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Short communication

Epitaxial growth of asymmetric α-silicon nitride nanocombs

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ABSTRACT

The asymmetric α-Si_3N_4 nanocombs have been prepared by direct current arc discharge method without the addition of any catalyst or template. The nanocombs are composed of closely packed Si_3N_4 nanowires, which grow perpendicular to the central axial nanorods in an epitaxial manner. The growth mechanism of the α-Si_3N_4 nanocombs can be considered as a combination of the vapor–solid mechanism and the secondary epitaxial nucleation process. The photoluminescence spectra of the nanocombs show a strong blue light emission peak at about 424 nm.

1. Introduction

Recently, considerable research efforts have been focused on controlling the morphology, structure, and crystallinity of one-dimensional (1D) nanostructures because these parameters have profound effects on the properties and applications of the 1D nanomaterials [1]. In the last few decades, many excellent researches on the shape-controlled syntheses of inorganic crystals have been reported, such as rods/wires [2], saws [3], flowers [4], triangles [5], plates [6], cubes [7], sheets [8], dendrites [9], combs [10] and so on. Dendrites and combs, as a kind of fractal structure, have been extensively investigated in recent years owing to their special significance in understanding the growth behavior of branched fractal patterns and their potential technological applications [9,10]. In general, there are two different routes to form hierarchical nanodendrites and nanocombs [11]. One is the formation of inner stems followed by the epitaxial growth of secondary branches. The other is the self-assembly of nanosized building blocks into hierarchical structures [12]. The subject of epitaxial nucleation and growth has been of great interest in recent years. Unique structural phases, unstable in the corresponding bulk materials, can be stabilized in thin films and nanomaterials by epitaxy onto a suitable substrate [11]. These structural phases, combined with the loss of the third dimension (and its associated bonds and symmetry) result in the possibility of unique chemical properties. Thus the combination of the self-assembly process [13] and the epitaxial nucleation and growth may open an effective route to synthesize new desirable materials and structures with potential applications.

Silicon nitride (Si_3N_4) is an important engineering ceramic for a variety of applications due to its excellent thermo-mechanical properties and chemical stability [14]. It exhibits a wide bandgap of 5.0 eV at room temperature [15]. 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 [16]. To date, one-dimensional Si_3N_4 in the shapes of wires, rods and belts have been synthesized through a series of sophisticated methods. In this paper, a simple and effective method, which is based on the conventional direct current (DC) arc plasma equipment, to produce α-Si_3N_4 nanocombs with a high aspect ratio is represented. The growth mechanism can be considered as a combination of the vapor–solid (VS) mechanism and the secondary epitaxial nucleation process without the designed addition of template or catalyst.

2. Experimental

The synthesis was carried out in an improved DC arc discharge plasma setup [17]. A tungsten rod with the purity higher than 99.99%, 8 mm in diameter and 30 cm in length, was used as the cathode. Si (mean size: 200 mesh, purity: 99.99%), SiO_2 (purity: 99.99%) and graphite powders (purity: 99.99%) were mixed with a molar ratio 1:1:1 in a ball mill and pressed into columns as reactants. A column, 18 mm in diameter and 4 mm in height, was placed into a water-cooled graphite crucible which acted as the anode. The reaction chamber was first evacuated to less than 1 Pa and then filled with argon several times to remove residual air completely. Then the working gas (N_2, purity: 99.999%) was introduced into the chamber until the inner pressure reached

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20 kPa. As the direct current arc discharge was ignited, the input current was maintained at 100 A and the voltage was a little higher than 20 V. The power supply was turned off 10 min later. After passivation in Ar for 6 h, the white powder samples were collected at the cathode.

Structural analysis of the products was carried out by powder X-ray diffractometry (XRD) on a D8 DISCOVER GADDS diffractometer. Scanning electron microscope (SEM) images of the sample were taken on a HITACHI S-4800 microscope equipped with an energy dispersive spectrometer (EDS). The morphology of the nanocombs, as well as the high-resolution transmission electron microscope (HRTEM) images and the selected area electron diffraction (SAED) patterns, was obtained via a JEM-2100F transmission electron microscope. The photoluminescence (PL) measurement of the synthesized product was conducted at room temperature under the excitation of a 300 nm UV fluorescent light by a Shimadzu RF-5301PC spectrophotometer.

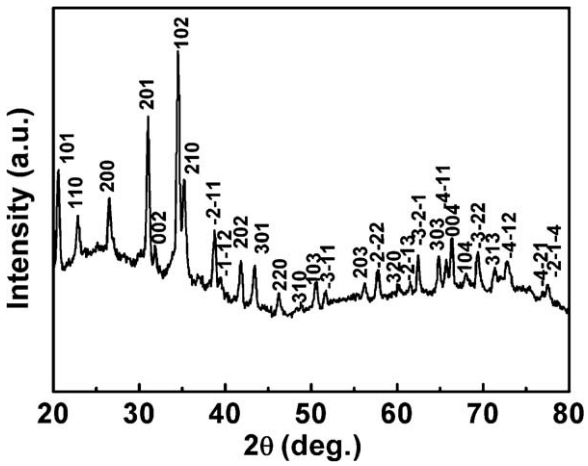

Fig. 1. The XRD pattern of the as-synthesized silicon nitride nanocombs.

3. Results and discussion

The XRD pattern shown in Fig. 1 reveals the overall phase composition and purity of the final white powder produced in this study. All the diffraction peaks can be unambiguously indexed to the hexagonal crystal lattice of α-Si_3N_4 with the space group $P31c$ (159) and the cell constants $a = 0.7766$ nm and $c = 0.5623$ nm, which is in good agreement with the standard values for bulk α-Si_3N_4 (JCPDS Card No. 83-0700, $a = 0.7765$ nm, $c = 0.5627$ nm).

Fig. 2 shows the SEM images and EDX spectra of the as-synthesized Si_3N_4 nanostructures. Fig. 2a is the typical low magnification SEM image of the samples. It can be seen that the product is composed of comb-like nanostructures with their stems and branches to be about several tens of microns in length. The most attention-getting feature of the nanostructures is that the branches grow unilaterally on one side of the stems to form a unique asymmetric nanocomb structure. The branches are very long and straight with high aspect ratios (Fig. 2b and c). Fig. 2c shows a high magnification SEM image of the typical nanocombs. The wire-shaped branches are very uniform in size with their diameters of 50–200 nm and distributed at one side of the stem. The chemical composition of the nanocombs is characterized by EDX. The results shown in Fig. 2d indicate that the nanocombs are composed purely of silicon and nitrogen elements. Semiquanti-

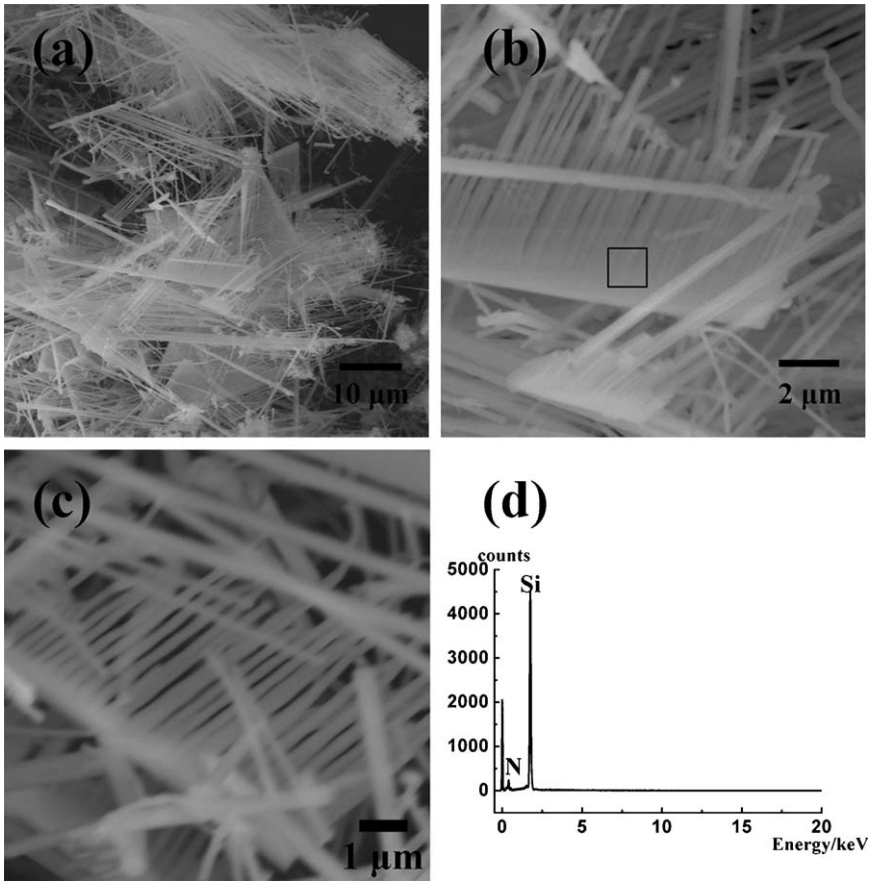

Fig. 2. (a–c) are the typical SEM images of the Si_3N_4 nanocombs with different magnifications showing their overall and detailed morphologies. (d) Shows the typical EDX spectrum obtained from the region marked with a rectangle in (b).