One-dimensional nanomaterials synthesized using high-energy ball milling and annealing process

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Abstract

One-dimensional (1D) nanomaterials including nanotubes, nanowires and nanorods have many new properties, functionalities and a large range of promising applications. A major challenge for these future industrial applications is the large-quantity production. We report that the ball milling and annealing process has the potential to achieve the mass production. Several examples including C, BN nanotubes and SiC, Zn nanowires are presented to demonstrate such capability. In addition, both size and structure of 1D nanomaterials can be controlled by varying processing conditions. New growth mechanisms involved in the process have been investigated and the high-energy ball milling has an important role in the formation of these 1D nanomaterials.

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1. Introduction

One-dimensional (1D) nanomaterials including nanotubes, nanowires and nanorods have many new properties and functionalities that lead to a large range of promising applications. Therefore, there is a strong demand for pure carbon nanotubes (CNTs) in large quantities and low costs [1], but this remains a major technical challenge so far. Many synthesis methods have been developed during the last decade. The popular processes include electric arc-discharge, laser ablation, chemical vapor deposition (CVD), and ball milling–annealing methods. Among them, the ball milling–annealing method, consisting of a pre-ball milling and a subsequent thermal annealing process, can produce much larger quantities of nanotubes due to a solid-state process without any vapor phase and the large milling capability [2]. Both single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) have been produced using the ball milling–annealing method [3,4]. Low production costs are also expected from the relatively simple milling equipment and low-temperature annealing process. In addition, the ball milling–annealing method can produce other nanotubes and nanowires such as boron nitride (BN) nanotubes [5]. It actually becomes a successful method for the large production of high yield commercial BN nanotubes [6]. Both nanotube size and structures (cylindrical and bamboo-type) can be controlled [7]. The ball milling and annealing method has been adopted by many research groups in synthesis of different nanotubes since it was first reported in 1999 [3,5]. Tang et al. [8] obtained BN nanotubes and horns from a mixture of B and Ga2O3 after first ball milling for 6 h and subsequent annealing up to 1550 °C in NH3 gas. Bae et al. [9] have produced BN nanotubes by first ball milling of B powder, followed by annealing in NH3 gas in the temperature range of 1000–1200 °C. Li et al. [10] have produced TiTe2 nanotubes by annealing the ball-milled mixture of Ti and Te powders, and they claim that the ball-milling treatment is essential for the nanotube formation. Multi-walled and open-ended TiSe2 nanotubes are also synthesized by using the ball milling–annealing method [11]. The above research works demonstrate that the ball-milling technique, which is generally regarded as a traditional technique with a history...
of several centuries [12], could become an important tool in 1D nanomaterial synthesis. One important reason is that most of the above research works uses actually a new ball-milling technique: high-energy ball milling (HEBM), which is very different from the traditional ball-milling technique.

The major differences between conventional ball milling and the HEBM include: (1) the impact energy of HEBM is typically 1000 times higher than the conventional ball-milling energy. The dominant events in the conventional ball milling are particle fracturing and size reductions, which correspond to, actually, only the first stage of the HEBM; (2) a longer milling time is generally required for HEBM to activate and complete the structural changes and chemical reactions; (3) HEBM requires the controls of milling atmosphere and temperature which are crucial to create the desired structural changes or chemical reactions. HEBM can cover most work normally performed by conventional ball milling. Therefore, conventional ball-milling equipment cannot be used directly to conduct any HEBM work and specially designed ball mills with a higher milling energy are used for HEBM purposes.

The new HEBM technique has produced many new metastable materials which cannot be synthesized using thermal equilibrium processes in past several decades [13,14], for example, amorphization of ZrNi alloys under a dynamic equilibrium between mechanical driven disordering or amorphization process and thermal reordering process [15], mechanical alloying of nanocrystalline compounds, nanoparticle-reinforced metal nanocomposite [16–18], and nanoporous materials [19]. Controlled reactive ball milling has produced nanosized particles of metal oxides [20], nitrides [21], hydrides [22] and carbides [23] at room temperature.

In addition to the direct synthesis of nanomaterials during the milling process, 1D materials (nanotubes and nanowires) can be produced by combining the HEBM and controlled thermal annealing processes. Large-quantity production of nanotubes in C and BN and nanowires in Zn and SiC has been achieved and related formation mechanisms will be discussed.

2. Experimental details

Different types of high-energy ball mills have been developed, including the Spex vibrating mill, planetary ball mill, high-energy rotating mill, and attritors [12,24]. In this study, two different types of HEBM mills have been used: a vertical rotating ball mill and a planetary ball mill. The rotating steel mill has a vertical rotating cell loaded with several hardened steel balls. As the cell rotates at a controlled rate, the balls drop onto the powder that is being ground. The action is illustrated in the schema shown in Fig. 1a. A magnet is placed close to the cell to apply a strong magnetic pulling force on the magnetic milling balls. An increased milling energy is thus achieved. Furthermore, different milling actions and intensities can be realized by adjusting the cell rotation rate and the magnet position.

Fig. 1. Schema of two high-energy ball mills: (a) a vertical rotating ball mill with a horizontal rotating axis and (b) a planetary ball mill (Pulverisette 5, Fritsch).

Much large quantity of materials can be treated using a planetary ball mill (Pulverisette 5, Fritsch), which employs strong centrifuge forces to create high-energy milling actions inside the container (Fig. 1b). Total four containers can be run at the same time to produce large quantities of materials. Because a large number (10) of the balls is used and the container rotates at a high speed of 300 rpm, the milling frequency is very high. A short milling time of 50 h is thus needed.

Crystalline structure of samples was investigated by means of X-ray diffraction (XRD) analysis using Co radiation (\(\lambda = 0.1789\) nm) at room temperature. A Hitachi S4500 field-emission scanning electron microscope (FES-EM) was used to study sample morphology. Nanostructures were examined using a high-resolution transmission electron microscope (TEM) (Philips, CM300 operated at 300 kV).

3. Experimental results

3.1. Carbon nanotubes

A graphite sample was first milled at ambient temperature for 150 h and then heated in a tube furnace at 1400 °C for 6 h in flowing N\(_2\) gas. CNTs were found in the final sample as shown by a typical TEM micrograph in Fig. 2.
The outer diameters of the multi-walled tubes are less than 20 nm. The inter diameter is in the range of a few nanometers. These nanotubes do not contain any metal particles inside, but some other nanotubes have nanosized metal particles at tips. These metal particles are iron and chromium as milling contaminants from steel milling balls and the container [4]. These metal particles have a positive effect in the current case and act as catalysts for promoting nanotube formation, similar to other synthesis processes [25,26]. Most nanotubes self-assemble into sub-micron sized clusters to minimize the total surface energy. No nanotube was found in the sample directly after the milling treatment without subsequent heat treatment. Also, direct annealing of the starting graphite powder without pre-milling treatment does not produce any nanotube. Therefore, the nanotubes should grow only during annealing process from the pre-milled sample with (or without) the help from metal catalyst particles. Because the annealing temperature (1400 °C) is much lower than the melting point of graphite (>3500 °C), carbon vapor should not be produced during the nanotube formation. The nanoporous and disordered structures created by HEBM [19] should have an important role in nanotube formation during annealing. Detailed growth mechanisms will be discussed later.

3.2. BN nanotubes

BN nanotubes have the same tubular structure as CNTs, as well as excellent mechanical properties. They are also a stable wide-band-gap semiconductor and very stable at high temperatures. However, BN nanotubes are difficult to be produced in large quantities using CVD or arc-discharge methods. In this study, high-purity boron (B) powders were used as the starting materials. Ball-milling experiments were performed at room temperature in a vertical rotating ball mill using hardened steel balls and a stainless steel container. A starting pressure of about 300 kPa of ammonia (NH₃) gas was established inside the milling chamber before each milling experiment. During milling, a huge amount of gas was absorbed onto the fresh surface of the powder created by high-energy ball impacts. The milling energy is so high that nitridation reactions are induced during the room-temperature milling process, which causes significant pressure decrease and re-increase inside the milling chamber [5]. Nanocrystalline BN was produced at the end of milling, which serves as seeds for nanotube growth during subsequent heating process. During the subsequent annealing in nitrogen-containing atmosphere, the nitridation reaction further proceeds and completes with the formation of high-density BN nanotubes, as been shown by the SEM image in Fig. 3a. The XRD analysis reveals the BN structure and the presence of catalyst Fe as indicated by the BN (0 0 2) and Fe peaks (Fig. 3b). Different milling and annealing conditions produce the BN nanotubes with different structures. When the as-milled sample was heated at a temperature of 1200 °C for 6 h under NH₃ gas flow, thin straight BN nanotubes with an external diameter less than 6 nm were produced. TEM reveals a tubular, multi-walled structure (Fig. 3c). Long bamboo-type nanotubes were also produced after heating at 1100 °C in N₂ gas (100 ml/min) from the B powder milled just for 50 h in NH₃ atmosphere using a planetary mill. The typical bamboo structure is shown in Fig. 3d. Selected area electron diffraction pattern of the tube end (head) in Fig. 3d identifies the catalyst particle as iron. The catalyst particle at the tip is responsible for the formation of this bamboo nanotube. Polygonal shape of the iron particle suggests that iron particle might be in the liquid or quasi-liquid state during tube growth. The lattice distance between two walls is determined to be around 0.34 nm from the inserted HRTEM image, very close to that of hexagonal BN powder indicating a well-crystallized structure. Some outer layers are terminated on the surface of the bamboo nodes (as shown in the enlarged image), leading to a more active chemical reactivity [27]. Both cylindrical and bamboo tubes can also be produced from crystalline BN compound as the precursor via the ball milling and annealing process [28]. The BN nanotube formation process in this case is similar to that of CNTs because of absence of nitridation reactions.

3.3. Zn nanowires

Nanowires in elemental metals or alloys can be used as interconnect materials in nanosized devices [29]. Zn nanowires in a large quantity and a high density have been produced from a mixture of amorphous B and ZnO powders with a molar ratio of 1:1.5. The mixture was first...
ball milled for 24 h in N\textsubscript{2} atmosphere (\sim 300 kPa) in a vertical rotating ball mill, and then heated at about 1050 °C for 2 h under a N\textsubscript{2} gas flow (500 ml/min). For comparison, the annealing experiment was also conducted on a sample of the same powder mixture without ball-milling treatment. The B and ZnO powders at the same molar ratio were mixed in a mortar by hand for about 30 min. After annealing of the milled sample, a thick layer of fluffy materials in gray-dark color was found depositing on the inner wall of the ceramic furnace tube near the tube end, where the temperature was estimated to be in the range of 200–350 °C. These deposition materials were characterized using XRD analysis and SEM. Fig. 4a shows a large number of nanowires obtained from the ball-milled starting sample, indicating a large-quantity production. The nanowires have a diameter about 150 nm and a length up to several micrometers. The high-magnification image in Fig. 4b clearly shows that the nanowire has a smooth surface and a hexagonal cross-section, suggesting a hexagonal single-crystal structure. In contrast, much less deposition was found from the unmilled starting sample after annealing. A mixture of nanowires and large particles was produced and a typical SEM image is shown in Fig. 4c. The faceted particles are associated with the Zn hexagonal structure too. Therefore, a higher yield of nanowires was produced from the starting material treated by ball milling.

The Zn nanowire structure was investigated using XRD. The XRD pattern is compared with that of the pure Zn powder in Fig. 4d. All diffraction peaks from both patterns can be attributed to the hexagonal Zn structure, confirming the nanowire composition as Zn. Interestingly, the two patterns have different strongest diffraction peaks. For the powder sample with a polycrystalline hexagonal structure, the strongest diffraction peak is (1 0 1), while the strongest peak in the XRD patterns of the nanowires is (0 0 2), which indicates the preferred growth of Zn (0 0 2) planes and this is in good agreement with the SEM observation of the hexagonal cross-section (Fig. 4b). The nanowire axis is parallel to the \langle 0 0 1 \rangle direction.

Possible formation mechanisms of these Zn nanowires are that boron first reacts with ZnO to form Zn and boron oxide (B\textsubscript{2}O\textsubscript{2}) vapor at a high temperature of 1050 °C [30]. Zn vapor is then carried by N\textsubscript{2} gas to the low-temperature zone of the temperature below the melting point of Zn (about 419 °C), and deposited on the furnace-tube wall to form Zn nanowires. The possible reaction is suggested as follows:

\[
2B (s) + 2ZnO (s) \rightarrow 2Zn (g) + B\textsubscript{2}O\textsubscript{2} (g),
\]

\[T > 900 ^\circ C, \ \Delta G < 0.\] (1)

It can be seen that the reaction is thermodynamically favorable process with a negative free energy at the
experimental temperature of 1050 °C. Furthermore, since there is no catalyst particle at the tips of the nanowires, these Zn nanowires should be formed via a vapor–solid (VS) mechanism [31]. It is clear that the ball milling treatment of the starting materials enhances the nanowire formation in both density and quantity, which could be associated with a faster reaction between B and ZnO, as well as a reduced reaction temperature. Detailed effects will be discussed later.

3.4. SiC nanowires

SiC nanowires (SiCNWs) are synthesized using CNT as template. A mixture of silicon monoxide (SiO) (Aldrich, 325 mesh, 99.9%) and iron (II) phthalocyanine, FeC_{32}N_{8}H_{16} (FePc) powders in a weight ratio of 1:1 were milled for 100 h in a vertical rotating ball mill using four steel balls. The milling was conducted in pure nitrogen gas at a pressure of 300 kPa at room temperature. The mixed powder was loaded in a ceramic combustion boat and placed in a horizontal tube furnace. The sample was first heated at 1000 °C for 30 min, and then the temperature was raised up to 1200 °C and held for 1 h. Si wafers were placed inside the furnace as the substrate to collect CNTs and nanowires.

During the first annealing at 1000 °C, cylindrical, multi-walled CNTs with a typical diameter of about 15 nm were produced. Detailed experimental procedure can be found in [32,33]. When the temperature increases up to 1200 °C, SiCNWs with a typical diameter of 40 nm were produced and some were in well-aligned bundles as shown in Fig. 5. The SiCNWs have a uniform diameter along the entire nanowire and no catalyst particle was observed at the tips as shown in Fig. 6a. The lattice image in Fig. 6b reveals the SiCNW has a β-SiC single-crystal core (diameter 15 nm) wrapped with a SiO_{x} layer. The inserted fast Fourier transform (FFT) pattern indicates the growth direction of the SiCNW is in \langle111\rangle direction with some stacking faults and twins perpendicular to the axis of the wire. The growth mechanism of SiCNWs appears to be a substitution reaction between SiO vapor and the CNTs. At 1000 °C,
CNTs were formed on the substrates during the pyrolysis of FePc via vapor–liquid–solid (VLS) mechanism [34], while SiO powder stayed in the combustion boat as it can only vaporize at a higher temperature between 1100–1400 °C. At 1200 °C, SiO started to vaporize and the vapor was blown onto the substrates where CNTs were already formed. At such a high temperature, SiO reacted with the CNTs through the reaction process: 2SiO + 3C → 2SiC + CO₂. As the reaction proceeds further, the whole CNT even transformed into a SiC nanowire. When no more CNT is available, the excess SiO vapor formed a layer wrapped outside of the SiC nanowire core. The HEBM process plays a very important role in the whole process. It refines the size of the starting materials and also increases the chemical reactivity of the powders, which leads to the occurrence of the reduction reaction and the formation of SiC structure at a low temperature of 1200 °C. In contrast, without this ball-milling process, bamboo-type CNTs can only be produced, and the final products are metastable amorphous SiO–C-NWs [35].

4. Discussions

The above experimental results show that HEBM has played an essential role in the formation of the above nanotubes and nanowires. Without the ball-milling process, many of them cannot be produced in the same annealing process. Therefore, the understanding of the role of ball milling is critical for the formation mechanisms and controlled production of nanotubes and wires. During the HEBM, material particles are repeatedly flattened, fractured and welded. Every time two steel balls collide or one ball hits the chamber wall, they trap some particles between their surfaces. The high-energy impacts severely deform the particles and create atomically fresh, new surfaces, as well as a high density of dislocations and other structural defects [36]. Such a high defect density can accelerate the diffusion process [37]. Furthermore, the deformation and fracturing of particles cause continuous size reduction and lead to reduction in diffusion distances. This can at least reduce the reaction temperatures significantly, even if the reactions do not occur at room temperature [38–40]. The detailed HEBM role on the nanotube and nanowire formation could be divided into three effects:

1. Creation of a precursor containing nucleation structures and catalysts: SEM and TEM observations found a high-yield of BN nanotubes in the heated samples but not in any milled samples, which suggest that the milling and annealing processes actually correspond to separate nucleation and growth processes, respectively [41]:
   - Ball milling → nucleation,
   - Annealing → growth.

Ball milling of graphite powder at room temperature produces a disordered and nanoporous structure through agglomeration of nanosized particles under ball impacts. The milling contamination acts as catalysts to promote nanotube formation during the subsequent annealing [42]. The nanosized metal particles and micropores are found to serve as nucleation structures. The amorphous/disordered phases are the source of free C, B and N atoms as no vapor phase is present. The growth process is in a solid-state process, possibly driven by surface diffusion [19]. This mechanism is supported by other experimental observations. Yin et al. [43] first ball mill graphite in NH₃ up to
120 h, in which a nitriding reaction between graphite and NH₃ gas occurs with the formation of amorphous CN phase. The milled sample is annealed in the temperature range of 300–450 °C under a flow of NH₃ gas to produce β-CN nanorods.

(2) Mechanical activation: HEBM produces smaller grain size, possibly higher surface area and disordered structure, which should all contribute a reduced reaction or vaporization temperature and a higher chemical reactivity in comparison with samples without the milling treatment. A larger amount of material is therefore vaporized at the same temperature and thus more nanowires or nanotubes could be formed from the larger vapor quantity. This effect was observed in the above enhanced formation of Zn nanowires. Same effect of nanowire yield improvement has also been observed in GaN nanowires [44]. In addition, because of the lower vaporization or reaction temperature, many nanowires such as SnO₂, Ga₂O₃, and GaN can be successfully produced from the milled precursors while only polycrystalline nanocrystals are formed without HEBM treatment [44–46]. Another effect of mechanical activation is the formation of well-crystallized structures in nanowires and nanotubes. High-quality, single-crystalline GaP nanowires and ZnO nanobelts are formed from the milled GaP and ZnO starting powders while polycrystalline curled GaP nanowires or ZnO plate-shaped chips are obtained from the unmilled powders [47,48].

(3) New chemical reactions: The ball-milled powders often have higher chemical reactivities and thus new reactions could take place during the subsequent annealing with the formation of various nanostructures as the end products. For example, the above SiC nanowires can only be produced from the milled mixture of SiO and FePc via the reaction of SiO⁺C(nanotube)→SiC(nanowire) + CO/CO₂ at 1200 °C. Without ball milling, SiOC nanowires are obtained at 1200 °C possibly because of the lack of sufficient activation energy. Some chemical reactions could take place even during the room temperature ball-milling process [43,49]. For example, nitriding reactions between B powder and NH₃ gas occurred during the ball-milling process with the formation of nanosized BN structures, which serve as nucleation structure for BN nanotube growth during the annealing [5].

5. Conclusions

Nanotubes and nanowires in large quantities and high densities have been produced using the ball milling and annealing process. HEBM creates a nanosized, disordered and more active structure in the precursor materials. The new metastable structure has different properties than unmilled materials including large surface area, reduced vaporization temperatures and a lower activation energy. These new properties enable the growth of 1D structure possible during the low-temperature annealing process.

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