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Growth of platelike and branched single-crystalline Si_3N_4 whiskers

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Abstract

In this communication, we report for the first time the growth of platelike and branched Si_3N_4 whiskers via catalyst-assisted pyrolysis of polymeric precursors. The as-prepared whiskers are single crystalline with a uniform thickness and width. The thickness and width of the Si_3N_4 whiskers range from 200 to 300 nm and 800 to 1200 nm, respectively. The platelike α-Si_3N_4 whiskers grew along [010] direction, while the branches grew along [001] direction. A growth mechanism based on solid–liquid–gas–solid reaction/crystallization is proposed. The formation of platelike whiskers instead of cylindrical whiskers is attributed to an anisotropic growth at an early nucleation/growth stage.

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1. Introduction

Due to its excellent thermal and mechanical properties, Si_3N_4 is an important engineering material for high temperature structural applications [1,2]. In addition, Si_3N_4 is also a wide band gap (5.3 eV) semiconductor in which midgap levels can be introduced to tailor its electronic/optic properties by properly doping [3,4]. Similar to the Group III-N compounds (such as GaN and AlN), Si_3N_4 could be an excellent host materials in terms of mechanical strength, thermal/chemical stability and high dopant concentration, thus promises for microelectronic/optic devices that can operate at high temperatures and radiation environments. In the recent years, extensive efforts have been devoted to the synthesis of one-dimension Si_3N_4 structures. Si_3N_4 nanorods [5–7] have been synthesized by mild benzene-thermal route [5], carbothermal reduction [6] and template method [7]. Si_3N_4 nanowires [8–17] have been synthesized by carbothermal reduction and nitriding reaction at high temperatures [8–13], combustion under a high N_2 pressure [14], hot-filament CVD and microwave plasma heating method [15–17]. Most recently, Si_3N_4 nanobelts have been synthesized via a vapor–solid thermal reaction between ammonia and silicon monoxide [18].

In this communication, we report the synthesis of platelike and branched Si_3N_4 whiskers via a new method, namely catalyst-assisted pyrolysis of polymer precursors. Si_3N_4 nanowires [19], Si_3N_4 nanobelts [20] and SiC nanorods [21] have been synthesized by using the similar technique. While branched structures have been synthesized in various materials [22–35], to the best of our knowledge, this is the first time that branched Si_3N_4 have been reported.

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Furthermore, the trunks and branches of the branched structures reported previously are nanowires [22–28], nanotubes [29], nanoneedles [30,31], or nanoprisms [35], both trunks and branches of the branched Si_3N_4 reported here possess belt-like morphologies. It is anticipated that the novel structures could be useful in fabricating three-dimensional composites and micro-/nano-devices.

2. Experiment

A polyureasilazane (Ceraset™, Kion Corporation, US) was used as the precursor in this study. The as-received Ceraset, which is liquid at room temperature, was first solidified by heat-treatment at 260 °C in N_2. The obtained solid was then crushed into fine powders by high-energy ball milling for 24 h with an addition of 3 wt% $FeCl_2$ powders (Beijing Bei Hua Fine Chemicals Company Lt. Beijing, China). The ball-milled powder mixture was then placed in a high purity alumina crucible and pyrolysized in a conventional furnace under flowing ultra-high purity nitrogen. The powder mixture was heated to 1450 °C at 10 °C/min and held there for 4 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, Japan), X-ray diffraction (XRD, Automated D/Max-RB, Rigaku, Japan) with Cu Kα radiation ($\lambda = 1.54178$ Å), and transmission electron microscope (TEM, JEOL-2010F, Japan) equipped with energy dispersive X-ray spectrum (EDS).

3. Result and discussion

Fig. 1(a) is a typical SEM image of the as-pyrolyzed products, showing that, relatively high-density whiskers have grown homogeneously on the top of the powder matrix. Closer examination under high magnification (Fig. 1(b) and (c)) reveals that the cross-sections of the Si_3N_4 whiskers are rectangular with the thickness ranges from 200 to 300 nm and the width from 800 to 1200 nm. Within each individual whisker, the thickness and width are uniform along its entire length, which can be up to several millimeters. The SEM observation shows that the surfaces of the whiskers are smooth and clean. Besides regular whiskers, intercrossed whiskers were also observed (Fig. 1(c)). Fig. 1(d) is a typical SEM image of the tip of the whisker, showing the triangle morphology. There are no liquid droplets at the tip, which was typically observed in vapor–liquid–solid (VSL) growth at the presence of catalysts [36], indicating the reported whiskers grew by fundamentally different mechanism.

Beside the platelike whiskers, the whiskers with branches were also observed (Fig. 2). It can be seen that the branches grow outward from the main stem, exhibiting T-shaped (Fig. 2(a)), cross-shaped (Fig. 2(b)), comb-like (Fig. 2(c)) and feather-like (Fig. 2(d)) morphology. The typical stem of the structures is platelike, and the thickness and width of the stem are about 200 and 1000 nm, respectively. In the comb-like and feather-like structures, the branches possess belt-like cross-section with a uniform thickness and width along the growth direction, which is are fundamentally different from those previously observed in other material systems, where the branches possess morphology of either wires or tubes or needles [22–30]. The branches are typically 50 nm in thickness and ~1000 nm in width, and the length can be up to more than ten micrometers. The branches are separated with a uniform distance on the stem and parallel to each other without sub-branches. The angle between the stem and branch is about 90°.

XRD pattern (Fig. 3) of the synthesized whiskers suggests that pyrolyzed products contain both α-Si_3N_4 and β-Si_3N_4 phases. The broad hump at lower angle regions suggests that the unconverted powders remains amorphous.

The structures of platelike and branched Si_3N_4 whiskers were further characterized with TEM. Fig. 4(a) shows the typical TEM image of the platelike Si_3N_4 whiskers. EDS analysis shows that the platelike whiskers consist of Si and N elements only. The inset picture in Fig. 4(a) is the corresponding select area electron diffraction (SAED) pattern that is identical over the entire whisker, indicating that the whisker is a single crystal and shows the hexagonal structure of α-Si_3N_4, where $a = 0.77541$ nm and $c = 0.56217$ nm (JCPDS Card No. 41-0360). Examination on more than 10 platelike whiskers suggests that [010] is the only growth direction for the platelike whiskers. Fig. 4(b) shows a Si_3N_4 stem at the stage to nucleate branches; numerous triangle droplets can be observed on the side of the stem. The inset picture in Fig. 4(b) is the typical EDS spectrum for the triangle droplets, which reveals that the droplets contain Fe element with a little amount of Cr and Ni (Cu elements come from the copper grid, and Cr and Ni may have come from the impurities of the $FeCl_2$ catalyst).

This result indicates the catalyst growth of the branches. Fig. 4(c) is a typical TEM image of T-shaped whiskers. The single crystalline nature of the branched structures is confirmed by SAED. SAED patterns recorded from different areas (indicated by the white circles) in a single dendrite are shown in Fig. 4(d). It is found that the SAED patterns recorded from different areas of the dendrite are almost identical, suggesting that the whole branched structure (stem + branches) is a single crystal. The SAED patterns can be indexed to the hexagonal structures of α-Si_3N_4. The growth directions of the stem and branch were [010] and [001], respectively.

No whiskers were formed in the samples without $FeCl_2$ additives, suggesting the catalytic growth of the Si_3N_4 whiskers.

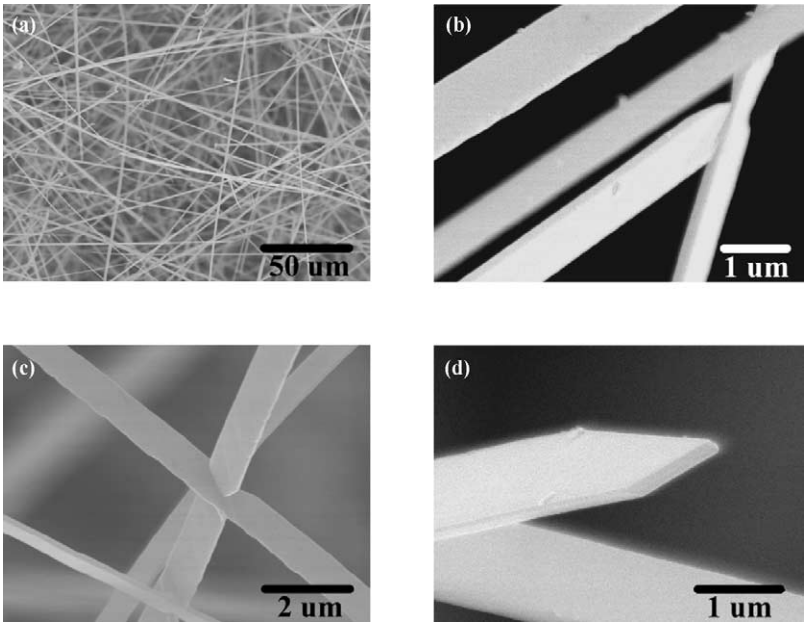

Fig. 1. SEM micrographs of platelike Si_3N_4 whiskers: (a) the morphology of the pyrolyzed product under low magnification; (b) shows rectangular cross section of the whiskers with clean surface; (c) shows the intercrossed platelike whiskers; (d) shows the triangle-shaped tip of the whisker without no liquid drop.

Typically catalyst-assisted growth of one-dimensional structures is through VLS mechanism [36], which is characterized by the presence of a catalyst droplet at the tips of the structures and requires the continuous supplement of gaseous species. Previous study [37] on the pyrolysis of Ceraset without catalyst revealed that the polysilazane was converted to an amorphous ceramic with an apparent composition of $SiC_{0.99}N_{0.84}$ at ~1000 °C at 0.1 MPa N_2. The material was stable up to ~1450 °C, where it crystallized to Si_3N_4 and free carbon [38]. It can be seen that at present heat-treatment conditions (1450 °C, 0.1 MPa N_2), there is no Si-containing gaseous phase. That, together with

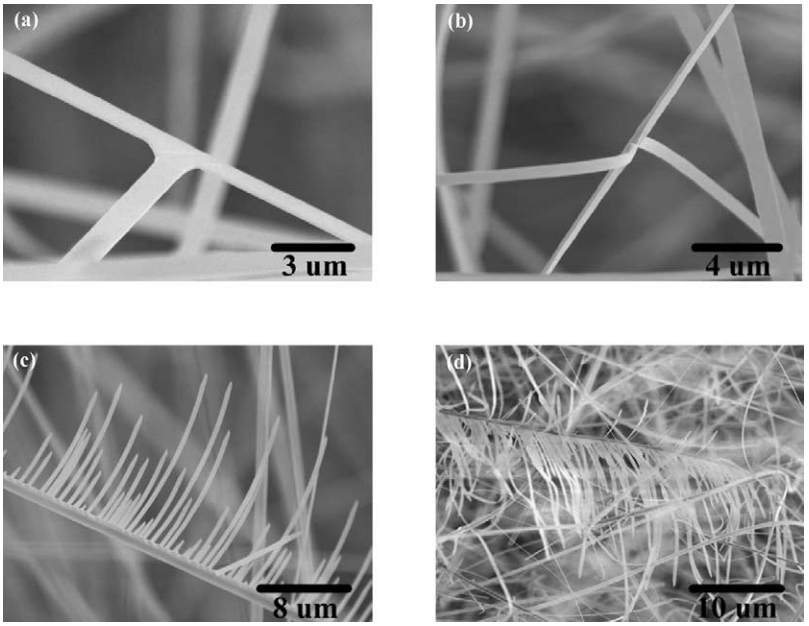

Fig. 2. SEM micrographs of branched Si_3N_4 whiskers: (a) T-shaped branched whiskers; (b) cross-shaped branched whiskers; (c) comb-like branched whiskers; (d) feather-like branched whiskers.

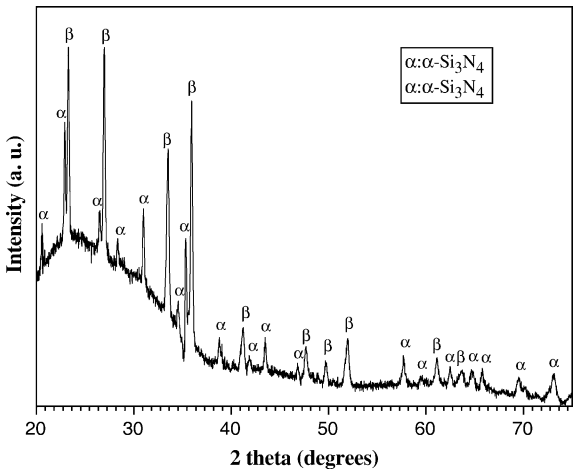

Fig. 3. XRD pattern of as-pyrolyzed products, indicating the coexistence of α- and β-Si_3N_4.

the fact of the absence of catalyst droplet at the tips of the whiskers (Fig. 1(d)), suggests that the growth of the whiskers reported here is not via VLS mechanism. In previous studies [19–21], we proposed a solid–liquid–gas–solid (SLGS) reaction/crystallization growth mechanism for the one-dimensional structures via catalyst-assisted pyrolysis of polymeric precursors. At the beginning of the process, the amorphous SiCN 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, meanwhile released N_2 gas. Further reaction of the solid SiCN and the liquid alloy resulted in a liquid supersaturated with silicon. This supersaturated liquid phase then reacted with N_2 gas to precipitate the Si_3N_4 whiskers (shown in Fig. 5(a)). The formation of silicon nitride, instead of silicon or silicon carbide, is due to that the silicon nitride is the most stable phase at the processing conditions. However, the mechanism that governed the formation of platelike instead of cylindrical whiskers is rather difficult to understand. The observation of the triangle-shaped tips (Fig. 1(d)) suggests a strongly anisotropy growth of the nuclei at earlier stage. It is believed [19,20] that at the beginning of the nucleation/growth of the Si_3N_4 nuclei, the growth of the nuclei occurs along all directions simultaneously. However, the growth rate along thickness directions is much slower than that along width direction due to the anisotropy nature of Si_3N_4 crystal structure. Consequently, the growth along axial and width direction resulted in the formation of triangle-shaped tips. The growth along width direction stops after it reaches a certain value limited by the confining effect of the liquid phase droplets and further growth only occurs along axial direction to form platelike whiskers.

Similarly, a two-stage SLGS growth mechanism is proposed for the growth of the branched structures. Firstly, silicon nitride platelike stems were formed via SLGS mechanism. Secondly, the impurity elements such as Fe, Ni and Cr were then deposited onto the surfaces of the stem uniformly. Another possible source for the impurity elements is the amorphous layer that generally formed on the surface of liquid–solid grown structures [39]. Such

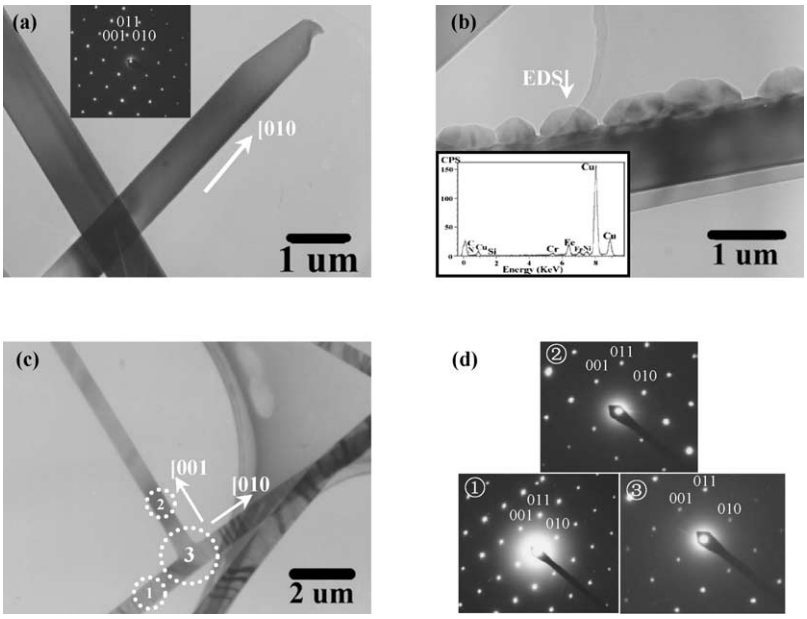

Fig. 4. TEM images and SAED patterns of the platelike and branched Si_3N_4 whiskers. (a) A typical TEM image of the platelike whiskers with the corresponding SAED pattern shows the single-crystalline structure with a preferred growth direction of [010]; (b) shows the nucleation stage of the branched whisker; (c) a typical TEM image of the T-shaped branched whisker; and (d) SAED patterns of the stem and the branch show the branched whisker is a single crystal with the preferred growth direction of [010] and [001] for the stem and branch, respectively.

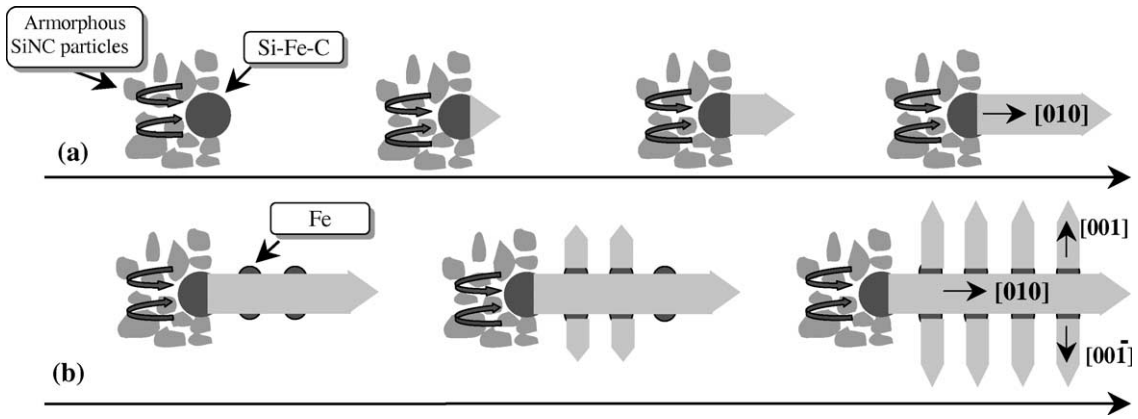

Fig. 5. (a) a schematic diagram showing the growth mechanism of the platelike whiskers; (b) a two-staged (based on a) growth mechanism of the branched whiskers.

impurities were then reacted with Si_3N_4 stem to nucleate liquid spots consisting of Si, Fe, Ni and Cr. Further reaction of the spots and the stem resulted in Si-supersaturated liquid. The belt-like branches then nucleated and grew via reaction of N_2 gas and the supersaturated liquid at the surfaces of the liquid droplets as shown in Fig. 5(b).

4. Conclusion

In summary, platelike and branched whiskers were synthesized via catalyst-assisted pyrolysis of polymeric precursors. The platelike whiskers are single crystals with a uniform thickness and width, ranging from 200 to 300 nm and 800 to 1200 nm, respectively. The preferred growth directions of the platelike whiskers are [010]. For branched structures, the whole structure is a single crystalline with the stem that grew along [010] direction and the branch that grew along [001] direction. The branches also possess belt-like morphology. A solid–liquid–gas–solid reaction/crystallization growth mechanism is proposed for both platelike and branched whiskers. The formation of platelike whiskers instead of cylindrical whiskers is attributed to the anisotropy growth at earlier stage.

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