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A simple technique to synthesize pure and highly crystalline boron nitride nanowires

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Abstract

Unlike various complex and extensive experimental procedures available in the literature, a simple experimental technique has been developed to synthesize boron nitride nanowires (BNNWs) on Si substrates in a short growth duration of 30 min via vapor–liquid–solid (VLS) growth mechanism. The surface morphology and diameter of BNNWs were obtained by field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscopy (HR-TEM). The as-grown boron nitride nanowires have a wire-like morphology with diameter in the range of ~20–150 nm. The Raman spectrum of the synthesized BNNWs showed a sharp and intense peak at 1380 (cm^{-1}) corresponds to the E_{2g} mode of vibration in h-BN depicted its highly crystalline nature. This work reveals that a modified CVD technique and short growth duration is suitable to synthesis nanowires with tens of nanometers in diameter.

Keywords: A. Chemical preparation; B. Electron microscopy; B. X-ray methods; E. Sensors; BNNWs

1. Introduction

The study of nanostructured materials has revealed that the electrical, mechanical and optical properties of these materials are totally different from their bulk counterpart due to electrons and holes confinement, surface effects and geometrical confinement of the phonon [1]. Therefore, the desired properties of materials can be achieved for potential applications through their size tailoring from bulk to nano [2,3]. Boron nitride is a promising material due to its remarkable properties for different applications in the modern world. These properties included the hardness, high melting point, low dielectric constant and large band gap etc. It exists in three different crystalline forms; hexagonal (h-BN), cubic (c-BN) and wurtzite (w-BN). Hexagonal boron nitride is a wide band gap semiconductor [4]. It has a direct band gap of 5.97 eV [5]. It is the normal phase of BN which is stable at room temperature and pressure. Its structure is similar to that of graphite but alternative boron and nitrogen atoms substitute for carbon atoms [6]. Boron nitride nanotubes (BNNTs) [7], and BNNWs are the low dimensional structures of h-BN. BNNTs are the hollow cylindrical structures of h-BN with diameter in the nanoscale range and length up to several micrometers [8]. It is found to be a very promising material [9], for different biomedical applications such as therapeutic or diagnostic procedures due to its possible non-cytotoxic nature [10–12]. The uniform distribution of Fe_3O_4 nanoparticles on the BNNTs surface introduced magnetic behavior in BNNTs [13]. This behavior of BNNTs might be very useful in Micro Electro Mechanical System (MEMS) and targeted drug delivery [14]. BNNTs, being nanostructure with improved properties, can be effectively used as a neutron sensing element in a solid state neutron detector [15]. Unlike BNNTs, BNNWs are the filled cylindrical structure of h-BN with at least one dimension in the nanoscale range. Its properties and advantages for different applications are dependent on its purity and size which in turn depends on the synthesis methods. In some of the synthesis methods, BNNWs are reported along with BNNTs. The production

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of the BNNWs in these techniques seem to be unexpected, as no separate method has been described or claimed for their synthesis [16]. BNNWs have been obtained over α-FeB nanoparticles by the reaction of a mixer of NH_3 and N_2; however, this method is a bit complex and quite lengthy as far as the synthesis of α-FeB or FeB and final product is concerned [17]. Ball-milling and annealing methods were also used, and BNNWs were synthesized on a stainless steel substrate covered by B solution [18]; however, again the method shown is quite lengthy and a bit difficult to be followed by other researchers. CVD technique was also utilized, and BNNWs were synthesized directly on stainless steel substrate. Stainless steel was used not only as a substrate but also as a catalyst. The overall method was claimed to be simple and useful for obtaining high quality BNNWs. However, the method is quite lengthy, especially in the milling of initial precursor and somewhat the duration of the final reaction [19]. Some other synthesis methods have also been reported for BNNWs [20–22], however, like all the above techniques, they are either very difficult or complex, or the used precursors are hazardous and may cause serious health problems.

In view of all the lengthy and complex procedures, a very simple and short procedure has been developed for the synthesis of pure BNNWs. The present experimental set up is quite different from the one already reported for the synthesis of BNNTs [23–25]. However, no further modification was done in it after it has been successfully used for the synthesis of BNNTs. The present findings focused on the influence of growth duration on the final product. In this study, we have successfully synthesized BNNWs in a short growth duration of 30 min, and then investigated the surface morphology, structural properties and elemental analysis in details.

2. Experimental details

2.1. Synthesis procedure

Boron nitride nanowires were synthesized via a simple catalytic chemical vapor deposition technique at 1200 °C in growth duration of 30 min. Amorphous Boron, MgO and γ- Fe_2O_3 nano-powder are used as the precursors. First, 400 mg of precursors are mixed in 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 [26]. The one end closed quartz tube is then inserted into the quartz tube chamber of the dual zone furnace in such a way that the open end of the one end closed quartz tube was toward the gas inlet. Before heating, Ar gas is flown through the system to remove the dust particle, and to create an inert atmosphere [27]. The precursors are then heated up to 1200 °C at a rate of 10 °C/min in the presence of Ar gas flow at a rate of 100–200 sccm. At 1200 °C, Ar gas flow is replaced by NH_3 gas flow at a rate of 200–300 sccm for a growth duration of 30 min. After 30 min NH_3 flow is stopped, and the system was allowed to cool down to room temperature in the presence of Ar gas flow. After cooling the furnace to room temperature, white color BNNWs were found on the Si substrate and on the inner wall of alumina boat (weighted approximately 80 mg in powder form), as shown in Fig. S1 (of the supporting material). The as-synthesized sample on the Si-substrate was then characterized by using FESEM, Raman spectroscopy, X-ray photoelectron spectroscopy and HR-TEM. The details of all the characterizations are discussed in the Results and discussion section.

2.2. Growth mechanism

A cap like morphology of BNNWs in HR-TEM image shown in Fig. 3(b) suggested that the nanowires growth is based on the vapor liquid solid (VLS) mechanism [19]. A detailed schematic diagram of VLS growth mechanism is shown in Fig. 1. The BNNWs have been synthesized by the various researchers based on same growth mechanism. Boron at higher temperature reacts with metal oxides catalyst particles and forms $B_2O_{2(g)}$ vapors, MgB_2 and partially melted Fe catalyst particles. The catalyst (Fe) particles react with Si-substrate and lose it catalytic properties. It then starts working as diffusion barrier that prevents other species or catalysts to react with the Si-substrate [24]. At sufficient partial vapor pressure, the partially melted MgB_2

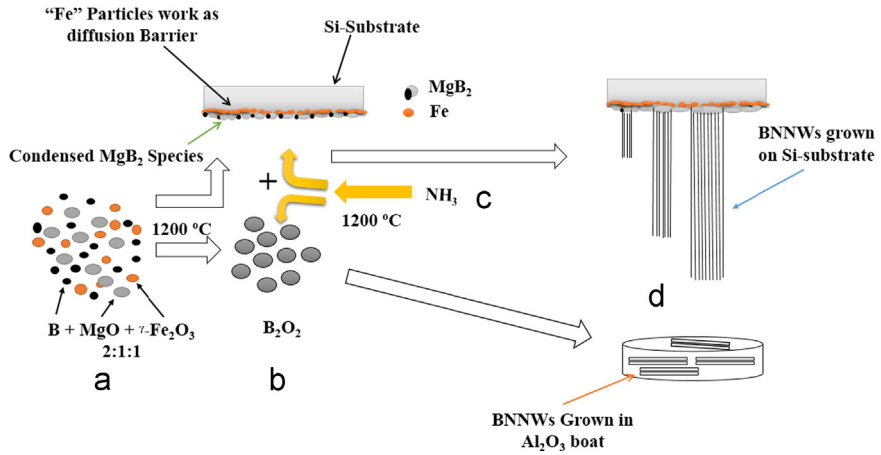

Fig. 1. Schematic diagram of vapor–liquid–solid (VLS) growth mechanism of BNNWs (a) Boron, MgO, γ-Fe_2O_3 are mixed in 2:1:1 ratio. (b) Formation of $B_2O_{2(g)}$ and Diffusion of Fe catalytic particle on Si substrate, condensation of as-formed partially melted MgB_2 species upon Fe catalyst on Si substrate. (c) Flow and decomposition of NH_3 at 1200 °C. (d) Growth of BNNWs from the reaction of MgB_2 and N_2 (from decomposed NH_3) on Si-substrate and from the reaction of B_2O_2 and N_2 (from decomposed NH_3) in Al_2O_3 boat.