



Remote catalyzation for growth of boron nitride nanotubes by low pressure chemical vapor deposition



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ABSTRACT

Direct deposition of high purity and quality boron nitride nanotubes (BNNTs) on Si substrate were obtained using low pressure chemical vapor deposition (LPCVD). We find Fe–Mg–O species may act as catalysts for growing BNNTs. This synthesis process conforms to vapor–liquid–solid (VLS) growth mechanism. As-grown BNNTs also show a large optical energy band gap of 6.12 eV, approaching to hexagonal phase BN single crystals. Meanwhile, as-grown BNNTs exhibit an intense UV-emission band located at 345 nm and a weak deep band at 237 nm. Their optoelectronic properties make them have promising for future nanoscale deep-UV light emitting devices.

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1. Introduction

Boron nitride nanotubes (BNNTs) are analog of carbon nanotubes (CNTs), which can be seen as alternating boron (B) and nitrogen (N) atoms entirely replace carbon (C) atoms in a hexagonal lattice structure. BNNTs have a large band gap (nearly 5.9 eV), which are insensitive to diameter, chirality and walls, approaching the hexagonal phase BN single crystals, which will be expected for the short-wavelength light-emitting device, UV detection and high temperature, high-power electronic devices [1–4]. In addition, BNNTs are known to have significant chemical stability and superhydrophobicity, which can be used in the biological systems as ideal delivery capsules of chemotherapy drugs [5–12]. Moreover, BNNTs have excellent thermal conductivity, high thermal resistance, and superb mechanical robustness [13,14], which make them suitable for insulating polymeric composition materials, protective shields encapsulating materials, radiation shielding in space vehicles, and nuclear reactor facilities [1]. Therefore, it is necessary to produce BNNTs with high purity and high quality in a large scale for BNNTs applications.

The conventional methods of synthesis of BNNTs include discharge [15], laser ablation [16], ball milling [17], and chemical vapor deposition (CVD) [18], etc. Recently, developed boric oxide

CVD (BOCVD) method can grow BNNTs with different diameter and morphology through tuning the precursors and ratios of the metal oxides under atmospheric chemical vapor deposition (APCVD), which is believed to have the potential for large scale synthesis of BNNTs [3,18]. The key feature of BOCVD is a chemical reaction of B₂O₃ (through heating a mixture of metal oxides and boron powder) with ammonia gas (NH₃) [19,20]. However, large scale production of high quality and long BNNTs still need further study by CVD. Therefore, it is highly desirable to develop a simple way to produce large amounts of high purity BNNTs.

Herein, we report a simple and efficient route for the synthesis of high purity and high quality BNNTs using the remote catalysts via low pressure chemical vapor deposition (LPCVD) method in a dual-zone furnace. Ammonia (NH₃) was applied as nitrogen source. Boron (B), magnesium oxide (MgO) and iron oxide (Fe₂O₃) powders as precursor materials were placed in the upstream gas flow to provide nitrogen source and metal vapors. The precursor vapor was introduced by carrier gas to low temperature zone and metal vapor was condensed into catalyst particles on the Si substrate to grow BNNTs. Under low-pressure conditions, the over-rapid reaction rate of B₂O₃ with NH₃ vapors can be effectively reduced by diluting molecule concentration and the unwanted gas-phase reactions were abated [21,22], which are beneficial to produce uniform BNNTs on the silicon (Si) substrates. Snow-white BNNTs were formed on the silicon (Si) substrates, which were fully characterized by Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction

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pattern (XRD). The optical properties of the BNNTs were also investigated by Cathodoluminescence (CL) spectroscopy and UV–visible absorption spectroscopy.

2. Experimental

2.1. Synthesis of BNNTs

The experimental setup is a horizontal alumina tube fitted with a dual-zone furnace that is 120 cm in length and 6 cm in diameter (Fig. 1a). A mixture of B, MgO and Fe₂O₃ was used as the precursor materials and placed into an open-ended alumina tube. The mixture was located at the center of the first heating zone (1400 °C) of the tube furnace. The molar ratio of B:MgO:Fe₂O₃ was fixed at 2:1:1 for all experiments. Several substrates were placed on the alumina boat, located at the second heating zone (1200 °C) for the deposition of BNNTs. The alumina tube chamber was evacuated to about 0.1 Pa, and then 200 standard cubic centimeter per minute (sccm) of N₂ and 200 sccm of H₂ were introduced into the chamber. Subsequently, the precursors were heated to 1400 °C and held for 3 h under the NH₃ gas, and all the above steps were carried out at pressure of 5 kPa. After that, NH₃ gas flow was stopped in order to terminate the reaction and the system was cooled down to room temperature under the N₂ flow. A large quantity of snow-white coatings was obtained on the Si substrates under the low pressure condition as shown in Fig. 1b. The experimental steps under the APCVD are the same as the LPCVD. The precursor materials were placed into an open-ended alumina tube that were located at the center of the first heating zone (1400 °C) of the tube furnace, and the Si substrates was located on the downstream (the second zone, 1200 °C).

2.2. Characterization

The products were characterized by scanning electron microscope (SEM, Hitachi S-4800), and high-resolution transmission electron microscope (TEM, Tecnai G2 F20 S-Twin) equipped with an energy-dispersive X-ray Energy Dispersive Spectrometer (EDS, Apollo 40SDD). The bright-field scanning transmission electron microscopy (STEM) images were taken using an energy-filtering electron microscope operating at an accelerating voltage of 200 kV. Raman spectroscopy was collected over the spectral range of 1000–2000 cm⁻¹ using LabRAM ARAMIS Raman confocal microscope (HORIBA JobinYvon) equipped with a wavelength of 532 nm. The crystal structure was characterized by X-ray diffraction (XRD, D8 Advance, Bruker AXS). The UV–visible absorption spectra of the products were characterized by UV–visible absorption spectroscopy (JascoV-466 Spectrophotometer). Cathodoluminescence (CL) spectroscopy was carried out at room temperature by a thermal field-emission electron microscope (TFE-SEM, JSM-6390) equipped with a high-spatial-resolution and low-energy cathodoluminescence (LE-CL) system inside of it. The beam current was kept at 200 pA. The Fourier transformed infrared (FTIR) spectroscopy were taken in a transmission mode on BNNTs under a FTIR microscope (IR, Thermo Scientific Instruments, model NicoletN10). Thermogravimetric analyzer (TGA) from NETZSCH Instruments, model 209 F1 Libra. The sample was heated from room temperature to 1000 °C at a heating rate of 10 °C/min in a steady flow of air.

3. Results and discussion

Fig. 1a is the schematic of experimental setup which is a dual-zone furnace fitted with a horizontal alumina tube, due to

the temperature of production of B₂O₂ vapor is different with the temperature of growth of BNNTs, which was reported by Huang [23]. Under optimal conditions, snow-white BNNTs were obtained on silicon substrate, as shown in Fig. 1b. In our work, the substrates with different areas were all completely covered with BNNTs as shown in Fig. S1. SEM was used to study the morphology of the as-synthesized BNNTs under low pressure and atmospheric pressure. As illustrated in Fig. 2a, silky like wires were clearly observed under SEM, indicating clean and long BNNTs can be grown under low pressure. TEM characterization also shows long and straight tubular structure, which is consistent with the above SEM result, indicating the high growth efficiency assisted by LPCVD. From TEM result, we can also observe some metal catalyst particles trapped inside of BNNTs, with few dark spots left in the pipe wall as shown in Fig. 2b, as observed in the literatures [18,24,25]. However, under atmospheric pressure, the purity and quality of the resulting BNNTs were much lower compared to the products grown under low pressure. As shown in Fig. 2c, BNNTs were covered by some BN clusters, revealing the low purity. From TEM image in Fig. 2d, except the particles in BNNTs were observed in SEM image, there were some amorphous contaminants coated on the tube surfaces. Moreover, the length of the tube was around 5 μm, which is shorter than the tubes grown from LPCVD.

Raman spectroscopy, FTIR spectroscopy, and XRD were employed to characterize the BNNTs structures. As shown in Fig. 2e, the dominant peak located at ~1366 cm⁻¹ with high intensity is attributed to the well-known E_{2g} in-plane vibration mode of the hexagonal BN (h-BN) [1,26], indicating the high quality of the BNNTs using the floating catalyst in the LPCVD. The FTIR spectra were also taken to characterize the BNNTs structures. As shown in Fig. 2f, three absorption frequency regimes were observed at ~800, ~1365, and ~1527 cm⁻¹. The weak absorption at ~800 cm⁻¹ is associated with the out-of-plan radial buckling mode. The absorption bands at ~1365 cm⁻¹ and ~1527 cm⁻¹ are attributed to the in-plane stretching modes of the hexagonal BN (h-BN) network. Absorption band at ~1527 cm⁻¹ is Raman inactive. It only shows up when the tube curvature induces a strain on the h-BN networks. Thus, highly crystalline BNNTs would have this absorption band [3]. In order to further confirm the structure of boron nitride nanotubes, the XRD pattern of BNNTs grown in LPCVD as shown in Fig. S2. The (002) peak around 27 cm⁻¹ can be indexed to h-BN with lattice parameters of $a = 0.2504$ nm and $c = 0.6656$ nm, which agrees well with that listed in the JCPDS Card (No. 34-0421). No other impurities, such as B or Fe were detected within the detection limit. The XRD analysis indicates that the as-grown product is pure, hexagonal BN structure. Thermogravimetry analysis (TGA) was carried out to investigate the oxidation behavior of the BNNTs at the temperatures from room temperature to 1000 °C, as shown in Fig. S3. The weight gain almost has not changed below 1000 °C, which shows the as-grown BNNTs have good anti-oxidation properties.

As-synthesized BNNTs in LPCVD were made of parallel and straight walls as shown in Fig. 3a. HRTEM characterization shows a tubular structure with inner diameter around 12 nm and outer diameter around 20 nm. The spacing between two neighboring layers is around 0.33 nm according to the inset image in Fig. 3a, which is the characteristics of $d(002)$ spacing of h-BN [4,27], indicating the high crystalline nature of BNNTs. The selected area electron diffraction (SAED) pattern of BNNTs confirms as shown in Fig. 3b the good crystallinity of as-synthesized tubes as well [28]. The perfectly ordered tubular shells of BNNTs in the ropes were preferentially assembled in a zigzag form with the 10 $\bar{1}$ 0 direction parallel to the tube/rope axis [28]. We find BNNTs display graphitic shells and many of them have zigzag or near zigzag arrangement of

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