

## 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  $\text{Si}_3\text{N}_4$  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  $\sim 800$  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  $\text{Si}_3\text{N}_4$  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 ( $\text{Si}_3\text{N}_4$ ) 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  $\text{Si}_3\text{N}_4$  nanostructures have been synthesized via different methods [12]. However, the mass production of high quality  $\text{Si}_3\text{N}_4$  nanobelts is still difficult.

In this paper, we report a method for producing high quality single-crystalline  $\text{Si}_3\text{N}_4$  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  $\text{Si}_3\text{N}_4$  nanobelts at high yield.

## 2. Experimental section

The  $\text{Si}_3\text{N}_4$  nanobelts were synthesized via pyrolysis of a polyaluminasilazane precursor, which was obtained by reaction of commercially available liquid polyureamethylvinylsilazane

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(Cereset, 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 N<sub>2</sub>, 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 $\alpha$  radiation ( $\lambda = 1.54178$  Å), 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 Si<sub>3</sub>N<sub>4</sub> nanobelts. The X-ray

diffraction pattern of the products reveals that the products are pure  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> 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 Si<sub>3</sub>N<sub>4</sub> 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 Si<sub>3</sub>N<sub>4</sub> (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  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>, where  $a = 0.77541$  nm and  $c = 0.56217$  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 Si<sub>3</sub>N<sub>4</sub> 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

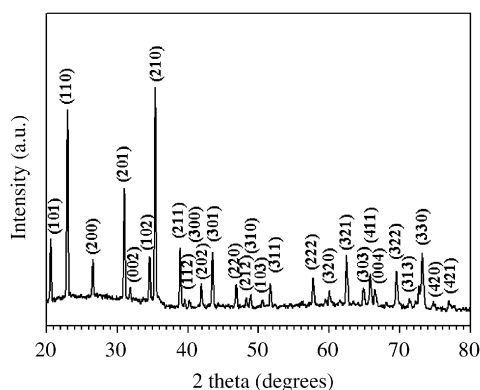


Fig. 1. XRD pattern of the obtained products.

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