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Short communication

Synthesis of multilayered hexagonal boron nitride microcrystals as a potential hydrogen storage element

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ABSTRACT

Top-down approach has been used to synthesize pure, highly crystalline, multilayered micron size crystals of hexagonal boron nitride (BNMCs) at the top of Silicon substrate at 800 °C by using bulk boron nitride powder as a precursor. The synthesized crystals have different interlayers spacing from left to right (0.33 nm, 0.37 nm and 0.35 nm) and at the center (~0.24 nm). The former spacing corresponds to $d_{(002)}$ spacing whereas the later corresponds to $d_{(010)}$ spacing in h-BN. The sharpness of the peaks in XRD, Raman and FTIR spectrums correspond to highly crystalline nature of BNMCs whereas the locations of the peaks verify the h-BN nature of BNMCs. The B-N bonded BNMCs with larger surface area can be an excellent choice as a hydrogen storage element.

1. Introduction

Type, purity, crystallinity and size of a material is very important for its use in any of its potential application [1]. Hexagonal boron nitride (h-BN) has high temperature stability, high electric insulation, low dielectric constant, hardness, large cross-section for thermal neutron and resistance to oxidation at high temperature [2–6]. All these properties enables h-BN an effective choice for a variety of application in microelectronic mechanical systems (MEMs), bio-medical, neutron sensing, lubricants, refractories, laser devices, catalyst supports and electrical insulators [4,7–10].

Like any other type of material, purity and crystalline nature of h-BN are some of the key concern before it can be used for any of its potential application. Numerous techniques have been adopted to synthesize pure and crystalline structures of h-BN. In this regard, Polyborazylene has been discovered as a precursor for high yield synthesis of boron nitride [11]. This idea later on resulted in borazine-based precursors for different h-BN structures. Thus, blend solutions of polyborazine/polyacrylonitrile were discovered as the most reliable precursors for the synthesis of h-BN fibers [12]. The health-risky nature of the precursors, their stiff chemistry to properly operate the chemical process and quality of the final product were some of the issues which have not only made the overall process complex but also lengthy. Boric acid and melamine have also been used as polymeric precursor for the synthesis of h-BN products [2]. However, the final product is found to contained carbon and nitrogen based compounds as impurities which have been very difficult or almost impossible to remove even at a higher temperature of 1600 °C.

Along with purity and crystalline nature, h-BN has inherent brittleness that demerit its uses in modern technology [2]. Thus techniques have been sought to not only synthesize pure and crystalline structures of h-BN but also to reduce or eliminate its brittleness. Researchers have shown that properties of materials can be changed to a great extent through the reduction of their size from bulk to nano (10^{-9}) or micro (10^{-6}). The reduced low-dimensional structures of h-BN have special characteristics due to their electrons and holes confinement [13], surface effects, and geometrical confinement of the phonon. The reduction in size is not only suitable to eliminate or reduce the inherit brittleness of h-BN but also make it a very useful material for a variety of applications in drug delivery, insulation,

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filtration, fuel cells, composite, information technology and hydrogen storage etc. [2].

Hydrogen is a clean fuel. It has emerged as the most suitable alternative for the existing carbon based energy sources. Hydrogen as a fuel has increased the demand for the preparation of storage devices for Hydrogen energy. Though, a few systems have already been adopted for this purpose, however, their capacity is not sufficient enough to be used in practical applications. This deficiency led to the development of nanostructured materials for Hydrogen storage via physisorption. As a first choice single walled carbon nanotubes (SWCNTs) and other nanostructures of carbon have intensively been studied due to its light mass, porous structure and excellent carbon-hydrogen molecular interaction. However, the Hydrogen storage properties of SWCNTs leads to controversy because of its complex electronic properties arises from its un-controlled diameter or helicity. Un-like SWCNTs, nanostructures of h-BN have diameter or helicity independent electronic properties suitable for a variety of applications in Hydrogen storage [14,15]. In view of the these facts, researchers have synthesized nanotubes, nanowires, nanosheets, microtubes [16] and microflakes of h-BN [17]. Following their excellent properties and potential applications, microcrystals of h-BN (BNMCs) have also been synthesized. However, to be used as a Hydrogen storage element, the synthesized BNMCs should be highly pure and crystalline along with its plate surface and porous structure.

Purity, size and crystalline nature of BNMCs are some of the serious issues if it to be synthesized from a mixture of different precursor's materials. In such a cases, it is found to contained different quantities of the as-used precursors or their compounds as impurities in the final product [16]. In order to avoid this, amorphous powder of h-BN is chosen as a precursor with argon gas as an inert and ammonia gas flow as a reaction atmosphere. Argon gas is used to flush the system before the experimental run [18]. It is found that the flushing will remove the dust particles and will prevent the precursor from oxidation due to its anti-oxidant nature [19]. The heat up removes stresses from the precursors. Ammonia as a reaction atmosphere also acts as an etching agent. The etching activity plus higher temperature help in making micron size crystal of h-BN. The decomposition of NH_3 at higher temperature though ends up the etching activity, however, the decomposition provides Hydrogen along with Nitrogen. To somehow Nitrogen acts as an etching agent in the coming process. During the processes, Hydrogen burns and adds up as heat energy [19]. The extra heat energy at final temperature helps in making fine and highly crystalline micron size crystal of h-BN.

2. Experimental details

Amorphous bulk-size h-BN powder of 99.999% purity and 200 mg of weight are taken in alumina boat as a precursor. Mono-crystal silicon wafer is cut into 2 cm×1 cm dimension. The as-cut substrates are standard cleaned and placed at the top of the alumina boat containing the precursor. Afterward, the boat is centered into one-end closed quartz test tube and placed inside quartz tube chamber of dual zone horizontal tube furnace. The furnace is flushed with the argon gas. Consequently, the system is slowly heated up to 800 °C. During the heat up, NH_3 gas flow (200 sccm) is used as a reaction atmosphere. After 30 min at 800 °C, the NH_3 gas flow is switched off and the system is cool downed to room temperature in the argon atmosphere. At room temperature, the argon gas flow is switched off and the synthesized sample deposited at the top of silicon substrates is collected from the system and characterized for shape, size, morphology, elemental compositions and phase.

3. Results and discussion

Field emission scanning electron microscopy (FESEM) shows BNMCs of various size and shape's in Fig. 1. Most of the BNMCs look-like pieces of polished diamonds. The crystal at the bottom right hand corner are formed in the shape of micron size particles. From bottom right hand to top right hand corner, the morphology changes to cylindrical from particle whereas from top right hand to top left hand corner the morphology almost remains the same however, the diameter increases. At the same time, from top left hand to the bottom left hand corner, the size, morphology and types of BNMCs are changing and becomes like flat surface.

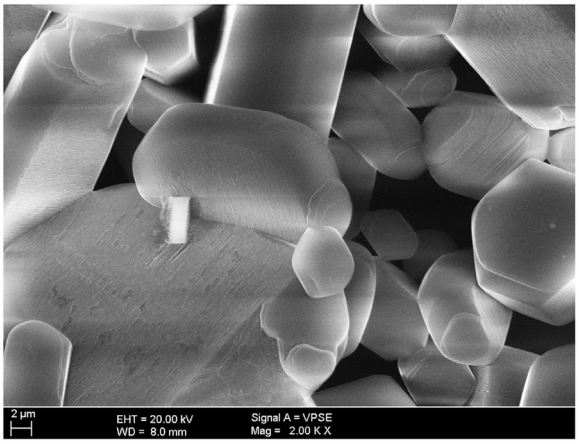

Fig. 1. FESEM micrograph shows BNMCs of various size that and morphologies. Most of the BNMCs look-like pieces of polished diamonds.

High resolution transmission electron microscopy (HR-TEM) is used to view the internal structure, lattice fringes, arrangement of different planes and their interlayer spacing in the synthesized BNMCs. Parts of a BNMC characterized with HR-TEM is shown in Fig. 2(a). The BNMC has a bending round edge from left to right with lattice fringes

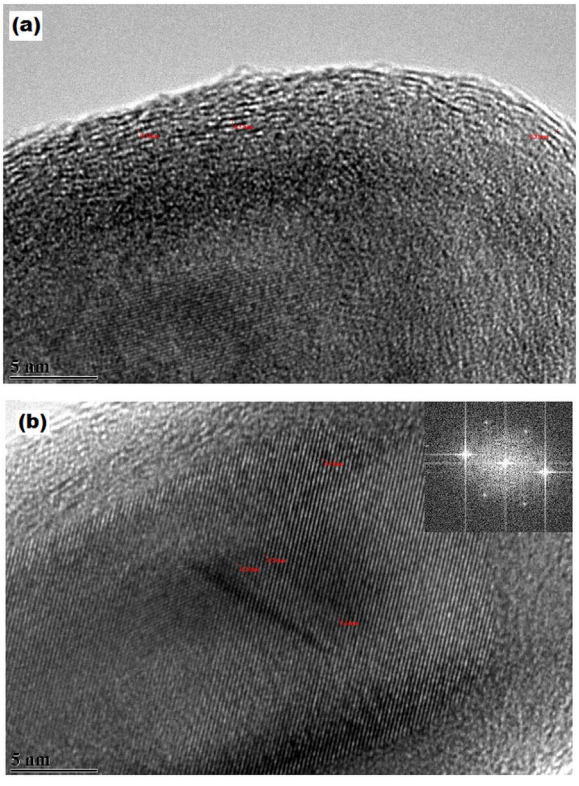

Fig. 2. (a) HR-TEM micrograph shows BNMC with bending round edge from left to right with different interlaye spacing i.e. 0.33 nm, 0.37 nm and 0.35 nm. **(b)** HR-TEM micrograph shows the central part of BNMC with an interlayer spacing of ~0.24 nm. The SAED image in the inset on the upper right hand shows the arrangement of atoms in the synthesized BNMC.