# 直流电弧自催化合成 $\beta$-SiC 纳米线

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**摘要**：采用 C,Si 和 SiO$_2$ 为反应原料,利用直流电弧法制备出长直的 $\beta$-SiC 纳米线。纳米线的直径为 100~200 nm,长度为 10~20 μm,并且沿着<111>方向生长。通过 X 射线衍射(XRD)、扫描电子显微术(SEM)、透射电子显微术(TEM)、拉曼光谱等手段,对 $\beta$-SiC 纳米线进行表征。探讨了 $\beta$-SiC 纳米线自催化气–液–固(VLS)生长机制。

**关键词**：β-SiC；纳米线；直流电弧
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## Self-catalytic Synthesis of $\beta$-SiC Nanowires by Direct Current Arc Discharge

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**Abstract**：Straight and long $\beta$-SiC nanowires were synthesized in direct current arc discharge using a mixture of graphite, silicon, and silicon dioxide as the precursor. The diameter of the nanowires is 100~200 nm, and the length is about 10~20 μm. The axis of the nanowire is preferentially along the <111> direction. The morphology and structure of the nanowires were characterized by X-ray diffraction(XRD), scanning electron microscopy(SEM), energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM) and Raman spectroscopy. The $\beta$-SiC nanowires are suggested to be formed via a self-catalyzed vapor-liquid-solid growth mechanism.

**Key words:** $\beta$-SiC; nanowires; direct current arc discharge

Silicon carbide(SiC) is an important semiconductor material. Its high saturation velocity, wide band gap and high thermal conductivity make it highly attractive at high-temperature, high frequency and high power display applications [1,2] as well as usages in harsh environments [3]. Furthermore, it is one of the best biocompatible materials with existing and potential medical applications[4]. SiC nanowires possess a higher elasticity and strength than those of bulk SiC[5], which makes them promising candidates for the reinforcing phases in ceramics, metals, alloys and polymer matrix composites. Recently, the fabrication methods as well as the optical and electrical characteristics of silicon carbide nanocrystals, nanowires, nanotubes and nanosized films have been reviewed[6].

Earlier, through a reaction between the carbon nanotubes and SiO or Si-I$_2$, Dai et al [7] successfully synthesized SiC nanorods with diameters similar to those of the carbon nanotubes used as templates. Later, by using a conventional furnace with a sintered alumina tube, a two-step reaction has been developed for the synthesis of SiC nanorods [8]. In that process, SiO$_2$ firstly reacted with Si, the produced SiO vapor then reacted with carbon nanotubes to form SiC nanorods.

Zhou et al [9] utilized hot filament chemical vapor deposition(HFCVD) to grow β-SiC nanorods from a solid source of carbon and silicon on a Si substrate. Recently, the synthesis of β-SiC nanorods by the pyrolysis of polymeric precursor in the presence of $FeCl_2$ as a catalyst has been reported [10]. SiC nanowires and nanowhiskers also have been synthesized by a number of other approaches, including chemical vapor deposition (CVD)[11,12] and arc-discharge[13,14]. In most of these approaches, either expensive raw materials, catalysts or sophisticated techniques were used. These drawbacks may hinder the massive fabrication and application of SiC nanowires. It is still a challenge for scientists and industrialists to synthesize SiC nanowires in large scale by using a simple and low-cost method. Direct current arc discharge is an effective method for the synthesis of nano-sized particles, nanowires[13,14] and nanotubes [15]. In this letter, we report a simple, but effective method to produce large quantities of β-SiC nanowires with a high aspect ratio. The method is based on conventional direct current arc discharge and self-catalytic vapor-liquid-solid (VLS) growth mechanism without any catalyst and template.

## 1　Experimental

　　The apparatus used in this work is shown in Fig.1. The copper crucible anode was cooled by water and kept at room temperature. A tungsten rod with a purity higher than 99.99%, a diameter of 8 mm and a length of 30 cm was used as the cathode. A mixture of Si(mean size: 74 μm(200 mesh), purity: 99.5%, impurities: Fe, Cr, Ni), $SiO_2$(purity: 99.99%) and graphite powders with a molar ratio of 1:1:1, which had been pressed into a column with 18 mm in diameter and 4 mm in height in advance, was placed into the crucible as the reactant. The graphite also makes the columns conductive so that the direct current arc may be started up. The reaction chamber was first evacuated to less than 1 Pa. Then, the working gas(Ar, purity: 99.95%) was introduced into the chamber until the inner pressure reached 10 kPa. When the direct current arc discharge was ignited, the input current was maintained at 100 A, and the voltage was a little higher than 20 V. As time went on, both the gas
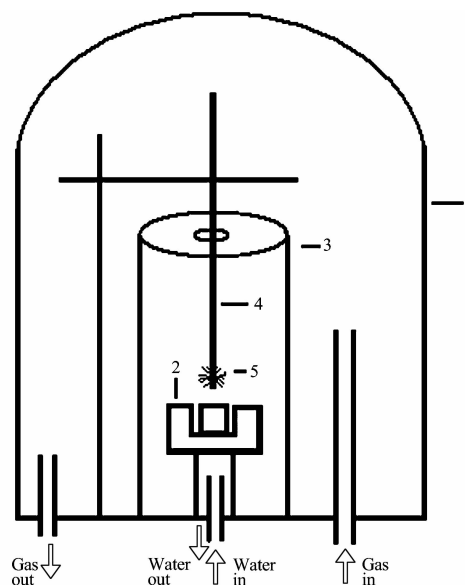


(1) reaction chamber; (2) water-cooled crucible; (3) water-cooled wall; (4) tungsten rod (cathode); (5) product collecting area

Fig.1　A sketch map of the direct current arc discharge system.

pressure and the arc voltage rose gradually. When the voltage reached 22 V and the pressure rose to 12 kPa the power supply was turned off 10 min later. After passivation in Ar for 6 h, dark gray powders were collected near the tip of the tungsten rod(see Fig.1).

　　Structural analysis of the products was carried out by powder X-ray diffractometry on a D8 DISCOVER GADDS diffractometer operated at 40 kV and 100 mA with Cu $K\alpha$ radiation($\lambda$=0.154 056 nm). The diffraction patterns were recorded on an image plate. The SEM images of the sample were taken on a JXA-8200 microscope operated on 10 kV and equipped with an energy dispersive spectrometer(EDS). The morphology of an isolated nanowire, as well as the selected area electron diffraction(SAED) pattern, was obtained via an H-8100 microscope using an accelerating voltage of 200 kV. The Raman scattering spectra were taken at room temperature on a Renishaw 1 000 spectrometer in a backscattering configuration, with the excitation wavelength of 514.5 nm produced by an Ar+ laser.

## 2　Results and discussion

　　A typical XRD pattern is shown in Fig.2. The peak around 25.95° is the characteristic diffraction of
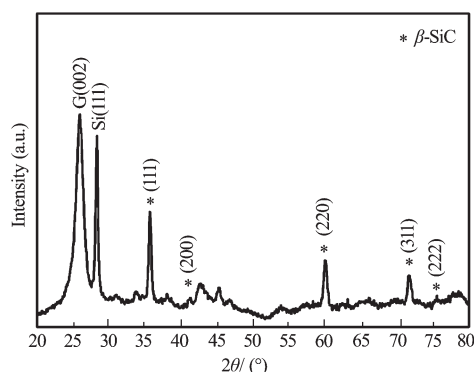
Fig.2　A typical XRD pattern of the synthesized product

graphite, corresponding to the(002) crystal planes. The peak centering at 28.32° is the characteristic diffraction of silicon, corresponding to the(111) crystal planes. The graphite and the silicon may come from the deposition of the unreacted source materials. There are five peaks at 35.69°, 41.29°, 60.06°, 71.68° and 75.52°, respectively, which are the characteristic diffractions of a face-centered cubic(fcc) lattice. The indexing of these peaks shows that they are the diffractions of the(111), (200), (220), (311) and (222) crystalline planes of a cubic lattice with the lattice constant $a$ =0.435 4 nm,

which is in good agreement with the known results(PDF # 742307) for $\beta$-SiC.

Fig.3(a) shows a typical SEM image of the sample. It can be seen that the sample consists mainly of nanowires, which are 100~200 nm in diameter and 10~20 $\mu$m in length. The nanowires are straight, randomly oriented. Provided that an over estimation of the growth time is 10 min, which is equal to a single experimental period, the nanowire growth rate($\sim$60 $\mu$m $\cdot$ h$^{-1}$) in the present work is about more than 20 times faster than that reported in an iron-catalyzed HFCVD synthesis($\sim$3.2 $\mu$m $\cdot$ h$^{-1}$)[16]. In that work, straight $\beta$-SiC nanrods of 20 ~70 nm in diameter and 1 $\mu$m in length were deposited on silicon substrates by HFCVD using a solid mixture of graphite, silicon, and silicon dioxide and iron particles as the catalyst. It has been reported that the addition of $SiO_2$ powders can not only produce straight nanorods, but also lead to a faster growth rate[16]. It is also of significance to find nanometer-scaled spherical droplets at the ends of the nanowires, which may have some implication on the growth mechanism of the $\beta$-SiC nanowires.
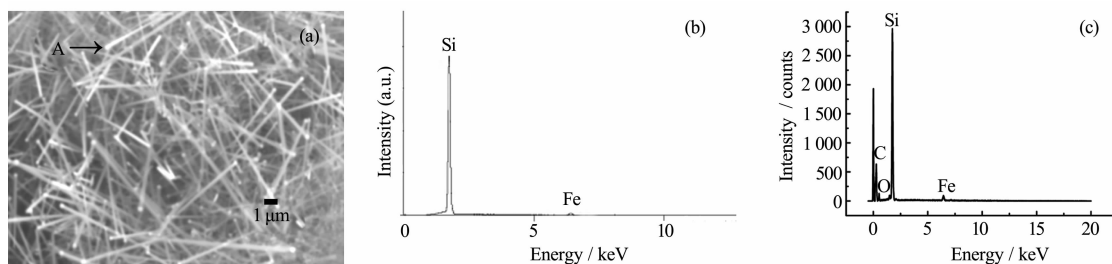


Fig.3　(a) A typical SEM image of the produced $\beta$-SiC nanowires; (b) The typical EDS spectrum from the tip of the nanowires (Point A); (c)The EDS spectrum from the nanowire stem

In order to study the growth mechanism of the $\beta$-SiC nanowires, the composition of the nanowires and droplets was measured using EDS. From Fig.3(c), it can be seen that the nanowire contains mainly C and Si elements. The EDS spectrum(Fig.3(b)) of a representative droplet(Point A) confirms that it contains mainly Si and only trace amount of Fe. The quantitative analysis demonstrates the predominance of silicon (99.34at% ), and a small amount of iron (0.43at% ). Presumably iron in the droplet comes from impurities in the initial Si powders. Although the traditional growth mechanism for nanowires is supposed to be a VLS

process with metal particles as catalysts, the formation of $\beta$-SiC nanorods undergoing a self-catalyzed VLS growth process with $SiCl_4$ and $CCl_4$ as reactants and Na as a coreductant has been reported[17]. It may indicate that metal catalyst is not indispensable in the formation of $\beta$-SiC nanowires. Thus, the EDS results here may indicate that the Si enriched droplets not only act as the reactant but also act as the catalyst. The $\beta$-SiC nanowires undergo a self-catalyzed VLS growth process in direct current arc discharge.

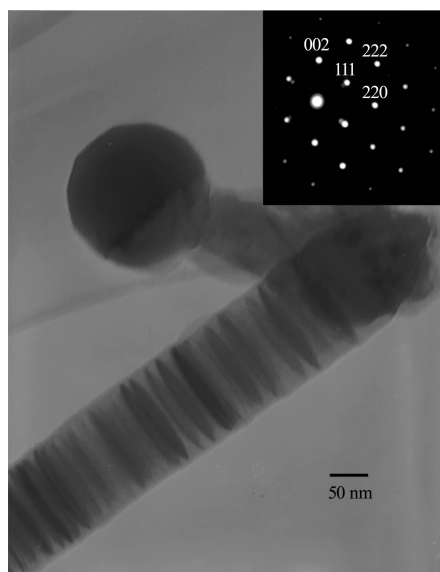Fig.4 shows the TEM morphology of an isolated nanowire. A droplet can be found at the top of the

Fig.4　TEM image of an isolated nanowire and its corresponding SAED pattern

nanowire as shown in Fig.3. The SAED pattern further confirms that the nanowire is $\beta$-SiC, with the axis parallel to the <111> direction. The growth orientation is consistent with that of $\beta$-SiC nanorods prepared by the pyrolysis of polymeric precursor in the presence of $FeCl_2$ as a catalyst[10].

Further evidence for the formation of $\beta$-SiC phase can be obtained through Raman scattering spectroscopy. A typical Raman scattering spectrum in Fig.5 shows a peak at about 795 cm$^{-1}$, which corresponds to the longitudinal phonon modes of $\beta$-SiC. As is well known, $\beta$-SiC is the most stable phase and its formation is more favorable in energy.
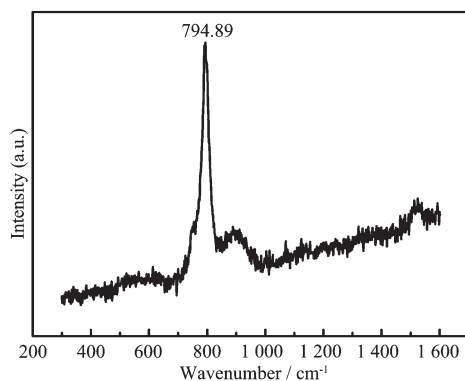


Fig.5　Raman scattering spectrum of the prepared nanowires

A proposed growth mechanism of SiC nanowires is as follows. In our experiment, the tungsten rod(cathode) and the source materials(anode) in the copper crucible are heated to $10^3 \sim 10^4$ ℃ within a few microseconds as soon as the arc discharge was started up. Then the stable arc discharge is established in space between the tungsten rod and the solid mixture at low gas pressure(~10 kPa). When higher gas pressure(~30 kPa) is chosen, no evidence of the growth of nanowires at the tip of the tungsten rod could be found. It means that the lower gas pressure is preferable for the synthesis of $\beta$-SiC nanowires.

The solid mixture of silicon, graphite and silicon dioxide are evaporated both thermally by the high temperature and by the bombardment of radicals of the arc zone. At the same time, the following reactions[8,18] might proceed among different particles.

$$SiO_2(s) + Si(s) \rightarrow 2SiO(v)$$
$$SiO_2(s) + C(s) \rightarrow SiO(v) + CO(g)$$
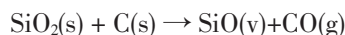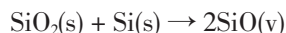
Reactive atoms and clusters are formed as a result of the ionization and decomposition of the radicals. Since pure Si boils at 2 355 ℃, pure $SiO_2$ and SiO boil at 2 233 ℃ and 1 880 ℃, respectively. These atoms and nanocluters are transported by convection to the cathode, forming a lot of Si rich nano-sized liquid droplets at the tip of the cathode, where the temperature is lower than 2 355 ℃. These Si-rich liquid droplets are preferred sites for disposition from the vapor. When the SiO and CO vapor molecules reach the vapor-liquid surface, they are dissociated into Si and C atoms. Both Si and C atoms are dissolved into the Si liquid droplets, which, induces precipitation of solid SiC at the liquid-solid interface upon supersaturation. Then the subsequent reaction may be possible:

$$SiO(v) + CO(v) \rightarrow SiC(s) + CO_2(v)$$
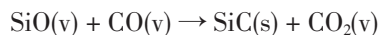
As precipitation continues, the nanowires grow, with their diameters proportional in size to the Si-rich liquid droplets. After the power supply is cut off, C atoms in the droplets are exhausted, thus resulting in Si riched droplets. As shown in Fig.3, the droplets are found at the end of $\beta$-SiC nanowires and the corresponding EDS results indicate that these nanowires are produced via a self-catalyzed VLS growth process.

# 3 Conclusion

In summary, straight and long $\beta$-SiC nanowires are directly synthesized in direct current arc discharge by using a mixture of graphite, silicon and silicon dioxide as the precursor. The diameter of the nanowires is 100~200 nm, and the length is about 10~20 μm determined through TEM and SEM studies. Droplets can be observed at the ends of the nanowires in the SEM and TEM images. EDS results suggest that they are Si rich droplets. The SAED pattern demonstrates that the nanowires grow along the <111> direction. The Raman scattering spectra confirm that the synthesized samples are $\beta$-SiC phases. The $\beta$-SiC nanowires are supposed to be formed via a self-catalyzed vapor-liquid-solid(VLS) growth mechanism.

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