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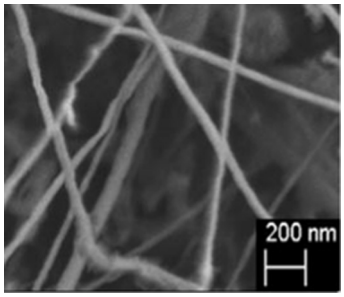
Synthesis of boron nitride nanotubes by Argon supported Thermal Chemical Vapor Deposition

Pervaiz Ahmad, Mayeen Uddin Khandaker*, Yusoff Mohd Amin

Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

GRAPHICAL ABSTRACT

The use of Ar gas as a reaction atmosphere has made BNNTs synthesis easy and ~ 18 % cost effective as compare to any other technique.



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ABSTRACT

Thermal Chemical Vapor Deposition technique is modified with the use of Argon gas flow inside the chamber as an alternative for vacuum and orientation of one end closed quartz test tube. The use of Argon gas not only simplified the experimental set up, but also made it ~ 18 % cost effective compared to the conventional set up. Field Emission Scanning Electron Microscopy micrographs show straight and long BNNTs along with some cotton like morphologies. Transmission electron microscopy revealed bamboo like structure inside the tube and ~0.34 nm interlayer spacing for highly crystalline nature of boron nitride nanotubes. X-ray photon spectroscopy shows B 1s peak at 191.08 eV and N 1s peak at 398.78 eV that represents h-BN. Whereas, Raman spectrum indicates a major peak at ~1379.60 (cm^{-1}) that correspond to E_{2g} mode of h-BN.

1. Introduction

Hexagonal boron nitride (h-BN) is a wide band gap semiconductor [1], with a direct band gap of 5.97 eV [2]. It is the normal phase of Boron Nitride (BN) that is stable at room temperature and pressure. Its structure is similar to that of graphite but alternative boron and nitrogen atoms substitutes for carbon atoms [1].

Boron Nitride Nanotubes (BNNTs) are the cylindrical structures of boron nitride having diameter in the range of below 100 nm and length up to several micrometers [3]. They were theoretically predicted in 1994 [4] and experimentally discovered in 1995 [5]. Their discovery has opened new ways for making devices with excellent properties. Properties of BNNTs are almost similar to Carbon Nanotubes (CNTs), however, CNTs can be conductor or semiconductor dependent on the chirality or helicity whereas, BNNTs are large band gap semiconductors independent of helicity [6].

* Corresponding author. Fax: +60 379674146.
E-mail addresses: mu_khandaker@yahoo.com, mu_khandaker@um.edu.my (M.U. Khandaker).

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BNNTs are found to be very useful material for different biomedical applications such as therapeutic or diagnostic due to its possible non-cytotoxic nature [7–9]. In boron nitride capture therapy, BNNTs are proposed to be the boron carriers. The BNNTs are first injected, and then transferred into the tumor cell, where it produces localized charged particles by the interaction of neutron beam from an external source. The as produced charge particles may then further be used to kill the tumor cells and cure the patient. The uniform distribution of Fe_3O_4 nanoparticles on the BNNTs surface introduced magnetic behavior in BNNTs. This behavior of BNNTs might be very useful in Micro-Electro Mechanical System (MEMS) and targeted drug delivery [10]. Moreover, BNNTs being nanostructure with improved properties can be effectively used as a neutron sensing element in a solid state neutron detector [11].

All these features and advantages of BNNTs for different application are dependent on its purity, size and alignment which in turn depend on the synthesis methods. The synthesis methods being used for BNNTs are Arc-discharge, Laser ablation, Template synthesis, Auto clave, Ball milling and Chemical vapor deposition using borazine as precursor [12]. However, all of these techniques either operate at higher temperature with complex and expensive experimental set up or require toxic and dangerous precursors. The BNNTs thus formed contained different materials as impurities. A major breakthrough, regarding the synthesis of pure BNNTs occurred with the development of Boron Oxide CVD (BOCVD) technique by Tang et al. [13]. This technique utilizes B, MgO and other metal oxides as precursors, and specially designed induction furnace with rapid heating and large temperature gradient as an experimental set up. The precursors are first heated at a temperature above 1300 °C. The B_xO_y vapors thus generated are transferred into the reaction area with the help of Ar (gas) career, where it reacts with NH_3 to form BNNTs [13]. Zhi et al. further developed the BOCVD technique with the introduction of B, MgO and FeO as an effective precursor [14]. Working on the same idea, Lee et al. [15] established thermal CVD technique for the synthesis of BNNTs. In this technique, induction furnace is replaced with a conventional horizontal tube furnace. Additionally, one end closed quartz test tube is used inside the chamber to get vapor trapped for growing of the BNNTs. During the experiment, the chamber is first evacuated to a certain level. Then, a 2:1:1 ratio of the precursor (B, MgO and FeO) is heated up to 1200 °C to form B_2O_2 vapors. At this temperature, NH_3 gas is introduced into the system. The B_2O_2 vapors react with NH_3 and form BNNTs [15]. The as-developed thermal CVD technique [15] is further applied for the pattern growth of the BNNTs by the same group. No change has been made in the previously used set up [15], except, the ratio of the precursors, growth duration, gases flow rates and nature of the substrate. Changes in these parameters with previously developed technique [15] was claimed to be used for controlled growth of the BNNTs [16]. Pakdel et al. studied the effects of precursor's ratios (1:1:1, 2:1:1 and 4:1:1) and temperature (1200, 1300 and 1400 °C) on the size and morphology of the BNNTs [17]. The major difference in their experimental set up and Lee et al. [16] was the use of inner quartz test tube. In the Lee et al. [16] work, the inner test tube used was closed at one end whereas the one used by Pakdel et al. was opened at both ends [17]. The use of both end opened inner quartz tube by Pakdel et al. [17] also denies the claim of Lee et al. [15] that BNNTs cannot be synthesized via their developed technique if the one end closed quartz tube is replaced with the one having both ends open. Both of these groups utilized vacuum or evacuation as a reaction atmosphere inside the chamber. The work of Pakdel et al. [17] on one side shows the effectiveness of thermal CVD technique for BNNTs growth, and on the other side suggests changes for further developments. To improve the quantity of the final product, Seo et al. [18] combined ball milling and annealing process (of the precursors) with thermal CVD (introduced by Lee et al. [15]). In their work, a mixer of milled precursors (B, MgO and FeO) was annealed in the presence of a gases mixer (N_2: 95% and NH_3: 5%) for 6 h. BNNTs were synthesized by the reaction of N_2 with solid phase of B. The production of impurities in the final product was a great concern. It was concluded that the quality of the final product can be improved by controlling the reaction parameters like: precursors, temperature and annealing time. Ozmen et al. [19] used thermal CVD with mass spectrometer, and synthesized BNNTs from the reaction of ammonia with powder mixer of boron and iron oxides in a wide temperature range of 900–1400 °C. Ar gas was used to purge the system before and after the experimental run. Also, during the experiment, Ar gas was used to remove the oxygen from the system [19]. Along with the lower quality of the final product, the as-used thermal CVD set up was a bit complex and expensive regarding the prices of mass spectrometer and arrangements for online analysis.

In the present study, thermal CVD technique [15] is further simplified with the use of Ar inert gas as an alternative for vacuum or evacuation (inside quartz tube chamber). This has also eliminated the use of vacuum pump in thermal CVD technique. Furthermore, the use of Ar gas prevents the oxidation of materials during a reaction [20]. Thus its (Ar gas) use on one side reduces the price of experimental set up by eliminating the use of vacuum pump, and on the other side, helps in growing longer BNNTs by preventing the oxidation of as produced Mg and Fe catalysts or their alloys.

2. Experimental details

A simple experimental setup is designed in the light of the work done by Lee et al. [15] and successfully used for the synthesis of BNNTs in the present work. A conventional horizontal dual zone quartz tube furnace along with one end closed quartz test tube is used as a major part of the experimental set up. During the experiment, Ar (inert gas) is used as an alternative for vacuum or evacuation.

Amorphous Boron powder, MgO and γ-Fe_2O_3 nanopowder of 99.9+% purities were bought from MTI Corporation and used as precursors. The aforementioned precursors having a total weight of 400 mg were first mixed at a weight ratio of 2:1:1 in an alumina combustion boat. The boat was covered with a few Si substrates and placed inside one end closed quartz tube near the closed end. The one end closed quartz test tube was then placed inside the quartz tube chamber of dual zone furnace in such a way that its open end was toward the gas inlet [21], as shown in Fig. 1(a). Furthermore, it was made sure that the precursors in the boat were exactly beneath the heating element. 2 min prior to the experimental run, Ar gas (with a flow rate of 100 sccm) was passed through the system to remove the dust particle and to create an inert atmosphere. Afterwards, the precursors were heated up to 1100 °C in the presence of Ar gas flow [19] at a rate of 100 sccm. At 1100 °C Ar flow was replaced by NH_3 at a rate of 100–200 sccm, and the precursors were heated up to 1200 °C. At 1200 °C, the system was kept for 1-h in the presence of ammonia gas flow.

After then, NH_3 gas flow was stopped, and the system was allowed to cool down to room temperature in the presence of Ar gas flow. At room temperature, white color BNNTs were found, deposited on Si substrate and the inner wall of alumina boat, as shown in Fig. 1(b).

The as synthesized samples are then characterized with the help of: Field Emission Scanning Electron Microscope (FESEM, Model: Zeiss Supra 55 VP) to study its surface morphology, Transmission Electron Microscope (Model: Zeiss Libra 200FE) to