Silicon carbide- from synthesis to application: a review

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Abstract. This paper provides a review of the synthesis techniques that are used to produce nanostructured silicon carbide. The synthesis methods, consisting of carbothermal reduction, chemical vapor deposition, laser ablation, sol-gel and microwave heating are described. The silicon carbide properties and application are also explained. The paper then discusses the limitations of previous studies which involved complicated equipment and processes, that limit their further application and act as a barrier to further research and development in many fields.

1 Introduction

In recent years, nanotechnology has been increasingly matured following intensive efforts by materials scientists, physicists, chemists and engineers who have been inspired by its importance in both basic research and technological applications. The borders between various subjects such as physics, chemistry, materials science, biology, become indistinguishable on the nanometer scale. Thus, breakthrough in any of these areas in nanoscale could have an impact on the others. In the case of nanoelectronics, the related semiconductor research has been the most important driving force [1].

In this modern day, nanotechnology has stimulated attention of many researchers worldwide and is said to be revolutionary, replacing conventional materials science. This interesting scientific research area became a phenomenon in the past decades when lijima had set a remarkable milestone with his first discovery of carbon nanotubes (CNTs) in 1991 [2], [3]. This was followed by exploration and production of identical geometrical compound namely SiC, BN, GaN and MoS2 to name a few [4]. Significant number of research works were recorded with large number of articles published internationally [5]. This shows nanotechnology has become a widespread relevant materials science study which has been explored by researchers and scientists alike.

Nanostructure material can be classified into its functionality and dimensionality. However, only low dimensionality like zero dimensional (0D), one dimensional (1D), two dimensional (2D) and three dimensional (3D) have taken the interest of researchers to explore. Since the majority of research works related to nanostructure are focusing on 1D [5], the various types of 1D-nanostructure have been established with many synthesizeation techniques developed from time to time including the sol–gel [12], vapor–liquid–solid [8],

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vapor–solid [2], laser ablation [6] and chemical vapor deposition (CVD) methods [9]. Among the various types of 1D nanostructure materials available, their specific names were classified based on their unique shapes and sizes such as nanowires, nanorods, nanocables, nanotubes and nanobelts [7], [8].

Different dimensions and shapes of nanostructure allow them to be applied in various applications. When a material is reduced to the range of nanometer, their properties changed significantly due to quantum confinement effect. 0D nanostructure is widely studied for its potential application in multifunctional nanoparticle probe. The charge carriers in 2D nanostructures are restricted to the direction perpendicular to the layer and can move freely in the layer plane. These 2D nanostructures, especially nanoporous materials have been studied for their applications in biosensors, nanophotonic andnanoelectronic applications. 1D nanostructures are known to exhibit quantum confinement effect like 0D nanostructures but for 1D nanostructures, the charge carriers can only travel in one direction along the wire, thus, making them useful as interconnects and critical devices in nanoelectronic and nano-optoelectronic applications [10]–[12].

2 Silicon carbide

Silicon carbide (SiC) is a non-oxide ceramic engineering material that has gathered a considerable amount of interest. It has a wide range of industrial applications [24] which plays a major role in high voltage, temperature and frequency semiconductor device applications.

SiC compound consists of a Silicon (Si) atom and four Carbon (C) atoms which are covalently bonded between two of them. The four C atoms surrounded the Si atoms through strong tetrahedral of sp3 combination bonds. Close-packed stacking structure between Si and C atoms can be considered in one period SiC crystallographic structure. Polytypes in SiC are formed when there are differences formed in crystallographic. More than 200 polytypes [13] or 250 polytypes in some reports claimed have been identified but only a few studied on them. Major polytypes of SiC are α-SiC and β-SiC, which are classified as hexagonal polytypes and cubical polytypes respectively. The most common polytype occured in α-SiC is 2H-SiC, 4H-SiC and 6H-SiC. Meanwhile, 3C-SiC owned zinc blend structure is the most synthesized polytype in β-SiC regime [14]. Another famous α-SiC polymorph type of SiC is 15R-SiC. The letter H, C and R in their name denoted as pure stacking of hexagonal, cubic, and rhombohedral respectively [3], [15].

2.1 Synthesize method

Up to the present, there are various fabrication methods that have been successfully conducted by the previous researchers. The synthesized products included micro and nano sizes with different dimensionality. However, with the recent advancement of nanotechnology, the race towards producing the nano level size SiC has become a phenomenon with the introduction of different synthesize techniques.

Composite powders which consist of a mixture in the Si-C-N system were produced by using a self-propagating high temperature synthesis (SHS). This process involved combustion reaction where it was started by an outer energy source in the powdery bed. Then, a reaction took place and followed by the propagation of high temperature thermal wave through the bed. Since it did not involve dilution, SHS was a simpler and more economical method. Four different compositions were prepared from the mixture of raw materials namely carbon black and silicon powder with C/Si vol.% ratio of 10, 20, 30, and 40.5 This mixture was then ball milled together with the grinding media which consisted of Si3N4 and isopropanol is added to wet homogenized them. The combustion process was performed
under a nitrogen pressure of 3 MPa in high pressure reactor. The result indicated that carbon content had influenced the temperature profile of the reaction front. As the ratio of carbon increased, the temperature profile became higher and narrower. The specific surface area was also increased in the product with higher carbon content. XRD analysis on the combustion products has revealed two phases; β-SiC and β-Si₃N₄. In addition, a small discrepancy of the SiC content was detected when compared to the predicted ones. This research had concluded that composite (i.e SiC-Si₃N₄) in the Si-C-N system with controlled morphology and high purity could be attained using SHS without inert solution[16].

Through metal catalyst free thermal evaporation technique, the SiC nanowires were fabricated from Si substrate. The experimental process began with the placement of Si wafer and graphite powder side by side in the columnar graphite crucible. The system was set up in a vacuum furnace. Prior to heating, the surface of Si was washed with acetone and ethanol and then air-dried. Argon gas was supplied to the vacuum furnace after evacuation to 10 Pa via rotary pump. The heating temperature was increased to 1000 °C at 10 °C/min of heating rate then gradually increased to 1500 °C at 3 °C/min and kept to 3 hours. SEM and field emission scanning electron microscopy (FESEM) analysis clearly indicated the formation of straight and curved nanowires with the size of several hundred microns and 50-100 nm in diameter. The structure was then analyzed by energy-dispersive X-ray spectroscopy (EDX). With composition of a single-crystalline SiC core wrapped in thin amorphous SiO₂ shell, the nanowire has been categorized as SiC–SiO₂ core–shell structure. Vapor-solid process has been suggested and proposed to be the growth mechanism for the overall experiment [12].

The complex structure namely SiC nanowires decorated with SiC polycrystalline nanoparticles were grown via chemical vapor deposition (CVD) using methyltrichlorosilane (MTS) as starting material. The method involved the cutting of specimen (C/C) into two, cleaned with ethanol and dried. The specimen was then hung in the CVD furnace with inert Ar atmosphere and temperature raised to 1000 °C for 2 hours. The as-product was analyzed in transmission electron microscopy (TEM) revealing two compositions labeled as nanowire and nanoparticle. EDX analysis had been conducted on both structures which suggested the presence of Si and C with a small amount of O. This was due to the oxidation of SiC to form SiOₓ during cooling process. The combination results of HRTEM and EDX safely concluded the appearance of many small single crystals with different orientations to form polycrystalline SiC and single crystalline SiC into SiC nanowires stem. However, the shift signal in Raman scattering indicated many stacking faults in the products. To conclude, the SiC nanowires decorated with SiC polycrystalline nanoparticles with diameters ranging from 50 nm to 200 nm and length up to several hundred micrometers was successfully synthesized through CVD with MTS precursor [17].

The inverted 3C-SiC nanoneedles with hexagonal structure were rapidly synthesized via a two-crucible heating technique. This study was conducted under high frequency and there was no catalyst involved. In this experiment, two different diameters hollow attached cylindrical graphite crucibles were used whereby the mixture of silicon monoxide and carbon coke was in smaller crucible and carbon fiber in the other. Then, the two crucibles were placed inside a quartz tube before heating to 1800 °C about 5 minutes dwelling time from room temperature under argon atmosphere. XRD pattern identified the structures as 3C-SiC in consistent with the standard. SEM images revealed hexagonal, spindle and thick portion of grown nanoneedle structure on the carbon fiber in the [1 1 1] orientation. The average length for each structure measured about 130 nm. The reaction process of SiO and carbon on the carbon fiber was believed to be the initial point forming SiC nuclei to SiC nanoneedle. Thus, with this synthesize effort, it has broaden the types of 1D nanostructure SiC [18].

Sol-gel method is one of the more versatile methods to synthesize SiC which offers several advantages including production of good chemical homogeneity, smaller particle size, and high-purity materials [19]. The sol-gel synthesis of nano-sized 3C-SiC has been
conducted using sol-gel technique silicon-bearing gel and nano-sized carbon particles obtained from soot. The preparation of silica bearing sol started by using alkaline ethylene glycol and fumed silica which then yielded in a silicon bearing gel. At a temperature about 1400 °C to 1580 °C, the major amount of 3C-SiC was observed with minor trace of 2H-SiC. The different ranges of nanosize structural dimension was observed at 1400 °C and 1580 °C with 30–50 nm (particles) and 15-17 nm (crystallite) respectively [15].

Carbothermal reduction process involved long hours of heating raw materials at extremely high temperatures around 2200 - 3300 °C. Quartz sand and petroleum coke were used as precursor materials for this technique [20]. The summary of latest carbothermal reduction synthesis methods were summarized in Table 1. There are few publications that conducted the synthesis of nanostructured 2H-SiC and most of them carried out other polytypes product mainly 3C-SiC. However, the required synthesizing parameters for 2H-SiC produced were not fully analyzed by Zhang [9]. Complex carbothermal reduction method were employed by Zhu et al, Omidi et al, Mostaghi et al and Zhang et al including combination of sol-gel technique and TEOS infiltration. The carbothermal reduction experiment grown major phase of β-SiC and only small amount of α-SiC traced. The growth of α-SiC was claimed to have initiates beyond 1400 °C in temperature.

<table>
<thead>
<tr>
<th>Product</th>
<th>Size</th>
<th>Method</th>
<th>T (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>6H-SiC</td>
<td>Diameter ranging from 60 to 160 nm and length up to tens of microns</td>
<td>Carbothermal Reduction infiltrated TEOS</td>
<td>&gt;1300</td>
<td>[14]</td>
</tr>
<tr>
<td>SiC</td>
<td>Ultrafine globular particles</td>
<td>Sol-gel technique and carbothermal reduction</td>
<td>1450</td>
<td>[19]</td>
</tr>
<tr>
<td>SiC nanoparticles</td>
<td>5-25 nm</td>
<td>Carbothermic reduction</td>
<td>1450</td>
<td>[21]</td>
</tr>
<tr>
<td>2H-SiC nanoribbon</td>
<td>Tens to hundreds of microns in length, a few microns in width and tens of nanometers in thickness</td>
<td>Carbothermal reduction</td>
<td>1400</td>
<td>[9]</td>
</tr>
<tr>
<td>β-SiC nanowires and nanocables</td>
<td>20 µm in length</td>
<td>Carbothermal reduction</td>
<td>1800</td>
<td>[22]</td>
</tr>
</tbody>
</table>

3 Silicon carbide properties and applications

Silicon carbide has been considered as a promising candidate material in industrial application due to its superior properties in mechanical, optical, chemical and electronic fields. In terms of size, SiC is light weight and normally has low dimensionality so it is commonly available in nano size devices [8]. This type of material achieved high evaluations in terms of mechanical strength [19], hardness [21], thermal stability [15] and conductivity [23], good thermal shock resistance [24] with low thermal expansion coefficient [9] and good wear resistance [21], [23]. Meanwhile, in view of chemical properties, SiC displayed chemical and oxidation resistance due to its inertness [25]. The strong bond of Si-C protected the structure from undergoing chemical reaction. The advancement of synthesization techniques has grown over time making SiC one of the more affordable materials in bulk volume [3].

On the other hand, in electronic properties and application, it is well known as a wide band gap material. 2H-SiC possessed the largest band gap among them compared to other polytypes like 3C-SiC, 4H-SiC, and 6H-SiC [3], [8], [12], [13], [17]. The simulation prediction done by Monte Carlo showed higher electron mobility in 2H-SiC than other polytypes [25]. Another most important parameter is thermal conductivity. As one material
being exposed to heat, the changes of physical properties will happen. Thus, the carrier mobility will be lower as the temperature increases [26]. In harsh environment application, it is a necessity for SiC to possess high thermal conductivity compared to other metals [18]. In fact, most SiC has proven as a promising material which has higher thermal conductivity compared to copper (4.0 W/cm-K) that was set as benchmarking material [26].

Other SiC electronic properties are high breakdown electric field [2], high thermal and electrical conductivity [35], low quantum confinement [3], high ionic mobility [36] and high saturation electron drift velocity of the latter [24]. These electronic properties give major contribution to be the best selected material in electronic devices application such as power electronics, field electron emission, sensor, MOSFET, MESFET and so on. Besides, SiC appeared to be applied as blue and ultraviolet (UV) emitting diodes due to ability to emit high-intensity and stable UV and blue green lights [38].

On the other hand, since no cooling and transformer are needed, nanotechnology-based SiC become a more economical and effective material in engineering and industrial applications [26], [35]. SiC also owns diverse properties in electronic and optical fields. Thus, the application of SiC in optoelectronics, microelectronics, nanodevices, nanocomposites, hydrophobic devices and biomedical engineering application is vital and useful [1], [27].

4 Conclusion

This paper has reviewed several synthesis techniques that have been used to produce silicon carbide nanostructured material. Carbothermal reduction is the most commonly used technique due to its simple setup and economical process. Other techniques that can be used are chemical vapor deposition, laser ablation, sol-gel and microwave heating. All the techniques discussed have their own advantages to improve the formation of various types of silicon carbide.

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