacancy-engineered SiC crystals are being investigated for use in spin-based qubits and photonic devices [20]. In biomedical devices, SiC films are enabling the development of robust and biocompatible implantable sensors and electrodes for long-term in vivo use [2, 14].

Figure 1 summarizes key aspects of SiC technology. As research on SiC progresses across different length scales, its role as an outstanding material for next-generation electronics becomes increasingly evident. The synergy between materials science and applied engineering defines the current and future relevance of SiC in nanotechnology and microelectronics.

Conflict of interest

The author declares no conflict of interest.

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Nanomaterials and Nanoelectronics: Synthesis, Properties, and Applications for Nanotechnology

Slah Hlali, Adel Kalboussi and Abdelkader Souifi

Abstract

As the field of nanoelectronics advances, it is increasingly focusing on overcoming fundamental challenges while leveraging the unique properties of nanomaterials to achieve superior performance and miniaturization in electronic devices. Recent innovations in nanoelectronics have demonstrated the potential for creating highly efficient, ultra-small devices by integrating novel nanomaterials such as two-dimensional materials (e.g., graphene and transition metal dichalcogenides) and one-dimensional nanostructures (e.g., nanowires and nanotubes). These materials offer enhanced electrical, thermal, and mechanical properties that are not achievable with traditional bulk materials. However, the practical implementation of nanoelectronics faces significant hurdles, including issues related to material synthesis, scalability, and integration into existing semiconductor technologies. Addressing these challenges requires a multidisciplinary approach, combining advances in materials science, electrical engineering, and fabrication techniques. Ongoing research aims to refine fabrication methods to produce high-quality nanomaterials consistently and to develop novel techniques for integrating these materials into functional electronic devices. As the field evolves, the successful resolution of these issues will be critical in unlocking the full potential of nanoelectronics and driving future technological advancements.

Keywords: nanomaterials, nanoelectronics, nanotechnology, nanoscale, quantum dots, carbon nanotubes, graphene nanowires, two-dimensional materials, material synthesis, device fabrication, electronic devices, miniaturization, interdisciplinary research, technological innovation

1. Introduction to nanotechnology

Nanotechnology is developing along two paths: nanomaterials and nanoelectronics. In many respects, these two paths exist independently now but will undoubtedly intersect soon [1]. Nanomaterials encompass a family of materials—many polymeric,

composite, or molecular-based—that are characterized by the presence of one or more nanoscale dimensions. These materials have unique physical or chemical properties that lead to novel solutions in fields such as structural materials, catalysts, sensors, electronics, photonics, optoelectronics, magnetics, and information storage. Exhibiting advanced properties, such as small feature size, high surface area, and quantum effects, has made nanomaterials offer very promising applications [2]. Various attempts have demonstrated the significance of their uses in different fields, especially as a technological base for developments in many sciences and a broad spectrum of nanotechnology applications.

Another speculative long-term significance of engineering systems and devices from many centuries of carbon is the development of carbon-based nanotechnology. With increasing miniaturization, the dimensions of the transistors designed with current technologies will soon be such that they will incorporate less than several thousand atoms for at least one of the transistor's features. Consequently, quantum mechanical tunneling effects will become particularly relevant, and one of the challenges will consist of limiting their negative impact [3]. Instead of doing so, in carbon-based nanoelectronics, one looks forward to exploiting the quantum properties of the different carbon allotropes that will form the basis of the devices.

1.1 Definition and scope of nanotechnology

Nanotechnology refers to the ability to work on a scale of 1–100 nanometers. Nanotechnology is recognized as a field right at the interface of condensed matter physics, chemistry, electronics, and biotechnology, which has a rather broad scope. Synthesis and study of novel materials on a nanometric scale represent an important aspect of nanotechnology, quite often referred to as “nanomaterials.” These materials are driven by dozens approaching toward 10 nm for novel discoveries. Beyond the bulk, they exhibit distinctive physical, chemical, mechanical, electrical, and optical properties. Pristine or hybrid nanomaterials have established a foundation for scalable nanotechnology and many breakthroughs in materials with widespread applications, that is, in nanoelectronics, spintronics, catalysis, photo- and electrochemical systems, optoelectronics, smart materials, medicine, and many others [4].

The classical theory of solid-state physics predicts that the stationary quantum state of electrons occupies a given energy band of atoms, and light does not penetrate inside the material. Our everyday perception confirms this when we look at the desk. The desk is roughly characterized by the electron sharing the fourth energy band (defense, like a night fox). Its subjects can ride freely and serve them with endless tea, but the transmission of light is nearly at zero. Then, nanometer dimensions should come to be lower than the free electron wavelength so that the energy gap of electrons in those small particles or their assemblies can inevitably depend on the radius. “Quantum-size effect” is the term defined for this case. Recently, semiconducting nanocrystals or metal nanoparticles that are now referred to as “quantum dots” (QD) have attracted a great deal of interest due to their unique dimension and size-tunable optical properties as well as the size-dependent fundamental electronic features. Those materials have been demonstrated to offer distinct advantages when used as an optical sensor in biological or environmental monitoring. In addition, both the QD synthesis based on biofunctionalization strategies, employing streptavidin-biotin and antibody-antigen affinity interactions, and the QD-based hybrid fluorophore with a wide biphoton absorption cross-section provide useful tools for scanning microscopy with high image resolution.

1.2 Historical background

Since the establishment of the science of condensed matter in the last quarter of the nineteenth century, it is well known that the electrical and optical properties of materials have differing properties with decreasing dimensionality [5]. For instance, the carrier concentration in metals with two or three dimensions and the density of states near the Fermi surface in semiconductor quantum wells show strong dependence on the thickness of the well. Geometric constraints make it possible to have stable two- or three-dimensional quantum confinement of the carriers and also to have the direct transitions between quantized energy levels leading to a variety of interesting physical properties that are important for possible electronic and/or optical applications.

The quantum effect of dimensional restrictions of the carriers in all three dimensions has been extensively explored for the research on new materials in the last decade of the twentieth century, under the name of “low-dimensional physics.” This area of research includes quantum wells of various semiconductors, rare gases, and also single-crystal metallic films. It deals with two-dimensional metal-insulator transitions induced by a magnetic field or an electric field in granular films. It also deals with quantum effects of point contact, using, for a good conductor, the scattering of surface electrons into the bulk or a two-dimensional metal-insulator transition. In one dimension, metallic nanowires of Cu, Ag, and Au, and semiconducting nanowires of InAs and carbon nanotubes are active research objects [6].

2. Fundamentals of nanomaterials

In this study, we will study nanomaterials and nanoelectronics. Upon successful completion of the chapter, you will be able to:

- Define basic and advanced concepts in nanomaterials, dealing with specifications and requirements.
- Understand the importance of advanced materials and their consequences from macro- to nano-level.
- Recognize the importance and formulation of advanced materials advantage.
- Mention applications of advanced materials or nanomaterials.

Introduction: The main aspect of nanotechnology is the knowledge and control over the properties of items measured in nanometers. Such nanomaterials, sized down to the nanoscale, have very intriguing optical, electrical, magnetic, chemical, and mechanical properties. Among many aspects and more fascination are the preparation of nanomaterials and also the way they are used. Due to such properties, nanomaterials have a variety of applications, from catalysis to medicine, and a long and important use can be foreseen. Nanotechnology covers a wide range of areas and has great financial importance, especially noting that it has already produced a substantial number of products. So, the future use of nanotechnology covers a variety of activities, including production, research, development, and application to manifold areas in science and industry.

2.1 Size effects and quantum confinement

Due to the high surface area to volume ratio and the related quantum size effects in small particles as well as small grains, nanosized crystalline materials, or nanocrystals, have unique and important properties, which are interesting and useful concerning their potential electronic, optical, magnetic, mechanical, chemical, and catalytic applications. Quantum size effects, the term used to describe the properties of materials with very small size dimensions in which classical ideas give place to quantum-mechanical descriptions, occur when the feature size of a structure becomes comparable to the wavelength of the electron or when the characteristic dimension of a solid is smaller than the de Broglie wavelength of the electrons. Quantum size effects and the resulting discrete energy levels are of importance in determining the average electron density, density of states, and other electronic behavior of particles [7]. From the formulas for the quantum dimensions of the particles, it can be estimated that the electronic properties and chemical reactivities are size-dependent in nanoscale materials.

Size effects play an important role in a wide range of basic research topics, such as phase transitions and critical phenomena, the operation of quantum zero-point-motion transducers, and interferometers. In the field of material research, size effects have important implications both for the electronic and optical properties of semiconducting clusters or quantum dots and for the thermal and mechanical properties of crystalline solids. For example, while the electrical conductivities of bulk silicon and germanium are quite different, the electrical conductivities of silicon nanowires and germanium nanowires exhibit a substantial super-exponential size dependence and converge as the nanowire diameter diminishes, consistent with classical electric-charge quantization on the nanowire radius. Quantum size effects observed in zero-dimensional systems such as quantum dots or one-dimensional systems such as quantum wires, or two-dimensional systems such as quantum well, point to the manifestation of properties completely different from bulk materials, which make these low-dimensional electronic systems promising candidates for novel electronic and optoelectronic devices in future nanoelectronics and related nanotechnology.

2.2 Types of nanomaterials

Inorganic materials are those that are not organic, such as metals, oxides, carbides, and some semiconductors. As a general rule, these materials are much more stable and durable than most organic materials, and this is clearly an advantage. There are several different types of nanomaterials, depending on their morphology, structure, size, or interactions. In other words, the different characteristics of a nanomaterial are responsible for the class of its nanomaterial. It can be classified by size, morphology, composition, nanostructure, organization, dimensions, composition and nanostructure, interactions, and origins [8]. We will now discuss the various types of nanomaterials considering their dimensional, morphological, compositional, and nanostructured classes.

In general, nanomaterials can be divided into three classes: zero-dimensional nanomaterials (dots), one-dimensional nanomaterials (wires, rods, and tubules), and two-dimensional nanomaterials (sheets, films). Although these are idealized descriptions of the principal classes of carbon-based nanomaterials, they represent a useful guide to the different structures that can be met in nanotechnology. In fact, materials with one dimension appreciably larger than the other two are called fibers or, if the

length is very long, threads. Similarly, materials that have two appreciably larger dimensions are called platelets or thin-film materials. These materials can be further divided into smaller classes such as biocomposites, ceramic-based, polymeric-based, and carbon-based nanomaterials.

3. Synthesis techniques for nanomaterials

Nanomaterials might be prepared using different synthesis techniques, which influence nanoparticles' properties. In this part, a review of different synthesis techniques and their operative conditions for appropriate applications was conducted. In addition, it offered an assessment of those methods: The benefits and drawbacks of several techniques were reported, providing some items to be solved by the scientific community. Chemical methods, including precipitation, sol-gel procedure, hydrothermal, and electrochemical, are simple, provide controlled-size particles, and allow for a wide range of materials. Every technique presents its particular bridging properties and applications, as illustrated in this section. The final part is dedicated to potential uses where the presence of nanoparticles shows the most benefit.

Regarding the concerning dimension of nanostructured materials, one of the critical issues in their practical applications is their synthesis. There are many methods for the preparation of metallic, alloy, and oxide nanoparticles with various physical and chemical properties that have been developed through the last several decades of intensive investigations.

3.1 Top-down vs. bottom-up approaches

The top-down approach for preparing nanoscaled materials is a modification of already existing materials or treatment of bulky parent material to produce smaller-sized specimens [9]. By comparing a top-down example to a similar bottom-up example, only one missed layer of TO is duplicated. Also, unlike the typical cinematic discharge in angular momentum transfer through a row, a bottom-up approach would have each of the atoms essentially coming into collision with the correct axial positions. Achieving more complex missing layers is a technical possibility but has not yet been mastered in a comprehensive experimental study. Conversely, in the top-down approach, the bulk target atoms can arrive within the node at one of the nodes of the space-lattice and, in many specimen conceptualizations, are allowed to keep reducing dimensions until a (p-d) next maximum is approached.

Due to technological considerations, materials originally have to be made much larger than their ultimate nanoscale domain, using bulk-size material, whose inherent properties become lessened (collective properties). Therefore, the optimal term in which phonon and roton interactions in the electron plasma are significantly influenced by the properties of the original quasi-discrete phonon and roton modes is determined during the process of achieving convergence to the next quantum level.

3.2 Chemical vapor deposition

Chemical vapor deposition (CVD) is an important technique to deposit thin films and coatings on a substrate from a vapor phase. The vapor phase precursors react with one another at or near the surface of the substrate to create the desired deposit. There are two variants of CVD: low-pressure chemical vapor deposition (LP-CVD)

and atmospheric pressure chemical vapor deposition (AP-CVD). A typical CVD system has a reaction chamber, a means to thermally or photochemically activate the reactants, and product recovery mechanisms. Thermal activation of the reactants is achieved by heating the substrates in conventional thermal CVD or by using microwaves or other sources of radiation. Photochemical activation utilizes the photons from a laser, an ultraviolet (UV) lamp, or other electromagnetic sources. The source and the temperature profile in the chamber depend on the type of CVD (LP-CVD or AP-CVD) and the nature of the desired deposit. The temperature profile in a CVD chamber is typically uniform or nonuniform.

CVD has been the most widely used technique for the synthesis of carbon nanotubes (CNTs) [10], boron nitride nanotubes (BNNTs), graphene, and several metal oxides such as SnO_2 and ZnO for different applications, particularly sensors. Nanocomposite (including nanocrystalline) thin films made up of organic and inorganic materials are also deposited using this technique. The thickness of the deposit could be a few nm to several μm . Contrary to CNTs and boron nitride nanotubes (BNNTs) syntheses, which require catalysts to bind the metal/metal oxide layer with the growing tube, nanostructured metal oxides can be easily deposited on a variety of substrates by the CVD process in the absence of the catalyst using metal organometallic precursors [11]. Commercial-grade vapor deposition systems are available for the synthesis of CNTs, BNNTs, nanostructured metal oxides, graphene, and nanocomposite and nanocrystalline films.

3.3 Sol-gel synthesis

Sol-gel synthesis is the preferred method for producing thin oxide films. Both sol-gel and dip-coating methods are cost-effective compared to physical vapor deposition techniques. A variety of amorphous, microcrystalline, and nanocrystalline metal-oxide films have been prepared through sol-gel techniques [12]. Uniform coatings can be deposited on a variety of substrates, regardless of their shapes or complexities. Essentially, the sol-gel process involves the controlled hydrolysis and condensation of metal precursors *via* solvation, which, in turn, results in a metalloid-oxide network [13]. The sol-gel synthesis is completed when the amount of hydroxyl groups is minimized, resulting in an lanthanum zirconate oxide (LZO) printable paste or stable sol. The sol-gel synthesis is somewhat unique as it assists in the formation of mixed oxide phases, is easy and cost-effective, can form thin films in the range of 10–400 nm, and offers a large number of options in terms of applications. The sol-gel process can consequently crystallize to obtain stable gel at 70°C, and the grinding of such nanoparticles is high-energy ball milled to obtain a homogeneous powder of LZO [14].

The final hydrolysis and polycondensations are defined as follows for a simplified, unimolecular acetylacetone precursor $\text{MX}_3.60(\text{OR})_5$: $\text{M-X-R} + \text{H}_2\text{O} \rightleftharpoons \text{M-X}\cdot + \text{ROH}$, followed by $\text{M-X}\cdot + \text{H}_2\text{O} \rightarrow \text{M-X}(\text{OH}) + \text{hydrogen X}_2\text{E}$ 7 and $\text{LXO} + \text{H}_2\text{O} \rightarrow \text{Oil} + \text{L-MX}(\text{O})\text{H} + \text{H}^+$ (7) for $\text{M} = \text{Li}$ and titanium ethoxide where X-OH is a hydrolyzed/functionalized acetylacetone precursor on the metal-derived portion, O is the oxygen atom from the hydroxy group, and LXO represents a hydrolyzed Lewis acidic titanium alkoxide such as a titanium ethoxide precursor. The presence of the acetylacetone chemical structure, aluminum alkoxide $\text{Al}(\text{OR})_3$, where R is a hydrophilic group) precursors, and the evolved water out of the solution during resonance are also solvent dependent. The formation of an amorphous, sol-gel-derived LZO involves two mechanisms—hydrolysis and condensation. Sol-gel-derived LZO films can offer a variety of attributes such as uniform structural properties over a relatively large area

of deposition, optimized growth orientation of crystallography, superior electrical properties, good adhesion strength to substrates, and relatively low decomposition temperatures.

4. Characterization methods for nanomaterials

Characterization is of utmost importance when dealing with nanomaterials. The size and structural features play a vital role in the resulting chemical, physical, and mechanical properties of the nanomaterial. As pointed out earlier, one of the main distinctions between the bulk materials and the ones with nanoscale is the large surface-to-volume ratio found in the nanomaterial. An example of this can be found in the melting point depression feature typically found in nanoscale metals [15]. The number of atoms on the surface increases with the decreasing size of the metal particle. This, in turn, lowers the melting point of the nanoscale metal.

Several characterization techniques are employed in the examination of the nanomaterials and identification of its structural features. The most commonly used techniques include both scanning and transmission electron microscopies, atomic force microscopy, high-resolution transmission electron microscopy, X-ray fine structure, X-ray photoelectron spectroscopy, electron energy loss spectroscopy, and transmission electron microscope scalar diffraction. With so far gained knowledge in nanomaterials, with the help of a number of advances in nanoelectronics, improvement in nanosystems handling, and applications draws to be versatile in biomedical, biotechnological, chemical, optical, and mechanical applications just to name a few. Navigating through the nanomaterial property terrain, the approach can have a bottom-up or a top-down approach. These techniques include mechanical or fractional approaches, chemical approaches mainly through liquid-phase and gas-phase synthesis, and physical approaches based on different types of vapor-phase techniques. Novel material designs employing biomimetic carbon fibers, carbon nanotubes or DNAs, dendrimers, and layer-by-layer thin film deposition with the help of hydrogen bonding just to name a few are making revolutionary advancements, providing us with unlimited functionalities [16].

4.1 Scanning electron microscopy

The goal of the course is to provide an overview of current and future developments in nanomaterials and their potential impact on emerging technologies and science [17]. The particular focus is on the properties and applications of nanomaterials and nanosystems with a special emphasis on special and exciting properties of matter at the nanoscale. The overall goal is to provide students with an understanding of present and future challenges and opportunities on nano-related topics with special relevance to scientific and industrial interests. Specifically, we explain the preparation of nanomaterials and their modifications. Their special properties are explained and summarized with reference to the possibilities and the goals of their application. The theoretical background is explained, and a detailed analysis is provided of the new phenomena and applications related to nanomaterials and nanotechnologies.

The scanning electron microscope (SEM) is an essential tool in the field of nanoscience and nanotechnology [18]. We begin our discussion of SEM with an introduction to electron beam analysis followed by a discussion of resulting signals. The operation and components of the SEM are then discussed in detail, as well as the

applications of SEM in the fields of nanomaterials and nanotechnology. We focus on two signal types that are typically detected: secondary electrons (SEs) and backscattered electrons (BSEs). The generation processes of these signals and their relationship to the properties of the sample are explained. The SEM apparatus consists of two essential parts: an electron optical column and a computer-aided imaging system to create an image from an incident electron beam impinging on the sample [19]. The capabilities of SEM are summarized with a focus on measurements of surface structures of topographical small features of sample surfaces.

4.2 Transmission electron microscopy

Transmission electron microscopy (TEM) is a high-resolution imaging technique for the nanoscale structural analysis of both materials and biological specimens [20]. TEM provides some unique features, such as high spatial resolution, imaging, and diffraction attributed to the short de-Broglie wavelength, and generally good contrast and depth of focus, which allow for the observation of defects, inclusions, and structures at both the micro- and nanometer scales, either in two or three dimensions. However, the principle of TEM cannot be explained in a few words. Here, the principle of TEM and typical detection systems of TEM are overviewed. Accelerated electrons are a powerful alternative to photons for the observation of structure in samples of a wide variety of materials. The wavelength of the diffraction of a beam of electrons accelerated in a vacuum within any modern electron microscope is generally less than 2 pm, compared with a wavelength of diffraction for an electron of 0.254 of the numerical value of that for photons employed in contemporary visible-light microscopes.

4.3 X-ray diffraction

An important aspect of the study of crystallinity is the use of X-rays. We have discussed the interaction of X-rays generally with materials. The utility of X-rays is that they cause diffraction when they impinge on a crystalline material [21]. This diffraction can be used to probe the inner structure of the material, particularly how the atoms are arranged within the crystal. This can be quite useful for identifying the nature of the constituents of the crystalline material and knowing their arrangement [22]. X-ray diffraction studies have also been performed on nanosized metal particles embedded in thin SiO₂ materials, such particles being created by ion implantation and subsequent high-temperature annealing. The particles were found to exist in face-centered cubic (FCC) geometry and the average particle size decreases with decreasing metal concentration, as was expected. But the XRD signals identified the average size of particles as the average crystallite size in the SiO₂ so the results deduced from the actual nanocluster array dimensions are not reflected in this comparing technique [23].

5. Properties of nanomaterials

In general, properties of materials in the nanometer regime are quite different from those found in bulk structure due to the quantum mechanical effects. In the study of nanomaterials, the bandgap, energy gap, and wave function of electrons should be employed. The properties can depend not only on the size or dimension

of nanoparticles but also on the degree to which they involve interactions between nanocrystals or force at the grain-clear surfaces [24]. Extensive studies on the features in various properties of nanoparticles, quantum dot lasers, and related optoelectronic devices are presented. In addition, there are a few well-known methods that are utilized for elucidating the size-dependent properties of nanocrystals that are extensively reviewed.

Many fundamental physical properties of nanometer-scale materials are qualitatively or quantitatively different from those of their conventional bulk-sized counterparts [25]. Over the past two decades, significant progress has been made toward understanding how the properties of a material evolve as its characteristic length scale becomes commensurate with relevant fundamental physical constants, such as the Fermi wavelength, the exciton Bohr radius, and the quantized energy levels of conduction and valence electrons in a small-box potential [26].

5.1 Mechanical properties

The mechanical properties of nanomaterials are not simply scaled-down versions of the properties of their bulk counterparts. Reduction in at least one, and often more, dimensions of the material leads to significant new material properties. Moreover, the small size of nanomaterials means their large surface area can control their properties, thus setting an entirely new paradigm for the mechanical properties. Assuming that the bulk material is a brittle, a power-law decrease showing in the stiffness of the nanosized long cylindrical structures with the fall in the radius of the cylinders. Also, assuming the bulk material to be brittle, Gurtin discusses the dependence of the effective elastic property of the material on the elasticity of the structural materials [27].

To develop a fuller understanding of the mechanical properties, one would start with the various types of nanostructures, like nanowires, nanotubes, and quantum dots [28]. Specifically, Gao et al. [29] have discussed the synergistic relationships of the possible coupling between length, radius, and the thickness of nanowires. Bergin et al. [30] have discussed the dependence of mechanical properties on the aspect ratio, that is, width relative to the length of the nanowire. Particularly, the mechanical stability of nanosized helices has been especially popular, largely based on the results of Greenwald and co-workers and Mohr and co-workers. In fact, we have a report of a dampening mechanism operative in a nanospring employed as a nanoscale AFM cantilever. Some modeling and experimental work has also shown that the mechanical properties of materials can change under the application of an electric field [31]. In the context of electronics, both classical metals and superconductors bordered by an insulator can provide the necessary quantum coherence. Moreover, a quantum version of the Hall Effect appears when the entire sample is in the superconducting state.

5.2 Optical properties

Nanostructures have unique optical properties. The photonic band structures are strongly affected by the reduced dimensions and can be designed at the micro- and sub-micro-scale [32]. The band structures of the low-dimensional photonic crystals, such as one-dimensional superlattices and two-dimensional photonic crystal slabs, are modified by the change of the superstructures in the silicon nitride multilayers. Colloidal silicon nanoparticles are not only perfectly good examples of quantum hetero-cluster ensembles but also the source of information about the phenomenon of

quantum confinement. Although silicon is not readily associated with a light-emitting device, we also describe the related optics phenomena with relatively higher quantum efficiency [33]. The model of a series-connected LED is analyzed. An electromagnetic image of silicon quantum dots observed in practice is demonstrated when embedded in a polymeric host beam.

The nanostructured metal films, consisting of periodically arranged metal nanodots, are capable of localizing the incident electromagnetic wave, promising for energy or information storage associated with enhanced Raman signals. The extinction can be modified, focused, and then resonant by changing the spacing distance between nanodots on the substrate [34]. Furthermore, the resonant positions are greatly influenced by the shape, size, and height of the nanodots. However, the strong near-field enhancement is restricted around each individual metal particle, which means that the sub-wavelength resolution is limited by far-field diffraction [35]. The usual near-field probing technique requires the tunable aspect ratio to image the nanoparticles; only the highest aspect ratio tips with high tensile strength have yet to be produced. The optical field enhancement at bound two-plasmon excitation as well as at field-induced surface plasmon oscillation is investigated. The considerable field enhancement at the wave-potential surface plasmon resonance predicts the performance of a sub-micron-sized multipurpose sensor in various display applications [36], such as a photodetector and nano-antenna array.

5.3 Electrical properties

In nanowires, because of their smaller cross-sectional area compared to bulk, the bandgap increases from thermal strain and quantum confinement. This makes it possible to change the material composition, crystal structure, or geometric size to tune the bandgap within the visible and much of the infrared region of the spectrum. Electrical transport measurements are also influenced by thermal strain and quantum confinement [37]. The smaller cross-sectional area compared to the bulk leads to an increase in the resistivity of the nanowires. Additionally, the nanowire resistivity vs. temperature dependence frequently deviates from that of bulk. In many cases, the increase in nanowire resistivity with decreasing temperature occurs at an increased rate compared to bulk [38]. This increase in resistivity with decreasing temperature is described mathematically by diffusive insulating behavior. These increases in resistivity and their temperature dependence are governed by the nanowire surface. The nanowire core has internal metallic conductivity, and tunable thermoelectric properties teach that electronics can dominate thermal transport and surface scattering in nanowires. Measurements of nanowire thermal transport have also shown that surfaces can be used to optimize the thermal conductivity and decrease the Lorenz number of nanowires to achieve a figure of merit greater than the bulk material [39]. Such enhancements are quite promising for thermoelectric applications in the cooler regions of electronics, radioisotopes, and waste heat recovery.

6. Nanoelectronics: Basics and components

The “Giant Leap” from passive metallization to active nanoelectronics brought with it requirements associated with extending the limits of semiconductor scaling. The drive toward smaller and faster devices with additional functionality would not be possible without the contribution of numerous microcomponents on one chip

location. Nanoelectronic components can have a dimension of approximately 100 nm or less, offering a substantial cost advantage due to a drastic reduction in the size of an integrated semiconductor. Unique mechanical, electrical, magnetic, or optical phenomena become affordable once the domain size reaches the nanometer level [40]. Semiconductor quantum dots, quantum wires, and quantum rings form a new class of materials for future versatile semiconductor device fabrication that could exhibit novel effects with advanced information processing capabilities [41].

Future devices such as quantum computers and optical microdevices with information transfer rates on the Terahertz scale will require dimensions on the order of 100 nanometers, preserving the advantages of many-qubit and long-lived energy level confinements. The International Technology Road Map for Semiconductors (ITRSTS) establishes the time plan projected to fabricate commercial integrated circuits with components at 90 nm before 2005 and 50 nm for the next decade. At flat-panel conferences, the proposed course of action for displays in 2020 will use devices with similar built-in dimensions. Once the storytelling abilities improve, these displays may reach the TV format. Nanotechnology proficiency is not only the key to advancing in semiconductor technology but is also an essential tool allowing a multitude of new applications for passive or active nanoelectronics, provided the material for nanoscale construction closely follows the forced dimensions.

6.1 Quantum dots

The pictures received from SEM/TEM seem to confirm this model. First, we observe the ample presence of the size quantization effects in the smaller nanoparticles due to the higher number of states below the energy gap. At the present time, it is possible to synthesize nanoparticles with controlled sizes always around 10% and also characterize the size relying on spectroscopic measurements (photoabsorption, photoluminescence, and some types of X-ray absorption measurements). In fact, the spectroscopic properties of these materials are strikingly different from the ones of the microcrystal. For example, the ability to synthesize quantum dots with stabilized luminescence properties has guided researchers toward developing a new generation of optoelectronic devices, in which photons are confined along the Z direction [42]. The N-dots are being developed with the property to be activated with the N₂ laser light. In the implantable devices, it is expected that patients with the implant will be able to work on desktop computers using the instructions provided by the light of the laser torch.

In this section, we will show some results prepared with nanocrystallites of Pb-chalcogenides. After this, it was used to explain the energy of phonons in anharmonic crystals and also employed to calculate the Franck-Condon equation. Later, it was used to explain the electronic transitions that are limiting Voigt and Verneev patterns of Cu-K α and La α emissions. More recently, it was used to predict the size dependencies of the option energy of semiconductors. In fact, all Schrödinger's equation solutions to rectangular potential well can be calculated using Box solutions and to construct valence and conduction bands wave functions and energies and adequate prefactors (options) [43]. Since then, we have been able to simulate some experimental results on micro- and nanoparticles of semiconductor materials and use them to confirm quantum well (QW), quantum ring (QR), waveguide harmonic generation (WHG), and conduction band (CB) and electron beam (EB) differences in the diffraction patterns. The systems that present the electronic confinement for the higher level of the valence band can present the CB cutoff (finite masses); that is,

they present the single defects limiting Osipov emissions and do not emit intermediate emissions, which is in total agreement with some V-excited electron energy loss spectroscopy (EELS) studies [44].

6.2 Carbon nanotubes

Carbon nanotubes, discovered by Iijima and colleagues in 1991 [45], have unique electronic properties due to their one-dimensional structure, high chemical stability, and high mechanical strength. The total energy of a nanotube is independent of the width of the graphene sheet in the same manner, and the curvature reflecting the edge deformation around the tube axis modifies the band structure of a carrier [46]. As a result, armchair- and zigzag-type carbon nanotubes have a metallic character, and armchair-type carbon nanotubes are more conductive than metal in the nanoscale. In fact, primitive nanotube fibers formed by rolling ink-coated nanotube sheets are conducting about 100 times better than copper [47].

On the other hand, zigzag nanotubes are semiconductive and are applied to field effect transistors. Metallic, as well as semiconductive, nanotubes possess ambiguity in their band structure coming from two degenerated subbands, or one in the case of zigzag-type tubes [48]. A small bias can induce a change in the band ordering, shifting charge transport from one-terminal to two-terminal conduction. Consequently, the cubic power of the current versus the voltage dependence holds in the finite temperature numerical simulation. The carbon nanotube junction, as well as the carbon nanotube itself, is also a subject of intensive experimental and theoretical studies. The strong bond existing between the two tubes is not essential to the current transport across the junction, and voltage vs. current dependence at zero or 180-degree rotation holds the cubic or quadratic character. Meanwhile, carbon caps or chemical treatment significantly modify the capping.

6.3 Graphene

The astonishing electronic properties of graphene, a single atomic sheet of carbon atoms arranged in the form of a honeycomb lattice, have attracted enormous interest [49]. Although the theoretical prediction of the electronic states of a minimal conducting band and high electron mobilities had been ascribed to graphene more than two decades ago, it took until 2004 for experimental groups to be able to synthesize monolayer graphene on a substrate, a sixfold increase in the electron field mobility with respect to the best theoretical and experimental results for the bulk form of graphite. A year later, it was demonstrated that other carbon structures, in the form of multiwall carbon nanotubes, are in fact collapsed carbon nanotubes and not carbon nanoparticles. Lastly, it was demonstrated that rolled-up sheets of graphene would indeed bind a C60 molecule at their open end [50]. These steps paved the way for the synthesis and the detailed studies of the electronic properties of other carbon structures with the aid of electron diffraction, high-resolution transmission electron microscopy, and C- and K-edge X-ray absorption measurements.

Unlike the individual encaged C60, their physical properties are described by considerably more complex, solid-state electronic states. In contrast to the aforementioned zero-dimensional, semiconducting properties of C60, the conducting properties of a nonlocally interacting two-dimensional graphene were predicted several decades ago [51]. However, to carry out definitive quasiparticle dispersion

experiments, one requires large, dimensionally stable samples, which were not to be obtained at that time. Nevertheless, some additional guidance toward the interpretation of the properties was gained from the study of fullerenes, multiwall carbon nanotubes, and twined carbon nanotube peapods [52].

6.4 Silicon carbide (SiC)

Silicon carbide (SiC)-based nanomaterials have garnered significant attention due to their exceptional mechanical, thermal, and electrical properties, making them ideal candidates for a variety of nanoelectronic applications. SiC nanostructures, such as nanowires, nanoparticles, and thin films, exhibit enhanced performance characteristics compared to their bulk counterparts, including improved charge carrier mobility and greater thermal stability. These properties facilitate the development of high-performance devices, such as transistors, sensors, and photonic components, capable of operating under extreme conditions. Furthermore, SiC's inherent wide bandgap enables its use in high-frequency and high-power applications, where conventional materials may fail. Recent advancements in synthesis methods, such as chemical vapor deposition (CVD) and sol-gel processes, have further enabled the tailored fabrication of SiC nanomaterials, opening up new avenues for innovation in the field of nanoelectronics. As research continues to explore the unique attributes and potential applications of SiC-based nanomaterials, their integration into next-generation electronic devices is poised to drive significant advancements in technology.

7. Fabrication techniques for nanoelectronics

The extraordinary electronic properties of nanomaterials make them candidates for use in disposable electronics and interfacing with biological systems. Toward the goal of disposable electronics, we have built wires made of 1 or 2 atomic layers of graphene that are processable and robust. These properties will be valuable in acid and temperature sensors being developed as part of the Extreme Environment Electronics Center [53]. As the size and density of field-effect transistors in integrated circuits decrease, leakage currents due to short channel effects and large power densities due to poor gate electrostatic control are increased. In low-power digital and analog circuit design, the subthreshold operation region is used to minimize the power dissipation to the minimum value that the circuit can provide.

However, these techniques have disadvantages such as low transconductance at the subthreshold region of operation, increased susceptibility to process variations, limited bandwidth, variation of transistor performance at different temperature environments, and output voltage swing trade-offs. The development of new transistor structures or emerging devices that could overcome these problems is imperative to maintain the performance progress in the semiconductor industry [54]. The advent of carbon nanotubes with their excellent mechanical, electrical, and thermal properties has opened a new chapter in transistor design. Circuits implemented with these devices can operate at high speeds and low power, and exhibit high drive capabilities.

7.1 Lithography

Lithography is a patterning process in which an energy source is used to modify specific regions on the surface of a substrate so that the modified regions can

then be selectively removed by a solvent or etching [55]. This selective removal process results in a pattern that can be subsequently transferred to the underlying substrate. Photolithography is a widely used patterning technique in the microelectronics industry. In this process, patterns on masks are transferred onto the surface of photosensitive organic materials by irradiation with ultraviolet light [56]. These organic materials conform to the patterns on the masks, and, after development, the transferred patterns on the surface of the substrates are then etched to form the microstructures. Recently, electron beam lithography, photolithography based on ultraviolet light that has a pattern resolution of several hundred nanometers, has been used to create extremely small features with nanometer lengths on photosensitive organic materials [57]. This technique is commonly employed to write patterns made by evaporated resists with a thickness of about 0.2 μm . The development of this technology requires expensive and large-scale equipment. It suffers from low writing speeds and is not practical for large-scale commercial production. Magnetic lithography and imprint lithography are used to produce nanometer-scale patterns on substrates [58]. Chen et al. [59] have employed nanosphere lithography to fabricate nanoscale silica droplet gratings with a period of 800 nm and a height of 300 nm. The authors used four-beam interference to create an array of micrometer-sized polystyrene beads and produce nanoscale patterns. The sizes of these particles and the holes on the substrates, corresponding to where the particles had previously been, were controlled by adjusting the sizes of the photoresist openings. The authors further used these arrays as templates to prepare highly ordered three-dimensional macroporous structures, nanoporous carbon, and nanostructured hollow members of titania and gold.

7.2 Self-assembly techniques

The auto-organization of molecules into higher organized structures is a visually captivating phenomenon and has long been the subject of scientific study. Over the years, a number of techniques for promoting self-assembly have emerged, permitting a degree of control over the final assembled structure. Self-assembly is the ultimate bottom-up approach. It is relatively simple to achieve and leads to a highly ordered structure with a minimum of external energy being used. It is not difficult to imagine then why self-assembly has become a popular technique for constructing new nanomaterials. Self-assembly leads to highly ordered structures, often in only one or two dimensions. This regularity is essential for constructing nanoelectronic devices. The ease and low cost of achieving self-assembled structures is an additional benefit.

Several techniques exist for self-assembling the nanoscale materials. In the case of nanowires, they have been demonstrated by growing them on various substrates that contain a patterned nucleating material [60]. This pattern defining the location of the nanowires can be created by optical lithography or other methods. Nanotubes have been shown to self-assemble in a silicon matrix, which was patterned using electron beam lithography. The self-assembly process then relies on the growth of the nanoscale material being promoted at the patterned locations. Other self-assembly techniques do not rely on promoting growth at specific locations. These include the evaporation of nanocrystals onto a substrate and subsequently annealing to drive them into ordered arrays, or more simply, allowing nanocrystals to settle onto a soap film, forming a nanocrystal monolayer during the film's lifetime. The soap film then serves to stabilize the nanocrystal array. The most powerful technique for self-assembling nanocrystals involves the use of a template. Two types of templates

are commonly employed. The first is a thin film that has been prepatterned, usually by lithographic methods, to form holes or trenches. Nanocrystals are then deposited onto the patterned template and driven into the patterned features by an appropriate postdeposition treatment. This is often an attractive method when the nanocrystals are to be incorporated into a device structure and require electrical connections. The second type of template is the templating self-assembled monolayer, which is based on the chemistry of the nanocrystal surface. This template allows for ordering in packing fairly arbitrary nanocrystal arrays but possesses greater flexibility and control compared to hard, lithographically patterned templates.

8. Applications of nanomaterials in electronics

Nanotechnology promises significant developments in a variety of industries, including medicine, electronics, and materials science. The major driving force of nanoelectronics is the advancement of devices including transistors, sensors, optical diodes, and other devices. The development of electronic technologies for computing and communications, for instance, is mainly driven by the improvement of existing devices and the development of new devices [61]. This, in turn, requires the use of new materials, an understanding of the chemistry of complex organic, inorganic, and metal materials, and solid-state properties.

With the development of technologies for producing smaller elements, the range of material problems is increasing fast. The concentration of these problems in the micro- and nanodimensions explains why researchers in the field are turning increasingly to methods for atomic-molecule growth of materials. Quantum dots and semiconductor quantum wells represent models for just a few so-called submicronic objects. In fact, practical use of such materials in technology will require new successful methods for fast, cheap, and large area growth. This is why the growth of thin films and multilayer films of such objects is an important aspect of the search for such methods. Such structures exhibit a set of the fundamental solid-state characteristics, namely (1) their size is approximately equal to the de Broglie wavelength in the center of the Brillouin zone, (2) bands whose energy width is less than or equal to the thermal energy, and (3) the enhancement of optical transitions between quantized levels.

8.1 Flexible electronics

The study of nanomaterials and devices smaller than 0.5 micrometers is an active and increasingly specialized field within nanoscience and nanotechnology [62]. This section aims to provide a snapshot of important research contributions and developments in the domain of nanoelectronics, especially materials synthesis, device fabrication, and applications that are part of the field of nanoelectronics. In the past years, the number of different nanomaterials and devices used in electronics has expanded significantly, and the respective applications have broadened to cover many areas. It can be stated that the continuous or even exponential speed of development in the area is only applicable to very specific subfields that largely correspond to Moore's "Law."

The "top-down" approach to the development of electronics uses existing bulk and planar materials and microfabrication techniques to make new devices in the nanometer range, while the "bottom-up" approach uses self-assembly techniques to grow the very small devices directly from even smaller atoms and molecules. The present

contribution is focused on ‘bottom-up’ synthesis methods, bottom-up nanodevices, and electronic materials and applications. The section is organized in the following manner. First, the goals of modern electronic devices and future devices are stated. Then, photonic and electrical properties of nanomaterials, including semiconducting, metallic, and insulating semiconductors, are described, followed by top-down and finally bottom-up electronic devices.

8.2 Sensors and detectors

Nanomaterials offer a large degree of diversity in terms of chemical composition, structure, and concomitant properties. This diversity, in turn, gives rise to a wealth of applications of concern to nanotechnology, such as innovative materials, intracellular probes, contrast agents for biological imaging, drug delivery agents, therapeutic agents, diagnostic tools for life sciences, and increasing the selectivity and sensitivity of miniaturized sensors for environmental surveillance, optical data storage, nanoparticle-tagged DNA processing, and nano-catalysis. In this chapter, we present chemical syntheses and some characteristic properties of the following nanomaterials commonly used in nanoelectronic devices and sensors: nanowires, nanotubes, nanoparticles, cluster-assembled films, and nanocrystals. For these materials, we describe future challenges by focusing on current concerns of nanotechnology.

Owing to their unique physical properties, preferably large specific surface areas, high surface energy, clean and new interfaces, and large interaction areas, highly responsive chemical and physical properties, and high electromagnetic strengths, sensors and detectors fabricated with nanomaterials are promising applications in the diversiform environmental species and undoubtedly attract numerous preliminary and exploratory studies in the world. In these investigations, progress has been made substantially in three aspects: the new type sensors and detectors based on the new properties of nanomaterials, the development of the functional nanomaterials and the integrated systems, and techniques for fabricating these sensors and detectors. Specifically, the distinctive traditional material properties converted from the unique physical properties of nanomaterials, the large effect caused by the steps of nanometer scale in the substrate environment, the wide areas for making the monitored physical and chemical processes being influenced by the surface or interface states of nanomaterials, and the potential space providing the wide dynamic range and exquisite selectivity of these nanomaterials used for chemical, physical, and biological species are usually referred to in these stunning studies. Our research is some of these typical cases that have happened in these three main directions. In this chapter, we will provide the powerful evidence to yoke the future clinic for these pioneering studies.

9. Nanomaterials in energy applications

Nanomaterials have been the heart of various scientific studies in the past few decades. The properties of noble metal nanoparticles have long been utilized in various major applications. This is a contribution to present generation nanotechnology. As we stand at a new frontier of controlled and customized material property engineering, there are prolific possibilities for these tiny materials in a wide variety of applications from catalysts to life sciences. This introductory chapter covers the synthesis, properties, and applications of various nanomaterials and gives a glimpse of what the following chapters entail.

Over the past few decades, nanomaterials have been the cornerstone for the evolution of various classes of commercial devices and industrial products. Nanomaterials, such as quantum dots, nanowires, carbon nanotubes, graphene, nanoplates, nanospheres, and nanorods, have been the central research focus for extensive cutting-edge materials research around the globe. These zero-, one-, and two-dimensional nanomaterials have unique size-dependent properties due to their small dimensions and quantum confinement effects, and have been utilized in a variety of unique and innovative applications. In general, nanotechnology illustrates the designing, creation, manipulations, and depositories of objects or materials only at the atomic, molecular, or macromolecular scales, wherein a new structure with fundamentally new properties and functionality can be exploited [63]. In other words, the properties and applications of nanomaterials are largely determined by their dimensions, size, morphology, and microscopic structures.

9.1 Solar cells

The use of antimonide-based nanomaterials in solar cells. Nanomaterials also promise new and better-performing light-harvesting technologies for solar energy conversion. The specific energy of the light absorbed in a solar cell is closely related to the bandgap of the absorbing material. Efficiency increases that can be gained in a given material by simply extending its energy absorption into the infrared portion of the solar radiation and complementing it with an efficiently solar up-converting component are far superior to other efficiency-increase options. However, this can only practically be accomplished in property-modifiable nanomaterials given the broad range of the solar emission spectrum. GaSb/ZnS colloidal quantum dots are synthesized and properties verified using optical absorption and photoluminescence methods. The proven monodisperse lead-salt pre-synthetic routes to these high-quality quantum dots translate into a high-resolution sample of quantum dots.

This large tuning range allows coverage of the infrared spectrum through liquid-state absorption of the basic quantum dot film. These materials, with the proper filter characteristics, are candidates to efficiently solar up-convert the infrared portion of the solar spectrum without disturbing the action of an underlying photonic-colloidal quantum dot solar cell. Swinging the solar cell charge mobility through a pinning effect (likely due to a mobility difference between the hole and electron transfer) near the donor/acceptor interface has increased the open-circuit voltage of a photonic-plastic solar cell. Absorbance filter characteristics have been shown experimentally for light as well as for minority solar electrons in the infrared pinning effect. These findings have implications for the design of efficient solar upconverters and for a new class of filter-enhanced photovoltaic solar cells [64]. Reported here are the synthesis and the optical and photovoltaic properties.

9.2 Batteries and supercapacitors

Two important uses of nanomaterials that take advantage of their several unique properties are for the electrodes of batteries and supercapacitors. The use of nanoparticles can give many advantages in comparison with larger structures. On the other hand, the small quantity of active materials incorporated in a battery is not the best use for these expensive materials. Four important uses of nanoforms are: the improved kinetics of the electrochemical reactions, a decreased diffusion distance for ionic transport, a higher electrical and mechanical stability, and increased electronic

conductivity. For batteries, the electrode capacity can be increased compared to that of the microforms, while supercapacitors store energy through double-layer formation and can also be charged much faster than a battery [65].

In the literature, there is considerable interest in the template-assisted preparation of nanostructured materials with different shapes, such as nanotubes, nanorods, nanowires, and nanoribbons. Researchers used to focus mainly on their physical and chemical properties and, of course, the technological relevance of the different manufacturing processes. During the last 10 years, though, there has been a rapidly increasing attention because of their potential applications in nanoelectronics, batteries, and nanocomposites. Among the possible applications of inorganic nanotubes, researchers are considering their integration in electronic devices, where the very high surface-to-volume ratio reveals better detection and sensing properties than those expected for bulk materials. To fabricate inorganic nanotubes, several techniques are proposed, based mainly on the employment of different kinds of inorganic templates.

10. Nanomaterials in biomedical applications

Biomedical research is expanding into new frontiers at a rapid pace. Recently, nanoscience and nanotechnology have been applied to various areas of biology and medicine. There is a growing interest in using nanomaterials for a wide range of therapeutic and diagnostic applications, including biosensing, bioimaging, targeted delivery, and controlled release of drugs or other important therapeutic agents. In particular, noble metallic nanoparticles have shown promising interest for utilization in these biomedical applications. Herein, this review focuses on using the representative noble metallic nanoparticles, including gold and silver nanomaterials, in various biomedical applications.

In recent years, there has been a growing interest in using noble metallic nanoparticles in various biomedical applications. These noble metal nanoparticles have unique localized surface plasmon resonance peaks, as well as high surface areas of nanoscopic sizes suitable for molecular imaging and therapy. Many groups, including ours, have demonstrated that metallic nanoparticles can be used to enhance the effects of optical focusing, which is useful for imaging in the near-infrared region. Furthermore, they could be used as a drug carrier for photothermal therapy and gene delivery through additional surface modification. Although inorganic nanomaterials could potentially be used in many applications, such applications can yield great efficacy only when these functional nanomaterials are specifically modified with antibody reagents. In this work, we discuss the most promising approaches to coat noble metallic nanoparticles with immune antibodies, which can then be effectively used for potential biomedical applications.

10.1 Drug delivery systems

The delivery way in cancer treatment is still limited today using traditional formulations, including not only particulate carriers such as micro-, nano-, and micelles but also liposomes capable of delivering a certain dose of drugs to the tumor site [66]. It is also well documented that not only drug delivery vehicle carriers but also other anionic carriers developed from certain hydrophilic charged molecules, including heparin, dextran, chondroitin, ferulic acid, and alginate, can be used. In general,

functionalizing the nanoparticulate with these anionic charged groups formulates the standard particle, making it able to avoid being trapped by macrophages.

Clinical shrinkage has been limited when using traditional drug formulations for two main reasons: limited water solubility and biodegradation, among others. In this regard, the applicability has been limited, as some are toxic to the patients. In this context, nanoparticles are used in cancer treatment not only as vehicles for chemotherapy drugs but also as an attractive system capable of releasing relatively high local concentrations of certain therapeutic agents to the cancerous solid tumor. The development of cancer cells releases particular chemical and structural molecules that are capable of suppressing immune response, with some patients having the capacity to escape from a condition of severe immune deficiency, including cyclophosphamide and temozolomide [67]. These are the most likely triggers for patient immune recovery.

10.2 Theranostics

Theranostics is the term used to mean a single detection/therapeutic probe. These are ideally suited and important in the context of cancer, and we showed examples of using nanoparticles for this purpose. Briefly, the idea here is that magnetically attachable gold and silver shells on magnetic cores can be used for cancer therapy—the magnetic component of the nanoparticle concentrates the particles at a fixed location, and the metal can be used for heating in order to boost the radiation dose received by the tumor. After a time delay, the metal nano-shells are cooled down and, by using upconversion to the important near-infrared wavelengths, imaging of the lesion to be treated is performed. Further, at various epochs of time, imaging is also accomplished by ultrasound.

These theranostic functions were performed using only a single entity, and the spatial resolution achieved in this study of $x \approx 25 \mu\text{m}$ shows the potential of the nano-metal surface energy transfer (NSET) concept. Our imaging results are very encouraging and offer solutions for specific tasks associated with nonionizing imaging, but further understanding of the basic physics and the development of better NSET-specific agents will need to be pursued further. Furthermore, in a clinical setting, logistics will help to decide whether the route of administration of the theranostic agent will be random or whether it will be a complicated targeted delivery. We expect that advances with the coating technology in the Laboratory for Multifunctional Nanomaterials in Medicine and the difficult problem of how to keep the particles in the blood flow until they arrive at the site of pertinent disease will provide the next significant steps in this direction.

11. Environmental applications of nanomaterials

Numerous environmental applications of nanomaterials have been proposed or demonstrated. This chapter briefly overviews these applications and introduces some issues regarding the impacts or environmental consequences posed by the use of engineered nanomaterials and nanotechnologies when released into the environment. Environmental applications of nanomaterials can generally be divided into a number of categories based on their functions. The toxicity risks of carbon-containing nanoparticles and nanotubes are reviewed. The viability of using both charged and

uncharged fullerenes as effective radical scavengers in some environmentally significant transformations is studied.

The present work focuses on the interaction of C₆₀ and C₆₀-C₆₀- with the main byproduct and purification stages of the water radiolysis in the nuclear reactor facility. OH radicals were detected. A degradation mechanism of the neutron irradiation of C₆₀ fullerenes in the near field of a reactor uranium-based target is described. Novel marginal decontamination reagents can be developed on this basis since the commercial C₆₀ fullerene-based preparations are environmentally safe, chemically inert, and most cost-effective. The former C₆₀-containing products used as radical scavengers practically are not degradable in the environment, and this group of compounds demonstrates stable behavior also, according to the results discussed.

11.1 Water purification technologies

Extremely high population growth has put significant pressure on the need for pure water worldwide. In some arid regions, people in underprivileged areas have limited access to potable water. Waterborne illness is a significant health issue, with millions of people worldwide dying from contaminated water every year. In specific countries, the contamination of metals, such as As, which is a widely distributed carcinogen, is causing frequent kidney and bladder cancer occurrences. Thus, water purification is a problem needing urgent attention.

Different technologies for water purification have already been developed, such as photocatalysts, a process where they purify water by irradiating with sunlight, and such nanomaterials are capable of degrading organic compounds, removing heavy metals, and destroying microorganisms. In conventional water treatment plants, the photocatalyst introduces limitations related to its poor performance. Nanotechnology enabled improvements in the radius of photocatalyst oxides to be confined in the range of visible light. By employing a combination with sunlight and granular activated carbon, the nanocomposites enable potential water purification. Photocatalytic disinfection has brought significant advantages compared to the traditional disinfection method with chlorination, involving creating a large number of low-hazard species, such as ozone, carbon dioxide, and water.

11.2 Air filtration systems

Nanotechnology has the potential to revolutionize the air filtration landscape *via* the creation of air filtration systems based on innovative functional nanomaterials. The benefits of nanomaterial-based air filter systems include low pressure drop, low energy cost, low mass, yielding high end-of-service-life capacity, reliable chemical bonding on non-activable media, and the ability to remove a great amount of harmful substances from the air [68]. Nanotechnology innovations have now enabled the development of materials and fiber-coating techniques that can perform these functions on a cost-effective and durable basis. These materials and fiber-coating techniques facilitate structure-property manipulation to produce self-cleaning, broad spectrum, and long-life air filter and purification systems for a wide variety of applications.

From a cost point of view, implementation of nanomaterials-based air purification systems can have a dramatic effect on filter and purifier costs, freeing funds for larger and more frequent filter changing and hence being more beneficial in terms of performance. In industrial applications, the ability to catch more pollutants at higher

flow rates through smaller filters would allow process designs to be more compact and energy-efficient, as well as less polluting. Carrying this argument further, one can then envisage many small stationary or mobile purifier units fitted into buildings or transport systems. This will reduce the peak concentrations of pollutants in cities, making possible taller, more compact buildings and thus freeing land for parks, farms, and wilderness while drastically enhancing public health and happiness.

12. Challenges and future perspectives in nanotechnology

The rapid progress and advances in nanoscience and nanotechnology have enabled the development of devices with increased complexity and decreased size. The enhanced performance has been achieved through major contributions from mankind, which has developed many techniques for the controlled generation and organization of structures with dimensions in the nanometer range. This allows for the integration of complex functionalities while taking advantage of quantum mechanics. In the case of BPN, the surface density of elements has been used to describe parallelism. By reducing the cell thickness of the nanowire, the circuit complexity is almost proportional to the square of the increasing number of transistors per unit planar area.

The electron mean free path (MFPs) of silicon at room temperature is approximately 0.4 μm . However, in one-dimensional devices, electrons can travel without being scattered over much longer distances than the MFP. In nanoscale transistors, the mean scattering time in silicon can be close to the upper limit given by the lifetime of electrons. This long mean scattering time in si-multi-gate metal-oxide-semiconductor field-effect transistor (MOSFETs) enables higher speeds because electrons have more time to propagate from the source to the drain along the channel axis, in search of an ideal low-energy path between the two terminals. The devices presented important performance features inspired by recent ideas in quantum theory, phenomena that would be disposable when the use of degenerated bands would extend the MOSFET up to the nanoscale.

12.1 Safety and ethical concerns

Huge strides in nanoscale science and engineering, involving major funding at both state and national levels, are providing the enabling technologies and tools that have significantly improved our ability to probe and manipulate matter at the atomic and molecular level. Increases in these capabilities are likely to demand enormous investments of human and economic resources, and are anticipated to bring forth unprecedented technological advancements and enrich our economy, quality of life, and global competitiveness. Great optimism permeates nanotechnology-enabled research on diverse applications as well as the commercialization of nanostructured products that significantly deviate—with respect to the composition, molecular structure, spatial and temporal distributions, or surface characteristics—from the otherwise closely related comparable bulk material with dimensions at least in the thousand angstrom range.

To guarantee continuous and steadfast progress in nanoscale science and engineering, including clear outcomes with wide societal benefits, inclusive efforts also need to be made to address and resolve concerned public's safety and ethical issues. These public concerns were succinctly outlined in the landmark British report that provided

the origin of the word “nanotechnology,” and these concerns have been echoed in the United States, which was the first country to fund a US\$1 billion National Nanotechnology Initiative. Managing the workforce and other public safety, health, regulatory, and ethical aspects of colloidal nanomaterial and nanoparticle handling with the corresponding environmentally and biochemically sustainable disposal and recycling, as well as mineral extraction and nanotechnology-based materials processing and manufacturing, are issues that have been seriously addressed at several nanointerface workshops over the past half-decade. Scientific and engineering stewardship and regulatory policies for nanotechnology-related worker health and safety were also examined in depth during the nano-transition metal chalcogenide research and development. The increased interest in coupling nanometrics with molecular and cellular biology and the emerging diagnostic and therapeutic benefits of biologically inspired and/or programmable materials have also raised public concern about genetic, future-meds, and military-technology uses.

12.2 Scaling-up production

The considerable activity directed toward the synthesis and properties of nanomaterials in recent years has focused on developing methods for synthesizing a variety of different types of carbon-based and nanometal materials. The natural evolution of those studies, which was a natural outgrowth of the desire to explore the use of these materials in a broad range of emerging nanotechnology-based applications, was the service of the demand to produce large-scale quantities of nanomaterials. Some of these applications, such as sensors, fuel cells, and catalysts, require the materials to be in the form of particles. The high specific surface areas of nanosized particles and their associated reactivity offer considerable advantages for those applications. Other applications, such as composites and electromagnetic interference (EMI) shielding materials, require the materials to be in the form of sheets or films, while other applications, such as high thermal and electrical conductivity materials, require the nanotubes to be in the form of ropes.

Pretreatment of the aluminum to remove the aluminum oxide layer is important for preparing an aluminum rod for use as a vaporization source. Microfiltration was then used to remove large, non-vaporized aluminum particles from the vapor cloud. The material properties for nanocarbon sheets and films can be controlled in a variety of different ways. For example, carbon films can have different mechanical characteristics depending on the orientation of the carbon fibers in the film, and the conductivity of the material can be changed by controlling the surface uniformity of the sheet or film. The purity of the carbon nanotubes used to prepare composite materials can significantly affect the mechanical, electrical, thermal, and gas permittivity properties of the composites. The use of loosely bound nanotube networks, prepared by selective microwave heating, can result in a dramatic decrease in the corrosive effect of the acid.

13. Conclusion

In summary, nanomaterials and nanoelectronics represent a transformative frontier in materials science and technology, offering unprecedented opportunities for innovation across various fields. The unique properties of nanomaterials, including their enhanced physical, chemical, and electronic characteristics, enable significant advancements in the design and performance of electronic devices. As research

progresses, the integration of these materials into nanoelectronic systems promises to drive the development of smaller, faster, and more efficient devices, potentially revolutionizing industries from consumer electronics to healthcare. However, realizing the full potential of nanoelectronics requires overcoming substantial challenges related to material synthesis, device fabrication, and integration. Continued interdisciplinary research and collaboration will be essential in addressing these challenges and ensuring the practical application of nanoelectronics. Ultimately, the ongoing advancements in nanotechnology and nanoelectronics will likely pave the way for a new era of technological innovation, with profound impacts on both scientific understanding and everyday life.

Author contributions

All authors were involved in conceiving and designing the study. INL and LMI conducted material preparation, data collection, and analysis. The initial draft of the manuscript was authored by LMI, and all authors provided feedback on earlier iterations of the manuscript. All authors have thoroughly examined and given their approval to the final manuscript version.

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Conflict of interest

The authors have not provided any information regarding competing interests.

Data availability

The datasets analyzed during the present study can be obtained from the corresponding author upon reasonable request.

Ethical approval

This study does not involve any human-related data, and no animals were utilized in the research.

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Silicon Carbide Thin Films: Innovations in Property, Process, and Applications

Alain E. Kaloyeros and Barry Arkles

Abstract

A systematic assessment is presented of the evolution and ongoing innovations for the silicon carbide (SiC) material system, focusing on emerging material and process technologies for thin films. To ensure an appropriate context for the drive to generate SiC thin films for a wide range of applications, we begin by tabulating the properties of the SiC material platform according to the corresponding primary structures. This is followed by recent results including both cumulative advances in established SiC applications as well significant developments in novel and potential SiC applications. Attention is directed to Si and C source chemistries, especially single source SiC precursors; novel nanoscale process intensification methodologies, and the corresponding effects on film properties and performance. Additionally, research and development efforts in which SiC materials are projected to play an enabling role in the introduction of new technological applications are discussed.

Keywords: silicon carbide, chemical vapor deposition (CVD), physical vapor deposition (PVD), semiconductor devices, high-power electronics

1. Introduction

Thin films of silicon carbide including non-stoichiometric compositions, henceforward referred to as SiC_x , remain a topic of intense academic investigation and industrial application in ever-expanding areas of traditional and novel commercial products [1–6].

The significant interest and wide-ranging allure of SiC_x is due to its many highly desirable and customizable properties. Of note is that its physical properties can be regulated by adjusting its, structure, texture, morphology, and compositions, including the incorporation of elements such as hydrogen (H), oxygen (O), and/or nitrogen (N) [7, 8]. Consequently, the desired development and deployment of technologically useful crystalline and amorphous SiC_x configurations with varying structures and chemical compositions have made the identification and optimization of SiC_x thin film processing techniques a critical and enabling research area.

Simply viewed, the key characteristics of SiC_x display intermediary values between Si and diamond, the C analog of crystalline Si. For example 3C-SiC and 4H-SiC, the two

most common forms of SiC, exhibit bandgaps of ~ 2.32 and ~ 3.24 eV, respectively, versus 1.12 eV 5.47 eV for Si and diamond, respectively [8–10]. However, this simplified view of the properties of SiC_x fails to take into consideration that it is a complex binary system with a bonding configuration that is 88% covalent and 12% ionic.

Figure 1 displays the bond lengths and energies of SiC_x , as well as those with H, O, and N, the elements that are most commonly incorporated into the matrix or surface of SiC_x . The comparatively long Si-C bond length creates various opportunities for multiple crystalline and amorphous forms, as well as polytypes and stacking errors.

SiC_x manifests over 200 polytype crystalline structures and numerous polycrystalline and amorphous phases [11]. Its hexagonal (4H-SiC) and cubic (3C-SiC) polytypes have so far been the most studied and incorporated in practical technological applications. The high electron mobility, wider bandgap, increased critical electric field, and isotropic electron mobility of 4H-SiC, and its availability in single crystalline wafer form, have made it extremely popular for usages such as high-power, high-temperature, and high-frequency devices [12]. More recently, the 3C-SiC polytype and amorphous SiC have been gathering more attention due primarily to the narrower bandgap of the former, [10, 13–15] and the variable optical bandgap as function of C content of the latter [9].

In the arena of hard protective coatings, SiC_x has long been incorporated as an encapsulating layer due to its remarkable hardness, minimal thermal expansion, superb chemical inertness, excellent oxidation resistance, and elevated thermal conductivity [15, 16]. These same properties have also made SiC_x one of the most common layers in integrated circuitry (IC), such microprocessor units (MPUs), systems-on-a-chip (SoCs), flash memory, three-dimensional (3D) device architectures, and systems-in-package (SiPs) [17]. To this end, SiC_x continues its use as diffusion barrier, protective coating, capping layer/etch stop in multilevel metal interconnect schemes [18].

The well-established reliability and endurance of SiC_x under extreme thermal and electrical conditions has also enabled incorporation of SiC_x into insulated gate bipolar transistors (IGBT) for use as inverters in electronic vehicle (EV) power systems [19, 20].

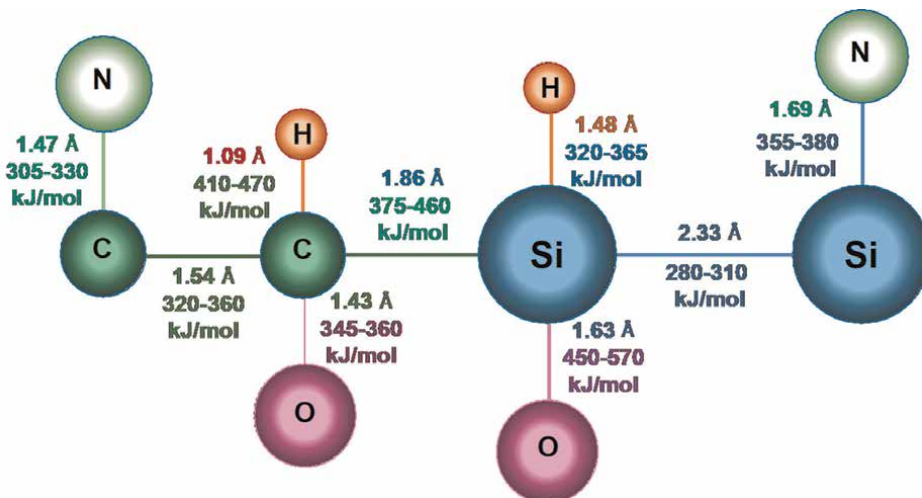


Figure 1. Illustrative molecular structure consisting of hypothetical molecular arrangements for Si and C bond lengths and energies for Si-C as well as the elements that are the most commonly incorporated in the SiC_x matrix, namely, H, O, and N.

These same properties, along with its much higher resistance to electrical breakdown than Si, [21] have made SiC_x the material of choice for high-power and high-temperature devices. The wider SiC_x bandgap compared to Si implies that the material can tolerate much stronger electric fields, namely, as high as 10 times the maximum for Si [22]. As a result, a SiC_x device is able to withstand 10 times the voltage of its Si counterpart of the same dimensions. In other words, a SiC_x device can carry the same voltage rating than a ten times thicker Si device. Additionally, thinner SiC_x devices boast higher speed, lower resistance, and higher operating temperatures than Si, leading to reduced Joule heat losses for SiC_x diodes and transistors [17, 19, 20].

Similarly, optical and optoelectronic devices, including inorganic and organic light-emitting devices (LEDs), optical waveguides, planar optical systems, and flexible electroluminescent panels employ SiC_x as permeation/encapsulation and passivation coating in because of its tunable bandgap and high electrical breakdown voltage [19, 20]. These characteristics have also made amorphous and polycrystalline SiC_x coatings quite popular in the renewable energy field, [21] particularly as efficient window protection and passivation layer in thin film solar cells [23]. SiC_x based composites, such as SiCO, are likewise emerging as effective host matrix in optoelectronic devices for white or blue light emission as function of dopant type and concentration [24].

In addition to the traditional industrial applications summarized above, SiC_x is witnessing a plethora of exciting usages in novel technological innovations in nano-scale photonics, quantum and nonlinear photonics, optically addressable spin qubits, and energy storage [17, 22, 25–27]. Unlike other commercially-available wide bandgap semiconductors, SiC_x is characterized by its biocompatibility since it is not cytotoxic and displays good resistance to biological fluids [28]. These properties make it beneficial for use in biocompatible devices for therapeutics and diagnostics, implantable sensors, drug-delivery, and neural interface devices [29–31].

Several informative reviews have been recently published pertaining to various industrial applications of the SiC_x material system, including micro-electro-mechanical-systems (MEMSs), [32, 33], power metal-semiconductor field-effect transistors (MOSFETs), [34, 35] and power electronics [36, 37]. This chapter is intended to complement the information provided in those reviews by offering a systematic and thorough presentation of recent developments and optimization of processing techniques for the fabrication and deployment of crystalline and amorphous SiC_x configurations with varying structures, chemical compositions, and properties, along with corresponding traditional and new technological applications. This chapter is also intended to update the two earlier review articles that highlighted the latest results and accomplishments in chemical vapor deposition (CVD), physical vapor deposition (PVD), and alternative processing technologies, as well as resulting film properties, performance, and usages [4, 5].

It should be noted that the reports on the SiC_x material system include crystalline (various polytypes), polycrystalline, and amorphous SiC_x configurations with varying structures and chemical compositions, including concentrations of elements such as hydrogen (H), oxygen (O), and/or nitrogen (N). Unfortunately, in many instances, the reports either neglect to include or incorrectly provide quantitative assessments of these elements, despite their measurable effects on the properties and performance of the corresponding SiC_x material system. As a result, there appear to be inconsistencies or contradictions in the findings outlined in different publications, although the SiC_x deposition methodologies, structures, and Si:C compositions are the same. The reader is therefore advised to exercise care when comparing and contrasting results from the publications cited.

This chapter is organized as follows:

- Section 2.0 and **Table 1** present fundamental properties of the SiC_x material system.
- Sections 3.0 and 4.0, as well as **Tables 2** and **3**, offer a high-level view of SiC_x CVD and PE-CVD processes and results, along with corresponding modeling and mechanistic studies. **Table 4** provides a classification of various precursor chemistries, thus facilitating comparison of critical properties and innovations in Si and C precursor chemistries. The information provided allows cross-reference to the chemistry literature outside the area of SiC thin films. Additionally, **Table 3** exhibits Si— and C— bond dissociation energies for pertinent SiC_x source chemistries.
- Section 5.0 as well as **Table 5** provide a high-level perspective on SiC_x physical vapor deposition (PVD) processing techniques, including current and emerging technological applications.
- Section 6.0 as well as **Table 6** provide a high-level perspective on SiC_x alternative (non-PVD and non-CVD) processing techniques, including current and emerging technological applications.
- Section 7.0 discusses challenges and opportunities for silicon carbide materials.
- Section 8.0 is an overall summary and commentary on SiC_x thin film technology.

2. Fundamental properties of the bulk and thin film SiC_x material system

In addition to compositional, dimensional, and environmental variables that affect measurements, the fundamental properties of SiC_x are dependent on form and phase. To assist in understanding the properties of the various SiC_x phases provided in **Table 1**, **Figures 2** and **3** visualize the basic configurations of the binary SiC system. The structural

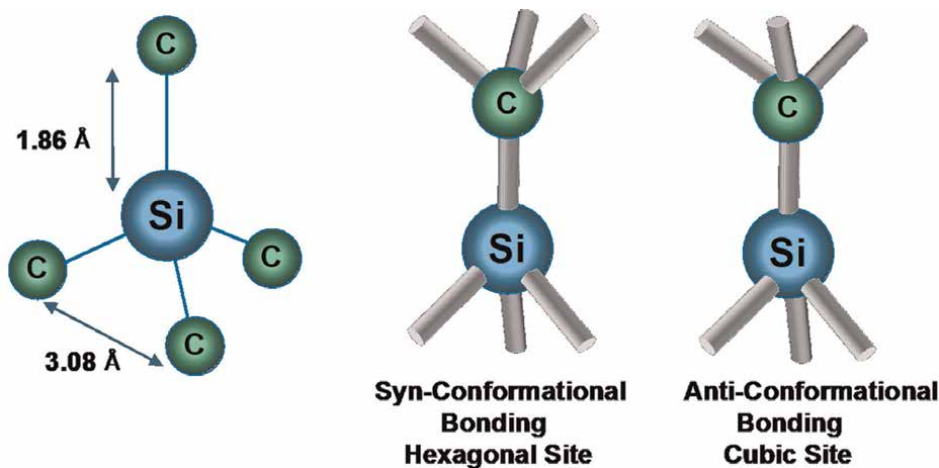


Figure 2.
Basic SiC_x tetrahedron along with sketches of the two most relevant C and Si bonding configurations.

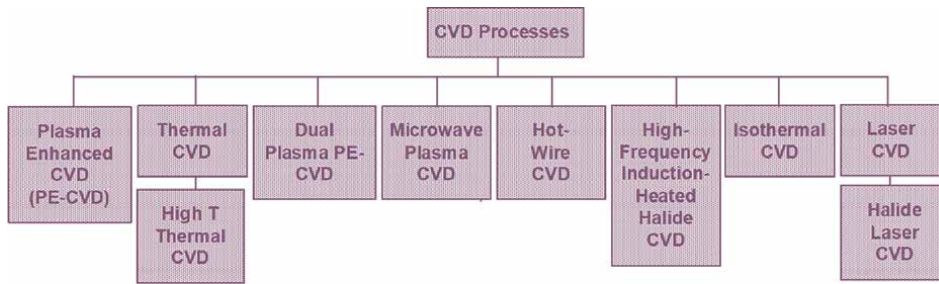


Figure 4.
Various CVD variants for generating SiC_x thin films.

hydrocarbons, and (2) single-source precursors comprising both Si and C atoms, such as carbosilanes and organohalosilanes.

As specified by the elevated bond dissociation energies of Si—Cl, C—C, and C—H as shown in **Table 3**, most of the Si and C source precursors require high substrate temperatures to decompose to yield SiC_x films. This increased thermal budget effectively limit their usage to the formation of chemically inert and/or thermally resistant devices and systems, including high-temperature and high-power devices and hard protective coatings. In any case, there are two sets of inherent challenges in the use of these precursors: (i) environmental health and safety problems because of their corrosive, pyrophoric, and exceedingly reactive nature, and (ii) technical issues attributed to the elevated thermal budgets needed to ensure efficient and complete decomposition. These problems prevent their use to deposit SiC_x on thermally, chemically, and/or electrically fragile substrates. Additional issues are related to their vapor pressure profiles and adsorption and decomposition mechanisms, which have so far prohibited the development of atomic-layer CVD (AL-CVD) processes for the growth of the nanoscale thickness SiC_x films needed for inclusion in IC and photovoltaic devices with aggressive design rules. Accordingly, there is an urgent demand for the design and fabrication of new SiC precursors that address and eliminate the problems and issues described above.

In this respect, the synthesis of precursors for CVD and PECVD SiC_x must take into consideration the specific application of interest and its related cost of ownership. There is a high level of interest in the formulation and development of stable Si— and C— precursors that can be transported controllably and dissociate thermally at low temperatures to yield device-quality SiC_x films. Latest developments in source chemistries for CVD SiC_x include single-source precursors that carry Si and C simultaneously to the substrate surface to enable the growth of SiC_x films while avoiding substitutional defects, i.e., defects consisting of Si—Si or C—C bonds.

Examples of such precursors include methyltrichlorosilane (CH_3SiCl_3) and hexamethyldisilane ($(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_3$). These single-source precursors can form SiC_x -based hard coatings. Unfortunately, they also produce a high defect density in semiconductor and photonic devices. Further, computational studies for methyltrichlorosilane, the most widely used single-source precursor for SiC, predict that low defect density is not achievable at temperatures consistent with device manufacture [140]. In contrast, precursors with structures consisting of alternating Si and C atoms have been shown to deposit films with reduced defect density. Two such single source silahydrocarbon precursors are 1,3,5-trisilacyclohexane (TSCH) and 2,4,6-trimethyl-2,4,6-trisilaheptane [94, 141]. Alternatively, for applications that require SiC:

OH films, precursors such as hexamethyldisiloxane $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ and hexamethyldisilazane $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$ were employed. In the case of hexamethyldisilazane, oxygen is substituted for nitrogen as a result of oxidative or hydrolytic chemical reactions.

Clearly, the field of single source precursors is still in its infancy and additional research is required to determine the driving adsorption and decomposition mechanisms for the formation of high-quality SiC_x films and serve as the foundation for the synthesis of new chemistries that can produce stoichiometric, H-free SiC_x thin films at temperatures below 500°C .

3.2 Summary and highlights of chemical vapor deposition (CVD) of SiC_x

Figure 4 and **Table 3** summarize a variety of CVD methodologies, the various structures of the corresponding SiC_x matrix, and related projected applications. Salient technology trends, key experimental conditions, and primary results are presented in what follows. The reader is again reminded that the summary and highlights are an update of the earlier review article by the current authors that highlighted the latest results and accomplishments in CVD processing technologies and resulting film properties, performance, and usages.

3.2.1 CVD SiC_x -based materials of various structures, compositions, and morphologies continue to be incorporated in well-known applications such as

- *Integrated Circuitry (IC):*
 - 3C- SiC_x thin films for inclusion as passivation layers, low-k dielectrics, etch-stop layers and dry-etching hardmask material in IC systems, including metal-oxide-semiconductor field effect transistors (MOSFETs) [10, 77, 90, 94].
 - Ultrathin films and nanowires (NWs) consisting of SiC_xO_y of various compositions for usage as etch-stops, passivation layers, and low dielectric constant thin films in IC systems [22].
 - a- $\text{Si}_{1-x}\text{C}_x\text{:H}$ coatings as dry etch hardmask materials and diffusion barrier/encapsulation layer [89, 90].
 - 4H-SiC epitaxial thin films for inclusion in MOSFETs and Schottky-barrier diodes (SBDs) [82].
 - Polycrystalline 3C-SiC thin films on Si for applications in IC and MEMS devices [109].
- *High-temperature, high-power electronics:*
 - 3C- SiC_x as base substrate for high-power electronic devices [10, 142].
 - 4H-SiC SiC_x , epitaxial coatings on n-type 4H-SiC substrates with 4° off-angle along the Si (0001) crystalline orientation high-power devices operating under elevated voltage and temperature conditions [8, 91].

- SiCN as protective cap for high-electron mobility AlGaIn/GaN transistors (HEMTs) for use in high-power devices operating under elevated frequency conditions [143].
- SiC thin coatings with no H inclusion for power electronics applications [94].
- SiC composites with diamond structure and adjustable thermal expansion coefficient for high-power electronics [95].
- SiC coatings of various polytypes for applications in MOSFET devices under extreme operating conditions [82, 96].
- β -SiC coatings for incorporation in high-power electronics operating under elevated temperature conditions [76].
- Epitaxial 4H-SiC thin films on 4H-SiC n-type substrates with 4° off-oriented Si-face for high-power and high-voltage SiC electronic devices for incorporation in power grids, electric vehicles and photovoltaic inverters [101, 102].
- (111) oriented 3C-SiC epitaxial layers on 4-inch Si substrates for inclusion in MOS devices for high-power electronics [14].
- 3C-SiC/4H-SiC stacked structures consisting of single-domain 3C-SiC on single-crystal 4H-SiC wafer with 4 degrees incline from the (0001) direction to the [1120] direction for power MOSFET applications [110].
- Single-crystal 3C-SiC layer on C-face 4H-SiC substrates for inclusion in 3C-SiC/4H-SiC heterostructures with carbon-face (C-face) for high electron mobility transistors (HEMTs) for use in high-frequency and elevated-power amplifiers for incorporation in broadband telecommunications, high-power radars, and high-resolution LiDARs [111].
- *Photovoltaics:*
 - a-Si_{1-x}C_x:H films for incorporation in heterojunction photovoltaics [74, 89, 90].
 - H-rich SiC nanocrystals (nc-SiC:H(n)) for incorporation as passivating transparent contacts in crystalline Si solar cells [23].
 - Activated SiC thin films as the Si¹⁴ C-Si barrier heterojunctions energy converters in betavoltaic cells [103].
 - N-type microcrystalline silicon carbide (μ c-SiC:H(n)) as part of transparent SiC/tunnel SiO₂ passivation layer for the front side of crystalline Si (c-Si) solar cells [88].
 - C-rich amorphous a-SiC films as antireflection and protective coatings for solar cells [108].

- Hydrogenated amorphous SiC (a -SiC:H) films with various Si/C ratios for incorporation in nanoelectronic and optoelectronic devices, including Si-based solar cells, Si-based light-emitting diodes [112].
- *Hard protective coatings:*
 - Hydrogenated amorphous silicon carbide (a -Si_{1-x}C_x:H) coatings for corrosion resistance [89, 90].
 - Silicon oxycarbide (SiOC) thin films for application as oxidation resistance protective coating on carbon or metal substrates [97].
 - SiC protective coatings for carbon/carbon (C/C) composites for applications in the aerospace field, including in components such as turbines and aeronautical brake systems [107].
- *Wide bandgap semiconductors:*
 - Homoepitaxial 4H-SiC thin films for inclusion in wide bandgap semiconductors [144].
- *Decorative applications:*
 - Hydrogenated amorphous silicon carbide (a -SiC_x:H) interlayers as adhesion promoter a -C:H/ a -SiC_x:H/ferrous alloy structures [104].

3.2.2 SiC_x materials grown by CVD in a variety of forms, structures, compositions, and dopant levels are also being examined for a plethora of novel applications such as

- *Medical, biological, and health-related applications:*
 - Epitaxial, polycrystalline, and amorphous 3C-SiC and 4H-SiC thin films and coatings for incorporation in biomedical devices, such as bone prosthetics, hybrid implantable systems that combine radio frequency and biosensor technologies, myocardial heart probes, coronary heart stents, neural probes, and implantable microelectrodes [57].
 - Intracortical SiC implants having 8–16 single shanks with either 4 or 6 μ m critical thickness for use as microelectrode arrays to record and stimulate neural activity consistently and reliably [80].
 - Implantable electronics for *in vivo* multiplexed cardiac electro-physiology recording with minimum invasive interfaces with recording, stimulation and reversible feedback control of how organs function [29].
 - Self-aligned extremely thin SiC nanowire arrays for medical diagnosis and nanoscale sensing [29].
 - Multilayered SiC thin films with various preferred growth orientations as hard coatings for biological devices and biosensors [98, 99].

- a-SiC:H thin films as protective coatings and passivation layers for biomedical devices, including neural implantable devices [105].
- *Ultrafast data processing and transmission:*
 - Non-stoichiometric SiC_x films for inclusion in an all-optical data-format follower and inverter based on a bus/ring waveguide resonator-based for ultrafast dual-functional wavelength and data-format conversion [9, 73].
- *Quantum optics and photonics:*
 - SiC as Si quantum-dots and nanocrystals host with pronounced quantum confinement effects for use in optical devices [75].
 - a-SiC coatings for quantum optics and non-linear and linear photonics [83].
 - Self-aligned ultrathin SiC nanowire (NW) arrays for quantum photonics, and quantum imaging and sensing [30, 31, 92].
 - 500-nm-thick a-SiC layer on a 2.5-μm-thick thermally oxidized SiO₂ layer on Si for applications in integrated functional SiC devices for integrated photonics, such as grating couplers, waveguides, power splitters, polarization beam splitters, and mode converters [106].
- *Specialized plates and mirrors:*
 - 200 mm in diameter × 3 mm in thickness SiC faceplate with monolithic cooling channels to serve as a deformable mirror for adaptive optics in high-power lasers [78].
 - Highly oriented and transparent, 0.025 cm thick, 3C-SiC bulks as frontal plates for hypersonic and supersonic domes and windows [79].

Electrochemical supercapacitors:

- SiC nanostructures of varying sizes, ranging from 0D (e.g., solid nanocrystals, core and/or shell nano-spheres, hollow nano-spheres, and hollow nano-cages), 1D structures (such as nano-ribbons or nano-belts, nano-needles, nano-tubes, nano-rods, and nano-wires), 2D (such as nano-flakes, nano-plates, nano-flakes, and nano-sheets), and 3D nanoscale architectures with controllable sizes and shapes as electrodes for electrochemical supercapacitors [100].

Table 4 presents a summary of recent CVD and PECVD processes and potential applications, organized by ascending publication date.

4. Modeling and mechanistic studies of CVD and PE-CVD

Table 5 presents a summary of relevant theoretical and experimental modeling and mechanistic studies of CVD and PE-CVD SiC_x that focus on elucidating gas-phase

and substrate surface reaction mechanisms that drive the adsorption and decomposition of source precursor and co-reactant(s) and resulting effects on film properties and performance.

5. Physical vapor deposition (PVD) of SiC_x

There are several PVD variants for generating SiC_x thin films, as shown in **Figure 5**.

Table 6 summarizes the different PVD processes, the structures of the resulting SiC_x materials, and the possible industrial applications. The reader is again reminded that this represents an update of the earlier review article by the current authors that highlighted the latest results and accomplishments in PVD processing technologies and resulting film properties, performance, and usages. Major technological applications, key experimental details, and important findings are also presented in what follows.

Sputtering and its variants are the predominant PVD technology used for the deposition of SiC_x structures, including nanocrystals and amorphous and crystalline thin films and coatings, except in IC devices, where nanometer-scale design rules and complex high-aspect-ratio topographies prohibit PVD usages.

5.1 PVD SiC_x materials of various structures, compositions, and morphologies continue to be incorporated in well-known applications such as

- *Hard protective coatings:*
 - a-SiC coatings as tritium permeation barriers (TBPs) [122] .
 - SiC thin films in a covalent multi-layer stack consisting of Al₂O₃ + SiC+B₄C as wear-resistant hard protective coatings for high-speed steel (HSS) rods [132].
 - SiC as protective coatings for C fibers employed to reinforce ceramic and metal matrix composites [124].

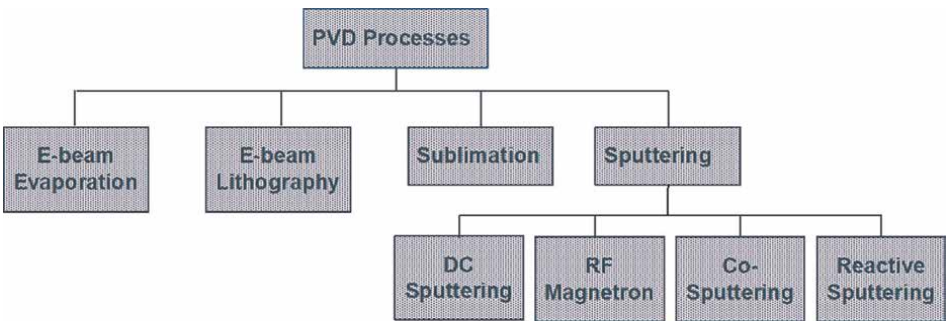


Figure 5.
Various PVD variants for generating SiC_x thin films.

- a-SiC_xN_y thin films for mechanical, electrical, and optical applications that require mechanically stable and durable SiC coatings [128].
- Nanocrystalline SiC (nc-SiC) and a-SiC phases as mechanical and optical protection coatings [126, 127].
- *Photovoltaics and light emitting diodes (leds):*
 - a-SiC thin films as protective or transition layers for LEDs and solar cells [79, 122, 126, 131, 133].
 - High-quality, ~1 mm-thick, crystalline 3C-SiC layers on 4° off-axis 4H-SiC substrates for solar-driven photoelectrochemical (PEC) water splitting for conversion of intermittent solar energy into renewable and storable chemical energy in the form of H₂ [130].
 - SiC films as a component of a double layer antireflection coating SiC/MgF₂ for solar cell applications [137].

High-power, high-temperature electronics:

- Nanocrystalline SiC (nc-SiC) and a-SiC phases for incorporation in optoelectronic devices operating in drastic environments such as high voltages and high temperatures [126].
- a-SiC and c-SiC thin films for incorporation in high-temperature electronics and sensors [127].

5.2 SiC_x PVD-based materials in various structures, morphologies, stoichiometries, and dopant levels are being examined for a plethora of novel applications such as

- *Radio-frequency (RF) electronics:*
 - Nanocrystalline rhombohedral 15R-SiC thin films for incorporation in high-frequency resonators and microwave absorbers [129].
- *Photonics and quantum optics:*
 - 530 nm-thick 3C-SiC thin films for monolithically integrated photonics, such as electro-optic (EO) modulators and electrically driven quantum emitters [134].
- *Biological and medical applications:*
 - Nanocrystalline rhombohedral 15R-SiC thin films for incorporation in bioimaging probes [129].
- *Supercapacitors:*
 - SiC nanocauliflowers (NCs) thin films as supercapacitor electrodes [123].

- *Photoelectrochemical CO₂ conversion:*
 - Amorphous a-SiC films on Si(100) as electrodes for use as photocathode in photoelectric catalysis reduction of CO₂ [136].

6. Summary and highlights of alternative (non-CVD and non-PVD) deposition techniques of SiC_x

There are several non-CVD and non-PVD processing technologies for generating SiC_x thin films, as shown in **Figure 6**.

Table 7 summarizes the different alternative (non-CVD and non-PVD) processes, the structures of the resulting SiC_x materials, and the possible industrial applications. The reader is again reminded that this represents an update of the earlier review article by the current authors that highlighted the latest results and accomplishments in non-CVD and non-PVD processing technologies and resulting film properties, performance, and usages. Major technological applications, key experimental details, and important findings are also presented in what follows.

6.1 Studies in recent years have examined the inclusion of alternative SiC_x deposition methods in traditional technologies as per below

- *Hard protective thin films:*
 - 3C–SiC cubic coatings as tool protective layers [48].
 - Substrate consisting of SiC(0001) with the Si face acting as basis for the formation of thermally conductive epitaxial graphene of atomic thickness for use as hard protective coatings in elevated-speed impact technologies, aeronautics, aerospace, body armor, and automotive applications [153].
- *LEDs, displays, and solar cells:*
 - 40–199 nm-thick epitaxial SiC on Si for electroluminescent devices [149, 150].

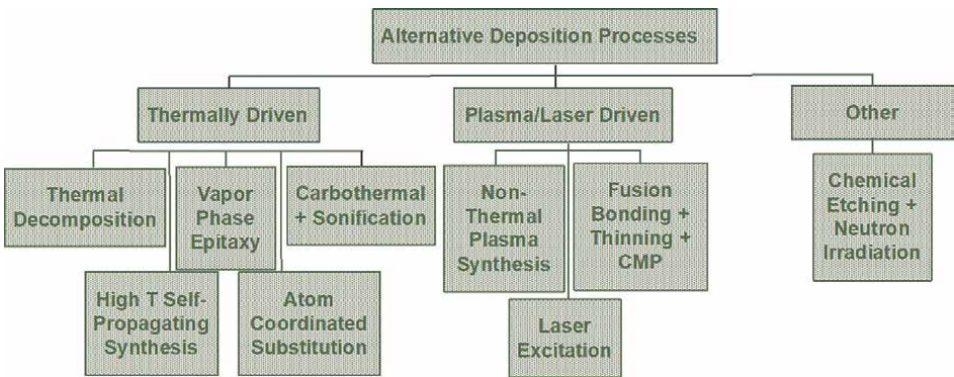


Figure 6.
Various non-CVD and non-PVD deposition technologies for generating SiC_x thin films.

- Controlled size (2–4 nm) SiC nanocrystals (nc-SiC) for incorporation in solar cells [156] .
- As-deposited then crystallized (via post-deposition annealing) a-SiC on p-Si (111) substrates for heterojunction photovoltaics [157].
- *Elevated-temperature, enhanced-power electronics:*
 - Epitaxial SiC phase with thickness ranging from 40 to 100 nm on silicon for elevated-temperature LEDs and integrated circuitry [149, 150].
 - SiC nanocrystals consisting of controlled sizes ranging from 2 to 4 nm for enhanced-power and elevated-frequency applications, including elevated-frequency field-emission-transistors and GaN light emitting diodes, and substitutes for Si integrated circuitry in electric vehicle systems [156].
 - SiC “nanoflakes” and nanosheets as a new category of 2D material systems for inclusion in elevated temperature applications and enhanced-power electronics [145, 146]
 - As-deposited then crystallized (via post-deposition annealing) a-SiC on p-Si (111) substrates for heterojunction solar cell applications [148].

6.2 Alternative SiC_x deposition methodologies are being investigated in novel applications such as

- *Quantum optics, photonics, and quantum information sensing and processing:*
 - Uniform SiC spherulites with thickness ranging from 700 to 1000 nm for incorporation in radiative passive cooling units and for inclusion in absorption and emission in mid-to-far IR range applications [16]
 - 4H-SiC on buried silicon oxide (SiO₂) multi-stacked system consisting of layer on Si for incorporation in spintronics for solid-state quantum information sensing and processing [147].
 - SiC porous nanoparticles a few nanometers in diameter formed through a two-step process (neutron irradiation and annealing) for incorporation in ultrasensitive nanosensors in magnetometry and thermometry, single-photon emitters, and quantum bits (qbits) [63]
 - Polycrystalline SiC thin films formed from 1 μm-thick Si-C bilayer stacks and consisting of a mixture of 3C-SiC(111) + 3C-SiC(220) + 3C-SiC(311) for applications in quantum electronics and photonics [154].
- *Biological and medical applications:*
 - Cubic 3C-SiC thin films for nuclear radiation protection and biocompatible applications [48]

- *Miscellaneous applications:*
 - Single crystal 3C-SiC(111) films on Si(111) substrates for applications in composite materials and as catalyst support [151].
 - Closed-pore and dense α -SiC grown by elevated-temperature pyrolysis from cross-linked Silres H62C methyl-phenyl-vinyl-hydrogen polysilsesquioxane for incorporation in three-dimensional (3D) printing applications [152].
 - Polycrystalline SiC thin films formed from 1 μm -thick Si-C bilayer stacks and consisting of a mixture of 3C-SiC(111) + 3C-SiC(220) + 3C-SiC(311) for applications as functional ceramic material [154].
 - Free-standing SiC membranes for harsh environment sensing applications [155].

7. Challenges and opportunities for silicon carbide materials

There is no question that silicon carbide will continue to occupy a prominent place in the realm of materials research in response to demands for improving manufacturing technology for existing applications and in meeting performance requirements for new applications across a plethora of industries. However, several challenges continue to hinder a broader and faster adoption of SiC technologies.

As discussed earlier, silicon carbide is a complex binary system with a bonding configuration that is 88% covalent and 12% ionic. It exhibits over 200 polytype crystalline structures and many polycrystalline and amorphous phases. And if this tremendous variety in form and phase is not complicated enough, many SiC processing techniques incorporate H, O, and/or N in various concentrations either intentionally to further customize the properties of the resulting SiC matrix, or unintentionally due to deficiencies and imperfections in the growth methodologies used. At an earlier stage in development, the main problem that was sought to be overcome in SiC fabrication was elimination of defects in the SiC crystals. The catalog of defects is long: edge dislocations, screw dislocations of different types, triangular defects, vacancies and basal plane dislocations. The effect of a less-than-perfect crystal is generally poor performance, making components electrically unusable. In other applications, particularly optical and photonic, controlled presence of specific defects at specific concentrations is essential to function. Unfortunately, in many cases, published work fails to detail, or report at all, trace elements and their concentration; and defects and their types and concentration, as well as the resulting SiC structure. These omissions lead to wide discrepancies in the literature available in the public domain and, as a result, cause confusion and create obstacles in establishing a true understanding of the various facets of the SiC system, leading to delays and interruptions in the development and deployment of reliable SiC material and process solutions. It is therefore imperative to compile a comprehensive library that clearly and thoroughly catalogs qualitative and quantitative statistics of the entire spectrum of structural and compositional issues associated with SiC. Such a library would act as a trustworthy record and streamline identification and commercialization of appropriate SiC solutions.

Additionally, the semiconductor industry is undergoing a rapid transition to the design and deployment of hetero-devices and systems-in-package (SiPs) for high performance computing (HPC). This transition is further enhanced by the industry's implementation of the concepts and drivers of the fourth industrial revolution (Industry 4.0). The fourth industrial revolution incorporates intelligent industrial manufacturing into IC R&D and commercialization through artificial intelligence, robotization, cloud computing, and cybernetics. This incorporation has significant repercussions for the identification, fabrication, and incorporation of SiC materials with higher levels of structural and compositional control necessary for the demonstration of hetero-devices and systems-in-package (SiPs). This includes the development of novel SiC process intensification techniques such as atomic layer deposition (ALD), atomic layer etching (ALE), molecular layer deposition (MLD), self-assembled monolayers (SAM) deposition, and other emerging manufacturing processes which have yet to be reported for SiC.

These SiC process intensification techniques may require the demonstration and deployment of an intelligent automated manufacturing paradigm for the real-time controlled production and concurrent consumption of highly toxic and/or unstable precursors that are needed to form these new materials and structures with exact composition and nanoscale precision, particularly at lower process temperatures. Such a paradigm involves a methodology and system for the simultaneous automated, closed-loop, end-point monitoring, sensing, and detection of the SiC thin film growth or etching in the thin film processing chamber and the precursor synthesis in the precursor synthesis chamber [158]. As such, this approach could overcome current manufacturing challenges associated with the management and utilization of effective but highly reactive precursors that exhibit a very short lifetime due or shock-sensitivity; and/or necessitate cooling to maintain their integrity prior to consumption. This intelligent manufacturing scheme would also enable the design and in-situ deposition of the multi-layered, near-zero thickness SiC films with varying structures, compositions and dopant profiles needed for novel technological applications, thus evolving and progressing the traditional in-situ dual-layered processes that proved highly useful for IC multi-level metallization schemes [159].

8. Summary and commentary

Sections 3.0 and 4.0 of this review summarizes the latest reports concerning the plethora of CVD deposition technologies for SiC_x coatings and material systems, along with CVD mechanistic studies and theoretical modeling. Similarly, Section 6.0 outlines and describes up-to-date peer-reviewed reports in the public domain referring to both PVD and alternative (non-CVD and non-PVD) deposition techniques for the multitude of SiC_x forms of interest. The latter includes the common 4H-SiC, 6H-SiC, 3C-SiC, and a-SiC structures in addition to distinct forms such as 21H polytype crystalline SiC, nanocrystalline rhombohedral 15R-SiC (nc-15R-SiC), SiC membranes, SiC two-dimensional materials, and micro- and nano-crystalline SiC systems.

In assembling the CVD SiC_x portion of this report, several clear trends emerge in Si and C chemistries, the various CVD deposition methodologies, and well-known and novel applications as follows:

- CVD SiC_x technologies continue their traditional use unabated in wide bandgap semiconductors, IC systems, enhanced-power and elevated-temperature devices,

hard protective thin films, and solar cells. Concurrently, SiC_x CVD structures consisting of different phases are being included into a myriad of emerging industrial products. The latter include biological and medical devices and systems, ultrafast data transmission and processing, and photonics and quantum optics.

- CVD in its many forms, including PE-CVD, Laser CVD, hot-wire CVD, and microwave CVD, has taken over from PVD as the method of choice for the various SiC_x forms of interest. Surprisingly, despite the urgent need for near-zero-thickness SiC_x films that exhibit atomic level uniformity, continuity, and coherence, work has yet to be reported on atomic layer deposition (ALD), atomic layer CVD (ALD-CVD), or molecular layer deposition (MLD). Such atomic layer vapor processing techniques must be identified and optimized to enable atomic level control and ensure high level of conformality for the extremely thin SiC_x coatings needed in nanoscale IC devices, solar cells, and elevated-temperature systems.
- With respect to Si and C sources chemistries, the lion share of SiC_x CVD precursors can be grouped into two categories: (1) Si chemistries including hydrihalosilanes, perhydridosilanes, and halosilanes, which react with C chemistries such as hydrocarbons, and (2) single-source chemistries that include C and Si simultaneously, for example, organohalosilanes and carbosilanes. Inherent challenges in the use of these precursors include environmental health and safety issues pertaining to their corrosive, highly reactive, and pyrophoric characteristics, and technological challenges attributed to the elevated thermal budgets needed to ensure efficient and complete decomposition. These problems prevent their use to deposit SiC_x on thermally, chemically, and/or electrically fragile substrates. Additional issues are related to their vapor pressure profiles and adsorption and decomposition mechanisms, which have so far prohibited the development of atomic-layer CVD (AL-CVD) processes for the growth of the atomic scale thickness SiC_x films needed for inclusion in nanometer scale MOSFETs and solar cell devices. Accordingly, an urgent demand exists to design and fabricate novel SiC precursors that address and eliminate the problems and difficulties discussed above.⁷²
- Accordingly, the design of precursors for CVD and PECVD SiC_x must take into consideration the specific application of interest and its related cost of ownership. There exists a high level of interest in designing and synthesizing C- and Si- precursors with the chemical integrity and thermal stability required to decompose at low temperatures to grow SiC_x films with the desired properties and performance. Latest developments in precursors for CVD SiC_x include single-source precursors that carry Si and C simultaneously to the substrate surface to enable the growth of SiC_x films while avoiding substitutional defects, i.e., defects consisting of Si-Si or C-C bonds. In this respect, precursors with structures consisting of alternating Si and C atoms have been shown to deposit films with reduced defect density.
- CVD of hetero-epitaxial 3C-SiC on Si has been garnering tremendous interest in recent years, in contrast to CVD 4H-SiC which has received limited attention due to its well-known properties and established use in several traditional industrial

applications. The overarching goal of the work is to design and demonstrate optimized CVD techniques that can address and resolve the challenges associated with lattice mismatch and disparity in thermal expansion coefficients between 3C-SiC and Si. In this respect, a number of material and process solutions have been reported that aim to remedy the issues pertaining to the pre-CVD 3C-SiC substrate surface carbonization process for 3C-SiC homo-epitaxy on Si.

In all these instances, it will undeniably be required to identify deposition techniques for good quality extremely thin SiC_x films using a low thermal budget environment without the application of plasma assistance with its many shortcomings, including undesirable H incorporation. Equally important is the ongoing identification and synthesis of single-source C and Si source chemistries along with effective substrate surface treatment recipes to catalyze hetero-epitaxial formation of 3C-SiC and 4H-SiC coatings on thermally, chemically, and/or electrically fragile substrates.

In terms of the PVD and alternative SiC_x processing techniques, sputtering in its many forms, including RF and direct current magnetron and reactive ion sputtering, continue to dominate the PVD arena. In this respect, ongoing R&D work aims to identify and deploy new sputtering processes for traditional as well as novel technological applications. In addition to sputtering, physical vapor deposition methodologies under investigation include direct sublimation and radio frequency assisted deposition, and e-beam evaporation and lithography. The latter seem to be promising solutions for ultimate use in large-volume manufacturing protocols that require high output to guarantee competitive cost of ownership. Alternatively, alternate SiC_x processing methodologies, including vapor phase epitaxy and elevated-temperature pyrolysis, are complex and require a large number of processing steps. As a result, they are too challenging for incorporation in industrial applications, in spite of their demonstrated ability at growing high-quality SiC_x systems. Efforts to simplify and streamline these techniques are essential for their potential adoption in manufacturing.

In all cases, it is obvious that the significant interest and wide allure of SiC_x thin films and nanostructures will continue to intensify, driven in part, by the desired development and deployment of technologically useful crystalline and amorphous SiC_x configurations with varying structures and chemical compositions. This desire has made the identification and optimization of SiC_x thin film processing techniques a critical and enabling research area, thus providing rewarding scientific and technological breakthroughs in basic materials understanding, atomic level deposition technology, and exciting new applications.

Properties	Alpha (non-cubic)			Beta (Cubic)	Amorphous	Not-Specified	Ref (s)	Comments
Physical/Structural								
Crystalline Form	Hexagonal	Rhombohedral	Cubic	<5% H	>5% H			
Polytype (Ramsdell notation)	2H-SiC	4H-SiC	6H-SiC	15R-SiC	3C-SiC	a-SiC: H	[38]	
Polytype Stacking	AB	ABCB	ABCACB	ABCACBCABACACBCB	ABC		[11, 39–41]	
Lattice Parameters @ 300 K	3.0763	3.0730	3.0806	3.080	4.3596		[42]	
Lattice Constant a (Å)	5.0480	10.053	15.1173	37.817	4.3596			
Lattice Constant c (Å)								
Space Group	P ₆ 3mc	P ₆ 3mc	P ₆ 3mc	R ₃ m	F ₄ 3m		[43]	
Atoms/Unit Cell	4	8	12	15	2		[42]	
Density @ 20–27°C (g/cm ³)	3.214	3.21	3.211	3.167–3.216	3.210	1.76–1.93	[42, 44]	[45] (PE-CVD)
Mechanical								
Hardness (Mohs)				9.2–9.3		9.08–9.5	[43, 46]	
Hardness- Knoop @ 100 g load (GPa)	24.6	29–31	29–31	14–16 (epi-CVD)		27.40–28.75; 24.0	[46–49]	
Modulus of Elasticity—1.29 mm thick (GPa)				442		62.1–91.6	[44, 46]	
Tensile Strength (MPa)				274 ± 58			[43, 50]	
Flexural Strength (MPa)						300–800	[46]	

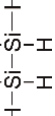
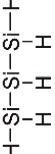
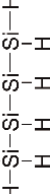
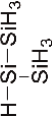
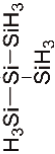
Properties	Alpha (non-cubic)	Beta (Cubic)	Amorphous	Not-Specified	Ref (s)	Comments
Physical/Structural						
Compressive Strength (MPa)	~			3900	[41]	
Shear Modulus (GPa)		140–190 ms			[46]	
Fracture Toughness (MPa·m ⁻²)				3.4–3.9	[46]	
Poisson Ratio				0.14	[51]	
Thermal						
Melting Point (°C)		1527°-phase change		~1800°-sublimes		No true mp-phase transitions, sublimation and dissociation occurs [52, 53]
Maximum Continuous Operating Temperature (°C)	1240°	1240°	1240°		[32, 46]	
Maximum Short-term, No-Load Operating Temperature (°C)				1650°		
Thermal Expansion Coefficient × 10 ⁻⁶ (25–500°C)	3.8		4.3	2.97; 3.8	[32, 46, 47]	
Thermal Conductivity (W/cm·K)	3.7	4.9	~5.0	1.25–1.30	[46, 47, 54]	
Specific Heat (J/Kg·K) @ 20°C			712 1084	750; 690	[43, 47, 51]	
Debye Temperature (°K)	1300°	1200°	1200°		[55]	
Electrical						

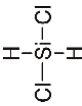
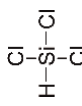
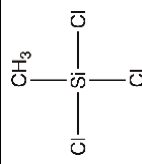
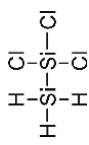
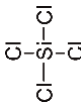
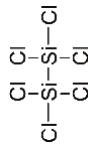
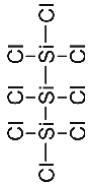
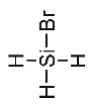
Properties	Alpha (non-cubic)			Beta (Cubic)	Amorphous	Not-Specified	Ref (s)	Comments
Physical/Structural								
Resistivity (ohm-cm)						>10 ⁸	[47]	
Dielectric Constant, Static	9.7	9.66 (perp c axis)	9.72	6.2			[44, 56]	
Dielectric Constant, High Frequency		6.52 (perp c axis)	6.52				[55]	
Dielectric Strength × 105 (V/cm)			~10	6.4				
Bandgap (eV) @ 20–27°C	3.30	3.26	2.86; 3.02	3.00	2.2–2.3	2.5– 2.6	[57]	
Electron Mobility-(axis) (cm ² /Vs)		720 (a); 650(c)	≤400	500	≤800		[43, 55]	
Hole Mobility (cm ² /Vs)		≤120	≤90	≤320			[55]	
Intrinsic Carrier Conc. (cm ⁻³) @ 300°K		5 × 10 ⁻⁹	1.6 × 10 ⁻⁶	1.5 × 10 ⁻¹			[57]	
Critical Breakdown Electric Field, (MV/cm)		2.2	2.5	2.12			[57]	
Saturated Electron Drift Velocity × 10 ⁷ (cm/s)		2.0		2.5				
Optical								
Color	colorless- amber	green- yellow	green	orange-yellow	canary yellow			
Refractive Index, @589.3 nm a;c	2.629;2.703	2.712; 2.659	2.690; 2.647	2.687; 2.650	2.6525	2.29	1.8–1.9 [58]	2H @ 601.5 nm
Optical Bandgap (eV)			2.0–3.02		1.34	1.51	[59, 60]	lower values for micro-crystalline compared to bulk

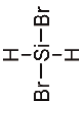
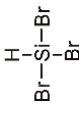
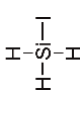
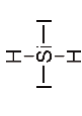
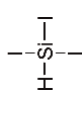
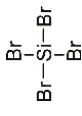
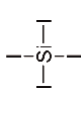
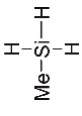
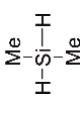
Properties	Alpha (non-cubic)		Physical/Structural			Beta (Cubic)	Amorphous	Not-Specified	Ref (s)	Comments
Optical Phonon Energy (meV)	104.2	104.2	102.8						[55, 61]	
Thermo-optic Coefficient $\times 10^{-5}/^{\circ}\text{C}$			5.1–7.3						[62]	
Photoluminescence, Max (nm)	~382 (Al-doped)	650 (porous) ~468 (B-doped) ~413 (Al-doped)	417.8 (Al-doped)	1540 (poly-crys; Er + induced) 1150 (nc-SiC)	~105				[31, 61–66]	
Other										
Coefficient of Friction @ 20°, Iron Mating								~0.3*	[67]	*preheated to 800–1500 °C, then cooled to RT
Acoustic Velocity (ms ⁻¹) @ 20–27°C	13,730	13,300	12,600*	10,340	9.4622				[42, 66]	*poly
Critical Surface Tension, dynes/cm								52 ± 5	[68]	
*The information presented should be viewed as relative not absolute. Variations and irregularities are the result of the various polytypes, structures, morphologies, and compositions of the SiC _x system. The reader should review the actual references cited for more relevant information.										

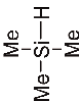
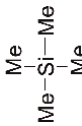
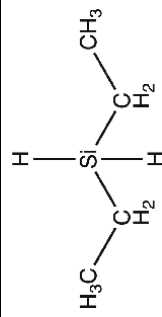
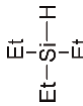
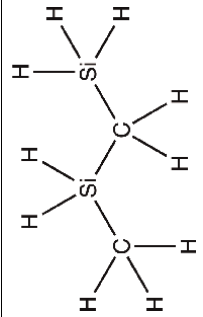
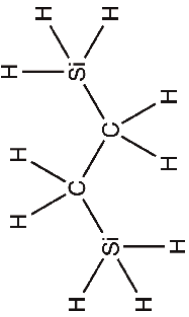
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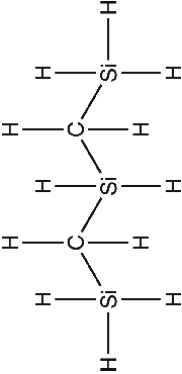
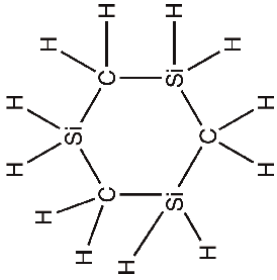
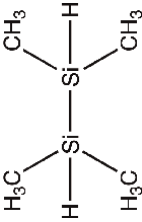
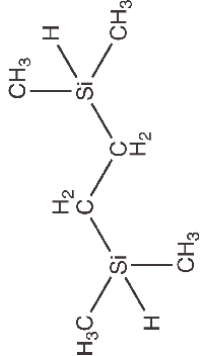
Table 1.
Properties of SiC_x in prominent forms*.

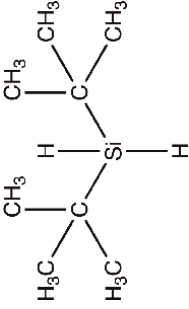
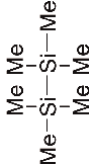
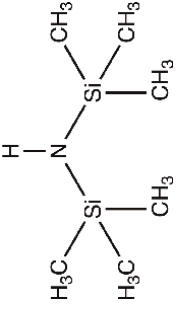
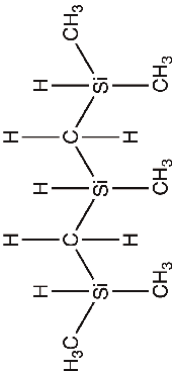
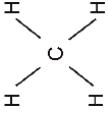
CVD SiC**	Name	Acronym	Formula	Chemical Formula	Molecular Weight (grams/mole)	% Si	Form	Boiling Point (° C)	Melting Point (° C)	Vapor Pressure (° C; torr)	Density (g/cm ³) @20 °C	CAS #
Perhydridosilanes												
**	Silane		SiH ₄		32.12	87.4	gas	-112°	-185°	20°; >760	0.680	7803-62-5
	Deutero- silane		SiD ₄		36.14	77.7	gas	-112°	-185°	-122°; 400	1.2	13537-07-0
**	Disilane		Si ₂ H ₆		62.22	90.3	gas	-14.5°	-132°	21.1°; 2586	0.686	1590-87-0
**	Trisilane		Si ₃ H ₈		92.32	91.2	liquid	52.9°	-117°	0°; 95.5	0.743	7783-26-8
	n-Tetra-silane		Si ₄ H ₁₀		122.42	91.7	liquid	106°	-85-95°	20°; 22	0.825	7783-29-1
	Isotetra-silane		Si ₄ H ₁₀		122.42	91.7	liquid	101°	-99°	20°; 25	0.825	13597-87-0
	Neopenta-silane	NPS	Si ₅ H ₁₂		152.52	92.1	liquid	132-134°	< -40°	25°; 15	0.805	15947-57-6
Halosilanes												
	Mono-chloro-silane	MCS	SiH ₃ Cl		66.56	42.2	gas	-30.4°	118°	20°; 4590	1.145	13465-78-6

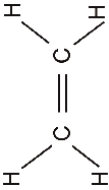
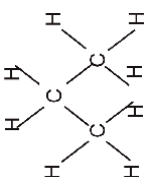
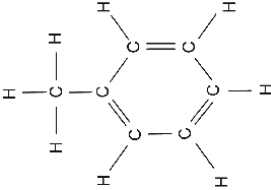
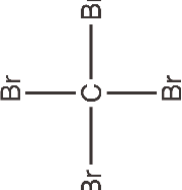
CVD SiC**	Name	Acronym	Formula	Chemical Formula	Molecular Weight (grams/mole)	% Si	Form	Boiling Point (° C)	Melting Point (° C)	Vapor Pressure (° C; torr)	Density (g/cm ³ @20 °C)	CAS #
	Dichloro-silane	DCS	SiH ₂ Cl ₂		101.01	27.8	gas	8.3°	-122°	-34°; 100	1.22	4109-96-0
	Trichloro-silane	TCS	HSiCl ₃		135.45	20.7	liquid	31.9°	-128°	14.5°; 400	1.342	10025-75-8
**	Methyl-trichloro-silane	MTCS	CH ₃ Cl ₃ Si		149.48	18.9	liquid	66.4°	-78°	13.5°; 100	1.275	75-79-6
	Penta-chloro-disilane	PCDS	Si ₂ HCl ₅		234.44	24	liquid	130°	N/A	25°; ~20	N/A	78228-96-3
**	Tetra-chloro-silane	SiTet	SiCl ₄		169.90	16.5	liquid	57.6°	-70°	20°; 194	1.481	10026-04-7
**	Hexa-chloro-disilane	HCDS	Si ₂ Cl ₆		268.89	20.9	liquid	144-6°	-1°	85°; 109	1.562	13465-77-5
	Octa-chloro-trisilane	OCTS	Si ₃ Cl ₈		367.88	22.9	liquid	213-5°	-67°	90°; 10	1.61	13596-23-1
Hydrido-halosilanes												
	Mono-bromo-silane	MBS	SiH ₃ Br		111.01	25.3	gas	1.9°	-94°	25°; 1700	1.533	13465-73-1

CVD SiC**	Name	Acronym	Formula	Chemical Formula	Molecular Weight (grams/mole)	% Si	Form	Boiling Point (° C)	Melting Point (° C)	Vapor Pressure (° C; torr)	Density (g/cm ³ @20 °C)	CAS #
	Dibromo-silane	DBS	SiH ₂ Br ₂		189.91	14.8	liquid	66°	-70.1°	25°; 166	2.17	13768-94-0
	Tribromo-silane	TBS	SiHBr ₃		268.81	10.4	liquid	118.8°	-73.5°	25°; 12	2.58	7789-57-3
	Monoiodo-silane	MIS	SiH ₃ I		158.01	17.8	liquid	45.8°	-56.5°	25°; 245	2.035	13598-42-0
	Diiodo-silane	DIS	SiH ₂ I ₂		283.91	9.9	liquid	149– 150°	-1°	55°; 25	2.834	13760-02-6
	Triiodo-silane	TIS	SiHI ₃		409.81	31.0	liquid	220°	8°	95°; 12	3.314	13465-72-0
	Tetra-bromo-silane		SiBr ₄		347.70	8.1	liquid	154°	5°	0°; 1.8	2.772	7789-66-4
	Tetra-iodosilane		SiI ₄		535.70	5.2	solid	287-8°	120-1°	125°; -30	4.198	13465-84-4
Carbosilanes												
X	Methyl-silane	1MS	CH ₆ Si		46.14	53.8	gas	-57°	-157°	20°; ~11000	0.628 @ (-58°)	992-94-9
	Dimethyl-silane	2MS	C ₂ H ₆ Si		60.17	46.7	gas	-20°	-150°	-80°; 30	0.68	1111-74-6

CVD SiC**	Name	Acronym	Formula	Chemical Formula	Molecular Weight (grams/mole)	% Si	Form	Boiling Point (° C)	Melting Point (° C)	Vapor Pressure (° C; torr)	Density (g/cm ³) @20 °C	CAS #
	Trimethyl-silane	3MS	C ₃ H ₁₀ Si		74.20	37.9	liquid	6.7°	-135.9°	25°; 1218	0.638	993-07-7
**	Tetra-methyl-silane	4MS	C ₄ H ₁₂ Si		88.22	28.0	liquid	26.6°	-99°	20°; 589	0.641	75-76-3
**	Diethyl-silane	2ES	C ₄ H ₁₀ Si		88.22	29.2	liquid	56°	-132°	N/A	0.684	542-91-6
	Triethyl-silane	3ES	C ₆ H ₁₀ Si		116.28	23.3	liquid	107-8°	-156.1°	20°; 40	0.728	617-86-7
**	1,3-disila-butane		C ₂ H ₁₀ Si ₂		90.27	56.0	liquid	44-5°	N/A	N/A	0.80	6787-86-6
**	1,4-disila-butane		C ₂ H ₁₀ Si ₂		90.27	56.0	liquid	45-6°	-15°	N/A	0.697	4364-07-2

CVD SiC**	Name	Acronym	Formula	Chemical Formula	Molecular Weight (grams/mole)	% Si	Form	Boiling Point (° C)	Melting Point (° C)	Vapor Pressure (° C; torr)	Density (g/cm ³) @20 °C	CAS #
**	1,3,5-trisila- pentane	TSP	C ₂ H ₁₂ Si ₃		120.37	63.6	liquid	100°	N/A	N/A	0.763	5637-99-0
**	1,3,5-trisilacyclo- hexane	TSCH	C ₃ H ₁₂ Si ₃		132.38	58.3	liquid	135°	-10°	20°: ~10	0.900	291-27-0
**	1,1,2,2-tetramethyl- disilane		C ₄ H ₁₄ Si ₂		118.32	42.4	liquid	86-7°	-93°	N/A	0.702	814-98-2
**	1,1,1,4- tetramethyl- 1,4-disila-butane		C ₆ H ₁₆ Si ₂		146.38	21.2	liquid	125-8°	<0°	N/A	0.743 (25°)	84677-98-5

CVD SiC**	Name	Acronym	Formula	Chemical Formula	Molecular Weight (grams/mole)	% Si	Form	Boiling Point (° C)	Melting Point (° C)	Vapor Pressure (° C; torr)	Density (g/cm ³) @20 °C	CAS #
	Di-tert-butyldisilane		C ₈ H ₂₀ Si ₂		144.33	17.0	liquid	128°	-38°	48°; 45	0.740	30736-07-3
	Hexamethyl- disilane		C ₆ H ₁₈ Si ₂		146.38	34.1	liquid	112-3°	12-14°C	20°; 22.9	0.729	1450-14-2
	Hexamethyl- disilazane	HMDZ	C ₆ H ₁₉ NSi ₂		161.39	31.1	liquid	126.6°	-80°	50°; 50	0.774	999-97-3
	2,4,6-trimethyl- 2,4,6-trisila- heptane		C ₇ H ₂₂ Si ₃		190.50	39.6	liquid	174°	N/A	N/A	N/A	31666-32-7
Hydrocarbons												
**	Methane		CH ₄		16.04	—	gas	-161.6°	-182.5°	-175°; 10	0.423 (-162°)	74-82-8
**	Acetylene		C ₂ H ₂		23.04	—	gas	-80.8°C	20°; 33,150	1.177 (0°)		74-86-2

CVD SiC**	Name	Acronym	Formula	Chemical Formula	Molecular Weight (grams/mole)	% Si	Form	Boiling Point (° C)	Melting Point (° C)	Vapor Pressure (° C; torr)	Density (g/cm ³ @20 °C)	CAS #
	Ethylene		C ₂ H ₄		28.05	—	gas	-103.7°	-169.2°	9°; 37,500	1.178 (15°)	74-85-1
**	Propane		C ₃ H ₈		44.10	—	gas	-42.1°	-187.7°	21°; 6300	0.564 (20°)	74-98-6
	Toluene		C ₇ H ₈		92.14		liquid	110.6°	-95°	20°; 22	0.867 (20°)	3101-08-4
	Carbon tetra- bromide		CBr ₄		331.63	—	solid	189.7°	94.5°	96.3°; 39.975	3.42 (20°)	558-13-4

*Tabulated data is primarily from reference [69]. Additionally included is information from references cited herein, in the public domain, or provided by the authors. **Indicates widely employed chemicals in vapor phase SiC deposition.

Table 2.
Properties of silicon carbide precursors for vapor phase deposition of SiC.^{*}

Precursors/sources	Bond dissociation energy (kJ/mole)
Carbon	
CH ₄ (C—H)	439
CH ₃ CH ₃ (C—H)	420
CH ₃ CH ₃ (C—C)	377
H ₂ C=CH ₂ (C—H)	464
H ₂ C=CH ₂ (C—C)	724
H—C≡C—H (C—H)	558
CBr ₄ (C—Br)	242
Silicon	
CH ₃ SiH ₃ (Si—H)	388
CH ₃ SiH ₃ (Si—C)	375
CH ₃ SiCl ₃ (Si—Cl)	258
SiI ₄ (Si—I)	284
SiBr ₄ (Si—Br)	367
SiCl ₄ (Si—Cl)	466
HSiCl ₃ (Si—Cl)	471
SiH ₂ Cl ₂ (Si—Cl)	472
H ₃ SiCl (Si—Cl)	466
H ₃ SiSiCl ₃ (Si—Cl)	409
Cl ₃ SiSiCl ₃ (Si—Cl)	397
SiH ₄ (Si—H)	384
H ₃ SiCl (Si—H)	458
SiH ₂ Cl ₂ (Si—H)	368
HSiCl ₃ (Si—H)	395
Si ₂ H ₆ (Si—H)	321
(H ₃ Si) ₂ SiH—H (Si—H)	352
(H ₃ Si) ₃ Si—H (Si—H)	343
(H ₃ Si) ₄ Si (Si—H)	363
Si ₂ Cl ₆ (Si—Si)	278
Si ₂ H ₆ (Si—Si)	310
H ₅ Si ₂ SiH ₃ (Si—Si)	297
H ₅ Si ₂ Si ₂ H ₅ (Si—Si)	284
HSi(SiH ₃) ₃ (Si—Si)	297
(H ₃ Si) ₄ Si (Si—Si)	297

*The data is intended as reference point for comparing bonding properties for the most investigated silicon and carbon precursors [69–71].

Table 3.
Bond dissociation energies for silicon and carbon for SiC_x source chemistries*.

Deposition technique	Applications	Summary description	Citation
Plasma-enhanced CVD	Coatings for wear resistance	a-SiC:H thin films on Ti–6Al–4 V alloy substrate	Nass et al. [72]
CVD and high-temperature CVD	Biomedical devices, including myocardial heart probes, bone prosthetics, coronary heart stents, implantable microelectrodes, hybrid implantable systems that combine radio frequency and biosensor technologies, neural probes	3C-SiC and 4H-SiC epitaxial, polycrystalline, and amorphous thin films and coatings, depending on the application	Review by Frewin et al. [57]
Plasma-enhanced CVD	Bus/ring waveguide resonator using an all optical data format follower and inverter for data-format conversion and ultrafast dual-functional wavelength	Non-stoichiometric SiC _x films	Su et al. [73]
Dual-plasma plasma-enhanced CVD: RF plasma to excite the substrate table coupled to on an Inductively-coupled RF plasma (ICP)	High-power electronics; high-frequency, high-temperature MEMS	a-SiC:H thin films	Frischmuth et al. [74]
Plasma-Enhanced CVD	Quantum-dots (QDs) or Si nanocrystals (ncs) host matrix with strong quantum confinement effect for optical devices	Broadband white and orange light band solid-state phosphor from stoichiometry detuned a-Si _x C _{1-x} films with buried Si and SiC nanocrystals	Tai et al. [75]
Laser chemical vapor deposition	Hard protective thin films proposed high-performance brake parts, and high-temperature, high-power electronics	3C-SiC (β-SiC) coatings	Zhu et al. [76]
Thermal chemical vapor deposition	Low-k dielectrics, passivation layers, and etch-stop layers in integrated circuitry	SiC _x O _y ultrathin films and nanowires (NWs)	Gallis et al. [77]
Thermal chemical vapor deposition	Deformable mirror with monolithic cooling channels for adaptive optics in high-power lasers	SiC faceplate with monolithic cooling channels 200 mm in diameter x 3 mm in thickness	Ahn et al. [78]
Halide laser chemical vapor deposition	Supersonic and hypersonic windows and domes	Transparent and highly oriented 3C-SiC bulks 0.25 mm thick	Cheng et al. [79]
Plasma-enhanced CVD	Microelectrode arrays that consistently and reliably stimulate and record neural activity	a-SiC intracortical implants with single shanks ranging from 8 to 16 with thickness of 4 or 6 μm	Deku et al. [80]

Deposition technique	Applications	Summary description	Citation
Plasma-enhanced CVD	High-field and high-power applications, photovoltaic devices, bus/ring waveguide resonator-based all-optical data-format follower and inverter	Review of literature on deposition and properties of non-stoichiometric SiC thin films	Review by Majid [9]; Cheng et al. [81]; Tai et al. [75]; Su et al. [73]
Warm or hot-wall chemical vapor deposition	Metal-oxide-semiconductor field effect transistors (MOSFETs) and Schottky-barrier diodes (SBDs),	4H-SiC epitaxial thin films	Tsuchida et al. [82]
Thermal chemical vapor deposition	Implantable electronic devices for electrophysiological stimulation and recording, <i>in vivo</i> multiplexed recording of cardiac electro-physiology with reduced invasive interfaces, and reciprocal feedback control over how organs function	3C-SiC single crystal nanomembranes deposited on Si substrates, then removed and transferred to an ultimate substrate (e.g., polyimide)	Phan et al. [29]
Hot-wall chemical vapor deposition	High-power electronic devices, MOSFETs	Thin films of 3C-SiC _x	Spera et al. [10]
Plasma-enhanced CVD	quantum optics, non-linear and linear photonics	Thin films of a-SiC	Xing et al. [83]
Laser chemical vapor deposition	Power electronics	Thick epitaxial 3C-SiC < 111> on Si(110) with morphology varying from mosaic to whisker to cauliflower-like as a function of deposition parameters	Xu et al. [84]; Sun et al. [85]
Three phase deposition: (i) 3C-SiC CVD seed layer on Si(100), then: (ii) total melting of the Si substrate to produce a 3C-SiC free-standing seed layer, then (iii) 3C-SiC homo-epitaxial CVD on seed layer	High-power devices operating under elevated frequency and temperature conditions	Epitaxial 3C-SiC on free-standing 3C-SiC seed layer	Anzalone et al. [86, 87]
Thermal Chemical Vapor Deposition nanosynthesis	Optical, biological sciences, electronics, energy harvesting, medical diagnostics. Quantum sensing and imaging, quantum photonics, and ultra-high nanosensing	Self-aligned extremely thin SiC nanowire arrays	Tabassum et al. [24]; Tabassum et al. [31]
Hot-wire CVD (HW-CVD)	Crystalline Si (c-Si) solar cells	n-type microcrystalline silicon carbide ($\mu\text{c-SiC:H}$ (n))	Pomaska et al. [88]
Plasma-enhanced CVD	Dielectric diffusion barriers, Heterojunction	a- Si _{1-x} C _x :H coatings	Leitl et al. [89]

Deposition technique	Applications	Summary description	Citation
	solar cells, corrosion resistant coatings, and/or micro sensors		
Plasma-enhanced CVD	Hardmask material for dry etching	a-SiC:H thin films	Kwon et al. [90]
Chemical vapor deposition	Wide-bandgap semiconductors	4H-SiC homoepitaxial coatings	Zhao [91]
Hot-wire chemical vapor deposition (HWCVD)	c-Si solar cells	highly transparent nc-SiC:H (n) passivating contacts	Köhler et al. [23]
Hot-wall low-pressure thermal CVD	High-power devices operating under elevated voltage and temperature conditions	Epitaxial 4H-SiC thin films on n-type 4H-SiC with an off-angle of 4° along the Si (0001) crystal direction	Zhao et al. [91]
Thermal CVD	Energy conversion, biotechnologies, nanophotonics, and quantum photonics	SiC NW-based nanophotonic structures doped with O and Er ions	Kaloyeros Jr. et al. [92, 93]
Metal-organic CVD (MOCVD)	High-power and high-frequency electronics	In-situ SiCN cap layer for AlGaIn/GaN high-electron mobility transistors (HEMTs)	Im et al. [93]
Thermal CVD	Power electronics, microelectromechanical systems (MEMS), nanophotonics, and quantum and nonlinear photonics technologies	H-free stoichiometric SiC thin films	Kaloyeros et al. [94]
Microwave plasma CVD	High-power electronic devices	Diamond-SiC composite materials with variable (within some limits) coefficient of thermal expansion (CTE) values	Popovich et al. [95]
High-frequency Induction-heated Halide CVD	Microelectromechanical systems (MEMS) and metal-oxide-semiconductor field-effect transistors (MOSFET) for use under extreme thermal and other conditions	4H-SiC thin film mixtures below 1800 K, 3C- and 4H-SiC mixtures between 1800 K and 1900 K, graphite above 1900 K	Tu et al. [96]
Isothermal CVD	Oxidation resistant thin films on carbon or metal substrates, biomaterials, lithium-ion battery anode materials, electromagnetic absorbing material, and sensors	Thin SiOC films	Wu et al. [97]
Thermal CVD	Hard protective coatings, biological devices and sensors,	SiC multilayered coatings with varying preferred growth orientations Highly <111>-oriented 3C-SiC coatings with distinct surface morphology	Huang et al. [98]; Huang et al. [99]

Deposition technique	Applications	Summary description	Citation
		consisting of hexagonally-shaped pyramidal crystals	
Various CVD and PE-CVD techniques	Electrodes for electrochemical supercapacitors	SiC nanostructures of dimensionality ranging from 0D to 3D	Ojha et al. [100].
Hot-wall thermal CVD	High-power and elevated voltage SiC devices for incorporation in electrical grids, inverters for photovoltaics, and EVs	Epitaxial 4H-SiC thin films on n-type 4° off-oriented Si-face 4H-SiC substrate	Yang, Chen et al. [101]; Chen, Yang et al. [102]
CVD, plasma-enhanced CVD, and their variants	Hard coatings; integrated circuitry including MPUs, SoCs, flash memory, 3D device architectures, and SiPs; high-temperature high-power devices; optical and optoelectronic devices; photovoltaics; nanophotonics, quantum and nonlinear photonics, and optically addressable spin qubits; implantable electronics for microbiology and medical diagnosis, and energy harvesting	Comprehensive review of latest results and accomplishments in CVD SiC _x processing technologies, as well as resulting film properties, performance, and usages	Kaloyeros et al. [4]
High-temperature CVD (HT-CVD)	Heterojunction betavoltaic Si ¹⁴ C-Si energy converter for integrated betavoltaic batteries and low-power cells	Activated heteroepitaxial SiC thin film structures	Dolgopolv et al. [103]
Si-substrate melting followed by carbonization step then hot-wall CVD	Power Electronics	(111) oriented 3C-SiC epitaxial layers on 4-inch Si substrates	Calabretta et al. [14]
Plasma-enhanced CVD	Decorative applications	Hydrogenated amorphous silicon carbide (a-SiC _x :H) interlayers as adhesion promoter a-C:H/a-SiC _x :H/ferrous alloy structures	Goldbeck et al. [104]
Plasma-enhanced CVD	Biomedical devices, including neural implantable devices	Amorphous hydrogenated SiC (a-SiC:H) thin films as passivation layer and protective coating	Greenhorn et al. [105]
Plasma-enhanced CVD	Optical applications, including bioimaging, optical communications, and quantum applications. Integrated functional SiC devices for integrated photonics, such as grating couplers, waveguides, power splitters, polarization beam splitters, and mode converters	500-nm-thick a-SiC layer on a 2.5-μm-thick thermally oxidized SiO ₂ layer on Si	Lu et al. [106]

Deposition technique	Applications	Summary description	Citation
Atmospheric plasma spraying and CVD	Carbon/carbon (C/C) composites for applications in the aerospace field, including in components such as turbines and aeronautical brake systems	SiC protective coatings	Qi et al. [107]
PE-CVD followed by annealing in air	Solar Cells	C-rich amorphous a-SiC films as antireflection and protective coatings	Lukianov et al. [108]
Low-pressure CVD (LP-CVD)	Advanced microelectronic and microelectromechanical system (MEMS) applications	Polycrystalline 3C-SiC thin films on Si	Moll et al. [109]
Synchronized lateral epitaxy (SLE) consisting of instantaneous nucleation of 3C-SiC(111) on 4H-SiC(0001) then step-controlled epitaxy	Power metal-semiconductor field-effect transistors (MOSFETs)	3C-SiC / 4H-SiC stacked structures consisting of single-domain 3C-SiC on single-crystal 4H-SiC wafer with 4 degrees incline from the (0001) direction to the [1120] direction.	Nagasawa et al. [110]
Thermal CVD	Heterostructures consisting of C-face 3C-SiC/4H-SiC for inclusion in high electron mobility transistors (HEMTs) for use in increased-power and elevated-frequency amplifiers for broadband telecommunications, high-resolution LiDARs, and high-power radars	Single-crystal 3C-SiC layer on C-face 4H-SiC substrates	Sazawa et al. [111]
Plasma-enhanced CVD	Nanoelectronic and optoelectronic devices, including Si-based solar cells, Si-based light-emitting diodes, nonvolatile memory and biosensors	Hydrogenated amorphous SiC (a-SiC:H) films with various Si/C ratios	Shan et al. [112]

Table 4.
 Overview of SiC_x chemical vapor deposition processes and applications.

Modeling protocol	Description	Citation
Theoretical modeling using self-consistent charge-based tight-binding density functional theory (SCC-DFTB)-based calculations	This review summarized earlier work that analyzed the effects of stoichiometry on surface morphology and electrical properties of the resulting SiC _x films. It was concluded that: (i) Si-rich surfaces displayed a metallic character, (ii) stoichiometric surfaces displayed semiconducting behavior, and (iii) C-rich surfaces were again semiconducting in character.	Majid [9] review of Rauls et al. [113]

Modeling protocol	Description	Citation
Iowa State University elementary gas phase reaction model and Scientific Research Associates reaction model	An investigation of available elementary gas-phase reaction models for CVD of SiC from methyltrichlorosilane (MTS). The models were analyzed by quadrupole mass spectrometry as they pertain to the MTS total decomposition rate constant, as examined in the temperature range from 960 to 1000°C.	Funato et al. [114]
Analyses based on ab initio density functional theory	An investigation of the SiC CVD mechanisms as a prerequisite for understanding the routes to future (ALD) of SiC. The study examined the reaction energetics of a number of Si and C precursors with bare and H-terminated 3C-SiC (011) surfaces.	Filatova et al. [115]
Density functional theory (DFT) based ab initio pseudo-potential plane-wave (PP-PW) method within the generalized gradient approximation (GGA)	A theoretical investigation of the thermodynamic and structural properties of 3C-SiC materials and their high compression and temperature dependences. Results derived for melting point, thermal conductivity, structural parameters, and Knoop micro hardness were compared with experimental findings.	Daoud et al. [116]
Molecular dynamics simulations using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code	A computational study consisting of a combination of theoretical molecular dynamic simulations with experimental scanning transmission electron microscopy (STEM) examined the structure of defects influencing the properties of 3C-SiC grown hetero-epitaxially on Si (001) substrate, iprimarily: (i) stacking faults characterized by bounding threading dislocation arms, including along unusual directions; (ii) inverted domain boundaries (IDBs); (iii) threading partial dislocations (PDs). The study analyzed TCVD grown 3C-SiC thin films at temperature of 1370°C from the reaction of ethylene (C ₂ H ₄) and trichlorosilane (SiHCl ₃ or TCS) as C and Si sources, respectively	Zimbone et al. [117] Zimbone et al. [118]
Lattice dynamics calculations along with molecular dynamics simulations	An investigation of the role of atomic coordination and mass density in thermal conductivity and fundamental vibrational characteristics of a-SiC by combining systematic atomistic simulations with experimental studies.	Thakur et al. [119]
Ab initio density calculations employing B3LYP Functionals with the 6-31G(d,p) basis set and empirical dispersion corrections D3	The study performed C ₆ H ₆ and CH ₃ quantum chemical calculations as the primary active C-carrying film forming entities in TCVD 3C-SiC _x from the reaction of either CH ₄ or C ₇ H ₈ with SiCl ₄ . The main objective was to derive the chemisorption characteristics of these active groups on several substrate planes, which resulted in a	Huang et al. [99]

Modeling protocol	Description	Citation
	fundamental insight into the morphology and structure of 3C-SiC _x films.	
Molecular dynamics modeling of the electrolytic deposition of SiC films on copper, nickel, and graphite substrates using a Lennard-Jones potential with a Coulomb term in a fluoride melt, while a Morse potential was applied to describe the interaction of deposited Si and C particles with the metal surface	A computer model was developed based on molecular dynamics to simulate the initial SiC film growth stages during its electrolytic deposition both on non-metal and metal surfaces. The model was also employed to determine the effect of various substrates on the structure and difference in the mechanisms of the SiC film growth and examine the role of the potential interaction during the SiC growth on a graphite substrate. Two forms of potentials (Morse and Tersoff) were applied to depict the film interactions with the graphite substrate. For the case of the Morse potential, the SiC film exhibited improved crystallinity and 1.5 times higher adhesion energy to graphite than what was measured for the Tersoff potential. The clusters growth rate on metallic surfaces was also derived.	Galashev et al. [120, 121]

Table 5.
Vapor phase silicon carbide modeling and mechanistic studies.

Deposition method	Applications	Summary description	Citation
Radio-frequency sublimation technique	Solar cell devices	3C-SiC coatings	Syv��rvi et al. [21]
Radio-frequency magnetron sputtering	Hard protective thin films for tritium permeation barriers	a-SiC thin films on tritium permeation barriers (TBPs)	Wu et al. [122]
Direct-current magnetron co-sputtering	Supercapacitors	SiC nanocauliflowers (NCs) as electrode material	Sanger et al. [123]
RF magnetron sputtering	Solar cells and carbon fiber coatings	a-SiC as carbon fiber coating a-SiC as a transition layer for solar cells	Cheng et al. [124] Cheng et al. [125]
Reactive radio-frequency magnetron sputtering	Photovoltaics and light emitting diodes; mechanical and optical protective thin films; optoelectronic devices operating under extreme conditions including high temperatures and elevated voltages;	Transition from a-SiC to nanocrystalline SiC (nc-SiC)	Kefif et al. [126]
Radio-frequency magnetron sputtering using one composite target	High-temperature electronics and sensors	c-SiC and a-SiC thin films	Akshara et al. [127]

Deposition method	Applications	Summary description	Citation
Reactive direct-current magnetron sputtering	Mechanical, electrical, or optical applications that necessitate SiC thin films with mechanical stability and durability	a-SiC _x N _y coatings	Tomastik et al. [128]
Radio-frequency magnetron sputtering	Bioimaging probes, radiation sensors, microwave absorbers, integrated optics and optoelectronics, high-frequency resonators, elevated temperature gas sensors, electronic devices, spintronics, integrated circuitry, micro- and nano-electromechanical systems (MEMS; NEMS), and supercapacitors	15R-SiC rhombohedral nanocrystals	Mourya et al. [129]
Sublimation-based deposition technique	Conversion of irregular solar energy into storable and renewable H ₂ chemical energy through solar-enabled photoelectrochemical H ₂ O splitting	~0.1 cm-thick 3C-SiC thin films of enhanced crystalline quality on 4° off-axis 4H-SiC substrates	Jian et al. [130]
Radio-frequency magnetron sputtering	Enhanced-temperature, high-power, and elevated-frequency electronic systems, x-ray masks, selective solar thin films, photovoltaics, elevated temperature. Gas sensors, phototransistors and optoelectronics, blue-light emitting diodes, and corrosion and wear resistant coatings	a-SiC coatings of different compositions	Tavsanoglu et al. [131]
Magnetron sputtering	Wear-resistant hard protective coatings	Al ₂ O ₃ , SiC, and B ₄ C covalent multi-layer coating	Manivannan et al. [132]
Radio-frequency magnetron sputtering	Aviation, aerospace, optoelectronics	Large-scale (120 mm) a-SiC thin films	Liu et al. [133]
Electron-beam lithography (EBL)	Monolithically integrated photonics: e.g., electrically driven quantum emitters and electro-optic (EO) modulators	530 nm-thick 3C-SiC layers	Powell et al. [134].
Electron-beam evaporation	Optoelectronic devices and solar cells	a-SiC thin films	Zheng et al. [135]
Reactive direct current magnetron sputtering	Photoelectric catalysis (PEC) for photoelectrochemical CO ₂ conversion	Amorphous a-SiC films on Si (100) substrates at room temperature from a high purity silicon carbide 6H SiC target as electrode for use as photocathode	Anas Boussaa et al. [136]
Radio-frequency magnetron sputtering	Solar cells	SiC films as a component of a double layer antireflection coating SiC/MgF ₂	Nussupov et al. [137]

Table 6.
Overview of SiC_x physical vapor deposition processes and applications.

Deposition method	Applications	Summary description	Citation
Horizontal vapor phase epitaxy (VPE)	Integrated circuitry, hard protective coatings for tools, bio-applications, nuclear radiation protection	3C-SiC (cubic) thin films	Geetha et al. [48]
Catalyst-free carbothermal method and post-sonication process	2D structures as a new class of valuable materials for incorporation in high-power electronics and high-temperature applications	2D SiC nanosheets and “nanoflakes”	Chabi et al. [145] Chabi et al. [146]
Fusion bonding followed by thinning and chemical-mechanical-polishing (CMP)	Spin-based quantum technologies for applications in solid-state quantum information processing and sensing	Stack consisting of a layer of 4H-SiC on top of a buried silicon oxide (SiO ₂) layer on silicon	Lukin et al. [147]
Pulse laser	Heterojunction solar cells	As-deposited a-SiC on p-Si(111) substrates and recrystallized by post-deposition annealing	Taha Yaseen [148]
Carbothermal reduction of silica (SiO ₂) and a carbon (C) source	Passive radiative cooling; absorption and emission in the mid-IR to far-IR range	Uniform spherical SiC structures 700–1000 nm in thickness	Feller et al. [16]
Chemical etching followed by neutron irradiation, then annealing	Single-photon emitters, ultrasensitive nanosensors in magnetometry and thermometry, quantum bits (qbits)	Neutron-irradiated and annealed porous SiC (“p-SiC”); SiC nanoparticles (NPs) a few nanometers in diameter	Cs��r�� et al. [63]
Coordinated substitution of atoms (chemical conversion of Si surface atoms to SiC)	High-temperature SiC diodes and transistors, electroluminescent devices	Epitaxial 40-199 nm thick SiC on Si	Kukushkin et al. [149] Kukushkin et al. [150]
Formation of stacking faults by mode-selective phonon excitation using mid-infrared free electron laser	Semiconductors, catalyst supports, and composite materials	Single crystal 3C-SiC(111) on Si(111) substrate	Maeda et al. [151]
High-temperature pyrolysis	3D printing	Cross-linked methyl-phenyl-vinyl-hydrogen polysiloxane as a precursor candidate for a-SiC	Vry et al. [152]
Thermal decomposition	Hard protective thin films for elevated speed impacts in body armor, and incorporation in automotive, aerospace, and aeronautic technologies	Thermally conductive epitaxial graphene of atomic thickness deposited on the Si-face of SiC(0001)	Rejhon et al. [153]
Self-propagating high T synthesis from binary Si-C-based reactive multilayers deposited by magnetron sputtering	Microelectromechanical systems, integrated circuitry devices, photonics, functional ceramic systems, sensorics, quantum electronics	Various forms of crystalline phases (3C-SiC(111), 3C-SiC(220), and 3C-SiC(311)) SiC coatings formed from a 1000 nm-thick Si-C dual-layer stacks	Shekhawat et al. [154]
N/A	Harsh-environment sensing applications	Free-standing SiC membranes	Medina et al. [155]

Deposition method	Applications	Summary description	Citation
Non-thermal plasma synthesis	Integrated circuitry applications under elevated power and frequency conditions, such as: GaN based light emitting diodes, high-frequency Field Effect Transistors, Si substitute in electric vehicle systems, and photovoltaics	SiC nanocrystals (NCs) of controlled 2–4 nm size	Petersen et al. [156]
Sputtering and e-beam evaporation, followed by high-temperature annealing	Power electronics	As-deposited a-SiC thin films on 4H-SiC substrates then recrystallized by post-deposition annealing	Usureau et al. [157]

Table 7.
Overview of SiC_x non-PVD and non-CVD processing methodologies.

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Electrical Properties in Heavily Al-Doped 4H-SiC by Hall-Effect Measurement

Hideharu Matsuura

Abstract

The author explores the temperature-dependent resistivity ($\rho(T)$) and Hall coefficient ($R_H(T)$) of heavily Al-doped 4H-SiC with Al concentrations (C_{Al}) between 2.4×10^{19} and $3.5 \times 10^{20} \text{ cm}^{-3}$ and discusses the underlying conduction mechanisms. At $C_{Al} \leq 1.5 \times 10^{20} \text{ cm}^{-3}$, electrical conduction is dominated by band conduction at high temperatures and nearest-neighbor hopping (NNH) conduction at low temperatures. In contrast, at $C_{Al} \geq 1.8 \times 10^{20} \text{ cm}^{-3}$, band conduction is observed at high temperatures, while variable-range hopping (VRH) conduction prevails at low temperatures. He characterizes the relationships between the electrical conduction mechanisms (i.e., band, NNH, and VRH conduction) and both T and C_{Al} . $R_H(T)$ is observed to become negative in both the NNH and VRH conduction regimes, even though Al-doped 4H-SiC is classified as a p-type semiconductor. A general physical model has been proposed to elucidate the underlying mechanism causing $R_H(T)$ to exhibit negative values in hopping conduction. At $5.2 \times 10^{19} \leq C_{Al} \leq 1.8 \times 10^{20} \text{ cm}^{-3}$, conversely, $R_H(T)$ becomes negative within certain temperature regions of band conduction, for which we present a proposed physical model. The purpose of the chapter is to review his research.

Keywords: heavily Al-doped 4H-SiC, electrical conduction mechanisms, temperature-dependent resistivity, quality of crystalline, temperature-dependent Hall coefficient, sign inversion of Hall coefficient

1. Introduction

As a power semiconductor device, Si n-channel metal-oxide-semiconductor field-effect transistors (MOSFETs) are used in adapter transformers for laptops and smartphones. In contrast, Si n-channel insulated gate bipolar transistors (IGBTs) are employed in inverters for electric vehicles and trains. As wide-bandgap semiconductors, 4H-SiC has recently demonstrated significant potential for high-power and high-operating-temperature electronic devices. Furthermore, 4H-SiC n-channel IGBTs are expected to offer considerably lower on-resistance than current 4H-SiC n-channel MOSFETs. To obtain high-performance SiC IGBTs, it is crucial to produce thick

p-type SiC substrates with extremely low resistance and high crystalline quality for use as IGBT [1].

Gaining a comprehensive understanding of electrical conduction mechanisms in heavily Al-doped 4H-SiC is crucial for reducing the resistance of p⁺-type SiC (i.e., collectors of IGBTs). Studies have been conducted on the electrical transport properties of Al-implanted 4H-SiC [2–4], Al-doped 4H-SiC fabricated using chemical vapor deposition (CVD) [5, 6], and Al-doped 6H-SiC synthesized via physical vapor transport (PVT) [7]. The author has also investigated the temperature-dependent resistivity ($\rho(T)$) and Hall coefficient ($R_H(T)$) of heavily Al-doped 4H-SiC prepared through CVD, PVT, and solution-based methods [8–19]. For heavily Al-doped 4H-SiC produced by CVD, research focused on the interaction among electrical conduction mechanisms (i.e., band, nearest-neighbor hopping (NNH), and variable-range hopping (VRH) conduction) as functions of measurement temperature (T) and Al concentration (C_{Al}) [9].

He has experimentally investigated the relationship between the sign of $R_H(T)$ and different electrical conduction mechanisms [12, 13]. Although Al dopants render 4H-SiC as a p-type semiconductor, heavily Al-doped 4H-SiC exhibits negative $R_H(T)$ values [2, 6, 7, 12, 13] for hopping conduction in two cases, namely, NNH and VRH conduction. He proposed a physical model to explain the sign of $R_H(T)$ for hopping conduction [14–16]. Additionally, he observed negative $R_H(T)$ in certain temperature ranges of band conduction in p-type 4H-SiC and has proposed a physical model to explain this phenomenon [18].

He found out that, in the band and NNH conduction regions, the activation energies ($\Delta E_{RH\text{Band}}$ and ΔE_{RHNNH}) related to $R_H(T)$ were comparable to those ($\Delta E_{\rho\text{Band}}$ and $\Delta E_{\rho NNH}$) for the corresponding $\rho(T)$ values, respectively [12, 13]. Using his proposed model [14–16], he examined the relationship between the net density of hopping charge carriers ($n_{NNH}(T)$) responsible for the NNH current and the density of charge carriers ($n_{HallNNH}(T)$) measured by Hall-effect experiments in NNH conduction. This analysis helps explain why ΔE_{RHNNH} is similar to $\Delta E_{\rho NNH}$ [16, 17]. Moreover, his study was the first to report that $\Delta E_{RH\text{Band}}$ for negative $R_H(T)$ in the band conduction region is approximately equal to $\Delta E_{\rho\text{Band}}$, and he has clarified the underlying reason for this phenomenon [18].

To reduce the fabrication cost of heavily Al-doped 4H-SiC, he has investigated the temperature-dependent resistivity and mobility of heavily Al- and N-codoped 4H-SiC synthesized by PVT, as well as heavily Al-doped 4H-SiC produced via CVD [10, 19] because the growth rate of PVT-grown 4H-SiC is significantly higher compared to CVD-grown 4H-SiC.

The purpose of the chapter is to review his research [9–18] on the electrical properties of heavily Al-doped 4H-SiC epilayers grown by CVD, as measured using Hall-effect measurements.

2. Experimental

Approximately 90- μm -thick Al-doped 4H-SiC epilayers were grown using a horizontal hot-wall CVD system (VP508 GFR, Aixtron) at a substrate temperature of around 1620°C on (0001)-oriented 3-inch n⁺-type 4H-SiC wafers with an 8° off-orientation toward [11 $\bar{2}$ 0] [1, 8]. Four Al/Ti/Al contact dots were deposited on the four corners of the square sample using electron-beam evaporation of Al and Ti in the

van der Pauw configuration [20]. The samples were then annealed at 1000°C under a N₂ atmosphere. The C_{Al} values for the nine samples, as determined by secondary-ion-mass spectrometry, were 2.4×10^{19} , 3.4×10^{19} , 5.2×10^{19} , 9.6×10^{19} , 1.2×10^{20} , 1.5×10^{20} , 1.8×10^{20} , 2.4×10^{20} , and $3.5 \times 10^{20} \text{ cm}^{-3}$, respectively.

The resistivity, $\rho(T)$, and Hall coefficient, $R_H(T)$, were measured using a Hall-effect measurement system (ResiTest8400, TOYO Corp.) over a temperature range of 20–1060 K. The $\rho(T)$ values were obtained using the van der Pauw method [20], while the $R_H(T)$ values were measured under an AC magnetic field with a flux density of 0.35 T and a frequency range of 0.05–0.25 Hz. The methodologies for achieving precise $\rho(T)$ and $R_H(T)$ measurements in heavily doped semiconductors are described in detail in the author's earlier works [10, 12]. The X-ray diffraction (XRD) patterns corresponding to (0004) lattice plane were measured using a high-resolution X-ray diffraction system (SLX-2000, RIGAKU).

3. Results and discussion

3.1 Electrical conduction mechanisms of heavily Al-doped 4H-SiC epilayers

Figure 1(a) illustrates the resistivity at 300 K as a function of C_{Al}. The broken lines in **Figure 1(a)** serve as guides to the eye to illustrate the trend in resistivity for C_{Al} values less than $2.4 \times 10^{20} \text{ cm}^{-3}$, showing that resistivity decreases with increasing C_{Al}, as expected. However, for samples with C_{Al} > $2.4 \times 10^{20} \text{ cm}^{-3}$, the resistivity does not continue to decrease. This observation prompts a discussion on how conduction mechanisms related to C_{Al}.

The electrical conduction mechanisms in semiconductors include band conduction, NNH conduction [21], and VRH conduction [21]. **Figure 1(b)** and **(c)** illustrate the density-of-states distribution ($N(E)$) and the energy band diagram around the valence band edge (E_V) for Al-doped 4H-SiC. The density-of-states, $N(E)$, includes the density of delocalized states within the valence band, the density of localized states in the bandgap above E_V (referred to as the bandtail, represented by a dotted line), and the density of Al acceptors (N_{Al}) at the Al acceptor level (E_{Al}), which does

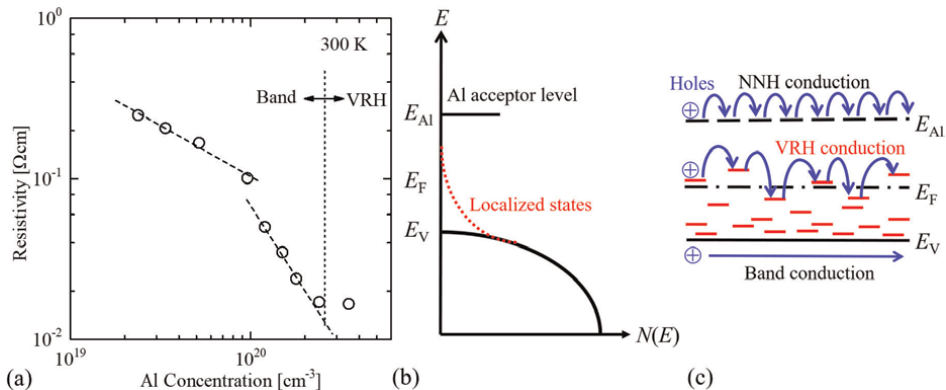


Figure 1. (a) Resistivity at 300 K as a function of C_{Al} for heavily Al-doped 4H-SiC epilayers, (b) density-of-states distribution, and (c) energy band diagram. As C_{Al} increases, the distance between nearest-neighbor Al sites decreases, leading to the hopping of holes between Al sites, and the density of localized states increases above E_V in the bandgap, leading to the hopping of holes between localized states around E_F . After [17].

not exceed the Al concentration (C_{Al}). At low C_{Al} , electrical conduction is dominated by holes in the valence band, corresponding to band conduction. This is attributed to the large distance between neighboring Al acceptor sites, which prevents holes from hopping to adjacent acceptor sites. Conversely, at higher C_{Al} levels, the reduced spacing between Al acceptor sites enables holes to hop between nearest-neighbor Al acceptor sites, resulting in NNH conduction. At very high levels of Al doping, significant local lattice distortion is expected due to the larger covalent radius of substitutional Al atoms (0.125 nm) compared to that of Si atoms (0.117 nm) [1]. This distortion can disrupt the lattice periodicity [11]. This disturbance in periodicity suggests that band tails have formed both above E_V and below the bottom of the conduction band (E_C). The Fermi level (E_F) has been reported to lie between E_V and E_{Al} , even at elevated temperatures in heavily Al-doped 4H-SiC [22]. Consequently, localized states are anticipated to exist near E_F , as depicted in **Figure 1(b)**.

Figure 1(c) depicts the various conduction mechanisms: band conduction, where holes move in the valence band; NNH conduction, where holes at Al acceptor sites hop to the nearest unoccupied Al acceptor sites; and VRH conduction, where holes in localized states near E_F transition to the most accessible unoccupied localized states. When currents from band conduction, NNH conduction, and VRH conduction flow in parallel in the valence band, at E_{Al} , and near E_F , respectively, $\rho(T)$ can be expressed as

$$\frac{1}{\rho(T)} = \frac{1}{\rho_{\text{Band}}(T)} + \frac{1}{\rho_{\text{NNH}}(T)} + \frac{1}{\rho_{\text{VRH}}(T)}, \quad (1)$$

where

$$\rho_{\text{Band}}(T) = \rho_{0\text{Band}} \exp\left(\frac{\Delta E_{\rho_{\text{Band}}}}{k_B T}\right), \quad (2)$$

$$\rho_{\text{NNH}}(T) = \rho_{0\text{NNH}} \exp\left(\frac{\Delta E_{\rho_{\text{NNH}}}}{k_B T}\right), \quad (3)$$

and

$$\rho_{\text{VRH}}(T) = \rho_{0\text{VRH}} \exp\left[\left(\frac{T_0}{T}\right)^{1/4}\right]. \quad (4)$$

Here, $\rho_{\text{Band}}(T)$, $\rho_{\text{NNH}}(T)$, and $\rho_{\text{VRH}}(T)$ represent the temperature-dependent resistivities associated with band conduction, NNH conduction, and VRH conduction, respectively. The terms $\rho_{0\text{Band}}$, $\rho_{0\text{NNH}}$, and $\rho_{0\text{VRH}}$ denote the pre-exponential factors for these conduction mechanisms. T_0 is a constant specific to VRH conduction, and k_B is the Boltzmann constant. As indicated in Eq. (1), the conduction mechanism with the lowest resistivity at a given T becomes dominant. At high temperatures, band conduction dominates due to a substantial increase in hole concentration ($p(T)$) in the valence band. Conversely, at low temperatures, hopping conduction prevails as $p(T)$ decreases significantly.

3.2 Temperature dependence of resistivity

Figure 2(a) presents the Arrhenius plots of $\rho(T)$ (i.e., $\ln \rho(T)$ versus $1/T$) for the 4H-SiC epilayers with C_{Al} values between 2.4×10^{19} and $1.5 \times 10^{20} \text{ cm}^{-3}$.

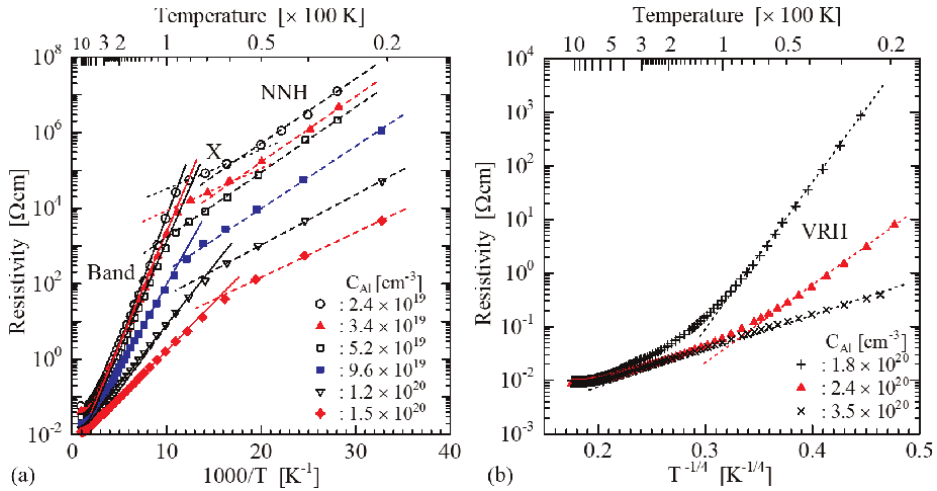


Figure 2. Temperature dependencies of resistivities by (a) Arrhenius plots for the epilayers with C_{Al} values between 2.4×10^{19} and $1.5 \times 10^{20} \text{ cm}^{-3}$, (b) Mott plots with C_{Al} values between 1.8×10^{20} and $3.5 \times 10^{20} \text{ cm}^{-3}$.

At $5.2 \times 10^{19} \leq C_{Al} \leq 1.5 \times 10^{20} \text{ cm}^{-3}$, the data in the Arrhenius plot of $\rho(T)$ can be adequately approximated by two straight lines, indicating that the values of $\ln \rho(T)$ are proportional to $1/T$, in accordance with Eqs. (2) and (3). Therefore, the electrical conduction mechanisms represented by the solid and dashed lines correspond to band conduction at high temperatures and NNH conduction at low temperatures, respectively. The temperature at which these solid and dashed lines, extrapolated from the high- and low-temperature regions, intersect is denoted as T_{BH} . The values of T_{BH} for the samples with C_{Al} values of 5.2×10^{19} , 9.6×10^{19} , 1.2×10^{20} , and $1.5 \times 10^{20} \text{ cm}^{-3}$ were 91.7, 84.7, 75.8, and 62.5 K, respectively.

At C_{Al} values of 2.4×10^{19} and $3.4 \times 10^{19} \text{ cm}^{-3}$, conversely, the data in the Arrhenius plot of $\rho(T)$ can be adequately approximated by three straight lines rather than two. The solid and dashed lines correspond to band and NNH conduction, respectively. According to the Hubbard conduction mechanism [21], the slope of the intermediate region between the band and NNH conduction regions should be less steep than the solid line (band conduction) but steeper than the dashed line (NNH conduction). However, the slope of the dotted line is the shallowest among the three, indicating that the electrical conduction mechanism between the band and NNH conduction regions does not follow Hubbard conduction. Therefore, we refer to this conduction as X conduction and propose alternative hopping conduction mechanisms (the dopant-concentration inhomogeneity model [9, 10] and the emission-hopping model [9]). The temperature where the solid and dotted lines intersect is denoted as T_{BH} , while the intersection of the dotted and dashed lines is referred to as T_{XN} . For the samples with C_{Al} values of 2.4×10^{19} and $3.4 \times 10^{19} \text{ cm}^{-3}$, the values of T_{BH} were 88.5 and 89.3 K, respectively, and the T_{XN} values were 52.9 and 56.8 K, respectively.

Figure 2(b) shows the Mott plots of $\rho(T)$ (i.e., $\ln \rho(T) - T^{-1/4}$ plots) for the 4H-SiC epilayers with C_{Al} values between 1.8×10^{20} and $3.5 \times 10^{20} \text{ cm}^{-3}$. In each Mott plot, the data at low temperatures are well approximated by a straight line. Therefore, according to Eq. (4), the electrical conduction mechanism denoted by the dashed line

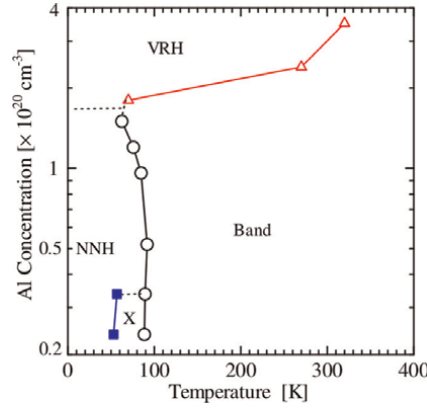


Figure 3. Relationship between electrical conduction mechanisms and values of T and C_{Al} . After [17].

is VRH conduction. T_{BH} can be estimated as the lowest temperature where the data follow Eq. (2) in the Arrhenius plots. At C_{Al} values of 1.8×10^{20} , 2.4×10^{20} , and $3.5 \times 10^{20} \text{ cm}^{-3}$, the values of T_{BH} were 70, 270, and 320 K, respectively [17].

Figure 3 shows the relationship between conduction mechanisms and the values of T and C_{Al} . At $C_{Al} > 2.4 \times 10^{20} \text{ cm}^{-3}$, the dominant conduction mechanism at room temperature is VRH conduction. This is attributed to the local disturbance of lattice periodicity caused by high levels of Al doping. This indicates that the resistivity in VRH conduction remains relatively stable with increasing C_{Al} , whereas it decreases in band conduction.

3.3 Parameters of $\rho(T)$ obtained from Arrhenius and Mott plots

From the slopes of the solid, dashed, and dotted straight lines shown in **Figure 2(a)**, the values of $\Delta E_{\rho\text{Band}}$, $\Delta E_{\rho\text{NNH}}$, and $\Delta E_{\rho\text{X}}$, respectively, can be estimated, where $\Delta E_{\rho\text{X}}$ is the activation energy in the X conduction region. **Figure 4(a)** shows the dependencies of $\Delta E_{\rho\text{Band}}$, $\Delta E_{\rho\text{NNH}}$, and $\Delta E_{\rho\text{X}}$ on C_{Al} . Here, straight lines are used as guides to the eye to illustrate the relationship between the activation energies and C_{Al} . The values of $\Delta E_{\rho\text{Band}}$ decrease with increasing C_{Al} , similar to the dependence of the Al acceptor level (i.e., $E_{Al} - E_V$) on C_{Al} [22, 23].

Similar to the two distinct relationships between $\rho(300)$ and C_{Al} observed in **Figure 1(a)**, there are also two distinct relationships between $\Delta E_{\rho\text{Band}}$ and C_{Al} . This suggests that the C_{Al} -dependence of $\rho(300)$ results from the C_{Al} -dependence of $\Delta E_{\rho\text{Band}}$.

From the dashed line slope shown in **Figure 2(b)**, T_0 values can be estimated. **Figure 4(b)** depicts the $\ln(1/T_0) - C_{Al}$ plot. It is found that $1/T_0$ increases with a power-law scaling as C_{Al} increases, as denoted by the dashed straight line. T_0 is a parameter for VRH conduction (Eq. (4)), described by [21].

$$\frac{1}{T_0} = g(E_F) \cdot \frac{k_B \alpha (E_F)^3}{\beta}, \quad (5)$$

where $g(E_F)$ represents the density of localized states at E_F , $\alpha(E_F)$ denotes the localization radius of a localized state at E_F , and β is a numerical coefficient.

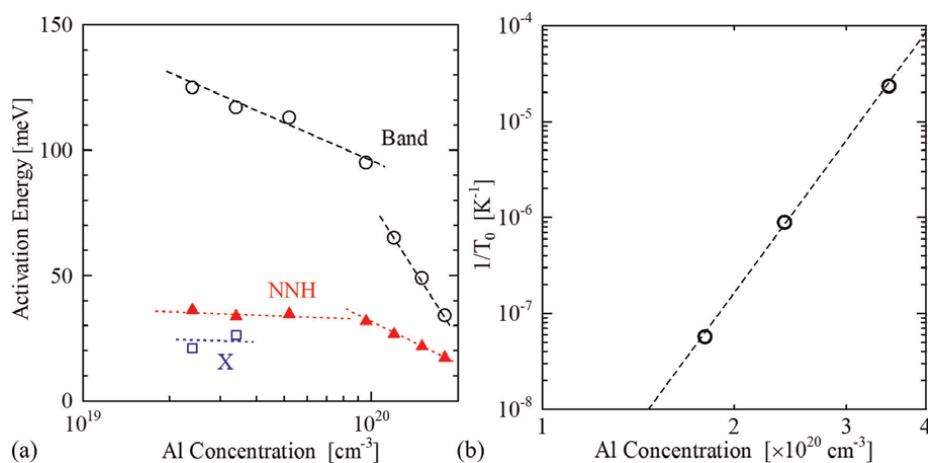


Figure 4. Dependencies of (a) activation energies for band, X, and NNH conduction and (b) T_o on C_{Al} for heavily Al-doped 4H-SiC epilayers.

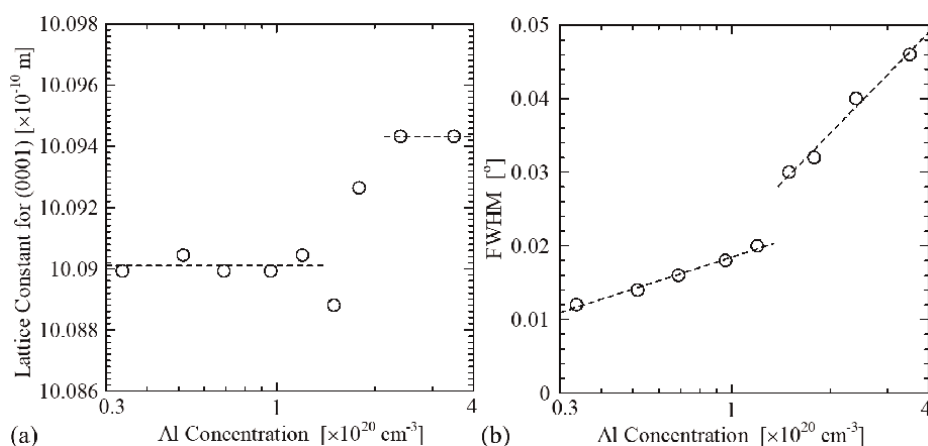


Figure 5. Dependencies of (a) d_c and (b) FWHM (after [19]) on C_{Al} for heavily Al-doped 4H-SiC epilayers.

Because $1/T_0$ is approximately proportional to $g(E_F)$ according to Eq. (5), the increase in $g(E_F)$ with higher C_{Al} suggests a rise in the density of localized states (i.e., the bandtail in **Figure 1(b)**) above E_V . This increase is likely due to the local disturbance of the periodicity of the 4H-SiC lattice.

3.4 Dependencies of (0001) lattice constant and FWHM on C_{Al}

The (0004) lattice constant ($d_c/4$) can be estimated from the peak angle (around 35.6°) of the XRD pattern. **Figure 5(a)** shows the dependence of d_c on C_{Al} . At $C_{Al} \leq 1.2 \times 10^{20} \text{ cm}^{-3}$, the average d_c value is 10.0901 Å, whereas at $C_{Al} \geq 2.4 \times 10^{20} \text{ cm}^{-3}$, the average d_c value is 10.0943 Å, which are denoted by dashed lines.

Figure 5(b) shows how the FWHM of the (0004) lattice constant depends on C_{Al} . The FWHM values increase with higher C_{Al} . Notably, there is a sudden change in

FWHM between C_{Al} values of 1.2×10^{20} and $1.5 \times 10^{20} \text{ cm}^{-3}$, as denoted by dashed lines. At C_{Al} higher than $1.5 \times 10^{20} \text{ cm}^{-3}$, the values of FWHM increase more steeply with rising C_{Al} .

The sudden increases in the lattice constant and FWHM are related to the onset of the VRH conduction at $C_{\text{Al}} \geq 1.8 \times 10^{20} \text{ cm}^{-3}$. This behavior is due to higher levels of Al doping, which disrupt the periodicity of the 4H-SiC lattice and enhance the density of localized states above E_V in the bandgap. Because E_F has been reported to be located between E_V and E_{Al} in heavily Al-doped 4H-SiC even at high temperatures [24, 25], localized states must exist near E_F . As a result, as C_{Al} increases, VRH conduction prevails according to Eq. (1) because $\rho_{\text{VRH}}(T)$ becomes lower than $\rho_{\text{NNH}}(T)$.

3.5 Temperature dependence of Hall coefficient

Figure 6 displays the plots of $\ln \rho(T)$ and $\ln |R_H(T)|$ against $1/T$ on a shared vertical scale for the samples with C_{Al} values of (a) 2.4×10^{19} and (b) $9.6 \times 10^{19} \text{ cm}^{-3}$. Similarly, **Figure 7** presents these plots for the samples with C_{Al} values of (a) 1.5×10^{20} and (b) $1.8 \times 10^{20} \text{ cm}^{-3}$.

In **Figure 6(a)** and **(b)**, the sign of $R_H(T)$ changes once. The temperature at which this sign change occurs is referred to as the $R_H(T)$ sign-inversion temperature (T_{inv1}). For a C_{Al} of $2.4 \times 10^{19} \text{ cm}^{-3}$, T_{inv1} of 76 K is near T_{BH} , whereas for a C_{Al} of $9.6 \times 10^{19} \text{ cm}^{-3}$, T_{inv1} (167 K) is significantly higher than T_{BH} . In **Figure 7(a)** and **(b)**, the $R_H(T)$ sign changes three times. These temperatures are designated as T_{inv1} , T_{inv2} , and T_{inv3} , representing the high, intermediate, and low $R_H(T)$ sign-inversion temperatures, respectively. At a C_{Al} of $1.5 \times 10^{20} \text{ cm}^{-3}$, T_{inv1} and T_{inv2} are approximately 173 K and 172 K in the band conduction region, respectively, where negative $R_H(T)$ is observed only at 172.26 K. T_{inv3} , measured at 67 K, is close to T_{BH} . For a C_{Al} of $1.8 \times 10^{20} \text{ cm}^{-3}$, the $R_H(T)$ values between T_{inv1} (187 K) and T_{inv2} (119 K) are negative, while T_{inv3} , observed at 64 K, is also close to T_{BH} .

In the figures, each dashed-dotted straight line for $|R_H(T)|$ is drawn with the same slope as the dashed straight line for $\rho(T)$ at the corresponding temperature region. It is evident from the figures that the data on $R_H(T)$ closely follow the dashed-dotted

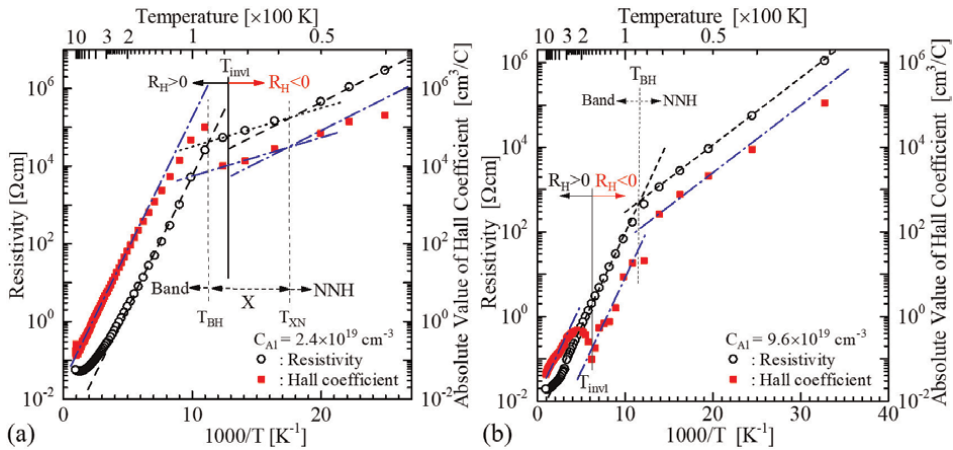


Figure 6. Temperature dependencies of resistivity and Hall coefficient for heavily Al-doped 4H-SiC with C_{Al} values of (a) 2.4×10^{19} and (b) $9.6 \times 10^{19} \text{ cm}^{-3}$ (after [18]).

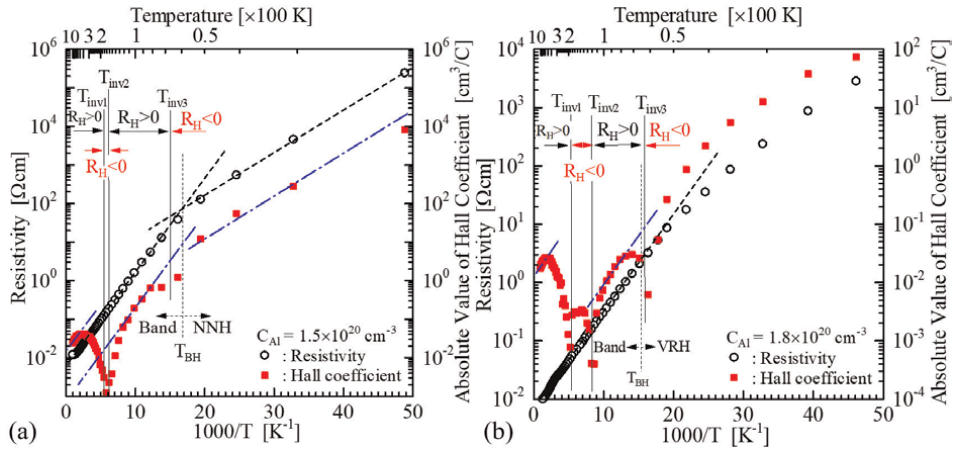


Figure 7. Temperature dependencies of resistivity and Hall coefficient for heavily Al-doped 4H-SiC with C_{Al} values of (a) 1.5×10^{20} and (b) $1.8 \times 10^{20} \text{ cm}^{-3}$. After [18].

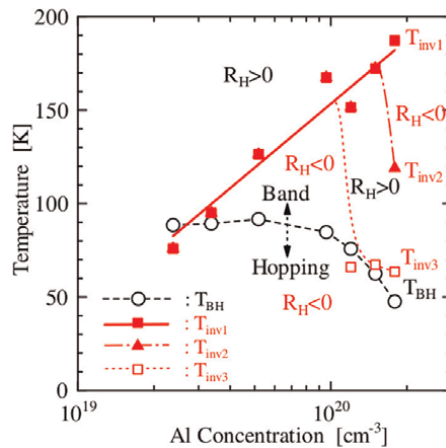


Figure 8. Relationship between the values of the transition temperature (T_{BH}) as well as the sign-inversion temperatures (T_{inv1} , T_{inv2} , and T_{inv3}) and the values of C_{Al} . After [13].

straight line, indicating that $\Delta E_{RH\text{Band}}$ and $\Delta E_{RH\text{NNH}}$ are very close to $\Delta E_{\rho\text{Band}}$ and $\Delta E_{\rho\text{NNH}}$, respectively.

Figure 8 shows the relationship between the transition temperature (T_{BH}) and the sign-inversion temperatures (T_{inv1} , T_{inv2} , and T_{inv3}) with the values of C_{Al} for the epilayers with C_{Al} values of $\leq 1.8 \times 10^{20} \text{ cm}^{-3}$. $R_H(T)$ becomes negative for NNH conduction. Although all T_{BH} values are below 100 K, T_{inv1} increases with the increasing value of C_{Al} and eventually exceeding T_{BH} , indicating that $R_H(T)$ is negative at low temperatures within the band conduction region. At C_{Al} values between 1.2×10^{20} and $1.8 \times 10^{20} \text{ cm}^{-3}$, $R_H(T)$ becomes negative between T_{inv1} and T_{inv2} in the band conduction region. As a consequence, $R_H(T)$ exhibits negative values in part of the band conduction region for heavily Al-doped p-type 4H-SiC with $C_{Al} \geq 5.2 \times 10^{19} \text{ cm}^{-3}$, which is unexpected for a p-type semiconductor where it should be positive in the band conduction region.

3.6 Hall coefficient

Three types of Hall coefficients: $R_{\text{HBand}}(T)$, $R_{\text{HNNH}}(T)$, and $R_{\text{HVRH}}(T)$, corresponding to band, NNH, and VRH conduction, respectively, are considered. **Figure 9** illustrates (a) the layout of the Hall measurement system and (b) the corresponding equivalent circuit for the Hall voltage ($V_{\text{H}}(T)$) being measured. In this configuration, w denotes the thickness of the epilayer, and four electrodes (labeled 1 through 4) are positioned at the corners of the sample. B is the applied magnetic flux density, and I is the applied current (i.e., $I = I_{\text{Band}} + I_{\text{NNH}} + I_{\text{VRH}}$), where I_{Band} , I_{NNH} , and I_{VRH} are the currents corresponding to band, NNH, and VRH conduction, respectively. Here, $V_{\text{HBand}}(T)$, $V_{\text{HNNH}}(T)$, and $V_{\text{HVRH}}(T)$ are the Hall voltages corresponding to band, NNH, and VRH conduction, respectively; and $r_{\text{Band}}(T)$, $r_{\text{NNH}}(T)$, and $r_{\text{VRH}}(T)$ are the resistances between electrodes 2 and 4 for band, NNH, and VRH conduction, respectively. Each resistance is regarded as an internal resistance for the corresponding Hall voltage source.

$V_{\text{H}}(T)$ and $V_{\text{HBand}}(T)$ are, respectively, described as

$$V_{\text{H}}(T) = R_{\text{H}}(T) \frac{IB}{w} \quad (6)$$

and

$$V_{\text{HBand}}(T) = R_{\text{HBand}}(T) \frac{I_{\text{Band}}B}{w}. \quad (7)$$

Similar to $V_{\text{HBand}}(T)$, $V_{\text{HNNH}}(T)$ and $V_{\text{HVRH}}(T)$ are defined as

$$V_{\text{HNNH}}(T) \equiv R_{\text{HNNH}}(T) \frac{I_{\text{NNH}}B}{w} \quad (8)$$

and

$$V_{\text{HVRH}}(T) \equiv R_{\text{HVRH}}(T) \frac{I_{\text{VRH}}B}{w}, \quad (9)$$

respectively. From the equivalent circuit diagram in **Figure 9(b)**, $R_{\text{H}}(T)$ can be derived as [13, 14].

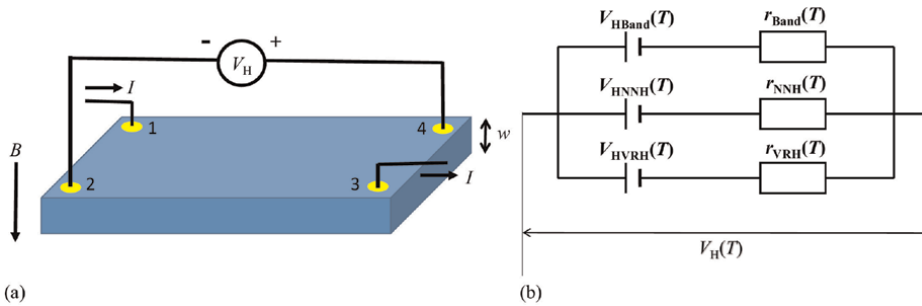


Figure 9. (a) Schematic configuration of the Hall-effect measurement system and (b) equivalent circuit for the Hall voltage. After [17].

$$R_H(T) = \left[\frac{\rho(T)}{\rho_{\text{Band}}(T)} \right]^2 R_{\text{HBand}}(T) + \left[\frac{\rho(T)}{\rho_{\text{NNH}}(T)} \right]^2 R_{\text{HNNH}}(T) + \left[\frac{\rho(T)}{\rho_{\text{VRH}}(T)} \right]^2 R_{\text{HVRH}}(T). \quad (10)$$

When band, NNH, or VRH conduction is dominant, $R_H(T)$ becomes $R_{\text{HBand}}(T)$ or $R_{\text{HNNH}}(T)$ or $R_{\text{HVRH}}(T)$ according to Eq. (10). It is evident from **Figures 6** and **7** that $R_{\text{HNNH}}(T)$ and $R_{\text{HVRH}}(T)$ should be negative in heavily Al-doped 4H-SiC. Therefore, we focus on discussing the sign of $R_H(T)$ in hopping conduction.

3.7 Physical model for the sign of $R_H(T)$ in hopping conduction

In the presence of an electric field ($\mathcal{E}$), an electron typically hops from a bandgap state (such as acceptor, donor, or localized state) to another unoccupied by an electron. Similar to the concept of holes in the valence band, an unoccupied bandgap state can be interpreted as being occupied by a hole. Consequently, hole hopping and electron hopping are analogous processes, differing only in their directions. This implies that the mathematical expression for the hopping probability of holes between bandgap states is identical to that for electrons. Since the density of hopping holes equals that of hopping electrons under $\mathcal{E}$, the net density of hopping charge carriers is referred to as $n_{\text{Hopping}}(T)$.

For a left-to-right hopping current (I_{Hopping}), both holes and electrons (of which n_{Hopping} consists) move upward when B is perpendicularly applied toward the rear of the plane. This motion results in a change in the charge state of the bandgap sites to which the holes and electrons transfer. When the charge state transitions to negative, corresponding to electron hopping under the influence of B , this change in charge state results in a negative Hall voltage. Conversely, when the charge state becomes positive, corresponding to the hopping of holes under B , it contributes to a positive Hall voltage.

Figure 10 shows the equivalent circuit for the measured Hall voltage due to hopping conduction ($V_{\text{HHopping}}(T)$). In this diagram, $V_{\text{Hh}}(T)$ and $V_{\text{He}}(T)$ are the Hall voltages due to the hopping of holes and electrons under B , respectively, while $r_{\text{Hopping}}(T)$ denotes the resistance between electrodes 2 and 4 due to hopping conduction in **Figure 9(a)**.

Assuming that under B holes or electrons, of which $n_{\text{Hopping}}(T)$ consists entirely, can hop, the absolute value of the ideal Hall voltage due to hopping conduction ($V_{\text{H0Hopping}}(T)$) is defined as follows:

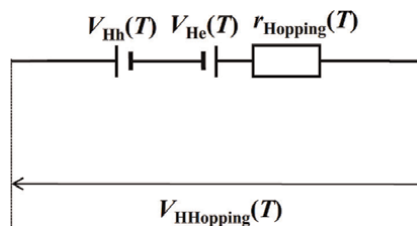


Figure 10.
 Equivalent circuit for the measured Hall voltage due to hopping conduction. After [17].

$$V_{H0Hopping}(T) \equiv R_{H0Hopping}(T) \frac{I_{Hopping}B}{w}, \quad (11)$$

where $R_{H0Hopping}(T)$ is the absolute value of the ideal Hall coefficient for hopping conduction, determined by

$$R_{H0Hopping}(T) = \frac{\gamma_{Hopping}}{qn_{Hopping}(T)}, \quad (12)$$

where q represents the elementary charge and $\gamma_{Hopping}$ denotes the Hall factor for hopping conduction.

Since B influences the hopping charge carriers with a density of $n_{Hopping}$, the ratio of the hopping probability for holes ($P_h(T)$) to that for electrons ($P_e(T)$) under B corresponds to the ratio of the density of hopping sites available for holes to that for electrons. Here,

$$P_h(T) + P_e(T) = 1. \quad (13)$$

Under B , the ratio of the number of holes to electrons accumulating at electrode 4 in **Figure 9(a)** corresponds to the ratio of $P_h(T)$ to $P_e(T)$. Since the internal resistance of the electronic voltmeter is sufficiently high to prevent current flow, the voltage drop across $r_{Hopping}(T)$ in **Figure 10** is nearly equal to 0 V. As a result, the ratio of $V_{Hh}(T)$ to $V_{He}(T)$ in **Figure 10** directly reflects the ratio of $P_h(T)$ to $P_e(T)$;

$$V_{Hh}(T) = V_{H0Hopping}(T)P_h(T) \quad (14)$$

and

$$V_{He}(T) = V_{H0Hopping}(T)P_e(T). \quad (15)$$

Consequently, $V_{HHopping}(T)$ can be expressed as

$$V_{HHopping}(T) = V_{Hh}(T) - V_{He}(T) = V_{H0Hopping}(T)[P_h(T) - P_e(T)]. \quad (16)$$

This phenomenon physically signifies the recombination of holes and electrons that have accumulated at electrode 4. Finally, the Hall coefficient for hopping conduction ($R_{HHopping}(T)$) is expressed as

$$R_{HHopping}(T) = R_{H0Hopping}(T)[P_h(T) - P_e(T)]. \quad (17)$$

Figure 11 presents schematic diagrams illustrating NNH conduction at E_{Al} under the influence of E_{Al} under $\mathcal{E}$ and B . Panel (a) shows the hopping of a hole or an electron for NNH conduction under $\mathcal{E}$ represented in an energy band diagram, while Panel (b) illustrates their hopping under $\mathcal{E}$ and B represented in real space. The inset in Panel (b) indicates the hopping direction of charge carriers, corresponding to the force (F) acting on them for a current (I) flowing from left to right when B is applied perpendicular to the plane.

In NNH conduction, as illustrated in **Figure 11(a)**, under the influence of $\mathcal{E}$, an electron transitions from a negatively ionized Al acceptor (Al^-) site to the nearest neutral Al acceptor (Al^0) site, or a hole transitions from an Al^0 site to the nearest Al^- site.

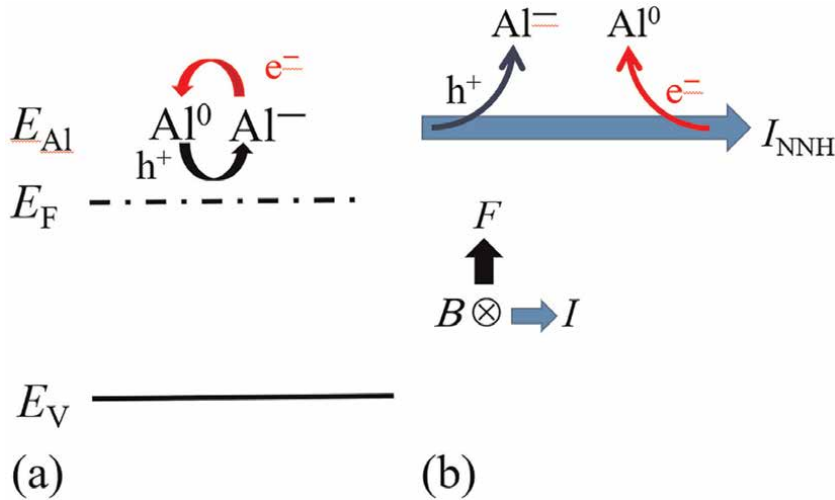


Figure 11.

Hopping of a hole or an electron for NNH conduction is depicted as (a) under $\mathcal{E}$ in an energy band diagram and (b) under $\mathcal{E}$ and B in real space. The inset in (b) illustrates the hopping direction of the charge carriers, representing the force (F) acting on them for a current (I) flowing from left to right, with B oriented toward the back of the plane. After [17].

In **Figure 10**, $V_{\text{HHopping}}(T)$ and $r_{\text{Hopping}}(T)$ are replaced by $V_{\text{HNNH}}(T)$ and $r_{\text{NNH}}(T)$, respectively. Additionally, $V_{\text{H0Hopping}}(T)$, $R_{\text{H0Hopping}}(T)$, γ_{Hopping} , and $n_{\text{Hopping}}(T)$ are replaced by the absolute value of the ideal Hall voltage ($V_{\text{H0NNH}}(T)$), the absolute value of the ideal Hall coefficient ($R_{\text{H0NNH}}(T)$), the Hall factor (γ_{NNH}), and the net density of hopping charge carriers ($n_{\text{NNH}}(T)$) for NNH conduction, respectively.

The existing probabilities of Al^- and Al^0 sites are $f_{\text{A}}(E_{\text{Al}})$ and $1 - f_{\text{A}}(E_{\text{Al}})$, respectively, where $f_{\text{A}}(E)$ denotes the Fermi-Dirac distribution function for acceptors. Since holes can hop from Al^0 sites to the nearest Al^- sites, and electrons can hop from Al^- sites to the nearest Al^0 sites, $P_{\text{h}}(T)$ and $P_{\text{e}}(T)$ are replaced by $f_{\text{A}}(E_{\text{Al}})$ and $1 - f_{\text{A}}(E_{\text{Al}})$, respectively. As a result, from Eq. (17),

$$R_{\text{HNNH}}(T) = R_{\text{H0NNH}}(T) [2f_{\text{A}}(E_{\text{Al}}) - 1]. \quad (18)$$

Consequently, in heavily Al-doped 4H-SiC, $R_{\text{H}}(T)$ becomes negative for NNH conduction because E_{F} is located between E_{Al} and E_{V} ; that is, $f_{\text{A}}(E_{\text{Al}}) < 0.5$.

3.8 Density of hopping charge carriers in NNH conduction

3.8.1 Net density of charge carriers hopping in NNH conduction

When the density of Al^0 (n_{Al^0}) is greater than that of Al^- (n_{Al^-}) (i.e., at $f_{\text{A}}(E_{\text{Al}}) < 0.5$), I_{NNH} can be explained by the hopping of all electrons from Al^- sites to the nearest Al^0 sites. Alternatively, the NNH conduction current can be expressed as the hopping of a fraction of the holes at Al^0 , with a density corresponding to n_{Al^-} , to the nearest Al^- sites. Consequently, these descriptions indicate that

$$n_{\text{NNH}}(T) = n_{\text{Al}^-} = N_{\text{Al}} f_{\text{A}}(E_{\text{Al}}). \quad (19)$$

When n_{Al^0} is less than n_{Al^-} (i.e., at $f_{\text{A}}(E_{\text{Al}}) > 0.5$), I_{NNH} can be explained by the hopping of all the holes from Al^0 sites to the nearest Al^- sites or alternatively by the hopping of a portion of the electrons from Al^- sites, with a density equal to n_{Al^0} , to the nearest Al^0 sites. Therefore,

$$n_{\text{NNH}}(T) = n_{\text{Al}^0} = N_{\text{Al}}[1 - f_{\text{A}}(E_{\text{Al}})]. \quad (20)$$

3.8.2 Density determined by hall-effect measurement in NNH conduction

For NNH conduction, analogous to band conduction, $\rho_{\text{NNH}}(T)$ can be defined as

$$\rho_{\text{NNH}}(T) = \frac{1}{\sigma_{\text{NNH}}(T)} \equiv \frac{1}{qn_{\text{NNH}}(T)\mu_{\text{NNH}}(T)}, \quad (21)$$

where $\sigma_{\text{NNH}}(T)$ represents the conductivity for NNH conduction and $\mu_{\text{NNH}}(T)$ denotes the mobility of hopping charge carriers for NNH conduction.

The density of charge carriers determined by Hall-effect measurements (i.e., $n_{\text{HallNNH}}(T)$) can be defined as

$$R_{\text{HNNH}}(T) \equiv \frac{\gamma_{\text{NNH}}}{qn_{\text{HallNNH}}(T)}. \quad (22)$$

From Eqs. (12), (18), and (22), the relationship between $n_{\text{HallNNH}}(T)$ and $n_{\text{NNH}}(T)$ is obtained as

$$n_{\text{HallNNH}}(T) = \frac{n_{\text{NNH}}(T)}{2f(E_{\text{Al}}) - 1}. \quad (23)$$

Here, the negative and positive values of $n_{\text{HallNNH}}(T)$ are regarded as the electron density and the hole density, respectively.

3.9 Relationship between $\Delta E_{\rho_{\text{NNH}}}$ and $\Delta E_{R_{\text{HNNH}}}$

It is evident from **Figures 6** and **7** that the $R_{\text{H}}(T)$ values can be approximated by the dashed-dotted straight line. This indicates that $\Delta E_{R_{\text{HNNH}}}$ is very close to $\Delta E_{\rho_{\text{NNH}}}$ because the slope of the dashed-dotted straight line matches that of the dashed straight line representing $\rho(T)$ in the NNH conduction region.

Because $\mu_{\text{NNH}}(T)$ depends on T much weaker than $n_{\text{NNH}}(T)$, $\Delta E_{\rho_{\text{NNH}}}$ is approximately equal to the activation energy of $n_{\text{NNH}}(T)$. Because E_{F} is located between E_{Al} and E_{V} , $f(E_{\text{Al}})$ is close to 0 at low temperatures, indicating that the absolute value of $n_{\text{HallNNH}}(T)$ approaches n_{NNH} according to Eq. (23). As a result, $\Delta E_{R_{\text{HNNH}}}$ is close to $\Delta E_{\rho_{\text{NNH}}}$.

3.10 Physical model for the sign of $R_{\text{H}}(T)$ in band conduction

3.10.1 The sign of $R_{\text{H}}(T)$ in the allowed (i.e., valence and conduction) bands

For an isotropic band structure, the effective mass (m^*) in an allowed band (i.e., extended states) is defined in terms of the electron energy ($E_{\text{e}}(k)$) as follows:

$$\frac{1}{m^*} \equiv \frac{1}{\hbar^2} \cdot \frac{\partial^2 E_e(k)}{\partial k^2}, \quad (24)$$

where k denotes the wave vector and $\hbar$ indicates the reduced Planck constant. Because the electron mass (m_e) is positive (i.e., $m_e = m^* > 0$) and the electron charge is negative (i.e., $-q < 0$), the motion of an electron under $\vec{\mathcal{E}}$ and $\vec{B}$ can be described as

$$m^* \cdot \frac{d\vec{v}}{dt} = -q \left[\vec{\mathcal{E}} + \vec{v} \times \vec{B} \right], \quad (25)$$

where $\vec{v}$ is the group velocity.

In the lower energy region of an allowed band (e.g., the conduction band around E_C), the $E_e(k)$ displays upward concavity, that is,

$$\frac{\partial^2 E_e(k)}{\partial k^2} > 0. \quad (26)$$

From Eq. (24), $m^* > 0$, indicating that the charge of the carriers is negative (i.e., $-q$) according to Eq. (25). Therefore, $R_H(T)$ becomes negative.

In the higher energy region of an allowed band (e.g., the valence band around E_V), the $E_e(k)$ displays downward concavity, that is,

$$\frac{\partial^2 E_e(k)}{\partial k^2} < 0. \quad (27)$$

From Eq. (24), $m^* < 0$, indicating that because the mass of the charge carriers should be positive,

$$m_h^* = -m^*, \quad (28)$$

where m_h^* is positive and represents the effective mass of the electron in the valence band. Substituting Eq. (28) in Eq. (25),

$$m_h^* \cdot \frac{d\vec{v}}{dt} = +q \left[\vec{\mathcal{E}} + \vec{v} \times \vec{B} \right], \quad (29)$$

indicating that mobile electrons in the valence band act as if they are positively charged carriers. As a result, $R_H(T)$ becomes positive.

3.10.2 The sign of $R_H(T)$ in allowed minibands formed by excited states of Al acceptors

According to the hydrogenic dopant model [18, 22, 24, 25], an acceptor exhibits a ground-state energy level (i.e., E_A) and the n -th excited-state energy level ($E_{AExc n}$), expressed as [18, 22, 24, 25].

$$\Delta E_A = E_A - E_V = \frac{q^4 m_h^*}{8\hbar^2 \epsilon_r \epsilon_0} \quad (30)$$

and

$$\Delta E_{AExc n} = E_{AExc n} - E_V = \frac{\Delta E_A}{(n+1)^2}. \quad (31)$$

Here, h represents Planck's constant, ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity, and n is a natural number ($1 \leq n < \infty$). The radii of the orbits corresponding to the ground state (a_A^*) and the n -th excited state ($a_{AExc n}^*$) are related as follows: [18, 22, 24, 25].

$$a_{AExc n}^* = (n + 1)^2 a_A^*, \quad (32)$$

where a_0 denotes the Bohr radius (herein, 0.053 nm) and $a_A^* = (4\pi\epsilon_r\epsilon_0\hbar^2)/(q^2m_h^*) = a_0\epsilon_r m_0/m_h^*$.

If the wave functions of the n -th excited states of Al acceptors strongly overlap and interact, they can form an allowed band around the n -th excited level. In particular, this allowed band is referred to as an n -th allowed miniband. This miniband consists of extended states rather than localized states typically found in the so-called impurity band [26]. In consequence, electrical conduction in these allowed minibands is regarded as band conduction.

In 4H-SiC with C_{Al} values on the order of 10^{18}cm^{-3} , the 1st through 4th excited states of Al acceptors are reported to remain localized [24, 25]. Moreover, when C_{Al} is below $5 \times 10^{19}\text{cm}^{-3}$, the first excited states of Al acceptors may remain localized. The allowed minibands formed by their higher-order excited states merge with the valence band, and E_V has been reported to approach E_A as C_{Al} increases [22, 23, 27].

The density of states (i.e., $N(E)$) around E_V is portrayed in **Figure 12**. In **Figure 12 (a)**, higher values of C_{Al} (i.e., $5.2 \times 10^{19} \leq C_{Al} \leq 1.5 \times 10^{20}\text{cm}^{-3}$) facilitate the formation of the first allowed miniband from the first excited states of numerous Al acceptors. This is due to the strong overlap and interaction of the wave functions of the first excited states. Conversely, higher-order allowed minibands are already incorporated into the valence band. As C_{Al} increases, moreover, the $N(E)$ for the first allowed miniband not only increases but also broadens energetically.

High levels of Al doping disrupt the periodicity of the 4H-SiC lattice, resulting in the formation of localized states (e.g., the bandtail) above E_V . Similarly, in **Figure 12(b)**,

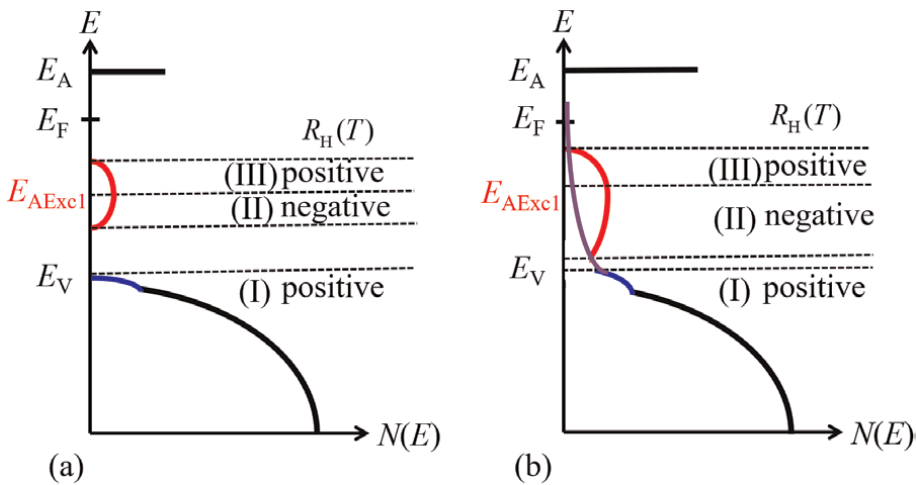


Figure 12.

Density-of-states around E_V for (a) higher C_{Al} (i.e., $5.4 \times 10^{19} \leq C_{Al} \leq 1.5 \times 10^{20}\text{cm}^{-3}$) and (b) much higher C_{Al} (i.e., $\geq 1.8 \times 10^{20}\text{cm}^{-3}$). After [18].

a substantially larger value of C_{Al} (i.e., $\geq 1.8 \times 10^{20} \text{ cm}^{-3}$) generates a pronounced bandtail above E_V , which contains these localized states.

Similar to the allowed bands, such as the valence and conduction bands, $E_e(k)$ in the electronic-energetically lower parts of the allowed minibands shows upward concavity, while $E_e(k)$ in the electronic-energetically upper parts of the allowed minibands displays downward concavity. Consequently, in the electronic-energetically lower part of the first allowed miniband (i.e., Region (II) in **Figure 12**),

$$\frac{\partial^2 E_e(k)}{\partial k^2} > 0$$

and $R_H(T)$ becomes negative, whereas in the electronic-energetically upper part of the first allowed miniband (i.e., Region (III) in **Figure 12**),

$$\frac{\partial^2 E_e(k)}{\partial k^2} < 0$$

and $R_H(T)$ becomes positive. The valence band is referred to as Region (I), wherein $R_H(T)$ is positive.

Consequently, $R_H(T)$ becomes positive, negative, and positive for currents flowing in Regions (I), (II), and (III), respectively, regardless of whether the charge carriers are electrons or holes. In the subsequent discussion, we will focus on understanding the sign of $R_H(T)$ using holes.

A. C_{Al} values of 2.4×10^{19} and $3.4 \times 10^{19} \text{ cm}^{-3}$ (**Figure 6(a)**)

At $T < T_{BH}$, as $\rho_{NNH}(T)$ is less than $\rho_{Band}(T)$, $R_H(T)$ equals $R_{HNNH}(T)$. Therefore, $R_H(T)$ becomes negative.

At $T > T_{BH}$, by contrast, a significant number of holes are present and flowing in the valence band (i.e., Region (I)). This indicates that $R_{HBand}(T)$ is positive. As $\rho_{Band}(T)$ is less than $\rho_{NNH}(T)$, $R_H(T)$ is equal to $R_{HBand}(T)$. As a result, $R_H(T)$ becomes positive.

B. C_{Al} values of 5.2×10^{19} and $9.6 \times 10^{19} \text{ cm}^{-3}$ (**Figure 6(b)**)

If T is substantially lower than T_{BH} , the Al acceptor sites, along with Region (III) in **Figure 12(a)**, are predominantly filled with holes. Some of these holes can hop between Al acceptor sites, suggesting that $R_{HNNH}(T)$ is negative. Meanwhile, other holes flow within Region (III), where $R_{HBand}(T)$ remains positive. As $\rho_{NNH}(T)$ is less than $\rho_{Band}(T)$ at these low temperatures, $R_H(T)$ equals $R_{HNNH}(T)$, indicating that $R_H(T)$ becomes negative.

At $T < T_{BH}$, as T increases, the density of holes in Region (II) also increases, contributing to electrical conduction and resulting in $R_{HBand}(T) < 0$. As $\rho_{NNH}(T)$ is less than $\rho_{Band}(T)$, however, $R_H(T)$ remains equal to $R_{HNNH}(T)$ and thus remains negative.

At $T_{BH} < T < T_{inv1}$, $\rho_{Band}(T)$ decreases to a value lower than $\rho_{NNH}(T)$, indicating that $R_H(T)$ is equal to $R_{HBand}(T)$. Therefore, $R_H(T)$ becomes negative.

When $T > T_{inv1}$, a significant number of holes excited to the valence band (Region (I)) participate in electrical conduction, causing $R_{HBand}(T)$ to become positive. Since $R_H(T)$ is equal to $R_{HBand}(T)$, $R_H(T)$ also becomes positive.

C. C_{Al} values of 1.2×10^{20} and $1.5 \times 10^{20} \text{ cm}^{-3}$ (**Figure 7(a)**)

When $T < T_{BH}$, holes are primarily located at the Al acceptor sites and in Region (III), where they can either hop between the Al acceptor sites or move within Region (III). $R_H(T)$ equals $R_{HNNH}(T)$, indicating that $R_H(T)$ becomes negative.

For $T_{BH} < T < T_{inv2}$, the energetic broadening of Region (III) due to high levels of Al doping allows holes in Region (III) to contribute to electrical conduction even at temperatures higher than T_{BH} , leading to $R_{HBand}(T) > 0$. $R_H(T)$ becomes positive because band conduction is dominant.

As T approaches T_{inv2} , the hole density in Region (II) increases, gradually contributing to electrical conduction. As a result, $R_{HBand}(T)$ shifts from positive to zero. If the hole density in Region (II) exceeds that in Region (III) due to the asymmetric distribution of $N(E)$, $R_{HBand}(T)$ turns negative. Furthermore, with increased Al doping, the allowed minibands broaden energetically, narrowing the energy gap between E_V and the lowest energy level of the first allowed miniband. This suggests an increase in the number of holes in the valence band. Consequently, $R_H(T)$ becomes negative only within a very narrow temperature range, specifically between T_{inv2} and T_{inv1} .

At $T > T_{inv1}$, a large number of holes are present and move through the valence band, suggesting that $R_H(T)$ becomes positive.

D. C_{Al} values of 1.8×10^{20} (**Figure 7(b)**)

When $T < T_{BH}$, holes are primarily located at the Al acceptor sites, near $E_F(T)$, and in Region (III). As shown in **Figure 7(b)**, the appearance of the VRH conduction region instead of the NNH conduction region indicates that $\rho_{VRH}(T)$ is lower than $\rho_{NNH}(T)$. Consequently, the holes predominantly hop between localized states near $E_F(T)$, where $R_{HVRH}(T)$ is negative [15]. Although some holes can flow within Region (III), contributing to a positive $R_{HBand}(T)$, $R_H(T)$ is equal to $R_{HVRH}(T)$ as $\rho_{VRH}(T)$ is less than $\rho_{Band}(T)$. Thus, $R_H(T)$ is negative.

At $T_{inv3} < T < T_{inv2}$, a significant number of holes are excited from the ground states into Region (III) and can flow in it, leading to a positive $R_{HBand}(T)$. Because $\rho_{Band}(T)$ falls below $\rho_{VRH}(T)$, $R_H(T)$ equals $R_{HBand}(T)$, signifying the inversion of $R_H(T)$ to positive.

For $T_{inv2} < T < T_{inv1}$, as T increases, the hole density in Region (II) grows, gradually contributing to electrical conduction. If the hole density in Region (II) surpasses that in Region (III) due to the asymmetric distribution of $N(E)$, $R_{HBand}(T)$ can shift from positive to negative. As a result, $R_H(T)$ becomes negative.

At $T > T_{inv1}$, a large number of holes are excited into the valence band, which primarily contributes to electrical conduction. Therefore, $R_H(T)$ becomes positive.

The aforementioned explanations are qualitatively consistent with $R_H(T)$ and $\rho(T)$, as depicted in **Figures 6** and **7**.

4. Conclusions

The underlying electrical conduction mechanisms in heavily Al-doped 4H-SiC epilayers with C_{Al} values ranging from 2.4×10^{19} to $3.5 \times 10^{20} \text{ cm}^{-3}$ are analyzed using $\rho(T)$ and $R_H(T)$ data obtained from Hall-effect measurements. For epilayers with $C_{Al} \leq 1.5 \times 10^{20} \text{ cm}^{-3}$, the conduction mechanisms are band and

NNH conduction at high and low temperatures, respectively. In contrast, for epilayers with $C_{\text{Al}} \geq 1.8 \times 10^{20} \text{ cm}^{-3}$, the mechanisms are band and VRH conduction at high and low temperatures, respectively. Higher Al doping causes local lattice distortions, resulting in a shift from NNH to VRH conduction at low temperatures. Although Al-doped 4H-SiC is a p-type semiconductor, the sign of $R_{\text{H}}(T)$ can be negative in the hopping conduction region. This behavior is attributed to the hopping of charge carriers (holes or electrons) influenced by the Lorentz force. Moreover, a negative $R_{\text{H}}(T)$ can be also observed within certain temperature ranges of the band conduction region, which is explained by the formation of the allowed miniband from the first excited states of Al acceptors.

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Rapid Thinning in SiC Wafering: Innovations and Impacts on the Value Chain

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Abstract

The semiconductor industry's demand for high-performance, cost-effective substrates has driven innovations in silicon carbide (SiC) wafer manufacturing. SiC's exceptional electrical properties make it an ideal material for high-power, high-frequency, and high-temperature applications. However, traditional wafer thinning methods like mechanical grinding and chemical mechanical polishing (CMP) are time-consuming and costly, limiting throughput and increasing the cost of production. The Rapid Thinning process (RTP) developed by Pureon represents a breakthrough in wafer processing technology, combining advanced pad technology with a diamond slurry to achieve high material removal rates and superior wafer quality. This method reduces cost of ownership of the process up to 40% compared to conventional techniques while minimizing subsurface damage and equipment wear. Integrating Rapid Thinning into the SiC wafering workflow not only streamlines production but also enhances yield and reduces contamination risks. This chapter explores the technical foundations, integration, benefits, and challenges of the Rapid Thinning process, supported by scientific research, highlighting its potential to revolutionize the semiconductor manufacturing value chain and meet the growing demands of next-generation electronic devices. The findings suggest that Rapid Thinning is a viable, cost-efficient solution for the evolving needs of the semiconductor industry.

Keywords: SiC wafering, wafer thinning, PowerElectronics, wafering, SiC, rapid thinning

1. Introduction

Silicon carbide (SiC) has emerged as a cornerstone material in the semiconductor industry, owing to its exceptional combination of electrical and thermal properties. Its high thermal conductivity, high breakdown voltage, and excellent electron mobility are unmatched by traditional semiconductor materials like silicon, making SiC a preferred choice for a wide range of applications. These include high-power, high-frequency, and high-temperature devices essential for electric vehicles, renewable energy systems, and high-performance communication networks. Additionally, there

are materials with similar properties to SiC, such as gallium nitride (GaN), zinc oxide (ZnO), aluminum nitride (AlN), diamond, and indium gallium zinc oxide (IGZO). These substrates have benefits and challenges as they transition into high-volume manufacturing and cost of ownership applications. They offer a range of physical properties that are critical for different applications, like high breakdown voltage, excellent thermal conductivity, and efficient light emission, making them suitable for high-power electronics and optoelectronic applications. These unique properties not only enhance device efficiency but also enable the development of more compact and robust systems, particularly in harsh environments where reliability is critical [1].

The manufacturing process of SiC wafers, however, remains a technical and economic bottleneck. It involves multiple intricate steps, including the growth of SiC boules, precise slicing of these boules into wafers, and subsequent thinning to achieve the desired specifications. Each step contributes significantly to the overall cost, complexity, and quality of the final product. Thinning is particularly critical as it directly affects the structural and electrical performance of the wafer. The challenges associated with these processes underscore the need for technological advancements to improve efficiency, reduce waste, and lower production costs [2].

Traditionally, mechanical lapping, grinding, and chemical mechanical polishing (CMP) have been the predominant methods for wafer thinning. While these techniques ensure high-quality surfaces, they are both time-intensive and costly due to their reliance on precision equipment and consumables. In response to these challenges, the industry has recently embraced innovative approaches to wafer thinning. Laser-based slicing methods can reduce the total material to be thinned. Rapid Thinning techniques, such as grinding and advanced mechanical processes, have gained traction as potential game-changers. These methods aim to enhance throughput and minimize material loss while maintaining the stringent quality standards required in semiconductor manufacturing [3].

This article delves into the Rapid Thinning process, examining its underlying principles and its compatibility with existing SiC wafer production workflows. By integrating Rapid Thinning into the broader semiconductor value chain, manufacturers stand to gain significant cost savings and productivity enhancements. Furthermore, this approach has the potential to redefine the competitive landscape of SiC wafer production by offering a compelling alternative to traditional thinning methods. Notably, substrates such as gallium nitride (GaN), zinc oxide (ZnO), aluminum nitride (AlN), diamond, and indium gallium zinc oxide (IGZO) can also benefit from this new Rapid Thinning process, further broadening its applicability across high-bandgap semiconductor materials. Comparisons between these novel techniques and established processes highlight key benefits, including improved cost efficiency, increased throughput, and superior final wafer quality. Collectively, these advancements underscore the transformative potential of Rapid Thinning in the evolution of the SiC semiconductor industry.

2. Traditional SiC wafer manufacturing process and its limitations leading to rapid thinning

Silicon carbide (SiC) wafer manufacturing is a highly specialized and intricate process designed to meet the stringent demands of high-power and high-temperature semiconductor applications. The traditional SiC wafering process is composed of several sequential steps, each addressing specific requirements for material removal, surface quality, and dimensional precision [4]. However, this process has

inherent limitations that have driven the development of more efficient techniques, such as Rapid Thinning.

2.1. Traditional SiC wafer manufacturing process

Figure 1 illustrates the entire traditional SiC wafer manufacturing process.

2.1.1 Boule slicing

The process begins with slicing SiC boules into thin wafers, a step that traditionally employs wire sawing or, less commonly, laser-based slicing. Wire sawing uses a wire with a specially formulated diamond slurry or an abrasive-coated wire to cut through the hard SiC material with high precision. While proven effective at producing cut wafer blanks, this method often introduces issues such as:

- Subsurface damage.
- Bow and warp in the wafers.
- High kerf loss, leading to wasted material.
- Laser slicing, an alternative technology, offers reduced kerf loss but can cause thermal damage, necessitating additional processing to remove induced defects [5].

2.1.2 Diamond mechanical polishing (DMP)

After slicing, diamond mechanical polishing (DMP) is employed to address subsurface damage caused during the sawing process. This technique typically involves two steps:

- DMP1: Aggressive lapping for bulk material removal.
- DMP2: Finer polishing for surface refinement to minimize the final CMP process time.

Although DMP is effective in preparing wafers for subsequent CMP polishing, it is highly abrasive and poses challenges, including:

- Risk of micro-crack formation
- Long process times
- Extensive reliance on precision equipment and consumables (**Figure 1**) [6].



Figure 1.
Legacy DMP process flow.

2.1.3 Coarse and fine grinding

With the increasing adoption of larger wafer sizes (e.g., 200 mm), coarse grinding (CG) and fine grinding (FG) have become intermediate steps to reduce wafer thickness while improving surface quality. Grinding is a single wafer process versus the batch process of DMP. Coarse grinding achieves rapid material removal but leaves surface damage, which must be corrected by fine grinding. Fine grinding provides better surface finish but requires:

- Increased processing time
- Sophisticated grinders capable of delivering the necessary performance for brittle and hard substrates [3]
- Single wafer process
- High consumable costs, including grinding wheels and abrasives (**Figure 2**) [7]



Figure 2.
Grinding process flow.

2.1.4 Chemical mechanical polishing (CMP)

The final step in the traditional process is chemical mechanical polishing (CMP). CMP achieves the desired wafer thickness and nanometer-level surface smoothness. It uses chemical etchants combined with mechanical abrasives to remove the remaining surface imperfections. Despite its precision, CMP faces several limitations:

- High cost of consumables such as slurries and pads
- Time-intensive processing
- Significant contribution to the overall cost of ownership (COO) for SiC wafer production [8].

2.2 Limitations of the traditional process

While the traditional SiC wafer manufacturing process has been the industry standard for years, its inherent limitations are increasingly challenging as demand for high-performance SiC wafers grows. Key issues include:

- High production costs: Each stage of the process requires expensive consumables and precision equipment, resulting in significant cumulative costs.

- **Material waste:** Kerf loss during sawing and excess material removal during DMP or grinding contribute to low material yield.
- **Time-intensive operations:** Steps like fine grinding and CMP are slow, limiting throughput and increasing production times.
- **Cumulative damage:** The highly abrasive nature of grinding and polishing processes can introduce micro-cracks, subsurface damage, or warp, which require additional corrective steps.

These limitations are particularly pronounced as wafer diameters increase. For instance, 200 mm wafers require tighter tolerances and more precise surface preparation, amplifying the inefficiencies of the traditional process [1].

2.3 The shift toward rapid thinning

To address these limitations, the industry is moving toward the adoption of Rapid Thinning techniques. These innovative methods aim to streamline the bulk material removal and surface preparation steps by combining or replacing traditional grinding and polishing processes with more efficient alternatives. Advantages of Rapid Thinning include:

- **Reduced costs:** By minimizing the reliance on multiple grinding and polishing stages, Rapid Thinning decreases the consumption of costly materials and high multiples of expensive capital equipment.
- **Enhanced throughput:** Faster processing times enable higher production rates, reducing bottlenecks in manufacturing.
- **Improved wafer quality:** Advanced thinning methods reduce the risk of subsurface damage and improve wafer flatness, bow, and warp characteristics.
- **Sustainability:** By optimizing material usage and reducing waste, Rapid Thinning supports greener manufacturing practices.

3. Development of the rapid thinning process

The Rapid Thinning concept has been in development by Pureon for over 2 years, driven by the understanding that the growing demand for silicon carbide (SiC) wafers in various applications necessitates innovative processing approaches. As the market transitions through its lifecycle—shifting from introduction to growth, and eventually toward maturity and commercialization—the need for cost-effective and efficient wafer production becomes increasingly critical. Traditional methods, such as diamond mechanical polishing (DMP), while reliable, face limitations in terms of cost, throughput, and cycle time. Grinding has aimed to address some of these challenges but introduces its own set of complexities.

Recognizing these constraints, the Rapid Thinning project was designed to meet future demands by addressing all critical factors affecting SiC wafer production, including removal rates, wafer geometry, surface and subsurface damage, tool

longevity, compatibility with existing double-side tools, and overall cost of ownership (COO). A major focus was on reducing slurry consumption, as it represents a significant portion of the total wafer production cost. The team identified that developing a composite pad requiring minimal slurry flow was a crucial step toward achieving cost reduction and efficiency.

3.1 Challenges in pad and slurry optimization

During development, it became clear that optimizing the interaction between the composite pad and slurry was paramount to the performance achieved. Similar to traditional DMP processing, this interaction has a profound effect on both removal rates and surface quality. The type and capabilities of the different thinning equipment also impact the performance of the pad and slurry combination. The challenge was to maximize removal rates while minimizing surface and subsurface damage. To address this, the team conducted trials on hundreds of wafers, exploring various configurations and materials, including:

- Pad composition: Testing multiple composite materials with varying physical properties to meet the project's requirements, ensuring durability and compatibility with high removal rates.
- Slurry formulation: Experimenting with different blends of diamond slurries, varying diamond types, concentrations, particle sizes, and carrier fluids to identify the optimal formulation.
- Abrasive-free pad materials: Notably, the composite pad was designed without embedded diamond abrasives, relying instead on slurry optimization to achieve desired performance metrics.

The iterative testing process refined both pad and slurry designs, ensuring the final materials and formulations met the stringent requirements of the Rapid Thinning concept. These cycles of learning were critical and used to optimize polish-ing tool capabilities and overcome their limitations.

3.2 Three-phase development process

The development of the Rapid Thinning concept was structured into three distinct phases, each contributing to the validation and optimization of the process.

3.2.1 Phase 1: In-house testing at Pureon's surface lab

The initial phase was conducted entirely in-house at Pureon's state-of-the-art Surface Lab. Equipped with advanced polishing equipment and metrology tools, including a Lapmaster Wolters AC 400 double-side polishing system, this facility provided a controlled environment for product and process development.

- Wafer testing: The first tests focused on 50 mm wafers, assessing characteristics such as removal rates, edge chipping, and surface quality. These trials allowed rapid feedback on modifications to both the composite pad and slurry formulations.

- Replicate trials: Conducting multiple replicate trials ensured the reliability and consistency of output data.
- Process kinematics: The team also observed that process parameters, particularly those affecting the kinematics of planetary motion, had a significant impact on performance. Adjustments were made accordingly to refine the process.

3.2.2 Phase 2: Collaborative scaling with Lapmaster Wolters

Once the optimal combination of pad, slurry, and process parameters was identified, the project entered its second phase: collaboration with the OEM Lapmaster Wolters. This phase focused on scaling the process to 150 mm and 200 mm wafers in high-volume production settings.

- Testing on AC 1200P tool: Several hundreds of wafers were processed using a Lapmaster Wolters AC 1200P double-side polishing system, replicating production-scale conditions.
- Validation in high-volume production: This phase was crucial for ensuring that the optimized pad-slurry combination and process parameters could meet the rigorous demands of large-scale manufacturing.
- Output alignment: Collaboration with the OEM ensured that the final process configuration achieved the desired throughput, surface quality, and cost-effectiveness to remain competitive in the market.

3.2.3 Phase 3: CMP post Rapid Thinning

The final phase of the project was aimed at understanding the impact of Rapid Thinning on the final CMP process, which is known to be both slow and adding significantly to the cost of the wafer. In addition, requiring the removal of more material to achieve an EPI-quality surface can introduce undesirable effects, such as wafer geometry degradation and increased costs. To mitigate these challenges, the incoming wafer conditions needed to match or exceed those achieved through conventional methods. This would ensure that the existing CMP process time would not need to be extended, maintaining efficiency and cost-effectiveness.

- Comparing the surface quality of Rapid Thinning with conventional DMP or fine grind processes.
- Assessing the impact of Rapid Thinning on the final CMP process step.
- Conducting comprehensive polishing tests and determining the depth of damage on wafers that had been processed in the Rapid Thinning process.
- Collecting detailed data to validate the technical and economic viability of the project.

These focus areas were essential to ensuring that Rapid Thinning could be adopted as a reliable alternative to conventional methods, contributing to a more streamlined and cost-effective manufacturing process.

The CMP testing began with wafers produced under the following conditions:

- Workpieces: 12 SiC wafers, 150 mm diameter
- Equipment used: Lapmaster Wolters AC 1200P
- Pressure applied: 425 daN
- Slurry dosage: 40 ml/min
- Carrier ring thickness: 300 μm
- Pad used: IRINO-PROSIC
- Slurry: PURE-DS-RT

During Rapid Thinning, the wafers were processed at rates of $\geq 1.5 \mu\text{m}/\text{min}$. Over a period of approximately 25 minutes, 40 μm of material was removed. The resulting wafers demonstrated an average total thickness variation (TTV) of less than 1.0 μm , while achieving a surface roughness of approximately 5 nm Sa. These metrics are critical for ensuring that the incoming wafer conditions meet the standards necessary for subsequent CMP processing.

Following Rapid Thinning, the wafers underwent further processing using the following parameters:

- Tool: IPEC 472 polisher
- Polishing pad: Commercially available Power1000
- Slurry used: Commercially available G7
- Downforce applied: 6.5 psi (with 1.3 psi back pressure)

Post-processing analysis and data collection were performed using a ZeGage μm , consistent with the results from conventional DMP processing methods. These findings demonstrate that Rapid Thinning can match or even exceed the performance of traditional processes. Refer to **Figures 3** and **4** for a detailed graphical representation of these results.

The study highlighted that the surface conditions achieved post-Rapid Thinning are comparable to those of conventional methods, offering significant potential for process optimization. Additional tests revealed that surface conditions could be further enhanced by adjusting the final stages of the process or incorporating specialized additives. These improvements would reduce the CMP burden, allowing for shorter CMP process times, lower slurry consumption, and minimized costs.

For instance, modifying the end-of-process parameters, such as reducing tool pressure or introducing optimized polishing additives, could result in smoother surfaces that require less material removal during CMP. This aligns with Pureon's overarching goal to create a more efficient and cost-effective SiC wafer production workflow.

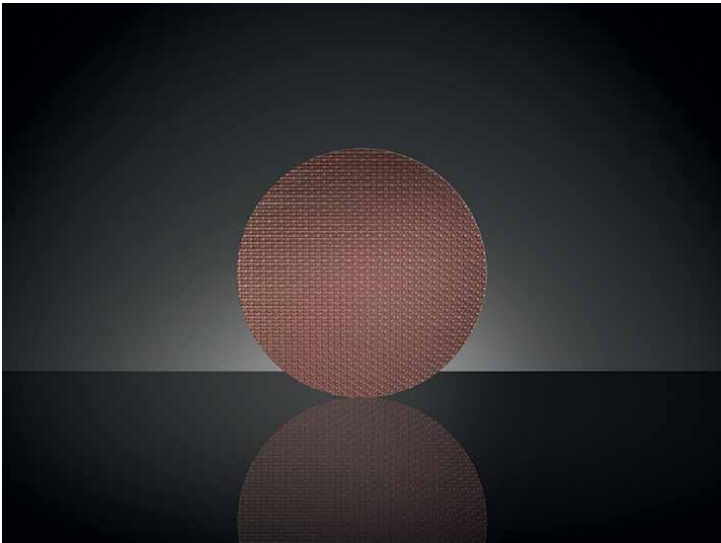


Figure 3.
IRINO-PROSiC pad.

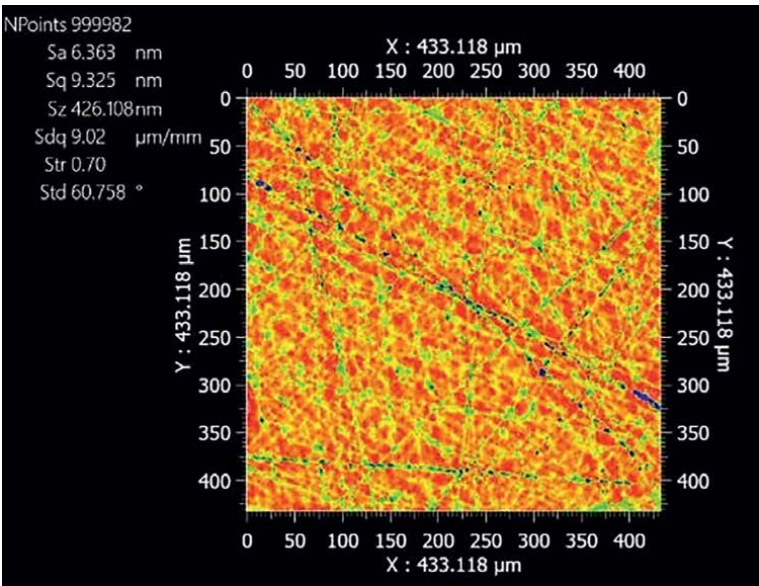


Figure 4.
Post rapid thinning.

Furthermore, implementing such refinements would pave the way for widespread adoption of Rapid Thinning as a robust alternative to traditional methods. By addressing both technical and economic challenges, this approach has the potential to revolutionize SiC wafer production, contributing to faster throughput and lower overall costs.

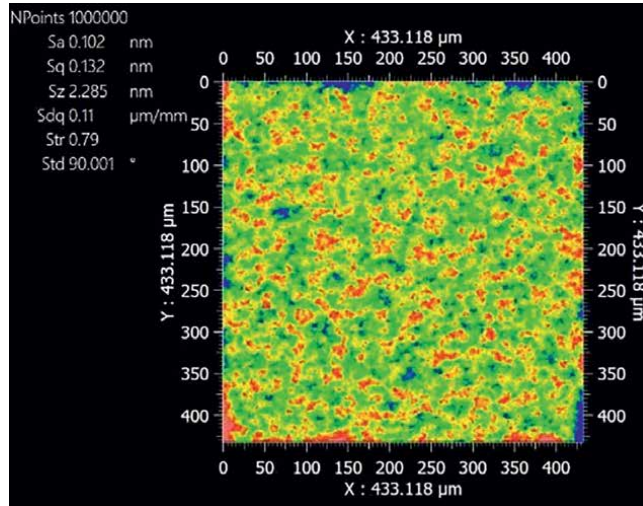


Figure 5.
Post CMP.

3.3 Building a data-driven approach

Over time, the project team compiled an extensive library of data, enabling them to predict and fine-tune removal rates while maintaining surface quality. This data-driven approach provided insights into the delicate balance between efficiency and defect prevention, offering a foundation for ongoing optimization.

While the work on the Rapid Thinning process is ongoing, Pureon has reached a stage where the process is ready for commercialization. The company is now prepared to bring the benefits of enhanced efficiency and cost reduction to the market, addressing the growing demand for high-quality SiC wafers in a competitive and scalable manner.

4. Benefits of the rapid thinning process

The Rapid Thinning process represents a transformative step in silicon carbide (SiC) wafer production, offering numerous advantages over traditional grinding, lapping, and DMP polishing methods. While the more apparent benefits include increased throughput, improved wafer quality, and reduced production costs, the process also provides less obvious advantages that significantly enhance its appeal. These include compatibility with existing equipment, shorter implementation timelines, reduced downtime, and substantial reductions in consumable use and waste management costs. One must also consider the facility impact and footprint of using the existing batch double side tools versus single wafer grinders. This can be significant depending on the number of wafers per run on the batch double side tool.

4.1 Increased throughput and cost reduction

The Rapid Thinning process enables significant improvements in throughput and cost efficiency. By streamlining wafer thinning, the process achieves

a material removal rate of up to 1.5 $\mu\text{m}/\text{min}$, dramatically reducing the time required for this step. These batch processing method can produce as many wafers per hour as up to 4 single station course grinding tools. Coupled with a surface roughness of less than 6 nm, the wafers can proceed directly to the CMP stage without additional processing. One could choose an additional pre-polishing step to minimize the CMP process time depending on the end wafer requirements. Key benefits include:

- Time savings: Traditional DMP processes can take hours, whereas Rapid Thinning reduces total processing time to less than 30 minutes per wafer to remove the same amount of material. It is also done in a batch process and can process up to 30 x 150 mm wafers per cycle.
- Cost efficiency: Rapid Thinning reduces the cost per wafer by up to 44%, driven by lower consumable cost versus grinding wheels and their excessive wear rate, reduced processing steps, and increased pad lifetime for a DMP process. See **Figure 5**.
- Higher material removal rates: Faster removal rates enhance productivity, allowing manufacturers to meet increasing demands for SiC wafers in less time.

These gains are critical as the demand for SiC wafers continues to grow in applications such as electric vehicles, power electronics, and renewable energy systems (**Figure 6**).

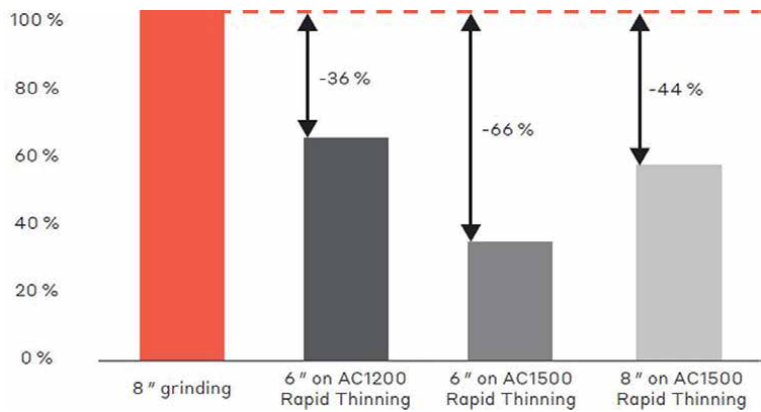


Figure 6.
Normalized COO per wafer rapid thinning versus grinding.

4.2 Seamless integration with existing equipment

One of the standout features of the Rapid Thinning process is its compatibility with existing double-side polishing tools, eliminating the need for costly equipment upgrades. This compatibility shortens the implementation timeline and reduces capital expenditures:

- **Faster deployment:** New equipment from OEMs often has lead times of 12 to 18 months or more, not including installation, training, and qualification. Rapid Thinning allows manufacturers to immediately upgrade their process using current tools.
- **Simplified approval processes:** Transitioning to new equipment often requires extensive customer qualification, potentially adding 15 to 24 months to implementation timelines. Rapid Thinning avoids this bottleneck.
- **Lower capital costs:** By eliminating the need for new equipment, manufacturers save on tool acquisition, spare parts, and operator training.
- **Facility utilization is optimized** by maintaining the batch double side process, the footprint for the equipment could be up to 25% less compared to single wafer grinding processes.

This streamlined integration enables manufacturers to achieve faster throughput and cost reductions without the delays and expenses associated with new tool installations.

4.3 Enhanced surface quality through planetary motion

A key technical advantage of the Rapid Thinning process is its ability to maintain the planetary motion characteristic of traditional polishing. This randomness minimizes the consistent artifacts and subsurface damage typically introduced by grinding processes:

- **Elimination of grinding patterns:** Coarse and fine grinding create parallel arced scratches that can persist after CMP, particularly at the wafer's center. These scratches require additional polishing time to remove.
- **Improved surface consistency:** Rapid Thinning leaves behind a surface similar to legacy polishing methods, ensuring better compatibility with CMP and reducing processing time.
- **Often times if wafers are taken straight from the wire saw step and placed on the vacuum chucks for course grinding, the wafer under vacuum will retain a nonuniformity surface signature from the wire saw, which will show up in the final wafer site flatness, LTV, and SBIR.**

This benefit enhances overall wafer quality while reducing the need for additional polishing, further streamlining the wafering process.

4.4 Reduced downtime and maintenance

The Rapid Thinning process also reduces tool downtime and maintenance requirements, thanks to the improved durability and performance of its pads:

- **Extended pad lifetime:** Rapid Thinning pads often last longer than conventional polishing pads, minimizing the frequency of pad changes.

- Less frequent conditioning: The IRINO-PROSiC pads require less conditioning or dressing between runs while maintaining removal rates and reducing interruptions in the production process.

These advantages translate into increased productivity and lower operational costs, making the Rapid Thinning process particularly attractive for high-volume production environments.

4.5 Lower slurry consumption and waste reduction

A major contributor to the reduced cost of ownership (COO) in the Rapid Thinning process is the significant decrease in slurry consumption:

- Optimized slurry flow rates: The process uses 60 to 80% less slurry compared to traditional DMP methods, with flow rates as low as 40 ml/min.
- Cost savings on consumables: Lower slurry consumption directly reduces costs, while the increased removal rates amplify these savings.
- Waste management efficiency: The reduced slurry flow decreases the volume of waste that must be processed or disposed of, cutting costs for waste treatment systems and logistics.

These reductions not only lower costs but also align with sustainability goals by minimizing environmental impact, making Rapid Thinning an eco-friendly alternative.

5. SiC wafers: Advancing efficiency and cost reduction

The Rapid Thinning process represents a significant leap forward in SiC wafer production. By bypassing traditional DMP and grinding stages, it consolidates multiple steps into a single, efficient process. With material removal rates of up to 1.5 μm/min, a surface roughness of less than 6 nm, and a total processing time under 30 minutes, the process reduces costs and cycle times while maintaining high wafer quality. These performance metrics make Rapid Thinning a compelling alternative for manufacturers aiming to optimize production (Table 1).

Process parameters						Consumables		Results	
n1	n2	n3	n4	Specific pressure	Dosage	Pad	Slurry	Removea rate L2	RA
A	-A	B	-C	0.2 Kg/cm ²	40 ml/min	IRINO PRO-SiC	Slurry #1	1.45 μm/min	4.7–5.9 nm
A	-A	B	-C	0.35 Kg/cm ²	150 ml/min	Suba 800	Slurry #2	0.47 μm/min	1.33–1.44 nm

Table 1.
Comparing the removal rate differences between rapid thinning and traditional DMP under similar process conditions.

6. Rapid thinning: Overcoming bottlenecks and enhancing production flow

Integrating the Rapid Thinning process directly after wire sawing offers a seamless solution to the bottlenecks and inefficiencies often encountered in traditional SiC wafering. By replacing coarse and fine grinding stages, Rapid Thinning improves process flow, reduces handling, and minimizes cycle times. Additionally, its ability to maintain high removal rates with low consumable use makes it a practical and cost-effective option for streamlining production.

7. Exceeding traditional methods: Key metrics

Preliminary testing of Rapid Thinning on 150 mm wafers demonstrates its ability to exceed the performance of traditional methods:

- **Material removal rates:** Achieves up to 1.5 $\mu\text{m}/\text{min}$, compared to 0.5 $\mu\text{m}/\text{min}$ for traditional DMP.
- **Surface roughness (Ra):** Maintains a value of less than 6 nm, eliminating the need for additional polishing.
- **Thickness variation (TTV):** Maintains an average of 1 μm , ensuring consistent wafer quality.
- **Cost savings:** Reduces the cost per wafer by up to 44%, thanks to lower consumable use and faster processing.

These metrics position Rapid Thinning as a superior alternative to conventional approaches, offering unmatched efficiency and cost savings.

8. Challenges and future directions

While the Rapid Thinning process delivers significant benefits, further research and optimization are required to expand its applications. Key areas of focus include:

- **Adapting the process for larger wafers:** With industry trends moving toward 200 mm and larger wafers, further development is needed to scale the process effectively.
- **Enhanced slurry and pad technologies:** Continued innovation in slurry formulations and composite pad designs will ensure sustained improvements in removal rates and surface quality.
- **Operator training and parameter optimization:** Successful implementation will require careful adjustments to process parameters and thorough training for operators.
- **As these challenges are addressed,** the rapid thinning process is poised to become the industry standard for SiC wafer thinning, offering unparalleled benefits in efficiency, quality, and cost reduction.

9. Conclusion

The Rapid Thinning process is a paradigm shift in silicon carbide (SiC) wafer production, overcoming critical challenges in efficiency, cost, and quality that have historically constrained the industry. By leveraging advanced pad and slurry technologies, this method enables high material removal rates of up to 1.5 $\mu\text{m}/\text{min}$, significantly reducing processing times while achieving exceptional surface roughness values of less than 6 nm. The process minimizes wafer subsurface damage, maintains total thickness variation (TTV) under tight tolerances, and ensures the incoming wafer conditions are optimized for the final chemical mechanical polishing (CMP) step. These breakthroughs directly address the need to lower cost of ownership of SiC wafers in high-power, high-frequency, and high-temperature applications, such as electric vehicles, renewable energy systems, and next-generation communication technologies.

One of the most significant advantages of Rapid Thinning is its seamless integration into existing wafering workflows. Unlike conventional or new grinding methods that require costly equipment upgrades or new equipment, this process is compatible with current double-side polishing tools, offering a practical and scalable solution for manufacturers. By streamlining production and reducing the need for additional steps, Rapid Thinning not only lowers capital expenditures but also accelerates implementation timelines. With shorter cycle times, reduced downtime, and lower consumable use, this approach yields cost savings of up to 44% per wafer, making it an economically attractive alternative for both established and emerging market players, not to mention the smaller facility footprint per wafer for Rapid Thinning compared to single wafer grinding.

Beyond immediate cost and efficiency benefits, Rapid Thinning also aligns with the industry's growing focus on sustainability. The significant reduction in slurry consumption—up to 80% less than traditional methods—decreases both material costs and environmental impact. Additionally, the process generates less waste, simplifying disposal and supporting greener manufacturing practices. These features make Rapid Thinning a forward-looking solution that addresses the industry's dual goals of operational excellence and environmental responsibility, making the EVs truly green.

The process further demonstrates its transformative potential by maintaining high levels of wafer quality. By replacing coarse and fine grinding stages with a single, efficient operation, Rapid Thinning minimizes defects such as micro-cracks and bowing while maintaining the planetary motion that enhances surface consistency. These attributes reduce the CMP burden, shortening polishing times and further lowering costs without compromising the stringent quality standards required for SiC applications. Testing has shown that the surface conditions achieved with Rapid Thinning are comparable to, or even better than, those obtained with traditional diamond mechanical polishing (DMP) and grinding methods.

While Rapid Thinning has already demonstrated its viability and readiness for commercialization, the technology also offers significant opportunities for further innovation and expansion. As the industry transitions to larger wafer sizes, such as 200 mm and beyond, continued research into scaling the process will ensure that Rapid Thinning remains a cornerstone technology in SiC wafer production. Similarly, advancements in slurry formulations, pad materials, and process parameters will refine removal rates, enhance surface quality, and expand the method's application to a broader range of devices and industries.

Looking ahead, challenges such as operator training, process optimization, and equipment adaptation for larger wafers must be addressed to fully unlock the potential of this groundbreaking technology. By overcoming these hurdles, Rapid Thinning can establish itself as the industry standard for SiC wafer production, delivering unparalleled benefits in cost efficiency, throughput, and environmental sustainability.

In conclusion, Rapid Thinning is more than a technical advancement—it is a comprehensive solution that redefines the SiC wafering value chain [1]. By bridging the gap between traditional methods and future industry demands, it supports the development of faster, more efficient, and environmentally friendly production workflows. As SiC continues to underpin critical applications in power electronics, electric vehicles, and renewable energy, Rapid Thinning is poised to play a pivotal role in meeting the evolving needs of the semiconductor industry, ensuring both technological progress and competitive advantage for manufacturers worldwide.

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Section 2

Applications and Emerging Technologies

Fluorescent Silicon Carbide Quantum Dots

*Mahdi Hasanzadeh Azar, Zimo Ji, Jahanbakhsh Jahanzamin
and Adrian Kitai*

Abstract

Fluorescent silicon carbide quantum dots have recently attracted attention due to their long-term chemical and optical stability, non-toxicity, biocompatibility, and ultra-low cost. More highly developed III-V and II-V quantum dots lack this combination of positive attributes. We review recent progress in the synthesis protocols and applications of silicon carbide quantum dots together with their resulting optical properties that aim to overcome the well-known indirect bandgap exhibited by all known silicon carbide polytypes. These advancements are accomplished by new approaches to preparing ultrasmall quantum dots that achieve quantum confinement. In addition, surface modifications may be realized by a rapidly growing range of functional groups, conjugated molecules, and shells. Recent advancements in the modeling of fluorescent nanoscale quantum dots using density functional theory are enabling unprecedented insights into fluorescence mechanistics. The application of engineered silicon carbide quantum dots to a range of problems is reviewed. Key target sectors include energy, electronics, optoelectronics, biomedical cell imaging and biosensors.

Keywords: silicon carbide, quantum dots, fluorescence, semiconductors, functional groups

1. Introduction

In the last two decades, silicon carbide (SiC) has emerged as a leading third-generation (wide bandgap) semiconductor due to its high mechanical, thermal, and chemical properties [1, 2]. Existing applications of SiC include turbine blades, engine parts, abrasives, Schottky diodes, and FET/MOSFET transistors [3]. Growth in the value of SiC-based power electronics for electric vehicles, windmill farms, solar farms, and other markets is leading to a cumulative annual growth rate of over 24% and is projected to reach a market value of almost US \$ 6 billion by 2027 [4, 5].

SiC optoelectronic properties are characterized by indirect bandgap behavior. Radiative recombination therefore requires the participation of phonons, defects, surface states, impurities, co-dopants, stacking faults, and controlled porosity have been studied in some detail [6–8].

Of key significance, the quantum confinement effect (QCE) in three dimensions has attracted extensive attention to enable efficient radiative recombination pathways

[9]. Although QCE is known to drive key optical properties in SiC quantum dots (QDs), surface states play a significant role in modifying the optical behavior of ultrasmall QDs. Surface chemistry changes through the use of functional groups, organic molecules, and shells are found to tune the emission wavelength and photoluminescence quantum yield (PLQY) [10]. In addition, SiC QDs have other advantages. SiC benefits from the natural abundance of silicon and carbon elements. While lead perovskites [11–13], CdSe [14], and PbS QDs [15] have achieved high photoluminescence quantum yields (PLQY), they suffer from toxicity and instability in harsh environments. In contrast, SiC QDs are biocompatible, photostable, chemically inert, and can remain stable in water for several months, making them highly suitable for biomedical applications.

Despite the advantages, the synthesis of SiC QDs is not straightforward since SiC single crystals are grown by sublimation from vapor rather than the solidification of a liquid as in the case of silicon. Ball milling, CVD, sol–gel, and carbothermal synthesis methods have been incapable of preparing small sizes of high-quality fluorescent SiC QDs [16]. Recently, a broad spectrum of sophisticated top-down (or bottom-up) and ex-situ (or in-situ) synthesis protocols have been introduced and found effective in synthesizing ultrasmall fluorescent QDs [17].

In this chapter, the recent advances in synthesis protocols, optical properties, and applications of SiC QDs is reviewed.

2. Structural properties of SiC

The substantially covalent Si-C bonds formed by sharing electron pairs in sp^3 hybridized orbitals make SiC one of the stiffest materials with a sublimation temperature of approximately 2700°C and the absence of a melting point [18]. SiC possesses more than 250 polytypes, which are identified by their layer-stacking sequences and relevant crystal structures but are identical in chemical composition. The most common polytypes formed spontaneously under suitable conditions in bulk crystal growth of SiC are 3C, 6H, and 4H.

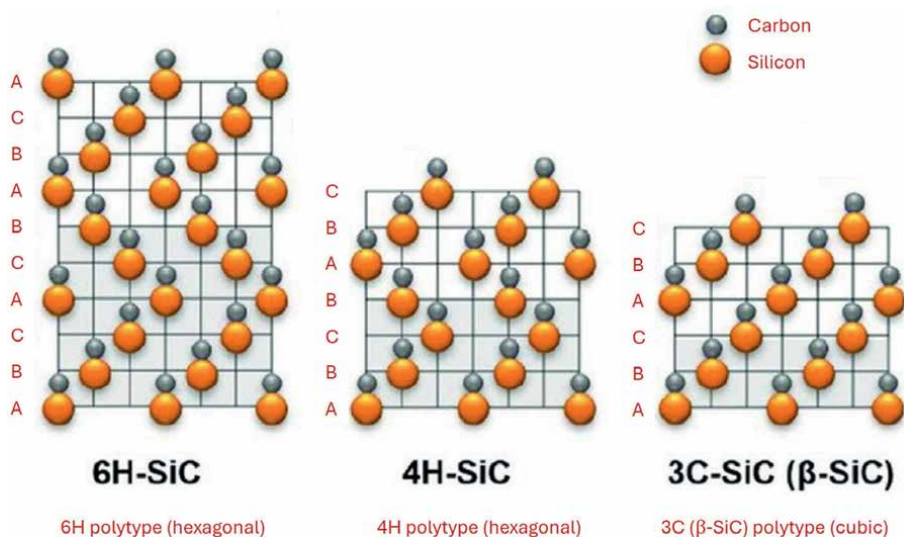


Figure 1.
Stacking sequence of the 3C-, 4H-, and 6H-SiC. After [20].

Property	3C-SiC	4H-SiC	6H-SiC
Space group	F-43 m (216)	P6 ₃ mc (186)	P6 ₃ mc (186)
Lattice constants (Å)	a = 4.3579	a = 3.0817 c = 10.0791	a = 3.0817 c = 15.1173
Band gap (eV)	2.36	3.23	3.02
Electron mobility (cm ² /Vs)	900	800	370
Hole mobility (cm ² /Vs)	40	120	80
Electron affinity (eV)	3.8	3.1	3.3

Table 1.
Physical, optical, and electrical properties of different SiC polytypes.

and 4H, expressed by indicating the number of layers in the unit cell, followed by a letter recording the symmetry of the lattice (C: cubic, H: hexagonal) [19]. **Figure 1(a)** and **Table 1** show the arrangement of atomic layers and various properties of SiC polytypes.

3. Optical properties of SiC

Figure 2(a) shows the electronic band dispersion of 3C-SiC, highlighting its indirect bandgap, which restricts efficient photon emission. Phonon-assisted transitions result in low photoluminescence quantum yield (PLQY) due to competing non-radiative recombination pathways. To overcome this challenge, several strategies can be adopted, including doping, defect introduction, etching, and size reduction.

3.1 Donor-acceptor-pair recombination

Cree Inc. pioneered the commercialization of blue LEDs in the 1980s using a donor-acceptor-pair (DAP) recombination mechanism. In this case, the emission wavelength is determined by the energy difference between donor and acceptor levels, as shown in **Figure 2(b)** [22].

To enhance radiative recombination, various factors should be examined. The first factor is selecting proper donor and acceptor dopants. For example, nitrogen (N)-aluminum (Al) and N-boron (B) doped 4H-SiC could generate green and yellow DAP fluorescence centers [25]. Another parameter is dopant concentration as it affects the average distance between donor and acceptor impurities, influencing the recombination rate. For instance, increasing the boron concentration from low 10^{18} cm^{-3} to mid 10^{18} cm^{-3} significantly doubles the emission intensity [26]. Additionally, photoluminescence (PL) studies show that n-type 4H-SiC produces a much stronger emission intensity than p-type 4H-SiC, even at higher concentrations [27]. This effect is attributed to the position of the Fermi level, which rises in highly n-type material, promoting electron population in the donor level.

3.2 Defects and impurities

Unlike the donor-acceptor pair (DAP) process, fluorescent defects that form isolated quantum systems in SiC emit light through electronic transitions within localized energy states in the bulk band gap [28]. Key defects include the divacancy (V_V),

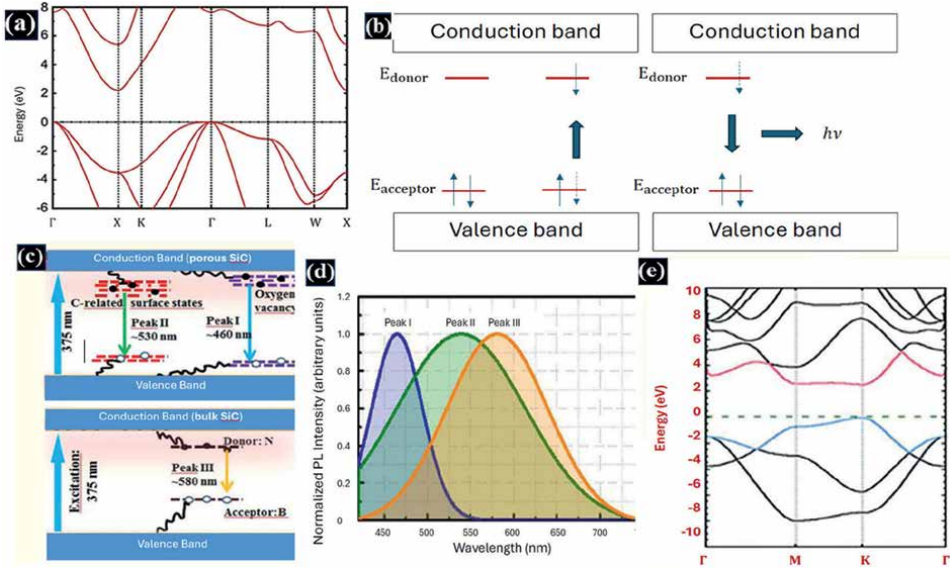


Figure 2. (a) Band structure of 3C SiC. After [21], (b) Mechanism of donor-acceptor recombination. After [22], (c) The possible pathways of radiative recombination in co-doped porous SiC with (d) corresponding PL spectrum. After [23], and (e) Computational band structure of 2D SiC. After [24].

silicon-vacancy (V_{Si}), antisite-vacancy pair ($C_{Si}V_C$), nitrogen-vacancy (N_V), and impurities from transition metals and rare earth elements such as vanadium, titanium, chromium, molybdenum, and erbium.

In addition to point defects, one- and two-dimensional defects also affect SiC optical properties. Some of these, like threading dislocations (TD), act as non-radiative defects, limiting radiative recombination by introducing competing non-radiative pathways [29]. In contrast, stacking faults (SFs) are known to induce radiative recombination in SiC by forming quantum wells [30]. For instance, the single Shockley stacking fault (1SSF) in 4H-SiC behaves like an atomically thin layer of 3C-SiC, which has a lower bandgap than 4H-SiC. SFs also assist in stabilizing the charge states of point defects [31], making them promising for robust room-temperature quantum information processing.

3.3 Porous structures

One approach to radiative recombination enhancement is forming a thin porous layer on bulk SiC. This porous structure was introduced as a promising candidate for blue and white light LEDs [32].

The physics behind porous SiC has been studied extensively. One theory suggests that quantum confinement within the porous regions leads to visible light emission [33]. Another model attributes the PL of porous SiC to surface defects or oxidized surface layers (**Figure 2(c, d)**) [23]. Therefore, the exact mechanism is under debate. Porous SiC on the surface of nitrogen-boron co-doped 6H-SiC can emit light at different wavelengths when excited by UV light. This emitted light may mix with bulk SiC emission to produce white light. Additionally, combining porous structures with other optically active configurations, like DAP-based devices, shows potential for further advancements in optoelectronics.

3.4 Nanostructures

Nanostructures have become a key area of research in SiC materials, with theoretical predictions suggesting various unique properties, including a direct band gap for 2D SiC due to quantum confinement effects (**Figure 2(e)**) [24].

SiC nanowires (NWs) have been widely developed. Photoluminescence (PL) properties of SiC NWs have been observed in both 3C-SiC [34] and 6H-SiC [35] varieties, with emission spectra ranging from 290 to 800 nm depending on the synthesis method and structure. While these optical properties are often linked to the QCE, surface states are likely to play a crucial role in modifying the optical behavior.

In addition to NWs, zero-dimensional structures such as SiC quantum dots (QDs) offer significant potential to modify and enhance the optical properties of SiC. A detailed discussion on SiC QD synthesis is provided in Section 4, followed by a review of their optical properties and applications in Sections 5 and 6.

4. Synthesis methods of SiC QDs

Both top-down and bottom-up methods have been employed to synthesize SiC QDs. Top-down methods involve breaking the strong covalent bonds in SiC wafers or powders. Bottom-up methods employ liquid-based silicon (Si) and carbon (C)-containing precursors to prepare SiC QDs using nucleation, growth, and crystallization processes.

Over the past decade, various techniques such as ball milling, sol-gel, microwave sintering, chemical vapor deposition (CVD), carbothermal reduction, and liquid phase sintering have been used. However, controlling the composition as well as reducing SiC nanocrystals (NCs) to sizes below 5 nm has remained challenging, hindering the emergence of desired optical properties.

To address these limitations, researchers have introduced new methods to efficiently produce stable suspensions of ultrasmall SiC NCs. **Table 2** provides a detailed summary of these processes for further study.

Regarding top-down synthesis, electrochemical or chemical etching methods can synthesize ultrasmall SiC QDs. To achieve this, SiC bulk (or powder) is exposed to a mixture of nitric and hydrofluoric acids under an electric field and UV irradiation. Ultrasonication is then used to break the resulting porous structure into smaller QDs [36].

In terms of bottom-up synthesis, various methods, including non-thermal plasma, electrical discharge in liquid, ion implantation, molten salt electrochemical, electron beam irradiation, laser ablation, and hydrothermal have been recently used to prepare colloidal suspensions of SiC QDs. Non-thermal plasma synthesis involves introducing argon and silicon-carbon-containing gas into the plasma zone, the subsequent application of an electric field which leads to the decomposition of precursors, followed by nucleation, and growth of NCs (**Figure 3(a)**) [45]. Hot electrons then bombard and selectively heat the NC surfaces, providing crystallization energy. Electric discharge in liquid is comprised of two facing Si and C electrodes in a dielectric liquid (**Figure 3(b)**) [39]. In this approach, high voltage pulses above 10 kV are applied, causing spark discharges. This process vaporizes atoms from the electrodes, followed by the nucleation and growth of SiC QDs from the plume of Si and C atoms. Growth stops when the particles are cooled out of the plasma plume. Electron beam irradiation of ionic liquid-based microemulsions is another effective method in

Synthesis method	Materials or media	Phase	Size (nm)	Ref
Chemical etching	1. SiC NPs Diameter: 100–500 nm 2. HNO ₃ and HF (v/v = 1:3)	3C	2.5	[36]
Electrochemical etching	1. n-type polycrystalline 3C-SiC wafer 2. HF/ethanol (HF:C ₂ H ₅ OH = 2:1) 3. DI Water, n-heptane, dichloromethane	3C	1–4	[37]
Non-thermal plasma	1. 1.4 sccm SiH ₄ gas 2. 275 sccm Ar gas 3. 150 sccm C ₂ H ₂ gas	3C	4.2	[38]
Electrical discharge in liquid	1. Pure silicon, carbon, and tungsten 2. Cyclohexane (CHX) and tetramethylsilane (TMS)	—	~10	[39]
Ion implantation	1. bulk-Si substrate 2. SiO ₂ coating 3. C ⁺ ions	3C-, 8H-, 6H-, and 4H-SiC	2–6	[40]
Molten salt electrochemical	1. SiO ₂ powder (15 nm) 2. Carbon powder (10 nm) 3. 15 wt.% polyvinyl butyral (PVB)	C	8–14	[41]
Electron beam irradiation	1. 1 g Trimethoxy[3-(phenylamino)propyl]silane 2. 18 g TX-100 3. 2 g [BMim]PF ₆ 4. 2 g [OMim]PF ₆	3C and H	7–14	[42]
Laser ablation	1. Non-doped 4H and 6H wafer 2. Acetone	3C 4H	10 30–80	[43]
Hydrothermal	1. SiC Powders 2. Water	2D 6H QDs	3 nm	[44]

Table 2.
Summary of synthesis methods of SiC QDs.

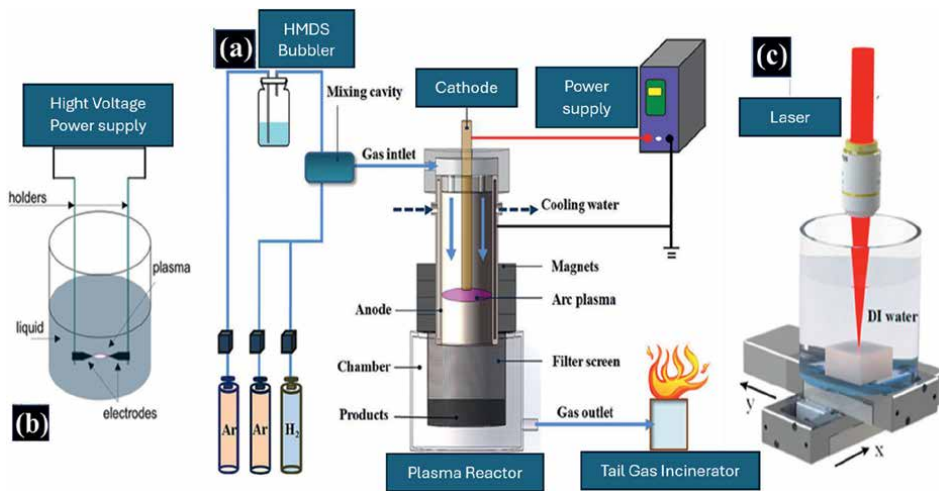


Figure 3.
(a) Schematic diagram of the non-thermal process design. After [45] and (b) electrical discharge setup for the synthesis of SiC NCs. After [39], and (c) Experimental setup for the PLA in liquid. After [43].

the synthesis of SiC QDs. In this process, a high-energy electron beam (10 MeV) is applied to a microemulsion, including 1-butyl-3-methylimidazolium hexafluorophosphate ([BMim]PF₆), TX-100, water, and Trimethoxy[3(phenylamino)propyl] silane, producing 3C-SiC QDs [42]. It was revealed that the optical properties of the final product are greatly dependent on the concentration and type of precursors. Despite the above ex-situ bottom-up processes, ion implantation was introduced as an in-situ method to synthesize SiC QDs. In this method, SiC QDs are prepared inside various substrates. For instance, 2 nm SiC QDs with a density of $2 \times 10^{12} \text{ cm}^{-2}$ were formed inside SiO₂ by double ion implantation of Si⁺ (dose: $6 \times 10^{16} \text{ cm}^{-2}$ with acceleration energy (AE) of 60 keV)/C⁺ (dose: $4 \times 10^{16} \text{ cm}^{-2}$ with AE of 25 keV) at temperatures between 200 and 400°C [40].

Apart from the abovementioned processes, pulsed laser ablation (PLA) and hydrothermal have been proposed. In the top-down case, a laser beam is used to ablate material from a SiC target in a solvent like ethanol (**Figure 3(c)**) [43]. PLA can be either a top-down or bottom-up method—detachment of fragments from the target is considered top-down, while nucleation and growth classify the process as bottom-up. In the latter case, the hydrothermal setup consists of a stainless-steel autoclave with a Teflon liner, solvent, precursors, and pH controllers. For top-down synthesis, powders are used as the starting material and the autoclave is heated in an oven at high temperatures (up to 250°C) and pressure, causing large SiC precursor particles to break down into smaller ones [44]. In contrast to top-down, a bottom-up hydrothermal approach uses silicon and carbon-containing compounds, offering better control over particle size, ease of use, and high photoluminescence quantum yield (PLQY). However, the final product has not been pure SiC but rather Si-doped carbon, Si, and silicon carbon QDs [46, 47].

5. Optical properties of SiC QDs

As a result of quantum confinement, excitons, or bound electron–hole pairs, are stabilized by confinement in quantum dots, thereby overcoming momentum differences and inducing radiative recombination. The exciton Bohr radius is a meaningful measure of the regime of the quantum confinement scale. For a QD radius above this Bohr radius, quantum confinement is controlled by an effective mass approximation [48]. But below the Bohr radius, more dramatic quantum confinement takes place. In addition to QCE, there is another mechanism of emission via surface state recombination in QDs. When the QDs are extremely small, a majority of the atoms reside on the surface of the QD, and due to the presence of various functional groups, the electronic structure and emission can be tuned. As a result of both quantum confinement and the wide range of surface states, the SiC NC has seen intense attention as a candidate for achieving high PLQY in SiC material.

The QCE which involves the spatial confinement of photogenerated electrons and holes within quantum dots (QDs) was initially introduced to explain the significantly higher photoluminescence (PL) intensity (over 1000x) of 3C-SiC QDs compared to SiC polycrystalline wafers. However, understanding the origin of emissions in QDs is much more complex [49].

Determining whether optical properties are controlled by quantum confinement or surface/defect states is challenging and can be misleading. While a PL emission spectrum offers basic information, factors like excitation spectrum, quantum yield, spectral FWHM (full width at half maximum), and Stokes shift

provide deeper insights into the underlying mechanisms. For instance, in one study, increasing the excitation wavelength from 340 to 400 nm caused a redshift in the 3C-SiC QD PL emission peak from 417 to 451 nm, indicating excitation-dependent photoluminescence (**Figure 4(a)**). This is due to the size distribution of QDs in the sample, where higher excitation wavelengths fail to excite QDs with larger band gaps, thereby shifting the PL peak towards the red, tending towards the properties of bulk SiC [50, 51].

In contrast to the above, in some studies, it was revealed that by increasing the excitation wavelength the PL peak slightly blueshift or remains constant, showing excitation-independent PL behavior. This is attributed to smaller NCs, where emission is governed by surface states rather than QCE (**Figure 4(b)**) [52].

Density functional theory (DFT) modeling, combined with experimental data for various SiC QDs, suggests that both surface states and core quantum confinement states contribute to “dual feature” PL spectra. Surface states dominate PL for smaller QDs where the core bandgap exceeds surface state absorption, while core states dominate in larger QDs, with an expected dependence on QD size [55].

Using both experimental and simulation surveys, the boundary between QC and surface state effects was quantitatively calculated. As shown in **Figure 4(c)**, ultrasmall QDs smaller than 2.85 nm exhibit molecular behavior and surface states primarily control radiative recombination. For QDs between 2.8 and 3.75 nm, there is a transition between the quantum confinement effect (QCE) and surface state recombination. Larger particles, up to 5.8 nm, close to the Bohr diameter of 3C-SiC (2.0 nm), follow the effective mass approximation. It is also predicted that QCE diminishes for NCs larger than 5.8 nm [53].

Regarding surface states, the effect of various functional groups on optical properties was assessed. **Table 3** shows that using various functional groups (H-, HO...C=O, Si-O, Si = O, -COOH, -OH, C=O, Si-C-O), shells (carbon or silica), and surface point defects (Si vacancies), a broad PL spectrum from blue to NIR is covered, and significant PLQY can be achieved (**Table 3** and **Figure 4(d)**) [54].

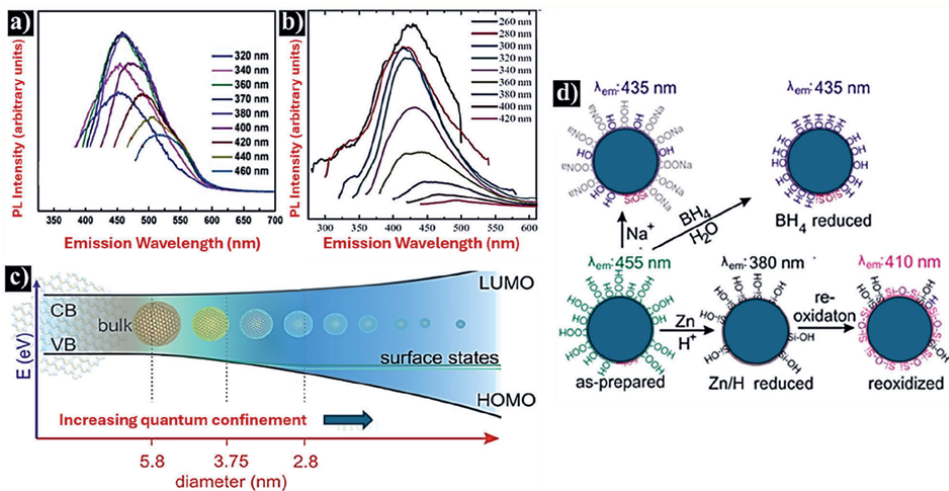


Figure 4. (a) PL spectra of 4H-SiC NCs. After [50] and various emissions under different excitation wavelengths. After [51], (b) PL spectra of SiC NCs synthesized by PLA [52], (c) The relation between band gap and size of SiC QDs. After [53], and (d) The effect of different surface terminations on the emission of SiC NCs. After [54].

QDs	D (nm)	Study	Emission mechanism	Surface groups and molecules	E_{exc} (eV or nm)	E_{m} (nm)	PLQY (%)	τ (ns)	Ref
3C	2 and 2.5–5.5	E	QCE and SS	—	260–300 (SS) 300–420 nm (QCE)	413–495	—	—	[52]
6H	3.2–9.7	E	QCE and SS	SiO ₂ -passivation	360–440 nm	440–560	0.58	6.4	[56]
3C	~14	E	SS	BSA-terminated	320 nm	350–500	—	—	[57]
3C	1.5	S	SS	H-terminated	$E_{\text{g}} = 5.97$ eV	—	—	—	[58]
3C	1.83	E	QCE and SS	HO...C=O	326 nm (SS)	438 (SS)	—	—	[59]
—	1–4	E	QCE and SS	COOH-terminated	320 nm	450	—	—	[54]
—	1–4	E	QCE and SS	OH-terminated	—	435	—	—	[54]
—	1–4	E	QCE and SS	Si-O-terminated	—	410	—	—	[54]
3C&H	3.2–9.7	E	SS	C=O	327 nm	429	0.22	15 ns	[58]
3C&H	3.2–9.7	E	SS	Unknown	365 nm	517	0.13	—	[58]
3C&H	3.2–9.7	E	SS	Si = O	503 nm	560	0.16	70 ns	[58]
C	2.3	E	SS	Si-C-O	340 nm	450–550	—	—	[60]
6H	10–250	E	SS	Si vacancies (V _{Si})	800 nm	850–1000	—	—	[61]

D = average size (nm), E = experimental, S = simulation, SS = surface states, QCE = quantum confinement effect, E_{exc} = excitation wavelength (nm), E_{m} = emission wavelength (nm), τ = carrier lifetime, N = not mentioned,

Table 3.
The optical properties of SiC QDs.

6. Key applications and potential applications of SiC

6.1 Cell imaging and detection

SiC QDs have been extensively studied for biological applications due to their small size, stable fluorescence, and biocompatibility. Fan et al. [62] demonstrated the use of 3C-SiC QDs (3.9 nm) as fluorescent labels for human fetal osteoblast cells, achieving bright fluorescence throughout the nuclei of the cell. QDs have a Gaussian size distribution (**Figure 5(a)**). Cytotoxicity tests indicated no significant impact on cell viability even at concentrations up to 100 $\mu\text{g/mL}$ after 48 hours. Similarly, Botsoa et al. [65] mixed 1.6 nm 3C-SiC QDs with fibroblast cells, observing efficient cellular uptake and strong fluorescence signals, both in the membrane and nucleus. Chen et al. [66] compared the performance of various sizes of SiC NPs (30, 80, 620 nm) for stem cell labeling and tracking. It was revealed that 620 nm NPs offered superior photoluminescent and photoacoustic performance. These NPs had negligible effects on cell viability and proliferation, even at varying concentrations, and enabled effective tracking of stem cell-derived adipocytes and osteocytes.

It was revealed that the interaction of SiC NPs with live cells is significantly influenced by SiC QDs surface functional groups. One study showed that while “as-prepared” SiC NPs led to almost complete cell death, amino- and hydroxyl-terminated NPs enhanced metabolic activity and altered cell morphology, with potential applications in immune cell therapies [67]. Bokseveld et al. [68] used

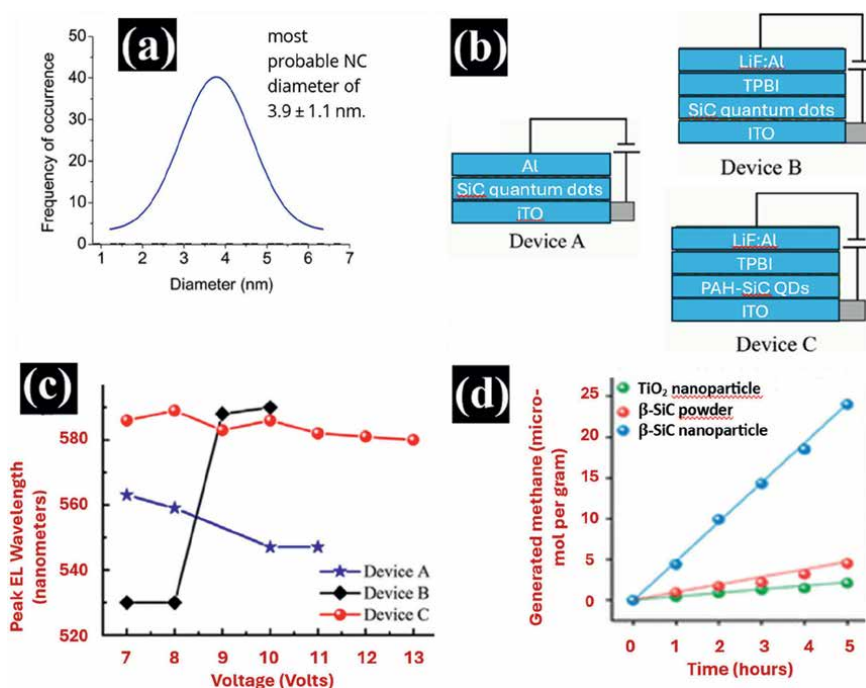


Figure 5.

(a) Strong fluorescence signal observed in the cytoplasm and nuclei of hFOB cells after 3C-SiC nanocrystals uptake. After [62], (b) Electroluminescent WLEDs featuring three different configurations: A, B, and C, (c) Performance of EL devices under varying voltage conditions. After [63], and (d) Methane (CH_4) evolution over time, compared to other photocatalytic materials. After [64].

PEG-folate functionalized SiC NPs to target cancer cells with multiphoton microscopy, effectively distinguishing cancer cells without affecting healthy cell proliferation. In another survey, HPG-coated NPs demonstrated reduced cytotoxicity even at high concentrations and were used in SiC-PDA-GNP complexes for photothermal applications, providing controllable heat output for various biomedical uses [69].

In addition to cell imaging, SiC QDs have been used in detection. For instance, Chen et al. [50] demonstrated a highly selective method for detecting Fe^{3+} ions. Fe^{3+} ions are crucial in various biological processes, including cellular oxygen uptake and metabolism, making their detection significant for monitoring abnormal levels in biological fluids. The reaction between Fe^{3+} and the oxygen-containing groups of 4H-SiC QDs led to fluorescence quenching of the QDs, with a linear decrease in fluorescence intensity observed as the Fe^{3+} concentration increased from 1 to 20 μM . In a similar approach, Yang et al. [70] investigated the use of 20 nm SiC NPs for detecting Au^{3+} ions through aggregation-induced fluorescence quenching. This method addresses concerns about environmental pollution and biological toxicity associated with gold used in industrial applications. The total fluorescence quenching and formation of a yellowish precipitate upon exposure to Au^{3+} ions confirmed successful detection with a limit of detection (LOD) of 10^{-5} M.

6.2 Optoelectronics and electronics

The integration of green and red quantum dots (QDs) into the backlighting of wide color-gamut liquid crystal displays has become increasingly common [13, 71]. Direct gap II-VI semiconductors such as CdSe and III-V semiconductors such as InP are widely used for this purpose. However, creating an electrically driven white-emitting light source that covers the full visible spectrum (RGB) using blue LED-excited fluorescent QDs followed by color filtering is not optimal in terms of energy efficiency. Interestingly, SiC QDs have also been explored as potential candidates for electrically driven WLEDs. Through careful design engineering, three different electroluminescent white LEDs utilizing SiC QDs were developed, featuring three distinct configurations (Devices A, B, and C) (**Figure 5(b)**) [63]. Device C indicated the widest emission spectrum, with a FWHM of 340–360 nm, covering the entire visible range (350–900 nm). Device C also showed better performance because for two reasons. Firstly, this is related to the introduction of TPBI with high electron mobility between QDs and LIF/Al. Secondly, the use of a mixture of the QDs and polycyclic aromatic hydrocarbons (PAHs) as an HTL which decreases the probability of non-radiative recombination and also mitigates imbalanced charge injection (**Figure 5(c)**).

The development of silicon-vacancy (V_{Si}) and divacancy (DV) centers in SiC NPs offers potential for SiC-qubit-based sensors. While V_{Si} emission can be seen in nanoparticles as small as 10 nm, zero-phonon lines and optically detected magnetic resonance (ODMR) signals are only observed in particles of 300 nm or larger. These signals indicate functional qubits through optical spin polarization and spin-selective fluorescence. Addressing these challenges involves advanced surface passivation to eliminate defects and optimizing synthesis methods for high crystal quality [72].

The potential of 3C QDs for use in metal–insulator–metal (MIM) charge-storage-type memory applications has been investigated. This approach focuses on enabling the deposition of charge storage materials at very low temperatures, specifically

utilizing SiC QDs in complementary metal-oxide-semiconductor (CMOS) devices. The synthesized colloidal QDs were incorporated into hafnium oxide (HfO₂)-based MIM structures. By applying varying potential differences across the electrodes and measuring capacitance within a frequency range of 0.01 to 1 MHz, the formation of conducting filaments facilitates charge transfer and storage on the NCs. This process leads to alterations in band bending, and the charge storage is evaluated by plotting the flat band voltage against the initial bipolar program/erase voltage. The projected retention time for this charge storage is estimated to be over 10 years.

6.3 Energy conversion

Semiconductor QDs have attracted considerable attention in energy conversion. In bulk photocatalysts, band bending allows for the generation of either holes or electrons. In contrast, colloidal semiconductor particles can simultaneously host both carriers on their surfaces, enabling multiple reaction pathways. In addition, QCE becomes pronounced when particle dimensions approach the de Broglie wavelength of carriers, leading to discrete energy levels that can enhance photocatalytic activity. This effect increases the energy gap between occupied and unoccupied levels, resulting in higher redox potentials. 3C-SiC was found promising for CO₂ reduction photocatalysis since the bandgap required for CO₂ reduction ranges from 1.23 to 3.00 eV. To optimize performance, silicon oxide (SiO_x) was applied to the surface of SiC nanoparticles. This coating not only traps photoinduced carriers but also protects the SiC core from photo-corrosion, extending its lifespan. As shown in **Figure 5(d)**, using 3C-SiC QDs, the CH₄ generation rate was recorded at 4.9 μmol g⁻¹ h⁻¹, which was remarkably higher than that of SiC powders and TiO₂ NPs [64].

6.4 Biosensors

As a result of having stronger responses compared with conventional dye molecules or fluorescent proteins, SiC QDs are also being extensively used in photoluminescent biosensing systems. Recent studies have not only used the good cellular uptake of SiC QDs, but also their superior optical properties in improving both sensitivity and selectivity of biosensors [73]. For example, Li et al. [57] developed SiC@BSA nanoparticles conjugated with GH12 peptides to detect *S. salivarius* for forensic saliva identification. Owing to the enhanced fluorescence intensity and stability of these peptide-functionalized SiC@BSA nanoparticles, the biosensing system achieved a limit of detection of 25 cfu/mL within 40 minutes. In another application in food safety, Yeo et al. [74] conjugated SiC QDs with aptamers for the detection of *P. mirabilis*, a potentially fatal foodborne pathogen. The results showed a stable fluorescence signal, enduring over eight weeks, alongside achieving a limit of detection of 526 cfu/mL with high selectivity in real sample matrices such as milk powder, blood, and urine. In contrast with the abovementioned platforms that used aptamers or peptides, the biosensor designed by Sun et al. [75] relied on the injection of holes by hydroxyl radicals into the SiC QDs, taking advantage of the high redox potential of these radicals. This system used SiC QDs synthesized via a one-step hydrothermal method to detect ambient particulate matter. These examples highlight the flexibility and efficacy of employing SiC QDs in biosensing systems, showcasing their potential for rapid, sensitive, and specific detection of various biological and environmental targets (**Table 4**).

Application	Platform	Device characteristics	Mechanisms	Ref
Live cell labeling and imaging	SiC QDs (2.5 nm)	• Strong green fluorescence on the cell membrane after QD incubation • No cytotoxic effects after 20 days in incubation	QD uptake into cell membrane	[36]
Biosensing	SiC@BSA NPs (14 nm) conjugated to peptides	• Target: <i>S. salivarius</i> • Linear range: 10^2–10^7 cfu/mL • LOD: 25 cfu/mL	Fluorescence quenching upon binding of target cells to peptide chains on SiC@BSA NPs	[57]
WLED	SiC QDs (3.1 nm)	• Improved charge injection balance by embedding QDs in HTL material PAH and inserting TPBI between QDs and LIF/Al	TPBI with high electron mobility between QDs and LIF/Al enhances device performance.	[63]
Memory devices	2–5 nm SiC NCs in HfO ₂ -based MIM	• Programmed state detected by determining flat band voltage • 10 years extrapolated estimate of memory retention	Charge storage	[76]
Quantum sensing	Divacancy defect in SiC QDs	• Detects magnetic field using magnetic resonance • 1180 nm fluorescence dips in intensity due to magnetic field.	Optically detected magnetic resonance spectroscopy	[72]
CO ₂ reduction	SiC@SiO _x core-shell NPs	• CO₂ selectivity: 94% • CH₄ generation rate: $4.9 \mu\text{mol g}^{-1} \text{h}^{-1}$	CO ₂ adsorption followed by reduction by photogenerated carriers	[64]

Table 4.
Applications based on SiC QDs.

7. Conclusions

SiC polytypes, along with their structural, chemical, and mechanical properties, are presented. A comprehensive overview of successful strategies to enhance radiative recombination in indirect bandgap SiC, including doping, porosity, defects, and nanoscale morphologies, is provided. Key mechanisms driving the superior optical properties of SiC QDs are discussed. Methods for synthesizing SiC QDs smaller than 5 nm are briefly outlined. The key aspects of quantum confinement effects and surface state effects are thoroughly explained and illustrated as the primary mechanisms of radiative recombination in SiC QDs. It is demonstrated how SiC QDs hold significant potential for a wide range of applications, including optoelectronics, biomedical, and energy-related fields.

For the fabrication techniques, even though there exist several strategies including laser ablation and etching, it remains the challenge for mass-production and real application due to the high requirement of laser sources, poor uniformity, inevitable defects and the difficulties of polytype control. Apart from that, surface engineering is also significant for application such as passivation and surface ligands, which also need further studies and research to build bridges.

Given the strong case for earth-abundant and non-toxic SiC QDs to play a major role in various sectors, these materials are expected to continue receiving significant attention and undergoing extensive development in the future.

Conflict of interest

The authors declare no conflict of interest.

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Silicon Carbide in Photoelectrochemical Water Splitting: Advances, Applications, and Future Horizons

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Abstract

Hydrogen is emerging as an outstanding sustainable energy alternative in the global shift toward renewable energy innovations. Photoelectrochemical (PEC) water splitting has gained attention as an environmentally friendly and efficient method for hydrogen production by harnessing solar energy. Among the various semiconductors investigated for PEC applications, silicon carbide (SiC) stands out due to its favorable energy band structure aligned with water redox potentials and exceptional chemical stability. Specifically, cubic SiC (3C-SiC) has drawn significant attention owing to its optimal bandgap of 2.36 eV, which allows for absorption of a portion of the visible spectrum. This chapter explores the recent advancements in SiC nanostructures, such as thin films, nanoparticles, and nanowires, for PEC water splitting applications. We highlight advanced fabrication techniques, examine the challenges encountered in integrating SiC into PEC systems, and discuss the practical outcomes. Focusing on future opportunities, this chapter aims to provide an overview of the current status of SiC technology's role in PEC water splitting, inspiring further exploration and innovation in this emerging field.

Keywords: renewable energy, photoelectrochemical (PEC) water splitting, silicon carbide (SiC), cubic SiC (3C-SiC), nanostructure

1. Introduction

In a scenario of transformative global energy landscape, the urgency to identify and implement sustainable, efficient, and environmentally conscious energy solutions has become of importance for researchers, policymakers, and industries alike. As the world grapples with climate change, depleting fossil fuel reserves, and heightened environmental awareness, alternative energy sources have transitioned from being supplemental to the essential components of our energy mix [1]. Among them, hydrogen stands out as a key element in the energy revolution.

Hydrogen is universally recognized for its clean and renewable attributes, which would justify its widespread use [2]. Its combustion results solely in water vapor,

making it an unparalleled candidate in the pursuit for greener energy alternatives [3]. This is evidenced by its multifaceted applications, from the expanding market for hydrogen-powered vehicles to its potential in decentralized energy systems for residential heating and large-scale industrial operations [4].

The ascension of hydrogen in the energy ranking is not solely due to its end-use benefits but also depends on sustainable and innovative production methodologies. In this context, photoelectrochemical (PEC) water splitting has emerged as a technique inspired by nature's photosynthetic processes, wherein plants harness sunlight to produce energy. PEC water splitting aims to replicate this balance of efficiency and sustainability by converting abundant solar radiation into hydrogen fuel [5, 6]. This method not only promises substantial renewable energy generation but also offers a clear solution to mitigate the environmental impacts of conventional fossil fuel consumption [7].

A critical aspect of the PEC water splitting process is the utilization of semiconductor materials. These materials are responsible for capturing solar photons and initiating electrochemical reactions that yield hydrogen [8]. Their selection is thus a subject of intense research interest. The semiconductor's properties, such as its bandgap, ability to absorb the solar spectrum, and stability in aqueous environments, determine its efficacy in PEC processes [9]. Among the multiple semiconductors explored, silicon carbide (SiC) has emerged as a potential competitor in PEC water splitting application. Its distinctive attributes, including an optimal bandgap and inherent chemical stability, combined with its compatibility with the water redox potentials [10, 11].

This chapter presents an overview of the multifaceted role of SiC in PEC water splitting. By reviewing its fundamental research, critically evaluating its current applications, and projecting future challenges and opportunities for innovation, we aim to provide a perspective on how the use of SiC can contribute toward a more sustainable energy future.

2. Historical overview

The exploration of SiC as a semiconductor material dates to the late nineteenth century. Initially discovered by Edward G. Acheson in 1891 during his attempts to synthesize artificial diamonds, SiC quickly found applications as an abrasive due to its exceptional hardness [12]. However, its semiconductor properties were not exploited until much later.

In the mid-twentieth century, with the advent of semiconductor technology, SiC began to attract attention for electronic applications because of its wide bandgap, high thermal conductivity, and excellent chemical stability. These properties made SiC an attractive candidate for high-temperature and high-power electronic devices [13]. Despite its potential, the difficulty in growing high-quality SiC crystals limited its widespread use in electronics for several decades.

The first significant studies of SiC in PEC applications emerged in the late 1990s and early 2000s. Researchers recognized that the wide bandgap of SiC, while limiting its absorption to the ultraviolet (UV) region, could be advantageous for stability and resistance to photo corrosion, which are the crucial factors for PEC materials operating in aqueous environments [10].

In 2001, Sebastian et al. conducted photoelectrochemical characterization of SiC and highlighted its potential for water splitting applications [10]. The study

demonstrated that SiC photoelectrodes could achieve stable photocurrents under UV illumination, reaffirming SiC's promise as a durable PEC material. This work sparked increased interest in exploring SiC's capabilities and addressing its limitations.

Throughout the early 2000s, research on SiC for PEC applications progressed, driven by advancements in material synthesis techniques such as chemical vapor deposition (CVD) and molecular beam epitaxy (MBE). These methods enabled the production of higher-quality SiC crystals and thin films [14, 15], allowing for better control over material properties and opening new possibilities for tailoring SiC's electronic and optical characteristics for PEC applications.

The development of nanostructured SiC in the late 2000s and early 2010s marked a significant milestone. Researchers began to investigate SiC nanowires, nanoparticles, and thin films, which offered higher surface areas and could potentially enhance light absorption and charge carrier dynamics [16]. Nanostructuring also provided avenues to engineer the bandgap and introduce defects or dopants to extend light absorption into the visible range.

In 2014, Wang et al. reported enhanced photoelectrocatalytic performance of etched 3C-SiC thin films for water splitting under visible light [17]. By heavily doping SiC with aluminum and employing surface etching techniques, they improved visible light absorption and increased photocurrent densities. This study demonstrated that with appropriate modifications, SiC could be made responsive to visible light, significantly broadening its applicability in PEC systems.

More recently, the integration of SiC with other semiconductors in heterojunctions and composite materials has been explored to overcome its limitations. Studies have investigated SiC/TiO₂ and SiC/CdS composites, aiming to harness the stability of SiC while benefiting from the visible light absorption of narrower bandgap materials [11, 18, 19]. These hybrid structures have shown improved photocatalytic activity and offer a pathway to more efficient PEC water splitting systems.

The historical progression of SiC in PEC water splitting reflects a broader trend in materials science: the continuous search for stable, efficient, and cost-effective materials capable of harnessing solar energy for sustainable fuel production. While early studies highlighted SiC's exceptional stability, ongoing research focuses on enhancing its light absorption and catalytic properties through advanced material engineering.

Today, SiC stands as a material of significant interest in PEC research. The combination of its inherent chemical stability and the potential for bandgap engineering and nanostructuring positions SiC as a promising candidate for future PEC systems. Continued advancements in fabrication techniques and a deeper understanding of SiC's properties are expected to further its development in the coming years.

3. The promise of 3C-SiC

Cubic silicon carbide (3C-SiC) has emerged as a particularly promising polytype of silicon carbide for PEC water splitting applications. Unlike its hexagonal counterparts (4H-SiC and 6H-SiC), 3C-SiC possesses unique properties that make it highly suitable for PEC systems aimed at sustainable hydrogen production.

3.1 Optimal bandgap for visible light absorption

One of the most significant advantages of 3C-SiC is its optimal bandgap of approximately 2.36 eV [20]. This bandgap is narrower than that of other SiC

polytypes, allowing 3C-SiC to absorb a portion of the visible light spectrum in addition to UV light. This expanded absorption range enables more efficient utilization of solar energy, which is predominantly composed of visible light, thereby increasing the photocurrent generation in PEC cells.

The bandgap of 3C-SiC aligns well with the solar spectrum, capturing photons with wavelengths up to about 525 nm [20, 21]. This capability enhances its photoresponsiveness compared to wider bandgap semiconductors that are limited to UV absorption. By absorbing more solar photons, 3C-SiC can generate more electron-hole pairs, which are essential for driving the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in PEC water splitting.

3.2 Favorable band edge positions

The conduction and valence band edges of 3C-SiC are favorably positioned relative to the redox potentials of water splitting reactions [22]. The conduction band edge is sufficiently negative to facilitate the reduction of protons to hydrogen gas, while the valence band edge is positive enough to oxidize water to oxygen gas. This alignment ensures that the photogenerated electrons and holes have the necessary energy to drive the respective half-reactions without the need for additional bias voltage.

3.3 Compatibility with silicon substrates

3C-SiC can be epitaxially grown on silicon substrates due to its relatively small lattice mismatch (~20%) compared to other SiC polytypes [23]. This compatibility with silicon allows for the integration of 3C-SiC into existing semiconductor manufacturing processes, potentially reducing production costs and facilitating large-scale fabrication of PEC devices. The use of silicon substrates also offers mechanical stability and the possibility of creating hybrid structures that combine the advantages of both materials.

3.4 High carrier mobility and crystalline quality

3C-SiC exhibits high electron mobility and excellent crystalline quality when properly synthesized [24]. High carrier mobility is crucial for efficient charge transport, reducing recombination losses, and enhancing the overall photocatalytic efficiency. Advances in fabrication techniques, such as CVD and MBE, have improved the quality of 3C-SiC films, enabling better control over defects and impurities that can act as recombination centers [15].

3.5 Chemical and photocorrosion stability

Like other SiC polytypes, 3C-SiC is chemically inert and exhibits exceptional resistance to photocorrosion in aqueous environments [25]. This stability is essential for the longevity and durability of PEC photoelectrodes that are exposed to harsh conditions during water splitting. The robustness of 3C-SiC reduces degradation over time, maintaining performance and reducing the need for frequent replacements.

3.6 Potential for bandgap engineering and nanostructuring

The bandgap of 3C-SiC can be further tuned through doping and the formation of nanostructures [26]. Doping with elements such as nitrogen or aluminum can

adjust the electrical and optical properties, enhancing visible light absorption and charge carrier concentration. Nanostructuring techniques, including the fabrication of nanowires, nanotubes, and porous films, increase the surface area and provide more active sites for the water-splitting reactions [20, 21, 23–25]. These modifications can significantly improve the efficiency of PEC cells based on 3C-SiC.

3.7 Integration into heterojunction and tandem systems

3C-SiC can be integrated into heterojunctions with other semiconductors to form tandem PEC systems [27]. For instance, coupling 3C-SiC with narrower bandgap materials like cadmium sulfide (CdS) or copper indium gallium selenide (CIGS) can extend light absorption further into the visible spectrum. In such configurations, 3C-SiC can serve as a protective layer, preventing photocorrosion of the underlying material while contributing to overall photocurrent generation.

3.8 Recent advances

Recent advances have significantly enhanced the photoelectrochemical (PEC) performance of cubic silicon carbide (3C-SiC) for water splitting applications. Comprehensive reviews, such as the one by Jian and Sun [28], have highlighted progress in improving 3C-SiC efficiency through strategies like doping, nanostructuring, and heterojunction formation. Plasma-induced nitrogen doping and the creation of carbon vacancies in 3C-SiC photoanodes have led to the substantial improvements in water oxidation performance, as demonstrated by Wu et al. [29]. Their work showed that these modifications enhanced charge separation and reduced recombination, resulting in higher photocurrent densities.

Li et al. further advanced the field by fabricating 3C-SiC photocathodes optimized for water splitting, showcasing the improved hydrogen production through careful nanostructuring and doping [30]. Ren et al. explored the use of strain tuned SiC/WS₂ heterojunctions, showing how strain engineering can improve band alignment and enhance light absorption and charge separation [31]. Similarly, Xu et al. introduced carbon-based hole storage engineering in SiC photoanodes, achieving an ultralow onset potential and high photocurrent density [32].

Heterojunction nanochannel arrays with SiC core-TiO₂ shells, developed by Sun et al. [33], have also been instrumental in improving PEC performance, demonstrating enhanced light absorption and charge separation. These innovations underscore the ongoing research efforts to optimize 3C-SiC for efficient hydrogen production through PEC water splitting.

4. Recent innovations in SiC nanostructure fabrication

The advancement of SiC nanostructure fabrication has been pivotal in enhancing the material's performance for PEC water splitting applications. Recent innovations have focused on developing novel synthesis methods, precise doping techniques, and intricate nanostructuring to overcome the inherent limitations of SiC, such as its wide bandgap and charge carrier recombination issues. This section explores into the latest fabrication techniques and how they contribute to improving the efficiency and viability of SiC-based PEC systems.

4.1 Nanostructuring techniques

4.1.1 Chemical vapor deposition

Chemical vapor deposition (CVD) has been extensively used to fabricate high-quality SiC nanostructures, including nanowires (NWs), nanotubes, and thin films. CVD introduces gas-phase sources, such as silane (SiH_4), silicon tetrachloride (SiCl_4), or methane (CH_4) for silicon and carbon precursors, into a reaction chamber, where they react to form SiC [34, 35]. Three distinct methods have been employed to synthesize 3C-SiC nanowires (NWs) using a thin nickel (Ni) film as a catalyst on a silicon (Si) substrate.

In the first method, 3C-SiC NWs are grown on a 4 nm Ni film deposited on a Si substrate in a vapor phase epitaxy (VPE) reactor using silane (SiH_4) and propane (C_3H_8) as precursors [34]. The resulting NWs are predominantly of the 3C polytype with a $\langle 111 \rangle$ growth axis. These NWs exhibit planar defects such as stacking faults (SFs) lying on $\{111\}$ planes, which are oriented perpendicular to the growth axis.

In the second method, 3C-SiC NWs are synthesized in a heated quartz tube using carbon tetrachloride (CCl_4) as a carbon source [34]. CCl_4 is decomposed at high temperature, reacting with the Si substrate to form silicon chlorides, which in turn reacts with carbon atoms to produce one-dimensional (1D) 3C-SiC NWs. These NWs are typically less than 80 nm in diameter and several tens of microns long.

In the third method, 3C-SiC/ SiO_2 core-shell NWs are obtained on a Ni-covered Si substrate in an open-tube configuration by flowing carbon oxide. The carbon oxide serves as the carbon source for the growth of the SiC core structures and reacts with the SiC core to form a thin SiO_2 sheath.

4.1.2 Physical vapor deposition

Physical vapor deposition (PVD) techniques, including pulsed laser deposition (PLD) and magnetron sputtering, have been widely utilized to fabricate high-quality thin SiC films with precise control over thickness and morphology [11, 36, 37]. PVD offers key advantages over CVD, particularly in terms of lower processing temperatures, making it ideal for depositing SiC on temperature-sensitive substrates. This lower temperature process allows for better integration of SiC films with a wider range of materials.

Recent advances in PVD, as highlighted by Kaloyeros and Arkles [37], have demonstrated improvements in film adhesion and uniformity, both critical factors for consistent performance in PEC applications. The ability to produce uniform SiC films with excellent adhesion helps mitigate issues related to delamination or uneven surface coverage, which can negatively affect charge transport and overall PEC efficiency. These advancements underline PVD's growing role in the fabrication of SiC thin films, contributing to more reliable and scalable processes for high-performance PEC water-splitting devices.

4.1.3 Molecular beam epitaxy

Molecular beam epitaxy (MBE) offers atomic-level control over the growth of SiC nanostructures. This technique enables the fabrication of high-purity, defect-free SiC layers with precise doping profiles [38]. MBE has been used to create heterostructures and quantum wells, which are beneficial for tailoring the electronic and optical properties of SiC. For example, Wang et al. utilized MBE to grow 3C-SiC films on

silicon substrates, achieving sharp interfaces and controlled thicknesses essential for optimizing PEC efficiency [39].

4.1.4 Electrochemical etching

Electrochemical etching is a versatile method used to create porous SiC structures with high surface areas, enhancing PEC water splitting performance [40]. By controlling parameters such as current density and electrolyte composition, it is possible to fabricate porous SiC films with tunable pore sizes, increasing active sites for the water-splitting reaction. Studies on advanced substrates highlight how optimized pore distribution enhances light absorption and promotes better charge separation. These structures result in improved photocurrent densities compared to non-porous films, demonstrating the benefits of nanostructured SiC photoanodes [41].

4.1.5 Laser ablation and nanolithography

Laser ablation and nanolithography techniques have proven highly effective for patterning SiC surfaces at the nanoscale. Femtosecond laser ablation allows for precise control over the geometry and arrangement of nanostructures such as nanorods, nanopillars, and nanowires. These ultrafast lasers offer significant advantages, including minimal thermal damage and high spatial resolution, making them ideal for processing SiC, which is known for its hardness and chemical inertness.

Recent research demonstrates the ability of femtosecond lasers to induce phase transformations in SiC, enhancing its performance in PEC applications. For instance, H. Quan et al. explored phase transitions in 6H-SiC through femtosecond laser processing and highlighted how it facilitates structural modifications critically for improving light absorption and carrier dynamics. This enhances PEC efficiency by reducing reflectivity and improving charge separation properties [42].

4.2 Doping and bandgap engineering

4.2.1 Elemental doping

Doping silicon carbide (SiC) with various elements has proven to be an effective strategy to modify its bandgap and enhance visible light absorption. Nitrogen (N) and boron (B) are commonly used as dopants for n-type and p-type SiC, respectively, with nitrogen playing a crucial role in improving SiC's electronic properties [11, 43]. In particular, Zhao et al. demonstrated how nitrogen-doped SiC nanowires exhibit enhanced field emission properties, which are highly dependent on the nitrogen content and morphology [44]. Their study utilized density functional theory calculations to explain how doping alters the electronic structure of SiC nanowires, leading to improvements in electrical conductivity and overall material performance.

Advanced doping techniques such as ion implantation and *in situ* doping during growth have been developed to ensure uniform dopant distribution and control over dopant concentration.

4.2.2 Co-doping

Co-doping with multiple elements can introduce synergistic effects that further enhance the SiC's properties. Co-doping with nitrogen and aluminum has been shown

to create additional energy levels within the bandgap, facilitating visible light absorption [45]. The introduction of co-dopants creates intermediate energy states near the valence band, which in turn improves visible light absorption and charge separation. This process mitigates charge recombination, thereby increasing the efficiency of the photocatalytic water-splitting reaction.

This enhanced performance can be attributed to the synergistic effect of co-doping, which not only adjusts the bandgap but also optimizes the electronic structure for better light absorption and charge carrier dynamics [46]. This research provides a promising avenue for developing more efficient SiC-based materials for PEC water splitting under visible light.

4.3 Material modification and catalysis enhancement

4.3.1 Noble metal heterojunction

Noble metal heterojunctions, particularly with SiC, have gained significant attention for enhancing PEC water splitting performance. The incorporation of noble metals, such as gold (Au) and platinum (Pt), onto SiC nanostructures enhances catalytic efficiency due to the formation of a Schottky barrier at the metal/semiconductor interface. This barrier promotes charge separation by facilitating electron transfer from SiC to the metal, preventing the recombination of electron-hole pairs.

A notable example is the formation of Au/SiC heterojunction nanocomposites. These composites, as demonstrated in the work of H. Dang et al., enhance the photocatalytic and PEC performance of SiC nanowires through the deposition of Au nanoparticles [47]. The Au nanoparticles generate localized surface plasmon resonance (LSPR), increasing light absorption in the visible spectrum and boosting charge transfer at the heterojunction interface. This results in higher hydrogen evolution reaction (HER) rates and improved overall PEC efficiency.

4.3.2 Transition metal catalysts

Transition metal doping in SiC plays a crucial role in enhancing its catalytic activity, particularly for PEC applications. Transition metals such as iron (Fe), cobalt (Co), and nickel (Ni) are frequently doped into SiC to improve its HER efficiency by facilitating charge transfer and reducing recombination losses.

According to the recent review on transition metal-doped SiC [48], doping introduces new energy states that narrow the bandgap of SiC, allowing for better visible light absorption. This enhanced absorption is critical for PEC water splitting, where efficient light harvesting directly correlates with increased hydrogen production. The electronic properties of transition metal-doped SiC are modified through hybridization between the 3d orbitals of the metal atoms and the SiC conduction band, improving the charge separation needed for catalytic reactions.

For instance, nickel-doped SiC shows the enhanced electron mobility and promotes HER by acting as active catalytic sites. Similarly, Fe and Co doping introduces the magnetic properties to SiC, which further improves charge transport and photocatalytic activity.

4.3.3 Surface passivation and protective coatings

Applying thin protective layers on SiC surfaces can prevent photocorrosion and improve stability. Materials such as titanium dioxide (TiO₂) and silicon dioxide (SiO₂) are commonly used for passivation [6]. These layers are applied using atomic layer deposition (ALD) or sol-gel methods.

4.4 Nanocomposite and heterostructure fabrication

4.4.1 SiC/TiO₂ heterojunctions

SiC/TiO₂ heterojunctions offer significant advantages for PEC water splitting, combining the stability of SiC with the photocatalytic efficiency of TiO₂. Pessoa et al. highlighted that TiO₂'s strong UV light absorption and catalytic activity for oxygen evolution reactions (OER) complement SiC's narrower bandgap and better stability in the harsh environments [11]. This synergy enhances the overall photocurrent generation and hydrogen production.

The heterojunction improves charge separation by facilitating electron transfer from SiC to TiO₂, reducing recombination losses. This results in higher efficiency in PEC systems, making SiC/TiO₂ a promising approach for sustainable hydrogen production. Additionally, advanced fabrication techniques such as CVD optimize the interface, further improving performance and durability under prolonged operation.

4.4.2 SiC/graphene composites

SiC/graphene composites have gained considerable attention due to their ability to enhance photocatalytic activity through improved charge separation and visible light absorption. The integration of graphene with SiC provides a large surface area and superior electrical conductivity, promoting efficient electron transport. In particular, research highlights that graphene oxide (GO) in these composites facilitates charge transfer at the SiC-graphene interface, resulting in higher photocatalytic efficiency for water splitting under visible light [49].

4.5 Advanced manufacturing techniques

4.5.1 3D printing of SiC structures

Additive manufacturing techniques like 3D printing have been explored to fabricate the complex SiC structures with high precision [50]. Stereolithography (SLA) and selective laser sintering (SLS) allow for the creation of SiC components with intricate geometries, which can improve light trapping and increase surface area. Qu et al. demonstrated the 3D printing of high-purity SiC structures, opening new possibilities for custom-designed PEC photoelectrodes [50].

4.5.2 Roll-to-roll processing

Roll-to-roll (R2R) processing offers a scalable method for producing flexible SiC thin films and coatings [51]. This technique enables continuous fabrication, reducing production costs and facilitating large-scale deployment. Bartesaghi et al. explored

the implementation of SiC layers using R2R processing for flexible thin-film solar modules, indicating potential applications in PEC systems [51].

4.6 Challenges in fabrication

Despite these advancements, challenges remain in the fabrication of SiC nanostructures:

- *Controlled doping*: Achieving uniform and precise doping without introducing defects is complex, requiring advanced techniques and careful process optimization.
- *Scalability*: Many nanostructuring methods are difficult to scale up for mass production, limiting their commercial viability.
- *Cost*: Fabrication techniques such as MBE and CVD are expensive due to high equipment and operational costs.
- *Material compatibility*: Integrating SiC with other materials in composites or heterostructures can be challenging due to differences in thermal expansion coefficients and chemical properties.

5. SiC applications in PEC water splitting

SiC nanostructures, especially thin films, have garnered significant attention due to their exceptional properties, including high thermal conductivity, chemical stability, mechanical strength, and wide bandgap as highlighted in **Figure 1**. These

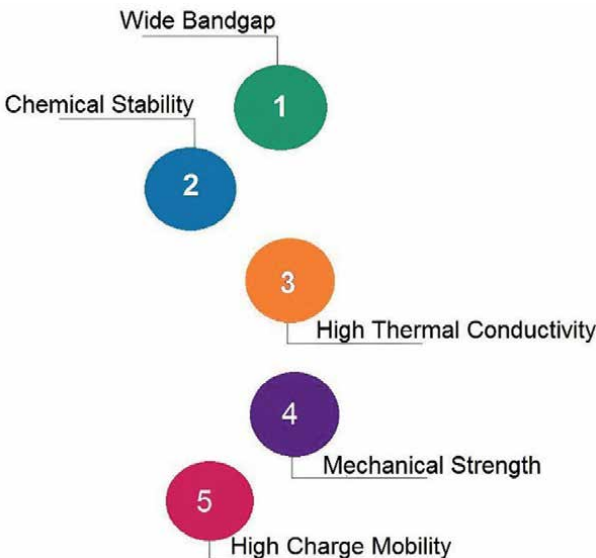


Figure 1.
Key properties of SiC for PEC water splitting applications.

attributes make SiC materials indispensable in harsh environments involving high temperatures, high voltages, and chemically corrosive conditions. Consequently, SiC has found applications across various industries, notably in power electronics, photonics, and sensor technologies. Recent advances have broadened their potential for use in emerging fields such as PEC water splitting, solar energy harvesting, and environmental monitoring [37].

In the PEC water splitting field, which uses solar energy to split water molecules into hydrogen and oxygen, SiC has emerged as a highly promising material [10]. This process offers a sustainable route for hydrogen fuel production but requires photoelectrodes capable of efficient light absorption, effective charge separation, and stability in harsh electrochemical environments. SiC films meet these criteria particularly well.

SiC's wide bandgap allows it to absorb high-energy photons, primarily in the ultraviolet (UV) range [52]. Its chemical resistance enables it to function in highly acidic or alkaline electrolytes, ensuring durability in challenging environments. Integrating SiC with other semiconductor materials has been observed to enhance its photocatalytic activity, improving the overall efficiency of hydrogen production—a critical advancement toward sustainable hydrogen fuel technologies [53].

For efficient PEC water splitting, materials must effectively separate and transport photogenerated electron-hole pairs to drive the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). SiC films, due to their excellent charge carrier mobility and crystalline structure, facilitate the transport of electrons and holes generated by solar absorption to the catalytic sites without significant recombination losses [54]. Additionally, SiC's bandgap can be tuned through doping or by forming heterojunctions with other semiconductors, such as titanium dioxide (TiO₂) or graphene, to enhance charge separation and increase catalytic efficiency [33, 54].

To further improve SiC's PEC performance, several studies have explored surface modifications and nanostructuring techniques. Nanostructured SiC films provide a larger surface area for reactions, increasing the availability of active sites for water splitting [55]. Surface functionalization with catalysts like platinum (Pt), nickel (Ni), or cobalt (Co) can significantly boost the reaction rates for HER and OER, overcoming SiC's intrinsic limitations in photocatalytic activity [56]. Such modifications make SiC films more competitive as photoelectrodes in PEC cells, enhancing overall water splitting efficiency.

One limitation of SiC is its limited absorption of visible light due to its wide bandgap. To address this, SiC is often used in hybrid structures or composite systems that combine it with narrower bandgap materials, such as cadmium sulfide (CdS) or perovskites, to extend the absorption range into the visible spectrum [57]. In these tandem PEC cells, SiC acts as a protective layer for the more photoactive materials while contributing to charge transport and enhancing overall stability.

6. Challenges and limitations

Despite its promising properties, SiC presents several challenges in PEC water splitting applications. While SiC's ability to absorb UV light and maintain stability in harsh environments is crucial for durability and long-term PEC performance, its wide bandgap limits absorption to the ultraviolet range, reducing photocurrents and overall efficiency [58]. This limitation makes SiC less competitive compared to materials like hematite (Fe₂O₃), which absorbs a broader portion of the visible spectrum.

To address these absorption limitations, researchers have explored bandgap engineering through doping [17]. However, doping SiC presents its own challenges. The process often requires high temperatures and achieving uniform and controlled doping can be difficult. Improper doping can introduce defects that increase electron-hole recombination rates and reduce carrier mobility. Additionally, developing stable p-type SiC is challenging due to the high doping concentrations required, which can compromise material stability. A study by Wang et al. reported the production of a robust p-type 3C-SiC thin film, heavily doped with aluminum, on a large silicon substrate using a low-temperature alternating supply epitaxy method [17]. This film achieved high conductivity and enabled photoelectrocatalytic water splitting for hydrogen production under visible light.

Surface recombination of charge carriers is another significant challenge [59]. Efficient separation and transport of photogenerated electron-hole pairs are essential to drive the HER and OER. Surface defects or impurities on SiC films can act as recombination centers where electrons and holes recombine before contributing to the electrochemical reactions, reducing the efficiency of water splitting. Addressing this issue requires meticulous surface engineering to minimize the recombination losses.

Furthermore, SiC exhibits relatively low intrinsic catalytic activity for both HER and OER [28]. To enhance the reaction rates, SiC often requires surface functionalization with catalysts such as platinum (Pt), nickel (Ni), or cobalt (Co). While these catalysts can significantly improve PEC performance, they can be costly, particularly Pt, raising the overall system cost and limiting the large-scale deployment. Achieving uniform and stable catalyst coatings is also challenging, as these layers may degrade over time, impacting long-term PEC performance.

The fabrication of high-quality SiC films suitable for PEC applications remains complex and costly. Techniques like CVD, necessary for producing crystalline SiC, involve high temperatures and sophisticated equipment, making it difficult to scale the production [28]. Controlling film thickness and uniformity is crucial for optimizing light absorption and charge transport properties, further complicating fabrication and increasing costs.

Finally, although SiC is chemically stable, long-term stability under continuous PEC operation remains a concern. Extended exposure to harsh acidic or alkaline electrolytes, combined with solar irradiation, can cause gradual degradation of the SiC surface, particularly when doped or functionalized with catalysts. Surface oxides or other degradation products can impair charge transfer efficiency, reducing photocatalytic performance over time.

While hybrid structures combining SiC with other semiconductors offer a potential solution for extending light absorption into the visible range, these composite systems introduce additional challenges [60]. Achieving efficient charge transfer between SiC and secondary materials can be difficult, especially if the materials have mismatched band alignments or differing chemical properties. These mismatches can result in recombination at the interface, reducing the benefits of the hybrid structure. Ensuring the mechanical and chemical stabilities of these hybrid systems adds further complexity to device fabrication.

7. Looking ahead: Opportunities in SiC and PEC water splitting

Despite the challenges, SiC continues to show immense potential in PEC water splitting, particularly as research advances in material science, surface engineering,

and system integration. Looking ahead, several opportunities stand out for enhancing the performance of SiC in this field, driving both its efficiency and broader adoption in sustainable hydrogen production.

One promising way is the continued development of bandgap engineering techniques to overcome the SiC's limited visible light absorption [17]. By refining doping strategies, researchers can tailor the electronic properties of SiC to improve light absorption while minimizing defects. Advancements in nanostructuring and the creation of heterojunctions with narrower-bandgap materials offer practical paths forward. Integrating SiC with semiconductors like cadmium sulfide (CdS), titanium dioxide (TiO₂), or perovskites in tandem structures can extend absorption into the visible spectrum while maintaining the stability that SiC provides. These hybrid systems present significant opportunities to design PEC cells that leverage both the durability of SiC and the superior light absorption of other materials.

Surface modifications and catalytic enhancements represent another key area for future research. As surface recombination continues to limit the efficiency of PEC systems, advanced surface engineering techniques—such as passivation layers or atomic-scale control of surface morphology—could significantly reduce recombination losses. Additionally, the development of cost-effective, earth-abundant catalysts, such as transition metal-based catalysts like nickel, iron, or cobalt, could enhance the HER and OER rates without relying on expensive materials like platinum [56]. These catalytic improvements would not only boost the overall efficiency of SiC-based PEC cells but also improve their scalability and commercial viability.

Nanostructured SiC, which offers increased surface area and active sites for the water-splitting reaction, is another exciting opportunity [55]. Employing novel fabrication techniques such as electrochemical etching or nanoscale CVD, researchers can create high-surface-area SiC electrodes optimized for maximum charge separation and transport. These structures can facilitate more efficient catalyst loading and better interface design, improving both the HER and OER.

Long-term stability is an important characteristic of SiC, particularly in harsh environments, but more research is needed to ensure this stability under continuous PEC operation. Future studies could explore protective coatings or advanced passivation layers that preserve SiC's chemical integrity without compromising performance. This is crucial for developing durable PEC cells capable of extended operation in industrial settings.

Finally, integrating SiC with advanced manufacturing techniques, such as 3D printing or roll-to-roll processing, holds potential to reduce the costs associated with SiC fabrication [50, 51]. These methods could enable large-scale production of SiC-based photoelectrodes with controlled thickness, surface morphology, and composition, making the technology more accessible for commercial applications. As the cost of SiC production decreases, its role in sustainable hydrogen production through PEC water splitting is likely to expand.

Although challenges remain, the opportunities for innovation in SiC-based PEC water splitting are vast. Continued interdisciplinary research into material design, surface engineering, and system integration will be critical in unlocking the full potential of SiC as a key material for the future of renewable hydrogen production.

8. Final remarks

Silicon carbide (SiC) has emerged as a material of significant interest in the field of PEC water splitting due to its unique combination of properties, including a

suitable bandgap, excellent chemical stability, and robust mechanical strength. While challenges such as limited visible light absorption, fabrication complexities, and charge carrier recombination exist, recent advancements in nanostructuring, doping, and composite material development have demonstrated promising pathways to overcome these obstacles.

The integration of SiC with other semiconductors and catalysts, along with innovative fabrication techniques, has the potential to significantly enhance PEC performance. As research continues to address the existing limitations, SiC stands poised to play a vital role in the advancement of sustainable hydrogen production technologies.

The future of SiC in PEC water splitting will depend on continued interdisciplinary collaboration, investment in advanced manufacturing methods, and a commitment to overcoming the material's inherent challenges. With these efforts, SiC could become a cornerstone material in the global pursuit of renewable energy solutions.

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Conflict of interest

The authors declare no conflict of interest.

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Silicon carbide (SiC) has emerged as an advanced material for nanotechnology and microelectronics, enabling new levels of performance, efficiency, and integration. This edited volume, *Silicon Carbide - From Materials Science to Nanotechnology and Microelectronics*, provides a comprehensive overview of recent developments in SiC materials, processing, and device applications. It offers a clear and accessible perspective on the unique properties of SiC and its role in driving the next generation of high-performance devices. The book highlights the interdisciplinary nature of SiC research, covering topics such as semiconductor materials, thin films, doping strategies, wafer processing, nanostructures, quantum dots, and sustainable energy applications. It presents key advances in fabrication methods, material characterization, and device integration. The volume also explores emerging applications of SiC in optoelectronics and energy conversion technologies, making it a valuable reference for both academic and industrial audiences. Combining contributions from leading researchers, this book serves as a practical resource for scientists, engineers, and students seeking to understand and apply SiC technologies. Its broad scope and accessible structure make it suitable for readers across various disciplines, including materials science, electrical engineering, energy, and nanotechnology. Whether for research or teaching, this volume offers a strategic overview of one of the most promising materials for the future of advanced devices.

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