

Asymmetric Silicon Nitride Nanodendrites

Weiyou Yang,^{*,†} Fengmei Gao,^{‡,§} Huatao Wang,[§] Zhipeng Xie,[§] and Linan An^{*,||}

Institute of Materials, Ningbo University of Technology, Ningbo, 315016, P. R. China, Laboratory of Excited State Process, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, 130033, P. R. China, State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing, 100084, P. R. China, and Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, Florida 32816

Received December 28, 2007; Revised Manuscript Received May 9, 2008

ABSTRACT: We have demonstrated the growth of asymmetric ordered Si_3N_4 nanodendrites via the catalyst-assisted pyrolysis of a polymeric precursor. The growth of the unique structure is due to the usage of a co-catalyst composed of a Fe–Al mixture. First, Si_3N_4 stems grow at an early stage via a gas–solid process with Al being the catalyst. Fe is then selectively deposited on the negatively charged ($0\bar{1}0$) surface of the Si_3N_4 stem to form catalytic droplets which promote the growth of the ordered nanowire branches. The novel nanostructures could be useful for the fabrication of nanodevices and nanocomposites. The principle demonstrated here is applicable for synthesizing ordered branched nanodendrites in other material systems.

Recently, extensive research efforts have been focused on controlling the morphology, structure, and crystallinity of one-dimensional (1D) nanostructures because these parameters have a profound effect on the properties and applications of the materials.¹ However, synthesis of nanostructures with controlled shapes/structures is not trivial. A promising approach to obtain nanostructures with unique morphologies and structures is a self-assembling process.² The driving forces for the self-assembly process can be van der Waals forces, hydrogen bonding,³ and surface energies.⁴ Self-assembly can also be achieved via surfactant assisted processes,⁵ by taking advantage of the surface charge of small particles⁶ and lattice mismatch.⁷ For ionic crystals, oppositely charged ions produce polar surfaces, which results in a divergence in the surface energies. Such surface polarities have been used as a driving force for the self-assembly of unique nanostructures such as asymmetric nanocantilevers,⁸ nanorings,⁹ and nanohelices.¹⁰

Silicon nitride is an important material with a set of excellent thermo-mechanical properties and chemical inertness.¹¹ The material exhibits a wide bandgap of 5.0 eV at room temperature.¹² Si_3N_4 has been considered as an excellent host material, in which midgap levels can be introduced by proper doping to tailor its electronic and optical properties.¹³ Because of these unique properties and potential applications in nanotechnology, 1D Si_3N_4 structures have been extensively explored.¹⁴ In previous studies on the catalyst-assisted pyrolysis of polymeric precursors, we demonstrated that the nanowires/nanobelts were grown when the Fe-containing catalyst was used via a solid–liquid–gas–solid (SLGS) process.¹⁵ In this communication, we report the synthesis of asymmetric Si_3N_4 nanodendrites by using a Fe–Al mixture as the co-catalyst. The obtained product exhibits a unique structure with ultralong ordered branches, which grow on only one side of the stem, which is different from most of the reported work in which the branches usually grew symmetrically on the stem. We find that the surface termination is a key factor for determining the asymmetric growth of the nanodendrites.

The asymmetric Si_3N_4 nanodendrites are synthesized via a catalyst-assisted pyrolysis of a polymeric precursor using a mixture of Al and Fe powders as the catalyst. The precursor is obtained by reaction of commercially available liquid-phased polyureamethylvinylsilazane (Ceraset, Kion Corporation, USA) and aluminum

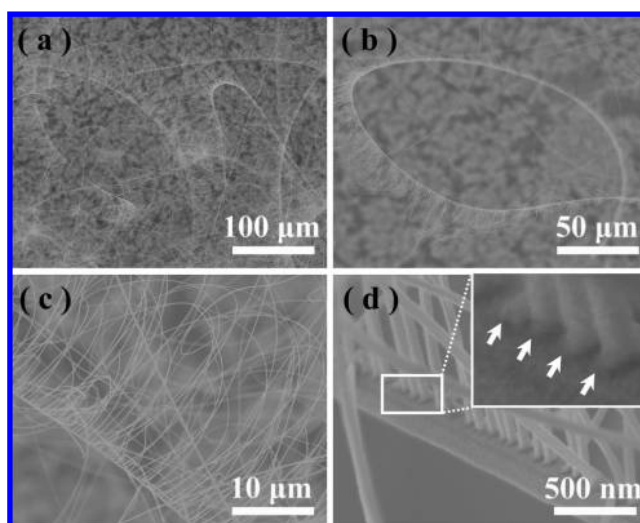


Figure 1. (a–d) Typical SEM images of the Si_3N_4 nanodendrites at different magnifications showing their overall and detail morphologies. The inset of (d) is the enlargement of the selected area; the arrowheads indicate catalytic droplets at the root of each branch.

isopropoxide powder (AIP, Beijing Bei Hua Fine Chemicals Company, Beijing, China) at the weight ratio of Ceraset-to-AIP = 2:1 using the procedure described previously.¹⁶ The obtained liquid-phased polyaluminasilazane is solidified by heat-treatment at 260 °C for 0.5 h in N_2 . The solid is crushed into a fine powder by high-energy ball milling for 24 h. 3 wt% of the metal mixture, which contains Al and Fe (both are 99.99% analytical purity, Beijing Bei Hua Fine Chemicals Company, Beijing, China) powders at the weight ratio of 1:1, is added during the milling. The mixture of the precursor and catalyst powders is pyrolyzed in a furnace of a graphite resistance under flowing ultrahigh purity nitrogen at 1350 °C for 2 h followed by furnace-cool to ambient temperature. The obtained products are characterized using field emission scanning electron microscopy (SEM, JSM-6301F, JEOL, Japan), and high-resolution transmission electron microscopy (HRTEM, JEOL-2011, Japan) equipped with energy dispersive X-ray spectroscopy (EDS).

Figure 1 shows typical SEM images of the as-synthesized sample at different magnifications. The most surprising feature of the product is that the branches only grew on one surface of the stem, to form a unique asymmetric dendrite structure. The branches are very long, up to several tens of microns (Figure 1b,c). The ultralong

* Corresponding authors. E-mail: weiyouyang@tsinghua.org.cn (W.Y.); lan@mail.ucf.edu (L.A.).

[†] Ningbo University of Technology.

[‡] Chinese Academy of Sciences.

[§] Tsinghua University.

^{||} University of Central Florida.

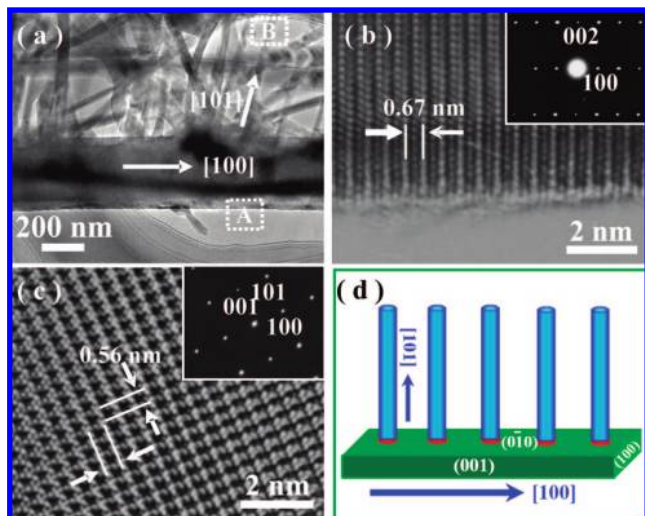


Figure 2. (a) TEM image of a Si_3N_4 nanodendrite. (b, c) HRTEM images of the stem and branch of the nanodendrite recorded from the areas A and B as marked in (a), respectively. The insets of (b) and (c) are the typical SAED patterns of the stem and branch, respectively. (d) Schematic model of branches grown on the $(0\bar{1}0)$ side of the preformed stem.

branches could be useful as connecting cables for nanodevices or as three-dimensional reinforcements for nanocomposites. The wire-shaped branches are very uniform in size with a diameter of ~ 50 nm and uniformly separated from each other by ~ 50 nm (Figure 1d). Closer observation shows that catalytic droplets exist at the roots of the branches (as indicated by arrows in the inset of Figure 1d), suggesting the branches grew via the SLGS process.¹⁵

The structure of the asymmetric nanodendrites has been further analyzed by TEM. Figure 2a is a low magnification TEM image of the nanodendrite with the surface that is opposite to the branch-growing surface facing the observer. The nanodendrite survives the severe ultrasonic treatment during TEM sample preparation and maintains its integrity, suggesting that the stem and branches are strongly bonded together. Figure 2, panels b and c are HRTEM images of the stem and branch, respectively. Both stem and branch exhibit smooth and clean surfaces without amorphous layers. The lattice spacing of 0.67 nm measured for both the stem and branch corresponds to the (100) planes of $\alpha\text{-Si}_3\text{N}_4$. The corresponding select area electron diffraction (SAED) patterns (the insets of Figure 2b,c) are identical over the entire stem and branch, indicating that both of them are single crystal in nature. The HRTEM and SAED show that the stem grows along $[100]$; the branch grows on the $(0\bar{1}0)$ surface of the stem along $[101]$. A schematic model on the corresponding crystallographic facets/direction is given in Figure 2d. The crystalline orientations of the stem and branch suggest that they are not one crystal, which is because the growth of branches is via the SLGS mechanism, instead of epitaxial growth on the stem.

Figure 3a is a low magnification TEM image of a typical stem formed at an early growth stage, which is typically found in the products obtained at very short pyrolysis time (~ 20 min) by stopping the process when the branches have not grown yet. Dark spots, which are uniformly distributed, are observed on its $(0\bar{1}0)$ surface (indicated by the white arrowheads in Figure 3a), but not on other surfaces. Energy dispersive spectrum (EDS) analysis reveals that the spots contain Fe, as well as Al and Si. These spots are apparently the catalytic droplets from which the branches will grow in the later stages. Consequently, the growth of the asymmetric nanodendrites is through a VS + SLGS process. VS and SLGS mechanisms are common mechanisms for the growth of 1D nanostructures. The VS mechanism is that the raw materials are first vaporized into gaseous phase(s); then the gaseous phase(s) was/

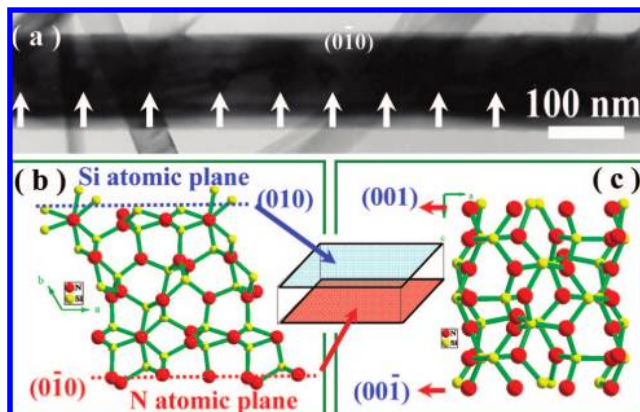


Figure 3. (a) A TEM image of a stem obtained in the early growth stage where the branches have not grown yet. (b, c) Structural models of $\alpha\text{-Si}_3\text{N}_4$ viewed from $[001]$ and $[010]$, respectively.

were condensed to form the nanomaterials. The SLGS mechanism was proposed by the current authors to explain the growth of Si_3N_4 nanostructures via catalyst-assisted pyrolysis of polymer precursors, in which the precursors were first reacted with the catalyst (such as Fe) to form Fe–Si–C catalytic droplets; then the supersaturated droplets reacted with N from the gas phases and raw materials to form Si_3N_4 .¹⁵ At the early stage of the current process, Si_3N_4 belt-shaped stems were first formed via a VS process, which consisted of the results when Al powders were used separately as the catalysts for the growth of the nanobelts, since products were only obtained on the walls of the alumina crucible and no catalyst droplets on both tips and roots of the belts were observed. The VS process is a fast process and the nanobelts can be formed in a relatively short time. Fe vapor was then selectively deposited on the $(0\bar{1}0)$ surface of the nanobelts which then reacted with the belts to form the catalytic droplets. Finally, the nanobranches were grown from the catalytic droplets via a SLGS mechanism.¹⁵ The growth of the nanowire branch is due to the small liquid droplet formed from the deposited Fe atoms on the stem and limits the earlier stage growth of the nuclei along the width and thickness direction by size confining effects; thus nanowires instead of nanobelts were formed.¹⁵ Here, we would like to point out that the successful synthesis of the nanodendrites lies in the use of the co-catalyst of Fe and Al. Only nanowires/nanobelts, instead of the nanodendrites, were obtained when they were used separately. The usage of the co-catalyst kinetically separates the growth stages of the stems and the branches, leading to a self-assembly process for the growth of the nanodendrites.

It is clear that the formation of the asymmetric nanodendrites is because the catalytic droplets can form only on the $(0\bar{1}0)$ surface of the stem. The selective deposition of the catalytic droplets on the $(0\bar{1}0)$ surface of the stem is a direct result of the difference between the surface terminations of Si_3N_4 (Figure 3b,c). $\alpha\text{-Si}_3\text{N}_4$ has a hexagonal structure and its (010) and $(0\bar{1}0)$ surfaces are terminated with Si and N and are thus positively and negatively charged, respectively (Figure 3b). Meanwhile, the (001) and $(00\bar{1})$ planes are both terminated with Si and N of equal numbers, and are electrically neutral (Figure 3c). The vapor of the catalytic elements, which is ionized to possess positive charges,¹⁷ is attracted by the negatively charged $(0\bar{1}0)$ surface to selectively deposit and form catalytic droplets on the surface.

In summary, we have demonstrated the growth of asymmetric ordered Si_3N_4 nanodendrites via the catalyst-assisted pyrolysis of a polymeric precursor. The nanodendrites are composed of plate-like stems and ultralong, fine wire-like branches of up to tens of microns long and a uniform size of ~ 50 nm. The unique usage of the Fe–Al mixture as the cocatalyst leads to a novel self-assembly process, in which the stems were grown first via the VS process with Al being the catalyst; the Fe was then selectively deposited

on the negatively charged (0 $\bar{1}$ 0) surface of the stem which resulted in the asymmetric growth of nanobranches. The obtained nanostructures could be useful in the fabrication of nanodevices and nanocomposites. The reported technique provides a novel and facile method to fabricate the ordered branched nanodendrites.

Acknowledgment. This work is financially supported by the National Natural Science Foundation of China (NSFC, Grant No. 50602025), Natural Science Foundation of Ningbo Municipal Government (Grant No. 2006A610059).

References

- (1) (a) Hao, E.; Bailey, R. C.; Schatz, G. C.; Hupp, J. T.; Li, S. Y. *Nano Lett.* **2004**, *4*, 327. (b) Hill, J. P.; Jin, W. S.; Kosaka, A.; Fukushima, T.; Ichihara, H.; Shimomura, T.; Ito, K.; Hashizume, T.; Ishii, N.; Aida, T. *Science* **2004**, *304*, 1481.
- (2) (a) Martin, B. R.; Dermody, D. J.; Reiss, B. D.; Fang, M. M.; Lyon, L. A.; Natan, M. J.; Mallouk, T. E. *Adv. Mater.* **1999**, *11*, 1021. (b) Pacholski, C.; Kornowski, A.; Weller, H. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 1188.
- (3) (a) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335. (b) Banfield, J. F.; Welch, S. A.; Zhang, H. Z.; Ebert, T. T.; Penn, R. L. *Science* **2000**, *289*, 751.
- (4) (a) Wang, Z. W.; Daemen, L. L.; Zhao, Y. S.; Zha, C. S.; Downs, R. T.; Wang, X. D.; Wang, Z. L.; Hemley, R. J. *Nat. Mater.* **2005**, *4*, 922. (b) Yin, L. W.; Bando, Y. *Nat. Mater.* **2005**, *4*, 883.
- (5) (a) Sun, D.; Riley, A. E.; Cadby, A. J.; Richman, E. K.; Korlann, S. D.; Tolbert, S. H. *Nature* **2006**, *441*, 1126. (b) Li, M.; Schnablegger, H.; Mann, S. *Nature* **1999**, *402*, 393.
- (6) Kalsin, A. M.; Fialkowski, M.; Paszewski, M.; Smoukov, S. K.; Bishop, K. J. M.; Grzybowski, B. A. *Science* **2006**, *312*, 420.
- (7) (a) Gao, P. M.; Ding, Y.; Mai, W. J.; Hughes, W. L.; Lao, C. S.; Wang, Z. L. *Science* **2005**, *309*, 1700. (b) Wang, H.; Liu, G.; Yang, W.; Lin, L.; Xie, Z.; Fang, J.; An, L. *J. Phys. Chem. C* **2007**, *111*, 17169.
- (8) Wang, Z. L.; Kong, X. Y.; Zuo, J. M. *Phys. Rev. Lett.* **2003**, *91*, 185502.
- (9) Kong, X. Y.; Ding, Y.; Yang, R.; Wang, Z. L. *Science* **2004**, *303*, 1348.
- (10) Kong, X. Y.; Wang, Z. L. *Nano Lett.* **2003**, *3*, 1625.
- (11) (a) Ziegler, G.; Heinrich, J.; Wötting, C. *J. Mater. Sci.* **1987**, *22*, 3041. (b) Govila, R. K. *J. Mater. Sci.* **1985**, *20*, 4345.
- (12) Zhang, L. G.; Jin, H.; Yang, W. Y.; Xie, Z. P.; Miao, H. H.; An, L. N. *Appl. Phys. Lett.* **2005**, *86*, 061908.
- (13) (a) Munakata, F.; Matsuo, K.; Furuya, K.; Akimune, Y. J.; Ishikawa, I. *Appl. Phys. Lett.* **1999**, *74*, 3498. (b) Zanatta, A. R.; Nunes, L. A. O. *Appl. Phys. Lett.* **1998**, *72*, 3127. (c) Yang, W. Y.; Wang, H. T.; Liu, S. Z.; Xie, Z. P.; An, L. N. *J. Phys. Chem. B* **2007**, *111*, 4156.
- (14) (a) Han, W. Q.; Fan, S. S.; Li, Q. Q.; Gu, B. L.; Zhang, X. B.; Yu, D. P. *Appl. Phys. Lett.* **1997**, *71*, 2271. (b) Zhang, Y. J.; Wang, N. L.; Gao, S. P.; He, R. R.; Miao, S.; Liu, J.; Zhu, J.; Zhang, X. *Chem. Mater.* **2002**, *14*, 3564. (c) Farjas, J.; Rath, C.; Pinyol, A.; Roura, P.; Bertran, E. *Appl. Phys. Lett.* **2005**, *87*, 192114. (d) Yin, L. W.; Bando, Y.; Zhu, Y. C.; Li, Y. B. *Appl. Phys. Lett.* **2003**, *83*, 3584. (e) Shen, G. Z.; Bando, Y.; Liu, B. D.; Tang, C. C.; Huang, Q.; Golberg, D. *Chem.-Eur. J.* **2006**, *12*, 2987. (f) Hu, J. Q.; Bando, Y.; Sekiguchi, T.; Xu, F. F.; Zhan, J. H. *Appl. Phys. Lett.* **2004**, *84*, 804.
- (15) (a) Yang, W. Y.; Xie, Z. P.; Miao, H. Z.; Zhang, L. G.; Ji, H.; An, L. N. *J. Am. Ceram. Soc.* **2005**, *88*, 466. (b) Yang, W. Y.; Xie, Z. P.; Li, J. J.; Miao, H. Z.; Zhang, L. G.; An, L. N. *J. Am. Ceram. Soc.* **2005**, *88*, 1647.
- (16) Dhamne, A.; Xu, W.; Fooks, B. G.; Fan, Y.; Zhang, L.; Burton, S.; Hu, J.; Ford, J.; An, L. *J. Am. Ceram. Soc.* **2005**, *88*, 2415.
- (17) Gennady, L. G.; Charles, W. B. *J. Phys. Chem. A* **2003**, *107*, 7013.

CG701276T