Ultra-long Si₃N₄ nanobelts prepared by nanosilicon, nanosilica and graphite

Ping Hu, Shun Dong*, Cheng Fang, Yuan Cheng, Boqian Sun, Guiqing Chen

Science and Technology on Advanced Composites in Special Environment Laboratory, Harbin

Institute of Technology, Harbin 150001, PR China

Abstract:

The composition and morphology of obtained products depended on the processing atmosphere using the raw materials of nanosilicon, nanosilica and graphite, with N₂-generating several millimeters long single-crystal Si₃N₄ nanobelts (NBs) and Ar SiC nanobelts. The width and thickness of in situ NBs ranged from 100 to 300 nm and 50 to 100 nm with an average width of 196 nm, while the width and thickness of ex situ NBs fluctuated from 150 to 500 nm and 80 to 200 nm with an average width of 436 nm. Alumina-assisted VS mechanism was proposed for the growth mode of in situ growth of Si₃N₄ nanobelts, while a combined mechanism involving VS and VLS was controlled the growth of Si₃N₄ nanobelts obtained on the inner walls of the crucible due to the presence of Fe₂O₃, which provides an effective means of fabricating ultra-long Si₃N₄ nanobelts on an industrial scale.

Keywords: Si₃N₄; Nanobelts; Atmosphere; Mechanism¹

*Corresponding author: Tel/fax: +86 451 86403016.

E-mail address: dongshunhit88@163.com (S. Dong)

1. Introduction

Recently, one-dimensional (1D) nanostructures have attracted tremendous attention due to their potential application for promoting the fundamental researches and for constructing nanocomposites and nanoelectronics devices [1-4]. The properties of nanostructures not only rely on their chemical composition but also on their morphology, such as microstructure, phase and size [5]. Owing to their unique morphologies with rectangle-like cross section, belt-like nanostructures could be used as a possible candidate material for nanodevices, which have been prepared through different chemical or physical routes [6]. Si_3N_4 is an important material for a number of applications because of its unique mechanical, optical and electronic properties, such as high dielectric constant, large electronic gap, and strong resistance against thermal shock [7-9]. Great efforts have been made to synthesize Si_3N_4 nanobelts with numerous methods, including pyrolysis of polymeric precursor, solvothermal synthesis, sol-gel method, chemical vapor deposition, and carbothermal reduction [10-12]. For example, Yang et al. obtained Si_3N_4 nanomaterials with the lengths up to several millimeters through FeCl_2 -catalyzed pyrolysis of a polysilazane precursor and ultra-long Si_3N_4 NBs were also successfully synthesized by Al-catalyzed pyrolysis of amorphous silicon carbonitride precursors [13,14]. Although high-yield and ultra-long Si_3N_4 NBs were obtained by these techniques, several

shortcomings could be listed as following sentences. For instance, much residual carbon usually remained in the final products during the method of pyrolysis of polymeric precursor, and severe demands of materials and equipments, such as inflammable gas and superatmospheric pressure, which hinder the further separation and application of Si_3N_4 nanomaterials [15]. Furthermore, the lengths on the order of millimeters or even centimeters long Si_3N_4 nanomaterials might be more valuable compared to short ones in some fields (e.g., connections for devices and reinforcements for composites) [16]. Inspired by this, other novel preparation approaches should be explored to prepare high-yield and ultra-long Si_3N_4 nanomaterials.

In this paper, we attempt to synthesis of several millimeters long nanomaterials just by inorganic powders with nanosilicon, nanosilica and graphite under the conditions of Ar and N_2 , respectively. The obtained nanostructures were characterized detailed by many methods, and effect of different atmosphere on the nanostructures was investigated, including flow rates. Moreover, the possible growth mechanisms for the obtained nanomaterials were also proposed, respectively.

2. Experimental

2.1 Preparation of ultra-long nanomaterials

Commercial available nanosilicon (100 nm, Hefei Kaier Nanometer Energy &

Technology Co., Ltd, China), nanosilica (25 nm, Aladdin Industrial Corporation) and the graphite flake (20 μm , Qingdao Tiansheng Graphite Co., Ltd, China) were used as raw materials to synthesize several millimeters long Si_3N_4 nanomaterials. A detailed synthesis process was described and the powder was mixed as follows: 13.92 wt% nanosilicon, 29.83wt% nanosilica and 56.25 wt% graphite flake. The mixture powder was ball-milled in ethanol for 6 h with SiC balls and dried in a rotating evaporator, and then the mixture powder (1 g) was put into a ceramic crucible (60mm $\times$ 30mm $\times$ 30mm) and the crucible was placed into a tube corundum furnace. The furnace was heated up from room temperature to 300 $^{\circ}\text{C}$ with 80 min and kept for 10 min, and then heated up to 800 $^{\circ}\text{C}$ with 120 min and kept for 10 min, and further heated up to 1500 $^{\circ}\text{C}$ with 230 min and kept for 2 h. The furnace was cooled to 500 $^{\circ}\text{C}$ firstly with 300 min and then naturally cooled to room temperature after the heating was terminated. High-purity argon or nitrogen gas was kept flowing during the experimental process. The products looked like white wools were found on the surface of mixture powder and on the inner walls of crucible.

2.2 Characterization of ultra-long Si_3N_4 nanomaterials

The composition, size and structure of the products were examined by X-ray diffraction (XRD, X'PERT PRO MPD, Holland), scanning electron microscopy (SEM, HELIOS NanoLab 600i, America), transmission electron microscopy and

high-resolution transmission electron microscopy (TEM and HRTEM, Tecnai G²-F30, America) equipped with energy dispersive spectroscopy (EDS).

3. Results and Discussion

3.1 Morphology and structure analysis of nanomaterials obtained under different atmosphere

The ceramic crucible with mixture powder was first send into a tube corundum furnace under different atmosphere to study the yield and composition of nanomaterials, and the products obtained at 1500 °C in 100 ml/min of Ar were revealed in Fig.1. From the macroscopic morphology, no obvious white wools were found on the surface of mixture powder and the inner walls of crucible, and a few several micrometers long nanomaterials were generated on the surface of mixture powder from SEM image. In order to confirm the microstructure of above nanomaterials, STEM and HRTEM were employed and the results were shown in Fig.2. Products exhibited a belt-like (so called nanobelt) shape with some stacking faults in Fig.2 and the composition of the nanobelt (NB) was measured by EDS under HRTEM. EDS spectrum of the stem of above NB was shown in Fig. 2c and the NB contained Si and C without any other elements suggesting that the product was SiC, which was similar to the previous literature [17-19].

The morphology of white wools obtained both on the surface of mixture powder

and inner walls of crucible were characterized by SEM and digital camera under the conditions of 1500 °C and 100 ml/min of N₂ was shown in Fig. 3. It can be seen that the lengths of nanomaterials range from hundreds to thousands of micrometers and the products presented a belt-like shape from the high-magnification observation, which was more complex than previous expected. The width and thickness of NBs growth on the surface of mixture powder, namely in situ growth, ranged from 100 to 300 nm and 50 to 100 nm as shown in Fig. 3a, respectively. A width distribution histogram of NBs provides an average width of 196 nm and a main distribution range of 180–240 nm was shown in Fig. 3b. As for the NBs growth on the inner walls of crucible as shown in Fig. 3c, namely ex situ growth, the width and thickness fluctuated from 150 to 500 nm and 80 to 200 nm, respectively. Similarly, a width distribution histogram of NBs with an average width of 436 nm and a main distribution range of 350–550 nm as in the case of Fig. 3d. A typical XRD pattern of the powders ground from the white wools was shown in Fig. 4 and the main XRD peaks can be indexed to the hexagonal α -Si₃N₄ confirming that the product was α -Si₃N₄ phase. Therefore, different composition and yield of nanomaterials with similar morphology were obtained with different protective gas, with Ar-generating single-crystal SiC NBs and N₂ several millimeters long Si₃N₄ NBs.

3.2 Si₃N₄ Nanomaterials obtained at different flow rate of N₂

Owing to successful preparation of several millimeters long Si_3N_4 NBs in N_2 atmosphere, the effect of flow rate on the nanomaterial was studied and the effect of N_2 flowing rate at $1500\text{ }^\circ\text{C}$ on the generation of Si_3N_4 NBs was studied, which was shown in Fig.5. Different yields of white wools were obtained under different conditions, and 100 ml/min was probably suitable to produce a certain amount of nanomaterials from the macroscopic morphology of products. It should be noted that the yields of white wools on the surface of mixture powder were approximate, while the production of white wools on the inner walls of crucible were obviously different. In order to illustrate the difference production in different areas, including the surface of mixture powder and inner walls of crucible, some tests were employed. Surprisingly, two remarkably different morphologies exhibited from SEM images as shown in Fig.6. The morphologies of nanomaterials obtained both on the surface of mixture powder and the inner walls of crucible showed a belt-like shape, while there were some droplets located at the tips of nanomaterial on the inner walls of crucible suggesting that the nanomaterials generated at different locations with different growth mechanisms [20-22]. Furthermore, SEM observation combined with EDS spectrum can be used to determine the nanochemical composition of the nanobelts and to ascertain their growth mechanism. From a typical EDS spectrum of the tip of NB as shown in Fig.7, the droplet contained Si, N, C, O, Au and Fe elements, in

which Au came from the treatment of samples but the source of Fe should be discussed. Since catalyst was not used, Fe should come from the crucible, which is mainly composed of alumina and a small amount of impurity, such as Fe_2O_3 and SiO_2 . As we all known, Fe_2O_3 could be reduced into active Fe nanoclusters under the reductive gas, and Fe nanoclusters can become suitable sites to absorb gaseous containing Si and C elements (e.g., SiO and CO) to promote nucleation and growth of nanomaterial, which indicates that the growth mechanism of ex situ nanomaterial could be attributed to VLS growth mechanism [23,24]. Moreover, silica contained in crucible might also take part in the formation of nanomaterials, and alumina may be also as a novel and highly effective mediator playing an important role in controlling the concentration of gaseous containing Si [25]. Therefore, the reason for high yield nanobelts obtained on the inner walls of crucible could be attributed to a combined growth mechanism (VLS and alumina–assisted VS).

Moreover, some comparative experiments were employed to confirm the above analysis. Firstly, one comparison experiment was carried out in an alumina crucible with some pieces of graphite papers affixed to the inner walls of crucible to confirm the source of Fe, while other experimental parameters were kept constant, and the macroscopic and microstructure morphologies of obtained products were shown in Fig. 8. The white wools obtained on the upstream graphite paper were tested by SEM

and no droplets were found on the tips of nanobelts as shown in Fig. 8c, while there were some droplets located on the tips of nanobelts growth on the inner wall of crucible as shown in Fig. 8b, which confirmed the above analysis and the source of Fe came from the crucible. In addition, the other comparison experiment with a graphite crucible (100mm×40mm×10mm) was carried out and the macroscopic morphology of obtained products was shown in Fig. 8d. It can be seen that there were no obvious white wools on the surface of mixture powder and the inner walls of graphite crucible suggesting that the crucible played an important role in the growth of nanomaterials with alumina, SiO₂ and Fe₂O₃. Therefore, two different yields of nanomaterials obtained on different locations (on the surface of mixture powder and on the inner walls of crucible) were attributed to different growth mechanisms, in which the nanobelts obtained on the surface of mixture powder were controlled by an alumina-assisted VS mechanism, and a combined growth mechanism (VLS and alumina-assisted VS) was proposed for the growth mode of a high yield nanobelts obtained on the inner walls of crucible.

3.3 Growth process of Si₃N₄ nanobelts

The growth process of ultra-long Si₃N₄ nanobelts can be concluded by following sentences, and the reactions involved are represented as below:

It should be noted that reactions (1)–(4) can take place to form Si_3N_4 , in which reactions (1), (2) and (4) all involve SiO or CO vapor and these gases can be generated by the following reactions (5)–(10) [26,27].

During the first stage, reactions (5)–(10) carry out gradually to form a suitable atmosphere, including SiO and CO, for the growth of Si_3N_4 nuclei. Si_3N_4 nuclei would be formed by reactions (1)–(4) when the concentrations of reactant gases are appropriate. Moreover, the change in Gibbs free energy of reaction (1) is always below zero in the reaction temperature and the change in Gibbs free energy of reaction (2) is negative until the reaction temperature rise to high enough without taking into account of the effect of size, while the changes in Gibbs free energy of

other reactions are both positive without taking into account of the effect of nanosize based on the thermodynamic data [28]. Therefore, reaction (1) may be mainly responsible for the formation of Si_3N_4 nuclei due to a lower change in Gibbs free energy compared with that of reaction (2), and then provides CO gas for the subsequent reactions (2) and (4). Meanwhile, reaction (3) would take place slowly to promote the formation of Si_3N_4 nuclei as a result of close contact of SiO_2 and C in mixture powder [28]. After the Si_3N_4 nuclei formed, Si_3N_4 nanobelts might grow subsequently along a fixed axis. Therefore, the last stage is Si_3N_4 nanobelts subsequent growth along the axis direction, and the nanobelts would grow subsequently along a fixed direction as long as the reactant gases continuously generated.

4. Conclusions

Ultra-long Si_3N_4 nanobelts were successfully fabricated using the raw materials of graphite, nanosilicon and nanosilica by a simple method. The atmosphere played an important role in the formation of nanomaterials, with N_2 -generating several millimeters long single-crystal Si_3N_4 and Ar several micrometers long SiC nanobelts. Si_3N_4 nanobelts obtained on the surface of mixture powder were governed by an alumina-assisted VS mechanism, while a combined mechanism with VS and VLS was proposed to illustrate the growth model of longer and higher yield of Si_3N_4

nanobelts growth on the inner walls of crucible. This approach provides an effective way of preparation Si_3N_4 nanobelts on an industrial scale.

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Figure Captions:

Fig.1 SEM image of products obtained on the surface of mixture powder at 1500 °C in 100 ml/min of Ar with macroscopic morphology.

Fig.2 STEM and HRTEM images, and EDS spectrum of the stem of products obtained on the surface of mixture powder at 1500 °C in 100 ml/min of Ar. (a) STEM image, (b) HRTEM image, and (c) EDX spectrum of the stem of obtained nanomaterials.

Fig.3 Typical SEM images with the macroscopic morphology and the width distribution histogram of products obtained at 1500 °C for 2 h. (a) SEM images of white wools growth on the surface of mixture powder, namely in situ growth, (b) the width distribution histogram of products obtained on the surface of mixture powder, (c) SEM images of the products obtained on the inner walls of the crucible, namely ex situ growth, and (d) the width distribution histogram of products obtained on the inner walls of ceramic crucible.

Fig.4 Typical XRD pattern of white wools obtained at 1500 °C for 2 h.

Fig.5 Photographs of products obtained at 1500 °C with different flowing rates of N₂. (a) 50 ml/min, (b) 100 ml/min, (c) 200 ml/min and (d) 400 ml/min.

Fig.6 SEM images of products obtained on the surface of mixture powder and the inner walls of crucible at 1500 °C with different flowing rates of N₂. (a)-(b) 50 ml/min; (c)-(d) 100 ml/min; (e)-(f) 200 ml/min; and (g)-(h) 400 ml/min.

Fig.7 EDS spectrum of the tip of Si₃N₄ nanobelt obtained on the inner walls of the crucible.

Fig.8 Analysis of products obtained from comparative experiments. (a) Macroscopic morphology of products; (b) SEM image of products growth on the inner walls of the crucible; (c) SEM image of products obtained on the surface of graphite paper; and (d) macroscopic morphology of products obtained with a graphite crucible.

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