

Rapid Communication

Mass production of very thin single-crystal silicon nitride nanobelts

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Abstract

We report the large-scale synthesis of very thin single-crystalline Si_3N_4 nanobelts with high yield via catalyst-assisted pyrolysis of polymeric precursors. The obtained nanobelts, which show a perfect crystal structure and smooth surface, are up to several millimeters in length with typical width and thickness of ~ 800 nm and tens of nanometers, respectively. It is believed that the nanobelts were grown via a vapor–solid process, in which Al catalyst played a key role. This result provides a possibility for mass producing high quality, very thin Si_3N_4 nanobelts.

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1. Introduction

The fabrication of one-dimensional nanostructures, such as nanowires, nanorods, nanotubes, and nanobelts has been a hot research area for the last decade because these materials are promising for many important applications and important for the understanding of fundamental physical concepts [1]. Among these one-dimensional nanostructures, nanobelts represent a special geometrical shape of a rectangular cross-section and have attracted extensive interest for their promising applications in building nanodevices and fully understanding dimensionally confined transport phenomena in functional nanomaterials [2]. Many research efforts have been put to the synthesis of nanobelts in different material systems, such as metal substances [3], oxides [4], nitrides [5], sulfides [6], carbides [7], and other compound nanobelts [8].

Silicon nitride (Si_3N_4) is an important engineering ceramic for a variety of applications owing to its excellent

thermo-mechanical properties and chemical stability [9]. The material is also a wide-band gap semiconductor with a band gap of 5.3 eV, in which the mid-gap levels can be introduced by doping for tailoring its electronic/optical properties [10,11]. To date, one-dimensional Si_3N_4 nanostructures have been synthesized via different methods [12]. However, the mass production of high quality Si_3N_4 nanobelts is still difficult.

In this paper, we report a method for producing high quality single-crystalline Si_3N_4 nanobelts via catalyst-assisted pyrolysis of polymeric precursors. The obtained nanobelts possess a perfect single-crystalline structure and smooth surface, and up to several millimeters in length with a very high width-to-thickness ratio. We believed that the technique reported here can be scaled up for mass production of Si_3N_4 nanobelts at high yield.

2. Experimental section

The Si_3N_4 nanobelts were synthesized via pyrolysis of a polyaluminasilazane precursor, which was obtained by reaction of commercially available liquid polyureamethylvinylsilazane

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(Ceraset, Kion Corporation, USA) and 5 wt% aluminum isopropoxide powder (AIP, Beijing Bei Hua Fine Chemicals Company, Beijing, China). The obtained polyaluminumsilazane, which is liquid as-synthesized, was then solidified by heat-treatment at 260 °C for 0.5 h in N₂, and then ball milled for 24 h to obtain fine powders. Three wt% of Al powder (99.99% analytical purity, Beijing Bei Hua Fine Chemicals Company) was added into the precursor during ball milling as the catalyst. The powder was then placed in a high-purity alumina crucible and covered with a graphite sheet. The pyrolysis was carried out in a conventional tube furnace at 1550 °C for 2 h in flowing ultra-high purity nitrogen. The experiment with similar conditions was also carried out without the Al powder additive for comparison.

The obtained products were characterized using field emission scanning electron microscopy (SEM, JSM-6301, JEOL, Tokyo, Japan), X-ray diffraction (XRD, Automated D/Max-RB, Rigaku, Tokyo, Japan) with CuK α radiation ($\lambda = 1.54178 \text{ \AA}$), and high-resolution transmission electron microscopy (HRTEM, JEML-2011, JEOL, Tokyo, Japan) equipped with energy-dispersive spectrum (EDS). The photoluminescence (PL) spectrum of the belts was recorded using a UV-lamb micro-zone Raman spectrometer under the excitation of a 325 nm He–Cd laser at room temperature.

3. Results and discussion

The crucible containing synthesized products was removed from the furnace after cooling down to room temperature. It was found that a fairly large amount of pyrolysis products were grown on the graphite sheet, which was placed on the top of the alumina crucible as a cover. In our typical experiments, several square centimeters with several millimeters in thickness of the highly packed products covered the entire graphite sheet. Weight measurements of the powder and the products suggest that ~38 wt% of the original materials has been converted into nanobelts. Such high yield has not been reported previously for synthesis of Si₃N₄ nanobelts. The X-ray

diffraction pattern of the products reveals that the products are pure α -Si₃N₄ without other phases (Fig. 1).

The morphology of the obtained product was first observed using SEM. Low-magnification SEM images (Fig. 2a–c) show that the products, which are up to several millimeters in length, are highly packed together. Closer observation at higher magnification (Fig. 2d and e) reveals that the products take a belt-like shape with a rectangular cross-section. Fig. 2d displays a typical flat and curved nanobelt, suggesting the high flexibility of the nanobelts. Fig. 2e shows the typical fluctuated nanobelts, which occupy a little amount of the final products. Both of the pictures suggest that the nanobelts are very thin and have a high width-to-thickness ratio, with an average width of ~800 nm and a thickness of tens of nanometers, respectively. These nanobelts possess a uniform size in width and thickness along the entire growth direction and smooth surfaces without any attached particles, suggesting they are of high quality. The typical tip of the nanobelt is clear without any droplets, shown as the white arrow marked in Fig. 2e, implying that the growth of the nanobelts should not be dominated by the vapor–liquid–solid mechanism [13].

The nanobelts were further characterized by using TEM and HRTEM. Fig. 3a shows a typical TEM image of the flat Si₃N₄ nanobelts. Fig. 3b and c display the fluctuated and curved nanobelts, respectively, which suggest that the high flexibility of the nanobelts. It is seen that the belts are highly transparent to electrons and the copper grid can be seen through the belts even the nanobelts are overlapped, confirming they are very thin. A typical EDS (Fig. 3d) obtained from an individual nanobelt reveals that the composition of the nanobelts are Si and N, confirming the products are Si₃N₄ (the Cu signals in the EDS spectrum come from the TEM grid used to support the sample). Fig. 3e is the HRTEM image of the nanobelts, revealing that the nanobelts possess a perfect crystal structure with few structural defects such as dislocations and stacking faults. The upper left inset picture in Fig. 3e is the selected area electron diffraction (SAED) pattern, which is identical over the entire belt, indicating the nanobelt is a single crystal. The lattice fringe spacing of 0.67 and 0.56 nm in Fig. 3e agree well with (100) and (001) planes of bulk α -Si₃N₄, where $a = 0.77541 \text{ nm}$ and $c = 0.56217 \text{ nm}$ (JCPDS card no. 41-0360). Both the HRTEM image and the SAED pattern suggest that the nanobelt grew along [101].

Fig. 4 is a typical PL spectrum of the nanobelts. The broad emission band can be split into three peaks which are centered at 1.95, 2.34, and 3.17 eV, respectively, similar to that reported previously [14]. These emission peaks are attributed to the transitions between four types of Si₃N₄ defects: Si–Si and N–N bonds, and Si and N dangling bonds [15].

Careful examination of the tips and roots of the nanobelts reveals that they are clear without any catalytic droplets, which are typically observed when liquid phases

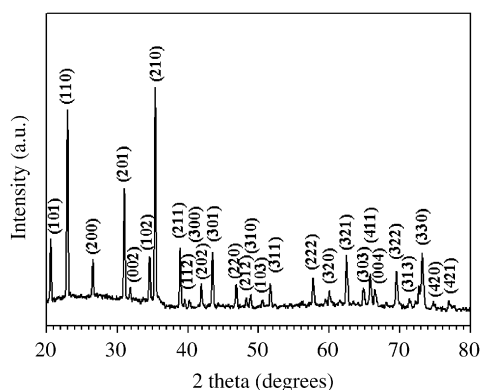


Fig. 1. XRD pattern of the obtained products.

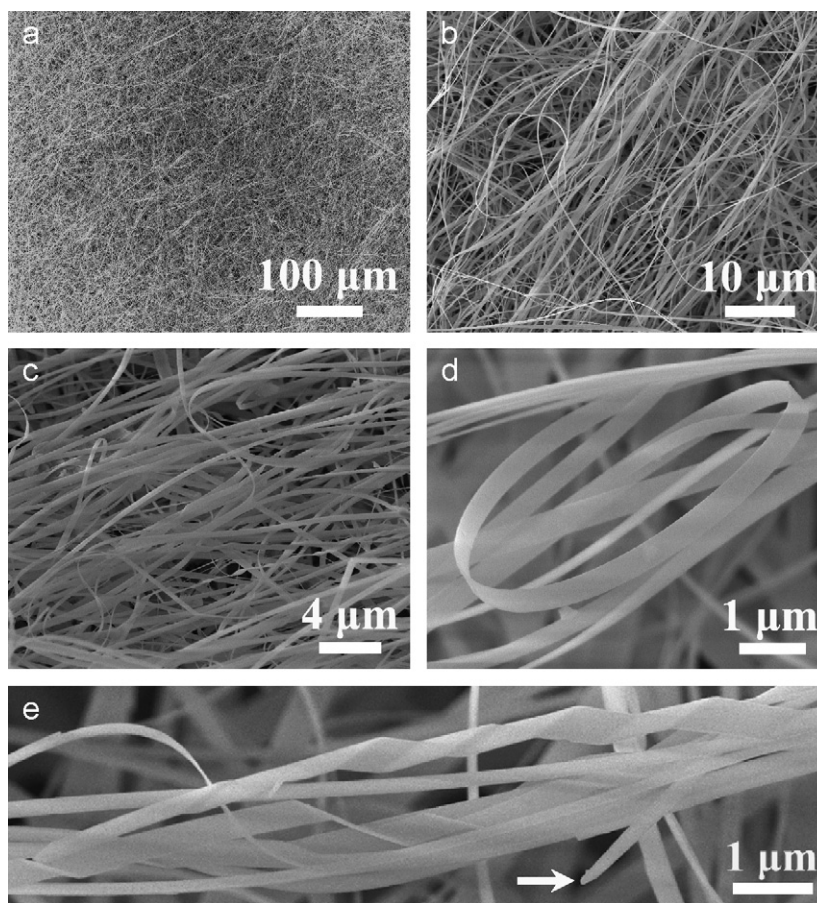


Fig. 2. (a–c) SEM images of the as-synthesized Si_3N_4 nanobelts under different low magnifications showing the large-scale and high-density growth of the nanobelts. (d) A typical SEM image displaying the flat and curved growth of the nanobelts. (e) A typical SEM image showing the fluctuating growth of the nanobelts.

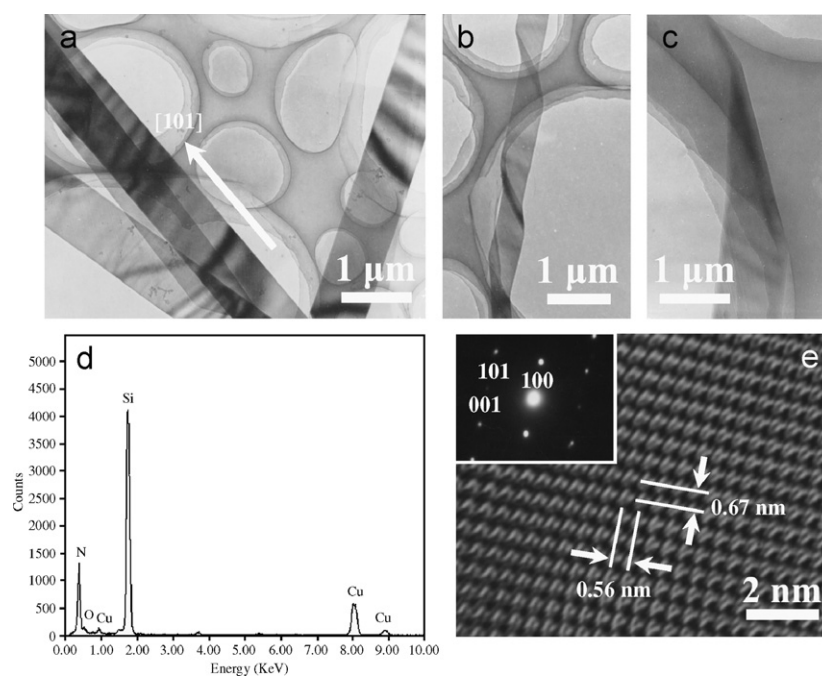


Fig. 3. (a) A typical TEM image of the flat Si_3N_4 nanobelts. (b and c) Two typical TEM image showing the flat and curved Si_3N_4 nanobelts, respectively. (d) A representative EDS spectrum obtained from an individual nanobelt recorded under TEM. (e) HRTEM image of the Si_3N_4 nanobelt with the corresponding SAED pattern recorded from a single nanobelt.

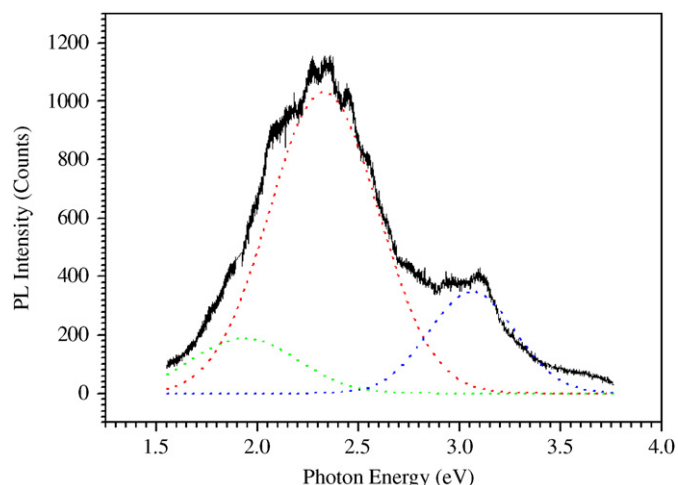
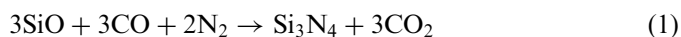


Fig. 4. PL spectrum of the Si_3N_4 nanobelts under excitation of 325-nm He–Cd laser at room temperature.

are involved in the growth. This, together with very high width-to-thickness ratio, suggests that the nanobelts should grow via a vapor–solid mechanism. In fact, the products are only found on the graphite sheet cover but not on the bottom of the crucible, consistent with the nanobelts growing via a VS process [16]. In the current study, it is believed that the starting precursor was first converted into amorphous SiCNs with a small amount of O at temperatures $\sim 1000^\circ\text{C}$ [17]. The amorphous SiCNs are metastable and released CO and SiO due to the presence of O in the material when heated to a temperature of 1550°C [18]. Then the CO and SiO react with N_2 to form Si_3N_4 nanobelts via reaction (1) [19,20]. The newly formed Si_3N_4 is easily nucleated on the graphite sheet since the latter provides heterogeneous nucleation sites. SiC would be expected to be formed via reactions (2) [21] and (3) [20] at temperatures higher than $\sim 1480^\circ\text{C}$. However, only Si_3N_4 formed in current experiments. This can be attributed to the lower $P_{\text{CO}}/P_{\text{SiO}}$ ratio within the SiCN system, which results in the higher phase equilibrium temperature favoring Si_3N_4 over SiC [18]. Al powder additives may play a key role in the success of the current processing. It is found that no Si_3N_4 belts were formed at the same pyrolysis condition when no Al powder was added [22]. Since no catalyst droplets were observed at either the tips or the roots of the belts, it is obvious that the role of the Al powder is not to form catalytic droplets and promote the formation of nanobelts via liquid phase growth mechanism as other catalysts did. It is possible that the Al may help the formation of the SiO vapor phase during pyrolysis. It is different from our previous work [11], in which the nanostructures grew via a solid–liquid–gas–solid (SLGS) mechanism when FeCl_2 was used as the catalysts and resulted in the Al-doped Si_3N_4 nanowires. This suggested that the growth mechanism might play a key role on the Al atoms doping into the single-crystal Si_3N_4 .



4. Conclusions

In conclusion, we realize the large-scale synthesis of very thin Si_3N_4 nanobelts with high quality via catalyst-assisted pyrolysis of polymeric precursors. The obtained nanobelts are up to several millimeters in length with a typical width and thickness of ~ 800 nm and tens of nanometers, respectively. The nanobelts possess a perfect crystal structure and a smooth surface. The growth mechanism of the nanobelts is attributed to a vapor–solid process. The current results could lead to a new way for mass production of high quality Si_3N_4 nanobelts with high yield.

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