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Influence of growth duration on size and morphology of boron nitride nanotubes grown via chemical vapor deposition technique

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ABSTRACT

Boron nitride nanotubes are synthesized on Si substrate via a chemical vapor deposition technique with different growth durations. Field emission scanning electron microscopy micrographs show a clear influence of growth duration on size and morphology of the synthesized nanotubes. It reveals that the diameter of the tubes decreases and length increases with an increase in growth duration. Total diameter of the tube has been reduced up to 31% and length increased up to 30% with an increase of 20 min growth duration. As a result, morphology of nanotubes has also been changed from curve like to straight. Transmission electron microscope confirms the tubular structure of the synthesized nanotubes with an interlayer spacing of 0.34 nm that corresponds to $d_{(002)}$ plane of hexagonal boron nitride and its crystalline nature. Energy dispersive X-ray spectroscopy indicates the presence of magnesium particles in the synthesized samples that refers to its catalytic growth. X-ray photoelectron spectroscopy confirms the elemental compositions of the sample. Raman spectra reveal a peak shift of 5.48 cm^{-1} towards higher region of wavelength that corresponds to E_{2g} mode of vibration in hexagonal boron nitride. This result also confirms the structural change in the synthesized boron nitride nanotubes with respect to the growth duration.

1. Introduction

The study of the nanostructured materials has revealed that the properties of these materials are totally different from their bulk counterpart due to quantum confinement of carriers [1,2], surface effects, and geometrical confinement of phonon. Therefore, the desired bulk properties of the materials can be improved through the reduction of their size and an increase in the surface area [3–10]. The discovery and synthesis of carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs), is one of the milestone achieved in nanoscience. CNTs have remarkable electrical and mechanical properties which have made it lying in the forefront of the researchers and scientists to use it in the development of different electronics devices and sensors [8,11,12]. The properties of BNNTs are almost similar to CNTs. However CNTs can be conductor or semiconductor depends on the chirality or helicity, whereas BNNTs are wide band gap semiconductor independent of helicity [13–15]. Being nanostructure enables material to have large number of atoms on the surface as compared to volume. The confinement of large number of electrons of the atoms in the surface states greatly enhance its absorption and emission properties, and also helps in improving its electrical and mechanical properties [4]. Therefore, applications of BNNTs as a sensing element in a radiation sensor for neutron will greatly improve its performance [16–18]. The possible role of BNNTs as an insulating protective shield has also been observed in the development of nanocables from semiconducting nanowires [19–25]. It is experimentally observed that the superplasticity of engineering ceramics increases to a great extent with the addition of BNNTs [26]. Due to the bipolar nature of B–N bond, BNNTs show stronger adsorption of hydrogen. Therefore, BNNTs are considered a very important material for hydrogen storage applications [27–31].

All these possible applications are based on the remarkable properties of the BNNTs. Most of these properties are determined on the size and morphology of the BNNTs, which are further dependent on the synthesis methods [32]. The BNNTs have been synthesized by various methods such as arc-discharge, laser ablation, template synthesis, auto clave, ball milling, chemical vapor deposition (CVD) etc. [33]. CVD is the most advanced and convenient technique for the synthesis of BNNTs. The BNNTs size and morphology can be changed in a controllable way with the change in different parameters of CVD. These parameters include: experimental set up, precursor's type, precursor's ratio and temperature [34]. Changes in BNNTs diameter and morphology have been observed in CVD technique with an increasing temperature in earlier studies [35,36]. A study showed that the diameter of the BNNTs reaches to micron size at higher temperature and

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converted to BN flakes at temperature above 1250 °C. Later on the size and morphology of the BNNTs have been observed at 1200 °C for a growth duration of 60 min. The as synthesized clean and long BNNTs were found to have diameter in the range of 10–100 nm and length of greater than 10 μm [37]. The size and morphology has also been observed at different temperatures of 1200, 1300 and 1400 °C for a growth duration of 30 min and precursors ratios of 1:1:1, 2:1:1 and 4:1:1. During that work the growth duration was kept fixed, however, different weight ratios of the (same) precursors and temperatures were used. For 2:1:1 ratio the diameter was found to be approximately 30, 60 and 20–100 nm at 1200, 1300 and 1400 °C respectively. A slight change in morphology has also been observed with respect to the changing parameters. A greater change in morphology and diameter was observed for 1:1:1 and 4:1:1 ratios of the precursors at 1300 °C. The diameter was found to be in the range of 100–500 nm with semi-erect flower like morphology for 1:1:1 ratio of the precursor and 50–150 nm with entangled curve like structure for 4:1:1 ratio of the precursors. The as-synthesized BNNTs were further found to have opened or closed tip with an encapsulated Mg particles. Synthesis of BNNTs with a particular size and morphology has also been reported by using 4:1:1 ratio of the precursor at 1200 °C for a growth duration of 30 min [38]. Using the same precursors, ratio, temperature, growth duration [38] and a slightly different experimental set up, BNNTs has been reported by Pakdel et al. Here, change in the experimental set up is assumed to be the possible reason in this regard. In all of the above studies, changes in diameter and morphology of the BNNTs were observed with respect to experimental set up, precursor's ratio and temperature. All of these are well known parameters, responsible for change in size and morphology of the BNNTs. Influence of growth duration on diameter and surface morphology of CVD grown BNNTs have been rarely studied till date. In the present study, BNNTs are synthesized via a simple catalytic chemical vapor deposition (CCVD) technique with different growth duration. The structural, morphological and elemental properties of as grown BNNTs on Si substrates have been studied in full details.

2. Experimental details

Boron nitride nanotubes are synthesized with different growth

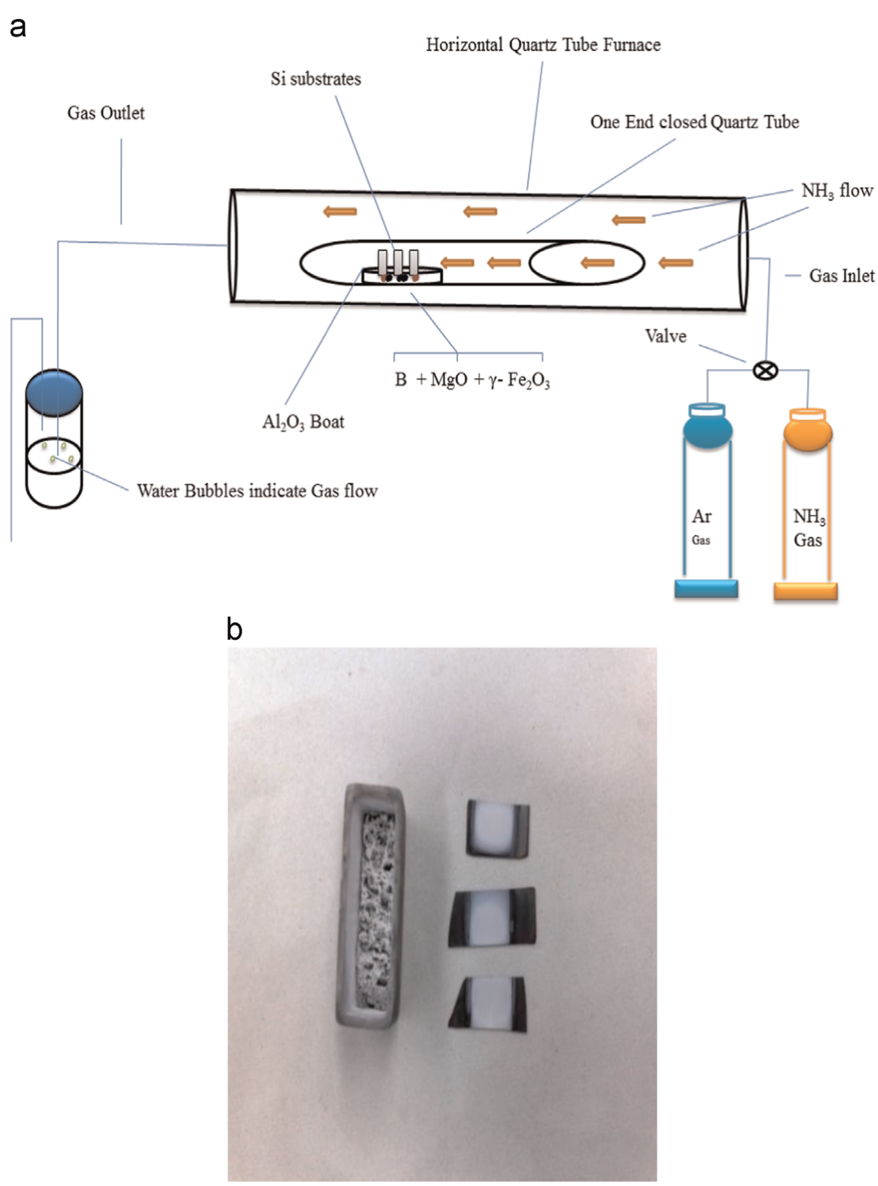

Fig. 1. (a) Schematic diagram of as-used experimental setup and (b) as-synthesized BNNTs in alumina boat and on Si substrate.