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Microstructures of the silicon carbide nanowires obtained by annealing the mechanically-alloyed amorphous powders

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ABSTRACT

Silicon, graphite and boron nitride powders were mechanically alloyed for 40 h in argon. The as-milled powders were annealed at 1700 °C in nitrogen for 30 min. The annealed powders are covered by a thick layer of gray–green SiC nanowires, which are 300 nm to 1000 nm in diameter and several hundred microns in length. Trace iron in the raw powders acts as a catalyst, promoting the V–L–S process. It follows that the actual substances contributing to the growth of the SiC nanowires may be silicon, graphite and the metal impurities in the raw powders. The results from HRTEM and XRD reveal that the products contain both straight α/β-SiC nanowires and nodular α/β-SiC nanochains. It is interestingly found that 6H–SiC coexists with 3C–SiC in one nodular nanowire. This novel structure may introduce periodic potential field along the longitudinal direction of the nanowires, and may find applications in the highly integrated optoelectronic devices.

1. Introduction

Silicon carbide ceramic attracts great attention, thanks to its excellent properties at normal and elevated temperatures, such as nice thermal conductivity, high mechanical strength, extreme hardness, high thermal and chemical stability, good field-emitting performance and favorable radiation resistance [1,2]. Over the past decades, various SiC one-dimensional nanostructures have been synthesized, such as nanowhisker [3], nanorod [4], nanobelt [5], nanowire [6–8], nanospring [9], beaded nanochain and nanoweb [10,11]. Novel properties and potential applications, which are greatly different from these of the bulk SiC ceramics, have been found to the abovementioned nanostructures. For example, SiC nanowires have stronger photocatalysis ability to degrade pollutants, higher mechanical properties approaching to the theoretical values, higher photoluminescence intensity, and stable field emission current density [6,12]. Thus, they are expected to find applications in the fabrication of nano-sensors, nano-laser devices, logic gate circuits, photochemical catalysts, functional composite materials, composite reinforcers, and field emission devices.

For the preparation of SiC nanowires, the methods mainly include the carbothermal reduction of the sol–gel derived silica xerogels [11], the reactions between carbon nanotube and gaseous SiO [13], the chemical vapor deposition (CVD) process with the solid or gaseous silicon source [14], the laser ablation of the targets containing silicon and metal catalysts [14], and the arc discharge technique using composite powder or SiC as the anodes [15]. By these methods, the average diameters of the prepared SiC nanowires vary from 20 nm to 100 nm, and the lengths are several hundred microns. Stacking faults are usually observed in the nanowires. In most cases, the obtained nanowires consist of single crystals of β-SiC, and the growth direction is normally along [111]. In some researches, the synthesized SiC nanowires have the core/shell structure, with β-SiC as the core and amorphous silica as the shell [16]. Spherical nanoparticles frequently exist on the nanowire tips, and this is often considered as the proof of the vapor–liquid–solid (V–L–S) growth mechanism [17]. Other mechanisms may also operate in the growth of the nanowires, such as the vapor–solid (V–S) process, the solution–liquid–solid (S–L–S) process, the oxide-aided growth (OAG) process, and the epitaxial growth process on crystal nucleuses [18–20]. Activated carbon, carbon nanotube, CCl_4 and CH_4 are popularly adopted as the carbon sources, but graphite is rarely used. Probably because carbon in graphite is more stable than that in other carbon sources, and is difficult to be involved in the growth of the SiC nanowires. Metal catalysts, such as Fe, Ni, Au and La, are selectively added into the raw materials, since they are believed to significantly influence the morphologies of the nanowires. For example, researchers have successfully introduced lanthanum nitrate into silica xerogels and use the carbothermal reduction method to prepare the beaded SiC nanochains [11]. It is generally accepted that the metal catalysts are able to promote the formation of alloy droplets at elevated temperature, and hence contribute to the growth of the SiC nanowires.

Current work adopted commercially available silicon, graphite and boron nitride powders as the raw materials. The mechanical alloying technique was employed to synthesize the amorphous composite powders, which was subsequently annealed at 1700 °C in nitrogen

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for 30 min to prepare the SiC nanowires. This method uses the mechanically-alloyed amorphous powders as the precursor and doesn't add any extra metal catalysts, being different from the abovementioned other methods.

2. Experimental procedures

The original purpose of the current research was to study the thermal stability of the mechanically-alloyed amorphous 2Si–B–3C–N powders. Hence, commercially available cubic silicon (45.0 μm, 99.0% in pure), graphite (8.7 μm, 99.5% in pure) and boron nitride (0.6 μm, 99.0% in pure) powders were adopted as the raw materials. Since during the manufacturing process of the above powders, metal impurities were hard to be completely removed, a small amount of Fe, Al and Cu were contained in the used raw powders. The composition was designed as Si:C:BN = 2:3:1 in mole ratio. The amorphous composite powders were synthesized in argon (99.99% in pure) by a planetary ball mill (Fritsch P4), equipped with high-quality silicon nitride balls and pots. The rotation speeds of the main disk and pots, the milling time and the ball to powder mass ratio were arranged as 350/600 rpm, 40 h and 20:1, respectively. The as-milled amorphous powders were placed in a graphite crucible and annealed at 1700 °C in nitrogen (1 bar) for 30 min. X-ray diffractometer (CuK_α, 40 kV/100 mA, Rigaku D/Max-γB, Tokyo, Japan), transmission electron microscopy (TEM, FEI Tecnai F30) and scanning electron microscopy (SEM, Hachi S-4700) were employed to study the phase composition, morphologies and microstructures of the prepared SiC nanowires, respectively.

3. Results and discussions

Since the original purpose of the current work is to study the structural stability of the mechanically-alloyed amorphous 2Si–B–3C–N powders, it is unexpected to find a thick layer of gray–green fluffs covering the powders annealed at 1700 °C, as shown in Fig. 1(a). Surface morphologies observed by SEM reveal that the fluffs are actually a large number of nanowires, which are 300 nm to 1000 nm in diameter and several hundred microns in length. This can be seen clearly in Fig. 1(b), (c) and (d). The nanowires have a large yield and are very straight along their longitudinal direction. However, it should be noted that the diameters are larger than those in other reported results. Perhaps it is due to the higher annealing temperature and hence the faster growth rate in the current experiment. The XRD spectrum in Fig. 2 indicates that the obtained nanowires are well crystallized α-SiC or β-SiC. The diffraction peaks at 35.6°, 41.1°, 60.0°, 71.7° and 75.5° represent the diffraction of the (111), (200), (220), (311) and (222) planes in β-SiC, respectively. This is consistent with the results in other published papers. However, diffraction peaks also appear at 33.6°, 38.1° and 65.5°, which are the features of α-SiC. These peaks denote the diffraction of the (101), (103) and (109) planes in 6H–SiC. It is inferred from the XRD pattern that the products may simultaneously contain α-SiC nanowires and β-SiC nanowires, a phenomenon rarely found in the previous researches. The diffraction peak at 25.6° is assigned to the turbostratic BNC, attaching to the nanowires while collecting samples. The quantity and quality of the SiC nanowires, obtained in the current work, are not inferior to those synthesized by other methods. Moreover, the used raw materials are cheap, extra metal catalysts are not used, and the processing time is just 30 min, much shorter than that

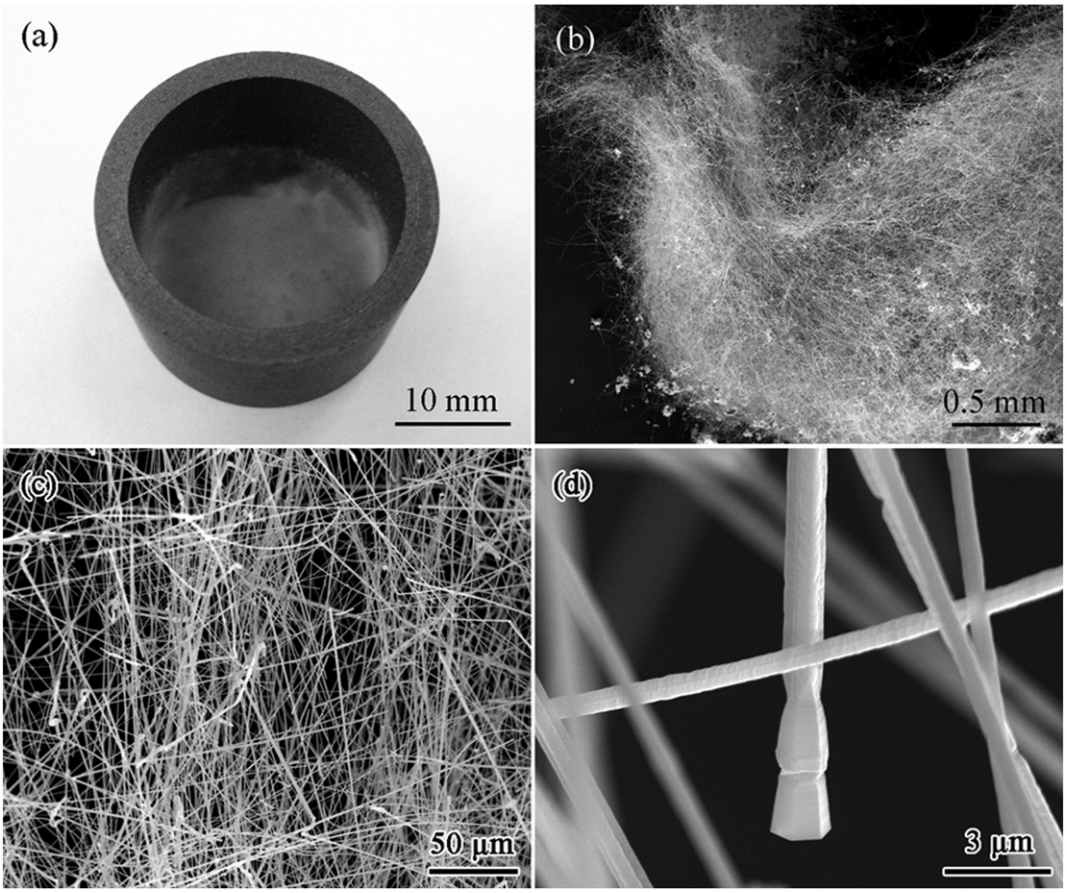

Fig. 1. The macro- and micro-morphologies of the obtained nanowires.