

Silicon Carbide and Its Nanostructures

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Abstract

Silicon carbide (SiC) is a promising ceramic for various industrial applications thanks to its excellent properties at high temperature, high power, high frequency, high radiation environment and chemically harsh conditions. Substantial efforts have been made to develop new approaches to the synthesis of SiC and its nanostructures. Nanostructured SiC including nanoparticles and one-dimensional (1D) structures are superior to their bulk counterpart in many properties, and have attracted considerable attention in recent years due to their important role in basic science and their potential applications in electronic and optoelectronic devices, and composite reinforcement. This paper outlines the various methods for fabricating SiC nanostructures.

1. Crystal structure

Silicon carbide (SiC) is a promising ceramic for various industrial applications thanks to its excellent properties. SiC is a binary compound semiconductor consisting of carbon and silicon, where each atom is sp^3 -hybridized and forms four bonds to four other atoms of the opposite kind (Fig. 1). On the other hand, the crystal structure gives rise to polytypism, which is a one-dimensional polymorphism. Unlike most other semiconductors, which only occur in one or two different crystal structures each, SiC exists in over 250 known polytypes^[1, 2]. The difference among the polytypes is the stacking sequence along the c-axis of the lattice. The cubic polytype is referred to as β -SiC, whereas the hexagonal and rhombohedral structures are referred to as α -SiC. Due to the low stacking-fault energy, it is easy to form different SiC polytypes, making it possible to obtain SiC crystals with different properties for various applications.

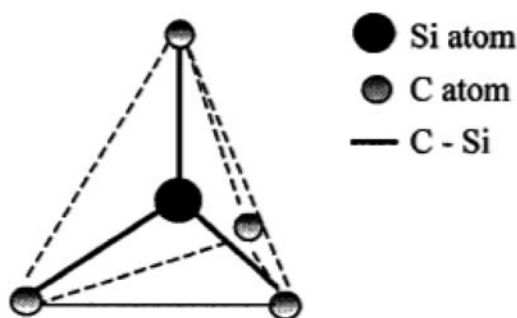


Fig.1 Unit cell structure of SiC single crystal^[1].

2. Properties and applications

SiC has been widely studied for various applications

because of its high Young's modulus and hardness, excellent oxidation and corrosion durability, high strength at elevated temperatures, and good thermal shock resistance^[3-5].

Moreover, SiC is a promising semiconducting material for application in areas of high temperature, high power, high frequency and harsh environments. Therefore, the synthesis of SiC for application in electronic devices has been widely investigated in recent decades. As a result of its large band gap (2.39, 3.02, 3.26, and 3.33 eV for 3C-SiC, 6H-SiC, 4H-SiC, and 2H-SiC, respectively, at room temperature), SiC shows a very high breakdown field (2.12, 2.2, and 2.5 MV/cm for 3C-SiC, 4H-SiC, and 6H-SiC, respectively)^[6].

In addition, the prominent thermal conductivity of SiC (3.2, 3.7, and 4.9 W/cmK for 3C-SiC, 4H-SiC, and 6H-SiC, respectively) is typically 2–3 times higher than that of silicon (1.5 W/cmK), which allows SiC to remove heat more efficiently^[7].

3. Synthesis of SiC

3.1 The Acheson process

Many studies have reported on the synthesis of SiC since the fabrication process initiated by Acheson in 1892. The overall formation reaction of SiC by the Acheson method can be described^[8] as follows:



Quartz sand and petroleum coke are generally used as the silicon and carbon sources, respectively. This process involves a carbothermal reduction reaction that takes

several hours and is usually carried out in an electrical resistance furnace at temperatures above 2000°C. Due to the high reaction temperature and long reaction time, the synthesized SiC powder has a large particle size and consists of mostly alpha-phase SiC. Therefore, extensive milling is needed to convert the as-synthesized product to sinterable powder with a particle size ranging from a few micrometers to submicrometers, which is inevitably accompanied by contamination from the milling media. The drawbacks of this industrial production process lie in the high energy consumption and low product purity.

3.2 SiC nanopowder

The physical and chemical properties of a material critically depend on the grain size of SiC because, for different grain sizes, a significantly different fraction of atoms forms the surface of the grain. Fine SiC nanopowder is beneficial for the sintering process as coarse powder is usually difficult to sinter. SiC nanoparticles are also important as a functional filler to improve the properties of materials such as polymers^[9, 10], ceramics^[11] and metals^[12].

SiC nanoparticles can be synthesized by chemical vapor deposition (CVD), sol-gel processes, laser gas-phase pyrolysis or laser evaporation processes. For example, Hollabaugh et al. synthesized pure SiC nanopowder by CVD using SiCl₄ and C₂H₄ as precursors^[13]. Zhu et al. synthesized SiC powder with an average particle size of 22 nm by conventional CVD^[14]. Viera et al. used a plasma technique to prepare SiC nanopowder from CH₄ and SiH₄ gas mixtures^[15]. Li et al.^[16] developed a two-step sol-gel process to synthesize SiC from phenol resin/SiO₂ hybrid gels. Jin et al.^[17] synthesized fine-sized β-SiC powder with a particle diameter of ~400 nm by combustion synthesis with the aid of a mechanical activation process.

The carbothermal reduction reaction has proven to be an economical and effective method for synthesizing nanosized SiC powder, using various carbon and silicon sources. Martin et al. synthesized nanocrystalline SiC powder from a solution of sugar in silica sol^[18]. Zhang et al. fabricated nanosized SiC powder by carbothermal reduction of SiO₂ and SiO₂-Al₂O₃ xerogels^[19]. Yoshioka et al. used a liquid carbon source of phenolic resin and various silica sources to synthesize SiC powders. Ultra-fine SiC powder with a grain size of 10–30 nm was obtained from TEOS and liquid C by carbothermal reaction at 1600°C^[20].

In addition, extensive research has been done to develop a method for reducing the temperature of the carbothermal reduction process. For example, high-energy reaction milling can synthesize nanosized SiC powder without heating^[21–23].

Microwave heating is another technique that produces fine and uniform SiC powder at lower temperatures and in shorter times than the conventional processes^[24, 25].

3.3 One-dimensional (1D) SiC nanostructures

Since the discovery of carbon nanotubes (CNTs)^[26], a great deal of attention has been paid to the formation and characterization of other one-dimensional (1D) nanostructures, including inorganic materials (metals, ceramics, glass) and organic materials (biomolecules, polymers)^[27]. Such 1D nanostructures are expected to improve our understanding of the fundamental concepts of the roles of both dimensionality and size on physical and chemical properties, as well as for potential applications in electronics, optics and materials science. Among the various 1D nanostructures, 1D SiC nanostructures have been extensively studied in recent years and are proven to have unique electronic^[28], field-emitting^[29], optical^[30], superhydrophobic^[31], and mechanical properties^[32], which can be ascribed to their low dimensionality, quantum confinement, and shape effects^[33–35].

Various techniques for fabricating 1D SiC nanostructures, particularly SiC nanowires (NWs), have been developed and can be classified as follows according to the formation mechanism.

3.3.1 Carbon nanotube/fiber confined reaction

Dai et al.^[36] succeeded in synthesizing SiC nanorods having similar diameters to those of CNTs (2–30 nm). The spatial orientation of the SiC nanorods was randomly distributed in agreement with that of the initial CNTs. Pan et al.^[29] used the same growth approach but spatially oriented CNTs as the starting material, and synthesized arrays of oriented SiC NWs.

Carbon fibers have also been used as a template for fabricating SiC NWs^[37]. The synthesized SiC NWs produced in this process have uniform cross sections, well-ordered structures, and very low concentrations of stacking faults. The carbon nanotube/fiber confined reactions contain no catalyst in comparison with 1D SiC nanostructures synthesized by the vapor–liquid–solid (VLS) mechanism.

3.3.2 1D SiC nanostructure growth via the VLS mechanism

The VLS growth process is the most well-established method for producing 1D SiC nanostructures. The VLS mechanism introduces a catalytic liquid alloy phase that can rapidly adsorb a vapor to supersaturation levels and crystal growth can subsequently occur. The use of a catalyst allows

the formation of the liquid phase at low temperatures and fast growth, contrary to the very slow growth of a crystal through direct adsorption of a gas phase onto a solid surface. The 1D SiC nanostructures grown by VLS usually have catalyst particles on their tips.

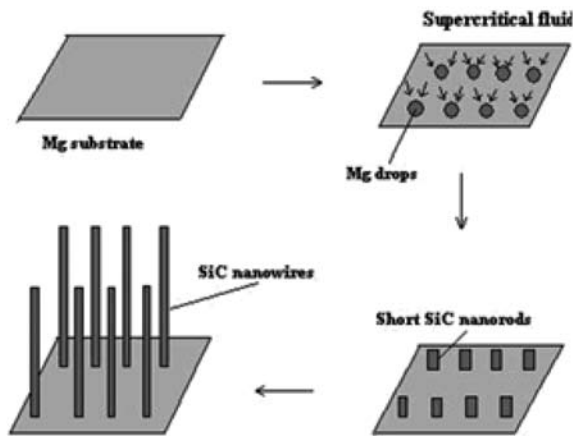


Fig.2 Schematic illustration of the growth process of the aligned 1D nanostructures via VLS mechanism^[38].

Xi et al. developed a novel magnesium-catalyzed co-reduction route for the large-scale synthesis of aligned β -SiC 1D nanostructures at a relatively lower temperature of 600°C (Fig.2)^[38]. By carefully controlling the reagent concentration, β -SiC rod-like and needle-like nanostructures can be achieved (Fig. 3) and the as-synthesized β -SiC nanostructures exhibit strong shape-dependent field emission properties. Li et al. synthesized large areas of centimeters-long SiC nanowires through pyrolysis of a polymer precursor with ferrocene as the catalyst by a CVD route^[39]. The NWs, with a length of several centimeters and a diameter of 100–200 nm, were composed of single-crystal β -SiC along the $\langle 111 \rangle$. The SiC NWs showed good intense-current emitting properties when a pulsed high-voltage electric field was imposed.

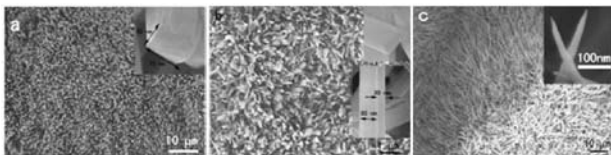


Fig.3 Representative SEM images of the as-synthesized β -SiC samples: (a) rod-like sample I, (b) rod-like sample II, and (c) needle-like sample.

3.3.3 1D SiC nanostructure growth via the vapor–solid (VS) mechanism

The VS mechanism corresponds to the case where silicon and carbon gaseous precursors react on a solid surface to form 1D SiC nanostructures. Growth starts at nanometer-sized nuclei created in situ and proceeds along

one crystallographic direction. An appropriate and well-controlled growth configuration must be employed in order to form nanosized nuclei for subsequent growth on top of them as well as to ensure growth along one axis. The most important feature is that the reaction develops without the presence of a metallic catalyst, which could be an advantage over other methods using a metal catalyst since the presence of the catalyst in the final product is considered deleterious for device application.



Fig.4 Schematic illustration of the SiC nanowires growth via VS mechanism^[40].

Yang et al. fabricated SiC nanowires by a simple catalyst-free method using detonation soot powder and silicon wafers (Fig. 4)^[40]. The nanowires have a diameter of 30–100 nm and a length of 0.5–1.5 μm . The axial growth direction of each nanowire is preferentially along the κ direction, while a low density of planar defects is detected. A relatively low threshold field of 6.2 V μm^{-1} suggests that it is a promising material for flat panel displays.

3.4 Synthesis of SiC from plant-based biomass

Plant-based biomass including rice husk (RH)^[41–43], coconut shell^[44], cotton fiber^[45], sugarcane leaf with rice straw^[46] and bean-curd refuse^[47] have proven to be good raw materials for the fabrication of SiC nanostructures. These agricultural byproducts contain large amounts of SiO₂ and C that naturally accumulate at the skin or outer layer and have a high surface area and close contact. It is possible to form SiC at a relatively low temperature that is far lower than that indicated by thermodynamic and kinetic calculations. Additionally, plant-based biomass is inexpensive and abundantly available all over the world. Among the different types of biomass, RH has been the most widely studied since the pioneering work by Lee and Cutler in 1975^[41]. The extensive studies performed on RH might be due to the high silica content compared to other agricultural byproducts.

The SiC synthesized by RH pyrolysis usually consists of a mixture of SiC particles and whiskers, with β -SiC as the main product. The effects of synthesis parameters such as pyrolysis temperature, holding time, heating rate and chamber atmosphere, etc. have been widely investigated. Our group synthesized nanostructured β -SiC including particles and 1D nanostructures by direct pyrolysis of RH in argon atmosphere

at different temperatures and durations [48, 49]. The results revealed that a complete carbothermal reduction reaction was achieved at 1500°C for 4 h or at 1600°C for 2 h. The β -SiC obtained on the bodies of pyrolyzed RH was mainly particles, as well as a small amount of β -SiC whiskers. We found that the pyrolysis temperature and duration greatly influenced the morphology and microstructure of the synthesized SiC. As shown in Fig. 5, the β -SiC particles obtained at 1600°C for 2 h had the smallest particle size of 100–200 nm. On the other hand, 1D β -SiC nanostructures were obtained from the vapor-deposited products formed on the graphite crucible walls (Fig. 6). The β -SiC/SiO₂ nanochains were synthesized at 1500°C for 2 h. Pure β -SiC whiskers with a diameter of ~160 nm and tens of micrometers in length were obtained at 1500°C for 4 h. As the pyrolysis temperature increased, β -SiC whiskers showed a shorter length, larger diameter and lower density of stacking faults.

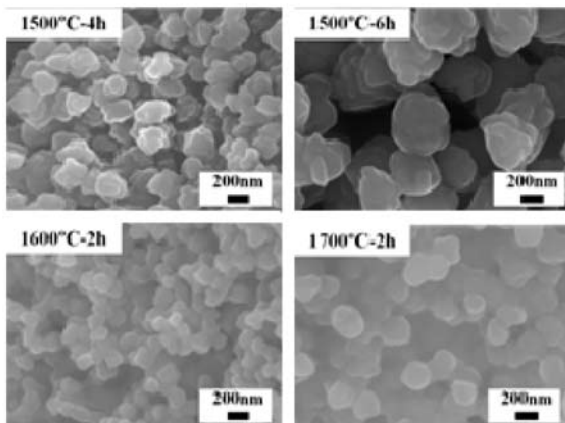


Fig. 5 FE-SEM images of β -SiC particles obtained at different temperature and duration.

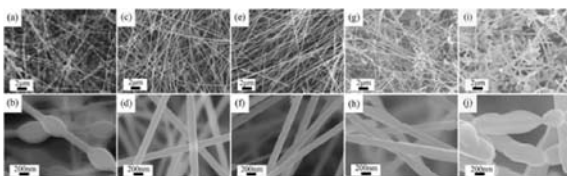


Fig. 6 FE-SEM images of the 1D nanostructures obtained on the inner walls of graphite crucible by direct pyrolysis of RH in argon atmosphere at different temperatures and durations: (a,b) 1500°C-2h; (c,d) 1500°C-4h; (e, f) 1500°C-6h; (g, h) 1600°C-2h; (i, j) 1700°C-2h.

Our group developed a two-step method for fabricating nanostructured SiC from RH by microwave heating [50]. First, the raw RH was carbonized in Ar at 700–1000°C by a vertical graphite furnace to obtain carbonized rice husk (CRH) and then was ball-milled to form CRH powder, which showed excellent microwave absorbance performance.

Microwave heating was carried out in a 2.45 GHz microwave furnace and the complete carbothermal reduction reaction could be achieved at 1300°C for 60 min or at 1500°C for only 15 min. As shown in Fig. 7, the products are a mixture of SiC particles and whiskers. The SiC particles are 60–130 nm in diameter and the whiskers, which are several to tens of micrometers in length, have a diameter of 110–170 nm. Compared to the conventional heating method, microwave heating proved to be an efficient approach for the synthesis of SiC in terms of energy and time saving, as well as for the fabrication of nanostructured SiC.

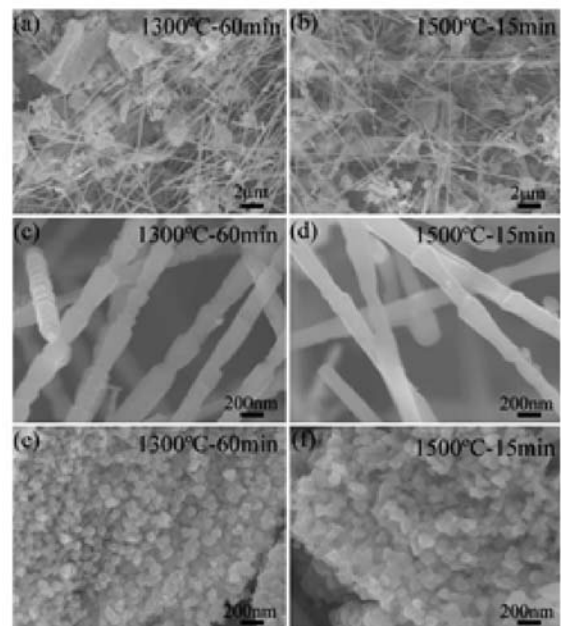


Fig. 7 Low magnification FE-SEM images of the β -SiC powders synthesized at (a) 1300 °C for 60 min and (b) 1500 °C for 15 min by microwave heating method; high-magnification FE-SEM images of (c and d) β -SiC whiskers and (e and f) β -SiC particles.

4. Conclusions

Various SiC nanostructures, especially 1D SiC nanowires, have been grown by a variety of methods via different growth mechanisms. Each method shows specific advantages and it is difficult to conclude which method and growth mechanism results in the best quality of nanostructured SiC suitable for all applications. The cost of precursors, the operation temperature, the yield and morphology of the products, and the feasibility of synthesis procedures on a large scale should be considered as a whole.

The synthesis of SiC and its nanostructures from plant-based biomass, especially rice husk, is an economical and simple approach due to its high activity and low cost. However, several matters still need to be addressed to improve this method, such as the purity of the product formed, the ability

to fully control the final product, the reduction of defects and the process of separating the particles and whiskers.

5. References

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