

Investigation on the Growth of Boron Carbide Nanowires

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Received May 29, 2002. Revised Manuscript Received August 13, 2002

Simple methods for preparing boron carbide nanowires have been investigated. The methods involve thermal evaporation of C/B/B₂O₃ powder precursors in an argon atmosphere with or without metal catalysts. High-purity nanowires (50–200 nm) were obtained by employing a precursor that has C:B:B₂O₃ molar ratios of 1:2:1. Less carbon content (C:B:B₂O₃ = 1:8:4) yielded products exhibiting different morphologies ranging from nanowires to platelet crystals. These nanowires were considered to grow via a vapor–solid (VS) mechanism. The addition of an Fe impurity into the precursor changed the growth from a VS mechanism to a vapor–liquid–solid (VLS) one, resulting in nanowires with smaller diameters (10–30 nm). We also found that boron carbide nanowires coated with boron nitride (BN) layers could be easily produced by adding B₄N₃O₂H into the starting materials and then subjecting the material to evaporation under a nitrogen atmosphere. The structural features of these nanowires were characterized by means of transmission electron microscopy.

Introduction

Boron carbide is a lightweight refractory semiconductor material with a high melting point, high strength and Young's modulus, and high-temperature thermoelectric properties.^{1–3} It has a rhombohedral structure (*R*3*m*, No. 166) consisting of a B₁₂ icosahedral and a C–B–C chain (B₁₃C₂ = (B₁₂)CBC, B₄C = (B₁₂)CCC). It has wide applications such as a ceramic armor for extreme conditions, a neutron absorbent in the nuclear industry, and potential for high-temperature thermoelectric energy conversion.^{1–4}

Synthesis and characterization of boron carbide nanomaterials has become a subject of recent interest.^{5–13} A plasma-enhanced chemical vapor deposition method was developed to grow various boron carbide nanomaterials including nanowires, nanonecklaces, and nano-

springs.^{5–7} In addition, Pender and Sneddon generated aligned boron carbide nanowires by pyrolyzing a single-source molecular precursor in porous alumina templates.⁸ More recently, Carlsson et al. performed a specific investigation on the growth of boron carbide nanowires via a carbothermal VLS growth mechanism starting with B₂O₃, carbon black, and catalyst metals of Co, Ni, and Fe.⁹

In addition, carbon nanotubes were employed as templates to form boron carbide nanowires.^{10–12} It was also found that boron carbide nanowires could be encapsulated into BN or boron carbonitride (BCN) nanotubes.^{12,13} Due to the chemical and thermal stability and insulating property of BN, these composite nanostructures are promising for advanced technical applications.

We report in the present study that boron carbides nanowires could be grown both via the VLS and via the VS¹⁴ mechanisms starting with C/B/B₂O₃ powder precursors with or without an Fe catalyst. We also introduced an effective route to yield boron carbide nanowires coated with BN layers. The growth mechanism and structural features of these nanomaterials will be discussed.

Experimental Section

Boron powders (99% purity), boron oxide powder (B₂O₃, 99.99% purity), and carbon black were used as the starting materials. The powder precursors were charged into an open cylindrical graphite crucible and inserted into a high-frequency induction furnace. The furnace temperature was raised quickly to 1650 °C within 15 min and maintained for 2 h under a flowing argon atmosphere. A grayish-black wool-like product deposited on the top wall of the crucible after the evaporation.

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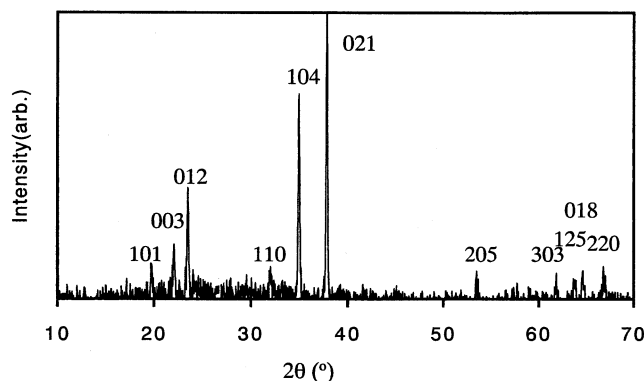


Figure 1. A typical XRD pattern of the deposit. This pattern can be indexed as a single phase of boron carbide.

Experiments employing different carbon contents in the starting materials, with C:B:B₂O₃ molar ratios of 1:2:1 and 1:8:4, were performed. Two kinds of carbon black, with ultrahigh purity or little metal impurity (Fe, 0.5 wt %; Ni, 0.1 wt %), were compared.

To produce BN coatings on boron carbide nanowires, B₄N₃O₂H^{13,15} (with a weight ratio of about 20% of the total starting material) was added into the precursor. The synthesis was then performed in a nitrogen atmosphere with other experimental parameters remaining the same.

The deposits were characterized by X-ray diffraction (XRD). The powdered samples were also observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A field emission JEM-3000F high-resolution electron microscope operated at 300 kV equipped with a Gatan-666 electron energy loss spectrometer (EELS) and energy-dispersive X-ray spectrometer (EDS) was employed to perform the microanalysis.

Results and Discussion

In all the synthesis processes, the deposited products were identified to be boron carbide. Figure 1 shows a typical XRD pattern. The pattern matches that of either B₄C ($a = 5.6003$ Å, $c = 12.086$ Å) or B₁₃C₂ ($a = 5.6330$ Å, $c = 12.1640$ Å). Due to the identical crystal structures and similar lattice parameters, it is difficult to distinguish the two phases. No other phase was detected in the spectrum. The products are therefore high-purity boron carbide materials.

The morphologies of the products differ depending on the carbon contents employed in the precursors. The SEM images (Figure 2) shows the product synthesized from starting materials with a C:B:B₂O₃ molar ratio of 1:2:1. It is obvious that the deposit consists of dense nanowire-like structures (Figure 2a,b). These nanowires are very smooth in the surface and uniform along the whole length. Figure 2c shows the high-resolution TEM (HRTEM) image and corresponding electron diffraction (ED) pattern (inset) of a typical nanowire. The electron pattern can be indexed as single-crystalline B₄C or B₁₃C₂ viewed along the [010] zone axis. The clearly resolved 0.40-nm distance between (003) planes is labeled. On the other hand, when the C:B:B₂O₃ molar ratios in the starting precursor were changed into 1:8:4, the morphology of the product varied greatly. Figure 3 shows the SEM observation results of the product. The product contains many flake or platelet crystals. Compared with that shown in Figure 2, the fraction of the nanowires

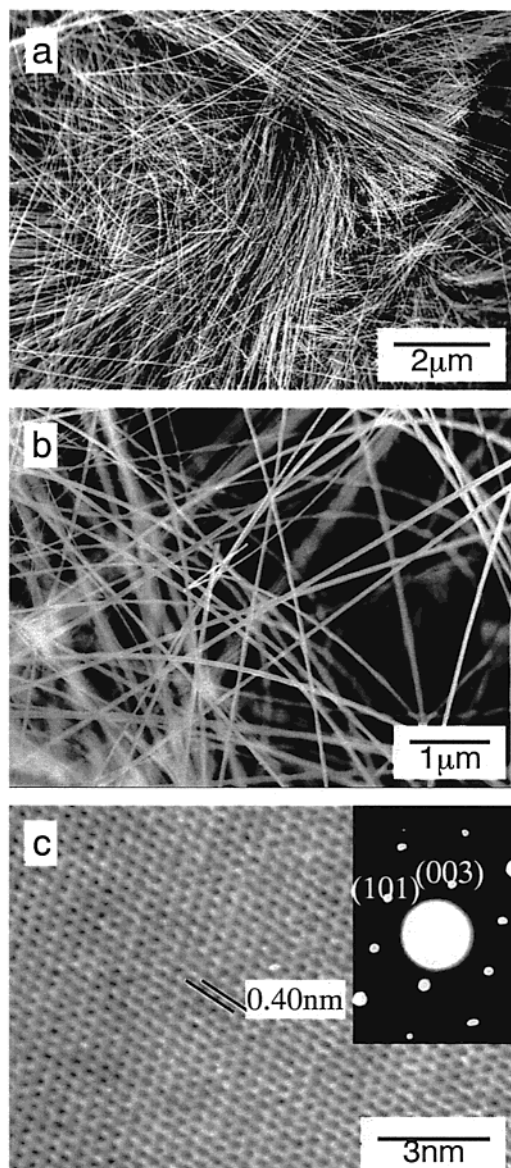


Figure 2. SEM images of the deposit started from the precursor with a C:B:B₂O₃ molar ratio of 1:2:1. (a,b) Dense nanowires were observed in the product. (c) The HRTEM image and electron diffraction pattern (inset) identify the single-crystalline nature of the boron carbide nanowires.

in the product was decreased significantly. Figure 3c shows a platelet crystal with the growth direction changing periodically. The crystal is somewhat thick and a high-quality HRTEM image could not be recorded. Tilting experiments identified that the growth directions might be changed between [012] and [101] as indicated in Figure 3c.

EELS analysis of the nanowires (Figure 4) showed that the nanowires were composed of B and C atoms. (The characteristic B and C K-edges at 188 and 284 eV are clearly visible.) The C/B atomic ratio was calculated as 0.23 ± 0.03 (the estimated error is due to the background subtraction), close to B₄C (C/B ~ 0.25).

In both of the above cases, the diameters of the nanowires are generally in the range of 50–200 nm. The tips of the nanowires are flat and no particle was observed at either end of the nanowires. We suspect that these boron carbide nanowires may be formed in a VS

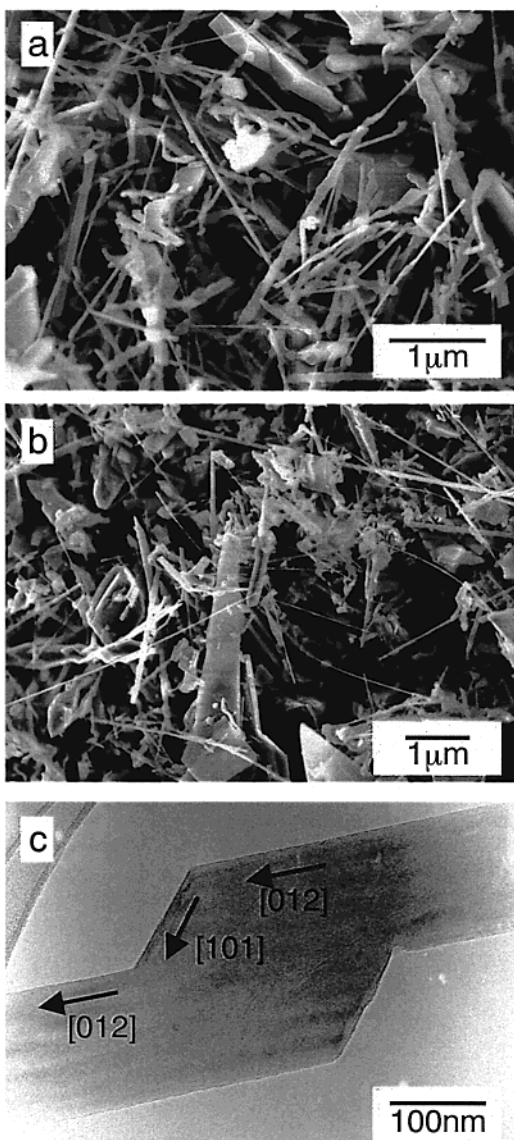


Figure 3. SEM images of the deposit started from the precursor with a C:B:B₂O₃ molar ratio of 1:8:4. (a,b) Besides the nanowires, the product also contains many flake or platelet crystals. (c) A platelet crystal changes the growth direction from [012] to [101], and [012] again.

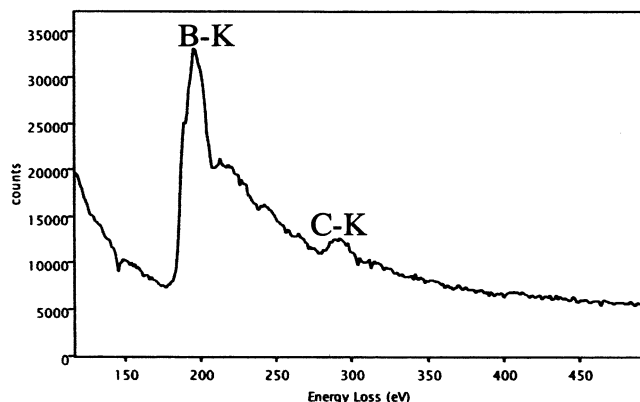


Figure 4. A typical EELS spectrum demonstrates the B and C K-edges at 188 and 284 eV, respectively.

mechanism.¹⁴ At high experimental temperature (1650 °C), the vapors of boron oxide or carbon oxide were generated from the starting materials and transferred

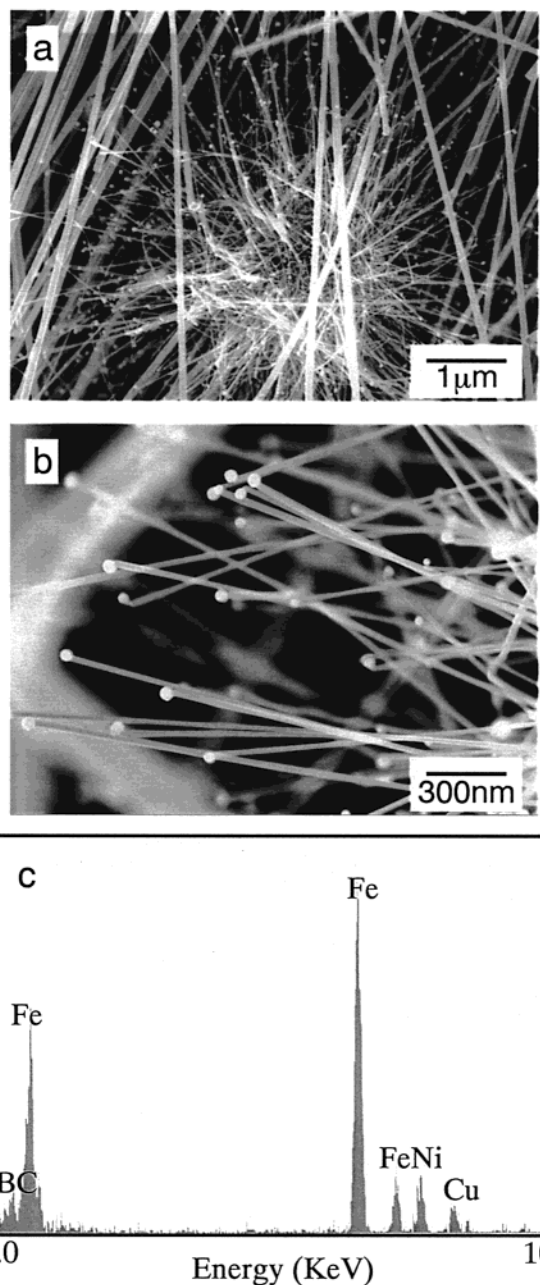


Figure 5. Nanowires obtained when carbon black with an Fe impurity was employed. (a) A typical SEM image. Nanowires in tufts with apparently smaller diameters, around 10–30 nm, were observed. (b) Almost every nanowire has a tip particle in brighter contrast. (c) A typical EDS spectrum identifies that the tip particle contains mainly Fe.

to a slightly low temperature region. There, the subsequent vapor–vapor (VV) reactions occur to form boron carbide solid nanowires, that is, via a VS mechanism. We consider that the decreased carbon content in the starting materials, that is, C:B:B₂O₃ molar ratios changing from 1:2:1 to 1:8:4, induced a less stable nanowire growth condition, causing the decrease of nanowire fraction.

When carbon black with an Fe impurity was used, abundant nanowires were also obtained. Figure 5a shows the typical SEM image. Besides the nanowires with diameter around 50–200 nm which grow in a VS mechanism as described above, nanowires in tufts with apparently smaller diameters, around 10–30 nm, were

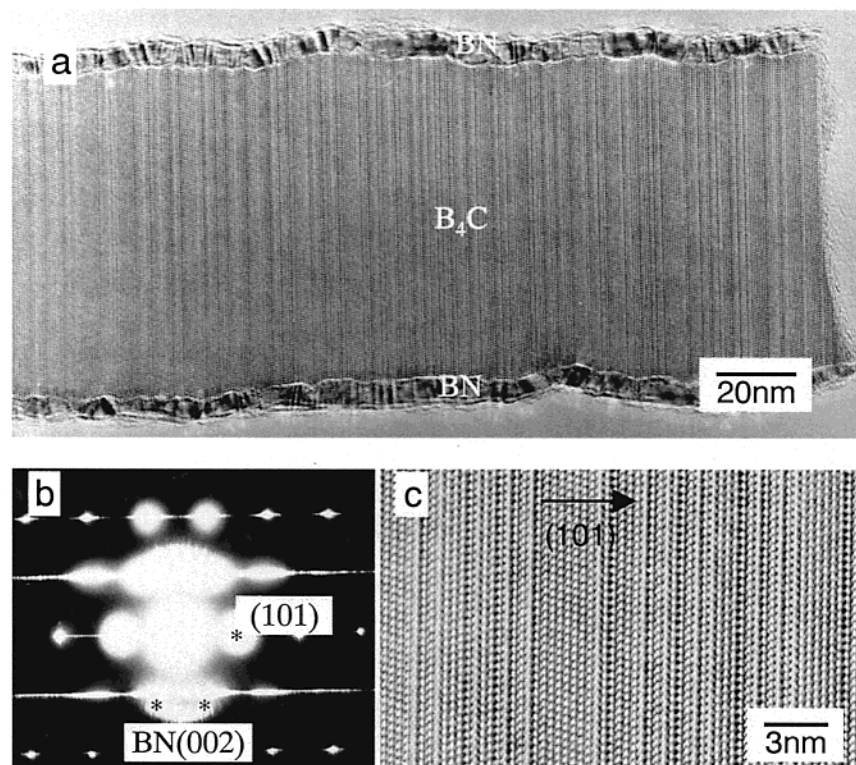


Figure 6. TEM characterization of boron carbide nanowires coated with outer BN layers. (a) A typical boron carbide nanowire coated with BN layers. (b) The electron diffraction. Note the twinned (101) planes in boron carbide and an arclike feature of BN (002) spots in the ED pattern. (c) A corresponding high-resolution TEM image.

observed (Figure 5a). The distinguishable feature of these smaller nanowires is that almost every nanowire has a bulbous tip. Figure 5b shows a higher magnification SEM image of these smaller nanowires. The tip particles in brighter contrast can be clearly seen. Figure 5c shows a typical EDS spectrum of these tips. Besides the elements boron and carbon, the particles are mostly enriched with Fe and a little Ni. The weak signal of Cu in this spectrum is derived from the copper grid used to support the specimen.

We propose that these smaller nanowires with Fe-rich tip particles attached are grown via the so-called VLS mechanism,^{9,16,17} in which a metal cluster or catalyst (Fe) serves as the energetically favored site for the condensation and precipitation of reactant vapors. Fe nanoclusters derived from the impurity in the precursor were initially deposited. Then the condensation and precipitation of boron carbide species from hot vapors occur on these Fe nanoclusters. Nanowire growth begins after the boron carbide species becomes supersaturated in the Fe nanocluster. During the reaction, the Fe nanocluster is always located at the growth front. As seen from the differences between the nanowires grown in Figures 2 and 3, where no catalysts were employed, the dimension of the Fe nanoclusters determines the diameters of the nanowires. This can reasonably explain the formation of such smaller nanowires.

After adding $B_4N_3O_2H$ into the precursor and carrying out the synthesis in a N_2 atmosphere, we also obtained a large quantity of boron carbide nanowires. However, most of the nanowires are coated with BN layers. The

outer BN layers coated on boron carbide nanowires are formed by pyrolyzing $B_4N_3O_2H$ in a N_2 atmosphere, which we employed to synthesize BN nanotubes in our earlier work.^{13,15} Different from the perfect crystallinity observed in those boron carbide nanowires without outer coatings, as shown in Figure 2c, most of the encapsulated boron carbide nanowires exhibit a high density of microtwins and stacking faults normal to the growth direction. Figure 6a shows a typical boron carbide nanowire coated with BN layers. The ED pattern (Figure 6b) is indexed as either rhombohedral B_4C or $B_{13}C_2$. Figure 6c is a corresponding HRTEM image of the encapsulated nanowire with obvious striations running normal to the length axis. Both the ED pattern and TEM images reveal the presence of twin defects on boron carbide (101) planes. Due to the presence of these defects, the outer surface of the boron carbide nanowire is composed of faceted areas. As BN layers coat the faceted surface, the BN layers are distorted on the atomic level. The ED pattern also indicates a twin diffraction of the BN (002) planes with an orientation difference (note the arclike feature of the BN (002) diffraction). It has been observed that interlayer distances in BN nanotubes could be deviated at 0.36 ± 0.03 nm for BN nanotubes depending on the curvature.¹⁸ The 0.36 ± 0.03 nm BN interlayer distances may match the lattice spacings of (003) planes (≈ 0.40 nm) or (012) planes (≈ 0.378 nm) in boron carbide nanowires. This gives some evidence that BN layers may coat on the boron carbide nanowire after some atomic-level surface reconstruction, though a detailed study on the crystallographic orientation is still needed.

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Conclusions

In summary, we investigated the growth of boron carbide nanowires starting from C/B/B₂O₃ powder precursors under an argon atmosphere with or without metal catalysts. The carbon content in the precursor has significant effect on the morphology of the product. High-purity boron carbide nanowires (50–200 nm) were obtained by employing suitable carbon content in the precursor. The addition of an Fe impurity into the precursor resulted in nanowires with smaller diameters

(10–30 nm). With the addition of B₄N₃O₂H into the starting materials and then evaporation under a nitrogen atmosphere, boron carbide nanowires coated with BN layers could be easily produced. These encapsulated boron carbide nanowires usually exhibited stacking defects. This study offers an effective route for synthesizing various boron carbide nanostructures for advanced technical applications.

CM020630V