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Review

Preparation of silicon nanomaterials by arc discharge

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A B S T R A C T S

Silicon (Si) has been occupying the central stage of semiconductor industries for many years. Si nanomaterials (SiNMs) have attracted great attention of many scientists and engineers for more than two decades, because of their unique properties. This review summarizes the preparation of SiNMs by arc discharge and their characterizations by different techniques. By changing arc discharge conditions, such as compositions and geometries of cathode and/or anode, voltage and current, and atmosphere in the chamber, etc., different types of SiNMs, including Si nanoparticles, Si nanowires, Si nanotubes, Si nanosheets, and some other nanomaterials containing Si, can be prepared. The formation mechanisms of these SiNMs are introduced briefly. Recent developments of arc discharge method will strongly promote its role in the preparation of SiNMs.

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1. Introduction

Si is a member of the main group IVA in the periodic table of elements and has been attracting the huge attentions of many scientists and engineers because of its physical and chemical properties. It is the extremely important and dominant component of semiconductor industries and also widely used in photovoltaic industries, due to its abundant reserves, low cost, and nontoxicity, compared with the semiconductors of other elements [1–4]. However, there are still several problems in some of its application areas, such as optics and optoelectronics, because of its indirect band gap structure. For example, the optoelectronic devices made of Si are less popular than those made of the elements of the main groups IIIA–VA, such as gallium arsenide with direct band gap structure, at the present time [5].

With the developments of nanoscience and nanotechnology, intense research efforts from both academic and technical sides have been devoted to SiNMs, in order to

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deeply investigate their properties and applications [6–8]. SiNMs have many physical and chemical properties different from those of bulk Si materials (BSiMs). For example, BSiMs show very poor luminescence in the infrared region at room temperature, due to their indirect band gap (~1.1 eV) between the conduction and valence bands and exciton binding energy (15 meV) [9]. When the sizes of BSiMs were decreased to nanoscale, the band gap energy was increased and the energy levels became discrete [10]. When the sizes of Si nanocrystals were decreased to 5 nm or less, they showed the differently optical properties due to the quantum confinement effects [10,11] and might even behave like the nanocrystals with direct band gap [12]. The size-dependent band gaps of SiNMs have been reported [13,14], e.g., the electrochemically etched and hydrogen capped Si nanoclusters with the sizes of 1.0, 1.67, 2.15, and 2.9 nm, have the band gaps of 3.44, 2.64, 2.39, and 2.11 eV, respectively [13]. SiNMs can exhibit photoluminescence from ultraviolet to visible regions [9,15–19]. For example, chain-like [15] and cubic crystalline [16] SiNMs can emit ultraviolet and red lights respectively, and some other SiNMs can emit violet, blue, green, and red lights [9,15–19]. In addition to photoluminescence, SiNMs also show some improved properties, such as field emission [20], mechanics [21], electrics [22], thermoelectrics [23,24], and catalytic activity [25], etc. Because of these properties, SiNMs may be used for many applications, including thermoelectricity [26], batteries [27], solar cells [28], catalysis [25], and sensors [29,30], etc. Some of these applications have been or will be commercialized.

SiNMs can be prepared strategically by two approaches, i.e., the top-down and bottom-up routes. But it is important to first consider which approach is more suitable for a specific application, as the properties of SiNMs are closely related with the approach adopted. Different methods can be used to reduce the sizes, improve the properties and enhance the yield of SiNMs. Some of the methods widely used to prepare SiNMs include chemical vapor deposition [31,32], liquid phase solution synthesis [33], arc discharge [34,35], hydrothermal deposition [36], electric field assisted growth [37], chemical etching [38,39], laser ablation [40,41], molecular beam epitaxy [42], and thermal evaporation [43], etc. Although each of them has its own advantages and disadvantages, the better method, i.e., simpler operation, lower cost, and higher quality and yield, needs to be developed.

Arc discharge, classified as a bottom-up approach, is an efficient method to prepare many kinds of novel nanostructures and nanomaterials. The arc discharge apparatus usually includes power supply, electrodes, chamber, cooling and vacuum-pumping systems, and desired medium (gas, mixture of gases or liquids). Although its design may vary from one research group to another, the basic principles are similar. Its major advantages are the convenient formation of very high temperature, relatively easy operations, easily available and cheap raw materials, and little special conditions. Its main disadvantages are usually the low selectivity and poor controllability of morphology, wide size distribution, low yield, inhomogeneous reactions, many byproducts, etc. These disadvantages greatly limit its role in the preparation of SiNMs. For more details about arc discharge, including arc discharge evolution, please read some of review papers recently published by other authors [44–47].

One of the two aims of this review is to attract more attentions of scientists and engineers on the preparation of SiNMs by arc discharge method, which include Si nanoparticles (SiNPs), Si nanowires (SiNWs), Si nanotubes (SiNTs) and Si nanosheets (SiNSs). The other one is to strongly promote the role of this method in the preparation of SiNMs, as our group recently used this method to successfully prepare the novel Si/N-doped graphene composite nanosheets [48], N-doped graphene [49,50], carbon encapsulated iron nanoparticles with different shell structures [51–54] and N-doped long bamboo-like carbon nanotubes [55], by using the anode with high content of SiO_2, increasing the temperature of nitrogen flowing into the arc discharge chamber, improving the homogeneity of anode or creating some special conditions, respectively. In fact, arc discharge method has been playing an important role in the preparations of carbon nanomaterials and nanostructures, especially fullerene (Nobel Prize in Chemistry in 1996, there are ca. 263 literatures in the online database of Science Citation Index (SCI)), carbon nanotubes (there are ca. 1350 literatures in the online database of SCI), graphene (Nobel Prize in Physics in 2010, there are ca. 206 literatures in the online database of SCI). It is very possible that this method will play an important role in the preparations of SiNMs in the future, if some or even all of its disadvantages can be overcome.

2. Si nanomaterials

Like any nanomaterials, SiNMs can be classified as zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) ones, according to their sizes in three-dimensional space. The preparations of 0D, 1D and 2D SiNMs by arc discharge have been reported. However, as a whole, the researches on the preparation of SiNMs by arc discharge are still at the primary stage until now, compared with other preparation methods. Therefore, there is a huge space for the development of such researches.

2.1. Si nanoparticles

0D SiNMs include SiNPs, Si quantum dots, nanodots or nanocrystals [7]. Sometimes Si nanoclusters are also categorized as SiNPs [7]. In the last decade the researches on SiNPs have been significantly increased [8], because of their luminescence, biocompatibility and easy surface functionalization. Due to their unique properties, especially luminescence, some remarkable breakthroughs have been obtained in some fields, such as detectors [56], light emitters [57,58], and waveguides [59].

The SiNPs were prepared by submerging electrodes about 10 cm below the surface of deionized water [60]. The adopted anode and cathode were Si rods with the diameters of 5 and 20 mm respectively. The deionized water was purged to remove the dissolved oxygen by continuously supplying argon (Ar). The arc discharge voltage and current were 25 V and 10 A respectively. The arc discharge was kept for 10 min and a pale yellow suspension was obtained. When the time was