

Ultra-Long Single-Crystalline α - Si_3N_4 Nanowires: Derived from a Polymeric Precursor

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Single-crystalline α - Si_3N_4 nanowires were synthesized by thermal decomposition of a polysilazane preceramic polymer using FeCl_2 powders as catalyst. The nanowires, which are 20–40 nm in diameter and up to several mm in length, possess smooth surfaces and uniform diameters along the entire length and contain no detectable structural defects such as dislocation or stacking faults. The study also revealed that all nanowires grow along [100] direction. The growth of the nanowires is attributed to a novel solid–liquid–gas–solid reaction/crystallization process. The mechanism that governs the formation of nanowires rather than nanobelts is discussed.

I. Introduction

RECENTLY, the synthesis of one-dimensional nanostructured materials has attracted tremendous interest.¹ Due to their unique and superior properties,^{1,2} this class of materials is promising for applications in multifunctional nanocomposites and nanodevices of new kinds. For example, carbon nanotubes have been incorporated into ceramics for improving mechanical properties.^{3–5} Semiconductor nanorods have been used to fabricate nanolasers.^{6,7} Most recently, Tong *et al.*⁸ have reported the use of SiO_2 nanowires as subwavelength-diameter low-loss optical wave-guide.

Silicon nitride possesses excellent thermal and mechanical properties and is one of the most important engineering ceramics.^{9,10} Recently, it has been demonstrated that wide-band-gap single-crystalline Si_3N_4 can be an excellent host material with high doping levels, similar to the III–N compounds (such as GaN and AlN).^{11,12} Synthesis of one-dimensional silicon nitrides has been explored in the last few years because of their potentials in applications where mechanical strength and high-temperature/corrosive durability are required. Si_3N_4 nanowires have been synthesized using various methods, such as carbothermal reduction and nitriding reaction at high temperatures,^{13–19} combustion under a high N_2 pressure²⁰, and by hot-filament CVD or microwave plasma heating method.^{21,22} Zhang *et al.*²³ have demonstrated that Si_3N_4 nanowires possess much higher bending strength than their bulk counterpart.

In this paper we report a new simple method to synthesize Si_3N_4 nanowires, namely catalyst-assisted pyrolysis of polymeric precursors. A similar technique has been used to synthesize SiC nanorods²⁴ and Si_3N_4 nanobelts.²⁵ The synthesized nanowires, which grew along [100] direction only, are 20–40 nm in diameter

and up to several mm in length and have no detectable structural defects. The growth mechanism is ascribed to the unique solid–liquid–gas–solid (SLGS) reaction/crystallization. The formation of nanowires versus nanobelts is discussed.

II. Experimental Procedure

The experimental procedure is similar to that reported previously.^{24,25} A commercially available polyureasilazane (CerasetTM, Kion Corporation, Huntingdon Valley, PA) was used as the starting precursor. The as-received CerasetTM, which is liquid at room temperature, was first solidified by heat treatment at 260°C for 0.5 h in N_2 .²⁶ The obtained solid was then crushed into fine powders by high-energy ball milling for 24 h. 3 wt% of FeCl_2 powders (Beijing Bei Hua Fine Chemicals Company Ltd., Beijing, China) was added as catalyst during ball milling. The powder mixture was then placed in a high-purity alumina crucible and pyrolyzed in a conventional furnace with a graphite resistance under flowing ultra-high-purity nitrogen of 0.1 MPa. The powder mixture was heated to 1250°C at 10°C/min and held for 2 h followed by furnace cool. The experiments were also performed on the samples without FeCl_2 additives for comparison. The morphology, structure, and composition of the pyrolysis products were characterized using field emission scanning electron microscopy (SEM, JSM-6301F, JEOL, Tokyo, Japan) and a high-resolution transmission electron microscope (HRTEM, JEOL-2010F, Japan) equipped with energy-dispersive spectrum (EDS) and electron energy loss spectrum (EELS).

III. Results and Discussion

The morphology of the obtained Si_3N_4 nanowires was first observed under SEM. Figure 1(a) is a representative SEM image of the pyrolyzed products, showing that relatively high-density nanowires have grown homogeneously on the top of the powder matrix. Closer examinations under high magnification (Fig. 1(b)) reveal the cylindrical shape of the nanowires. The diameters of the nanowires are in the range of 20–40 nm with an average value of 30 nm, and the length of the nanowires can be up to several millimeters. The diameter within each individual nanowire is uniform along its entire length. The SEM observation also reveals that the surfaces of the nanowires are smooth and clean without any attached particles. The inset in Fig. 1(b) is a typical tip of the synthesized nanowires. No droplet was observed on the tip of the wires.

Further characterization of the morphology and crystalline structure of the synthesized nanowires was carried out using TEM and HRTEM. Figure 2(a) shows a typical TEM image of the Si_3N_4 nanowires. It can be seen from the image that the catalytic liquid droplet associated with the vapor–liquid–solid growth process²⁷ is not present at the tips of Si_3N_4 nanowires, suggesting there should be other growth mechanisms. The EELS

L. C. Klein—contributing editor

Manuscript No. 11272. Received August 16, 2004; approved November 18, 2004. Supported by the National Natural Science Foundation of China (Grant No. 50372031) and “Hundred Person” program of Chinese Academy of Science.

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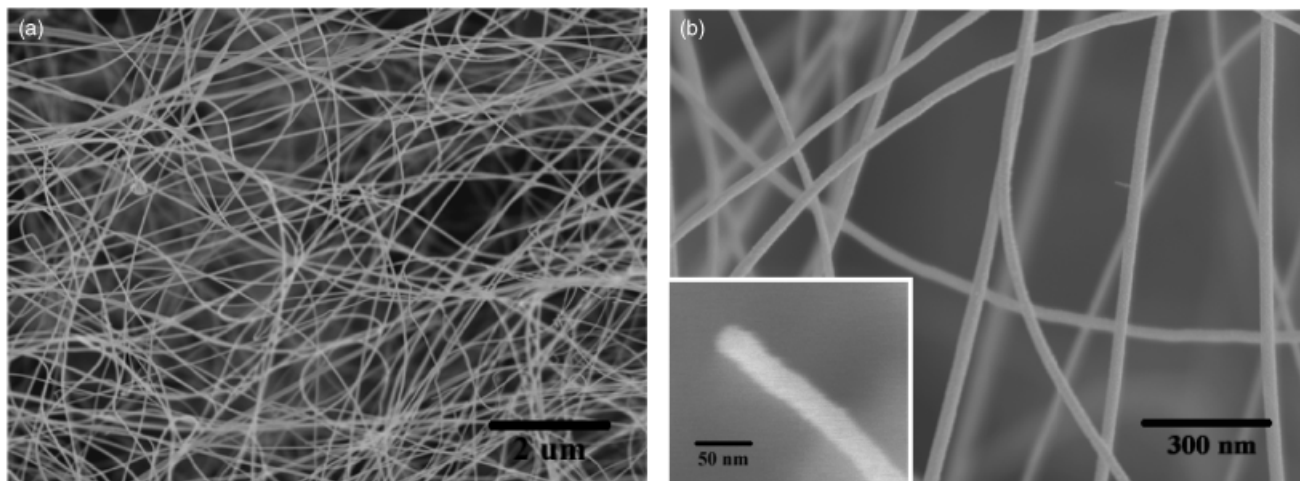


Fig. 1. (a) Low magnification scanning electron microscopy (SEM) image of the Si_3N_4 nanowires shows the homogeneous growth of Si_3N_4 nanowires and (b) higher magnification SEM image of the Si_3N_4 nanowires shows that the surfaces of nanowires are smooth and clean. The inset picture shows a typical nanowire tip; no liquid droplet has been observed.

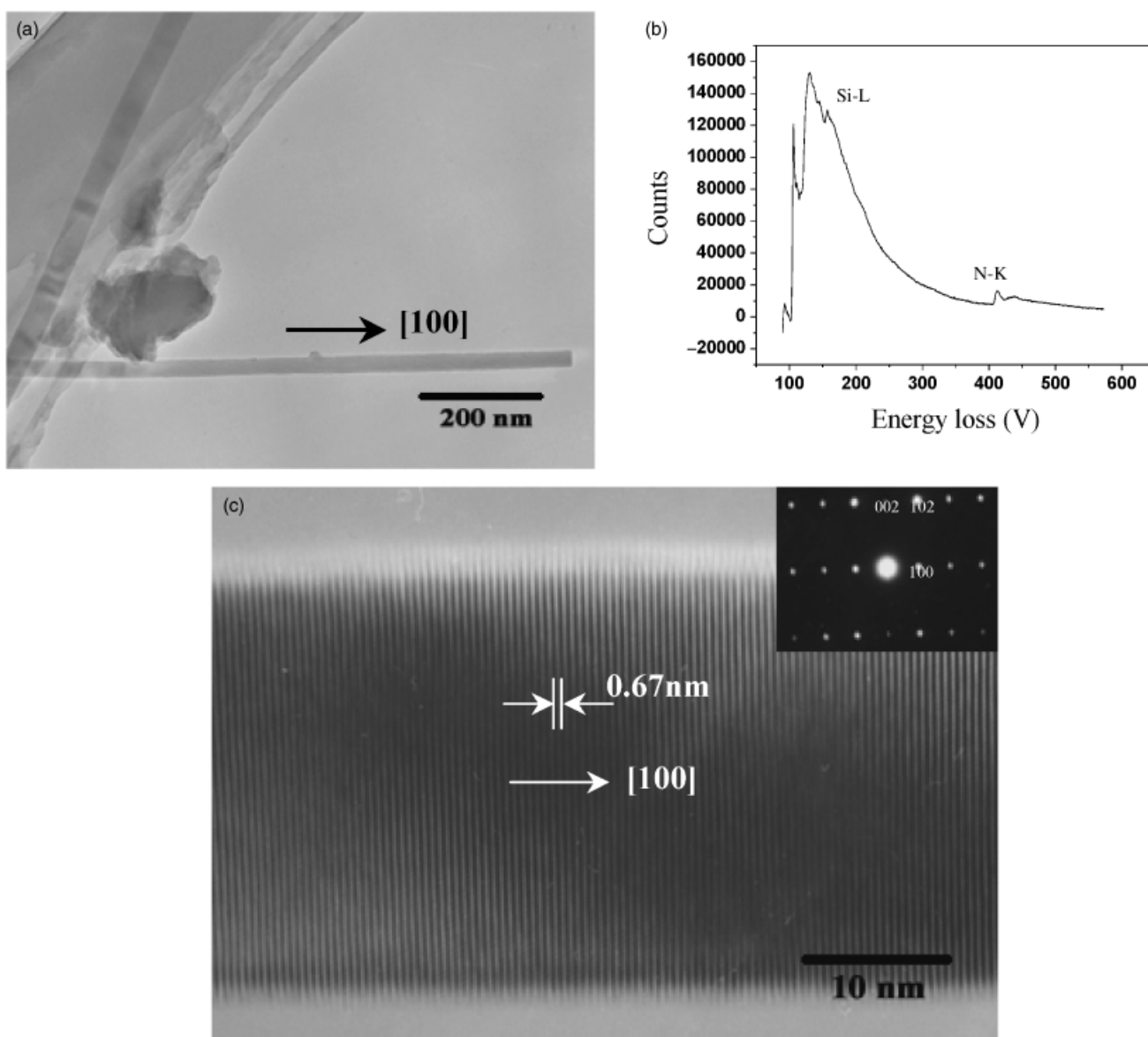


Fig. 2. (a) A typical transmission electron microscope image of Si_3N_4 nanowires; (b) the electron energy loss spectrum reveals that the wire consists of Si and N elements only, and (c) high-resolution transmission electron microscope images and corresponding selected area electron diffraction pattern of the $\alpha\text{-Si}_3\text{N}_4$ nanowire show that the nanowires possess perfect crystal structures and grew along [100] direction.

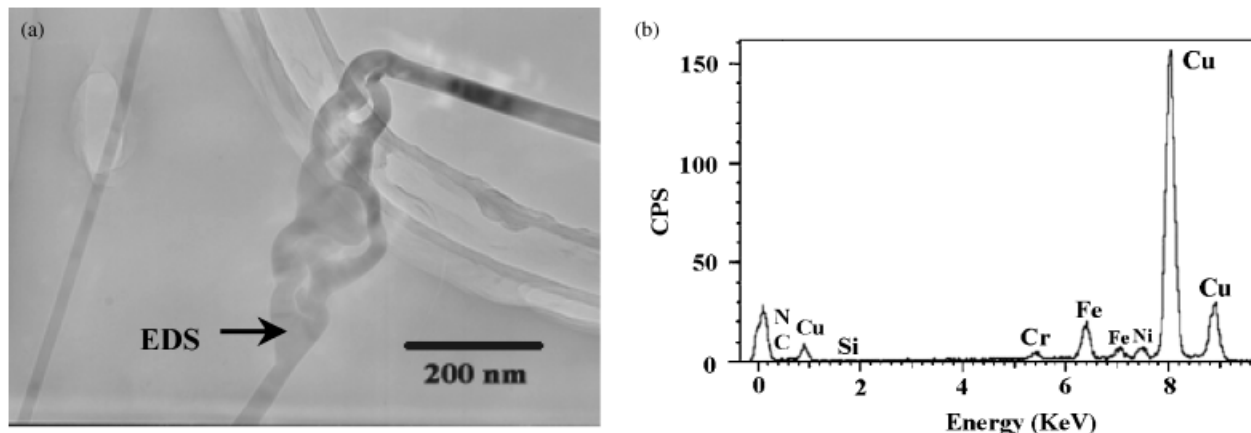


Fig. 3. (a) A typical transmission electron microscope image shows the roots of the Si₃N₄ nanowires. (b) A typical energy-dispersive spectrum obtained from the root of a nanowire suggested the existence of Fe.

spectrum of the nanowires (Fig. 2(b)) indicates that the nanowire consists of Si and N elements only. Figure 2(c) is a typical HRTEM image of the nanowires. The HRTEM image reveals that the nanowires possess a perfect crystal structure with few structural defects such as dislocations and stacking faults. The surface of the nanowire is clear and no amorphous layer is found. The inset in Fig. 2(c) is the corresponding selected area electron diffraction (SAED) pattern, which is identical over the entire wire, indicating the wire is single crystal. The lattice fringe spacing 0.67 nm in Fig. 2(c) agrees well with (100) planes of bulk α -Si₃N₄, where $a = 0.77541$ nm and $c = 0.56217$ nm (JCPDS Card No. 41-0360). The lattice fringes and the inserted SAED patterns suggest that the nanowires are of α -Si₃N₄ phase and grew along [100] direction. The examinations of more than ten wires reveal that [100] is the only growth direction for the nanowires.

No nanowires were formed in the samples without FeCl₂ additives, suggesting the catalytic growth of the Si₃N₄ nanowires in this study.

Previous studies^{24,25} suggested that the growth mechanism of one-dimensional nanomaterials via catalyst-assisted pyrolysis of polymeric precursors is a unique SLGS reaction/crystallization process. In this process, the Ceraset was first decomposed to amorphous SiCN at 1000°C.²⁶ The amorphous SiCN then reacted with Fe to form a liquid Si-Fe-C alloy at a temperature higher than the eutectic temperature of Si-Fe-C ternary system, and meanwhile released N₂ gas. Further reaction between the SiCN and the liquid alloy formed a liquid phase supersaturated with Si and C. This supersaturated liquid phase intends to precipitate crystalline phase. Since at the current heat-treatment conditions, namely 1250°C and 0.1 MPa N₂, silicon nitride is the most stable phase,²⁸ the supersaturated liquid phase reacted with N₂ gas in the protection atmosphere on the liquid/gas interface to form crystalline Si₃N₄. Due to the size confining effect of the liquid phase on the growth of the crystalline phase, the crystalline Si₃N₄ can only grow along length direction into a one-dimensional nanostructure. In order to further demonstrate this growth mechanism, the root of the nanowire was observed under TEM and the compositions of the root were measured using EDS. A typical TEM image of the root is shown in Fig. 3(a). The EDS spectrum (Fig. 3(b)) obtained from the root of the wires reveals that the droplet at the root contains Si, C, Fe, and a small amount of Cr, Ni (Cu element comes from Cu grid).

In our last point, we discuss the formation of nanowires versus nanobelts. A previous study²⁵ reported the formation of Si₃N₄ in a condition similar to the current one, except that the heat-treatment temperature was 1450°C in Yang *et al.*²⁵ instead of 1250°C used in this study. It is known that α -Si₃N₄ has a hexagonal structure and grain growth rates are dramatically different along different crystalline directions. Therefore, the growth along width and thickness directions at an earlier stage

promoted the formation of nanobelts in the previous study.²⁵ In the current study, the cross-section of the nanowire is close to a perfect circle, suggesting no grain growth along width and thickness directions at an earlier stage of the growth of the nanowires. We believed that the difference between the previous study²⁵ and the current one is that the sizes of the liquid phase formed at different temperatures are different. At higher temperatures, the saturated liquid alloy contains a higher amount of Si and C and forms a larger droplet than at lower temperatures. The smaller liquid droplet formed in this study limited earlier stage growth of the nuclei along width and thickness direction by size confining effect; thus nanowires instead of nanobelts were formed. Another possible explanation is that higher temperature favors anisotropy growth. A controlled experiment regarding this issue is undergoing.

IV. Conclusions

In summary, ultra-long α -Si₃N₄ nanowires have been synthesized via catalyst-assisted pyrolysis of a polymer precursor at 1250°C in 0.1 MPa N₂. The nanowire is single crystal, and contains no detectable structural defects such as dislocations or stacking faults. The diameters of the Si₃N₄ nanowires range from 20 to 40 nm with an average value at 30 nm and the lengths are up to several millimeters. The growth direction of the α -Si₃N₄ nanowires is [100]. The growth mechanism is a SLGS reaction/crystallization. The formation of nanowires instead of nanobelts is attributed to the small size of the liquid phase, which confined the growth in width and thickness directions.

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