Synthesis of \( \beta \)-SiC nanowhiskers by high temperature evaporation of solid reactants

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Abstract

\( \beta \)-SiC nanowhiskers were synthesized in large scale by evaporating the solid mixtures of silicon and silicon dioxide in a graphite crucible heated by a high-frequency induction system. Carbon source used for formation of the nanowhiskers came from the cheap common high-purity graphite at 1600 °C. XRD and TEM show that the nanowhiskers are crystalline \( \beta \)-SiC, and have diameters ranging from 15 to 50 nm and length up to several micrometers. Most of the nanowhiskers were wirelike and some nanowhiskers have high density stacking faults in the structure. The normal direction of the stacking layers ([111]) tilts by 12° with respect to the growth orientation ([223]). The growth mechanism of nanowhiskers is based on the reaction between silicon monoxide and carbon monoxide.

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1. Introduction

Silicon carbide (SiC) nanowhiskers have been extensively studied in recent years because of its remarkable electronic and mechanical properties with high hardness, high thermal stability, good flexibility and large band gap [1–3]. These nanowhiskers are being evaluated for a host of applications from semiconductor and field emission devices [4] to structural composites [5]. A variety of methods have been reported for the synthesis of \( \beta \)-SiC nanowhisker, including the carbon nanotube confined reaction method, carbon thermal reduction method, floating catalyst method and SiO thin film method [6–9]. In the process of preparing SiC nanowhiskers, the selection of carbon source is very important. At present, carbon sources used in the above-mentioned methods are usually carbon nanotubes, activated carbon, \( C_6H_6 \) and highly ordered pyrolytic graphite (HOPG). Although the high-quality \( \beta \)-SiC nanowhiskers could be obtained by using carbon nanotubes as carbon source, carbon nanotubes are too expensive to be employed in mass synthesis of \( \beta \)-SiC nanowhiskers. Using activated carbon easily makes the \( \beta \)-SiC nanowhiskers connect to either chains or fragments of SiC nanoparticles. \( C_6H_6 \) is poisonous. HOPG can easily produce amorphous carbon as by-products, which reduce the purity of products. Therefore, from a viewpoint of an actual application, suitable carbon sources are still under investigation for the large-scale production of \( \beta \)-SiC nanowhiskers. In the present paper, we report a novel synthesis technique of \( \beta \)-SiC nanowhiskers by evaporating a mixture of Si and SiO\(_2\) in common high-purity graphite crucible. In this method, common high-purity graphite was used as carbon source.

2. Experimental procedure

A high-frequency induction heating system was designed, as schematically depicted in Fig. 1. The growth of \( \beta \)-SiC nanowhiskers happened in a vertical heatronic reactor of quartz tube. In the middle of the quartz tube, there located an inductively heated cylinder crucible of high purity graphite (99.99%). A physical mixture of SiO\(_2\) and Si powder with molar ratio of 1:1 was put inside of the graphite crucible. The quartz tube was pumped down to a pressure of \( 4 \times 10^{-2} \) Torr. Argon gas flowed through the quartz tube at 100 sccm for keeping 20-Torr inert atmosphere. The mixtures in the graphite crucible were heated at 1600 °C for 15 min. The white-blue \( \beta \)-SiC nanowhiskers on the surface of graphite...
crucible were collected. The production rate is up to 0.0067 g/min. The morphology and the structure of the nanowhiskers were analyzed by X-ray diffractometer using Cu Kα radiation (XRD), transmission electronic microscopy (TEM), selected area electronic diffraction (SAED) and field emission scanning electron microscopy (SEM).

3. Results and discussion

Fig. 2 is an SEM image of the as-prepared β-SiC nanowhiskers growing on the surface of graphite. It is seen that there is a thick layer of β-SiC nanowhiskers on the surface of graphite, which indicates that the formation of SiC nanowhiskers is by growth on some random spots of the graphite crucible surface.

X-ray diffraction pattern of obtained nanowhiskers is shown in Fig. 3. All the strong intensity peaks can be indexed as β-SiC. The refinement gave the cell constant \( a = 4.358 \) Å, which is very close to the standard value for β-SiC (4.359 Å). There is a low intensity peak near \( 2θ = 33.5° \) marked with *, which is also observed by Liang et al. [10]. They confirmed that the occurrence of this peak results from the stacking faults. Some very weak peaks of silicon monoxide may also be observed in Fig. 3. This would result from the deposition of a small amount of gaseous silicon monoxide on the surface of as-prepared β-SiC nanowhiskers.

Fig. 4 is a TEM image showing the typical features of the β-SiC nanowhiskers synthesized in the present work. It can...
be easily seen that the product consists of high purity nanowhiskers, and other byproducts can hardly be identified. Most of the β-SiC nanowhiskers look wirelike and uniform, and have diameters ranging from 15 to 50 nm and length up to several micrometers.

Fig. 5a shows the TEM image of a single nanowhisker and the corresponding selected area electron diffraction (SAED) pattern. It can be seen that the nanowhisker exhibits a corrugated surface morphology and has a preferential growth along the direction of its axis. High-density stacking faults (striations) were observed. There is an interesting phenomenon that the normal of stacking faults [223] is tilted with respect to the direction of SiC nanowhisker axis [111] by about 12°. Similar tilt was also reported by Wang et al. [11]. However, their results show that the growth direction of SiC nanowhisker is tilted relative to the normal of stacking faults by about 30°, which is larger than our results. In most of the presently reported literatures, the axis direction of SiC nanowhisker runs parallel with the normal direction of the stacking faults [7–9]. The occurrence of tilted angle between axis direction of SiC nanowhisker and the normal direction of the stacking faults would be attributed to the relative shift between the blocks of atomic layers. A schematic figure is plotted in Fig. 5b. This also explains why the corrugated surface morphology can be observed in the nanowhisker. The nanowhisker observed in Fig. 5a is very straight, indicating that the translation between adjacent blocks of atomic layers seems to be able to keep a constant in the process of growth; that is to say, the latter SiC layer always inherits the characteristic of the former one. The reason resulting in this phenomenon is unclear at present.

According to Refs. [7,12–14], the formation of β-SiC nanowhiskers strongly depends on the selection of carbon source. In the present work, we observe that β-SiC nanowhiskers easily grow on the surface of graphite crucible. That is to say, the common high-purity graphite may provide the C species for β-SiC nanowhiskers. This is because the reaction temperature in our experiments (1600 °C) is higher than that in the carbon nanotube confined reaction method (1400 °C) [6], and the carbon thermal reduction method (1380 °C) [7]. Such high reaction temperature may make the carbon atoms on the graphite crucible become so active that they can react with gaseous SiO, which comes from the reaction between Si and SiO2 in 1600 °C, to produce SiC nucleus and supersaturated CO, and finally form SiC nanowhiskers. Therefore, we suggest that the increase of reaction temperature is a key factor for preparing the SiC nanowhisker by using normal high-purity graphite as carbon source. At present, there is not an effective and low-cost method for preparing high-quality β-SiC nanowhiskers yet. Most of methods reported need to use expensive carbon source or catalyst, which is hard to be removed completely in final production and therefore affects the purity of products. In present work, no catalyst is used and the high-quality β-SiC nanowhiskers can be produced in large scale by using cheap common high-purity graphite as carbon source only by elevating the reaction temperature.

4. Conclusions

β-SiC nanowhiskers were grown on the surface of a common high-purity graphite crucible by high temperature evaporation of solid mixtures of Si and SiO2. Common high-purity graphite was used as carbon source. Numerous stacking faults were observed in some β-SiC nanowhiskers with a preferential growth orientation [223], whose angle with stacking fault normal is about 12°. The large-scale high quality β-SiC nanowhiskers may be easily produced at low cost by using present method.

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References