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Tunable magnetic properties of SiC obtained by microwave heating

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ABSTRACT

To improve the magnetic properties of SiC-based semiconductor without any metal impurity, Si, SiO_x and graphite powders were used as raw materials and heated to 1400 °C under microwave irradiation. Ball-milling pre-treatment was employed to obtain high growth rate of SiC. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to analyze the crystal structure and morphology of the as-obtained SiC products. The results show that the products are mainly composed of 3C-SiC particles. The vibrating sample magnetometer (VSM) analysis revealed that the SiC products can exhibit ferromagnetism around room temperature with saturated magnetization of 0.9 emu/g. Corrosion treatment and coating with oxide were also performed to further study the origin of the ferromagnetism of the SiC-based materials. It is found that the saturated magnetization can be clearly reduced by corrosion treatment and reinforced by coating post-treatment without any transition-metal dopants or ion-implantation.

1. Introduction

Ferromagnetic semiconductors have drawn considerable interest due to their promising use in magnetic devices, such as spintronic devices and magnetic sensors [1–3]. Since the diluted magnetic semiconductors were proposed, much effort has been devoted to preparing magnetic semiconductors based on various compounds, including SiC [4,5], GaN [6], ZnO [7], etc. As a promising magnetic semiconductor, the SiC-based semiconductors may be employed as high-temperature and high-frequency magnetic devices due to its excellent fundamental properties, including high thermal stability [8], high thermal conductivity [9], etc.

For the practical application of SiC systems in magnetic devices, effective methods for improving room-temperature magnetism and a better understanding of the origin of their magnetism are desirable. The most common methods for improving magnetism include doping transition metals (Mn, Fe, etc.) or introducing point defects in SiC [10–12]. Most of the methods involve complicated procedures or extreme conditions, and the precipitates and secondary phases may affect the understanding of the origin of magnetism when transition metals are employed as dopant.

Considering that point defects or low crystallinity in SiC can induce ferromagnetism and rapid reaction rate may lead to badly-crystallized SiC, ferromagnetic SiC may be obtained by increasing the reaction rate. Governed by novel heat mechanism [13], raw materials can be rapidly heated under high-energy microwave irradiation if there exists an effective microwave absorber, such as metal or graphite powders, in them. Thus, microwave heating method may be an effective approach for the formation of ferromagnetic SiC.

Besides their preparation by introducing point defects and transition metal ions, ferromagnetic semiconductors can also be prepared by overlaying another diamagnetic material. A novel magnetism phenomenon, defined as “interface magnetism” several years ago, has been found in several systems including CuO/ZnO [14], Cu_2O/CuO [15], Si/SiO_2 [16], etc. The mechanisms of interface magnetism have not been totally understood, nevertheless, coating an oxide layer may also be an effective way to prepare ferromagnetic SiC-based materials.

In this study, the microwave heating method was employed to synthesize ferromagnetic SiC-based materials, without any metal impurity. Compared with the saturated magnetization of SiC nanowires reported previously [17], that of the as-obtained SiC particles was enhanced four-fold to 0.9 emu/g, approximately. The

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results also revealed that the ferromagnetism of SiC particles can be reduced through the corrosion treatment with hydrofluoric acid (HF) solution, but the saturated magnetization can be picked up through coating with SiO_x layer. The origins of the magnetism of the SiC based systems will be discussed in details.

2. Experimental sections

2.1. Synthesis of 3C-SiC products

High purity silicon (≥99.99%), silica (≥99.0%) and graphite powders (≥99.85%) (in the mole ratio of 1:1:2) were used as raw materials. The raw materials were mixed by high-energy ball-milling pre-treatment with rotation speed of 400–500 r/min. An agate jar and grinding balls were used in the ball-milling process. A ceramic crucible filled with the mixed powders was then placed at the center of the microwave oven. The furnace cavity was evaluated to approximately 10^4 Pa by a water circulating pump. Then, the powders were heated to 1300–1400 °C and kept at that temperature for 1 h. The as-obtained product, which exhibited light-green powders was designated as SCP.

2.2. Corrosion and coating post-treatment

To obtain detailed information of the micro-structure and magnetic properties of the SCP, analyses were carried out after corrosion and oxide coating processes. After the synthesis of SCP, a part of the as-obtained products was immersed in the HF solution (40 wt %) for 20 h to remove the SiO_x on the surface. The corroded product was designated as SCP-HF.

Si and silica powders were used as the raw materials for the oxide coating post-treatment. The corroded powders (SCP-HF) mixed with the ball-milled Si and silica powders were put into a ceramic crucible. The crucible was then put on a ceramic plate covered by graphite powder, which was used as microwave absorber. The crucible and the plate were then placed at the center of the microwave oven, and the furnace cavity was evaluated to about 10^4 Pa. The system was then heated to approximately 1000 °C using a microwave power of 4–5 kW. The whole coating process was conducted for 1 h, and the obtained product was designated as SCP-O.

2.3. Characterizations

All the specimens were analyzed by field emission scanning electron microscopy (SEM) with the type of XL FEGSFEG-SIRION instrument (FEI Ltd., Eindhoven, The Netherlands). Energy-dispersive spectroscopy (EDS) attached to the SEM apparatus was used to confirm the element components of the products. X-ray diffraction (XRD) patterns of the products were recorded with a D8 ADVANCE X-ray diffractometer (Bruker Co., German) with Cu Kα radiation (λ = 1.5418 Å). Data were collected in the 2θ range of 20–80°, with a step width of 0.2° and count time of 12 s/step. Transmission electron microscopy (TEM) analysis was performed with a FEI Tecnai T20 microscope (FEI) operated at 200 kV acceleration voltages using a LaB6 filament. The images were recorded using a Megaview III CCD camera.

The magnetization versus magnetic field (M-H) curves were measured using a LakeShore 7407 vibrating sample magnetometer (VSM) (Lake Shore Cryotronics, Inc., Westerville, OH, USA) at room temperature. Data were collected over the magnetic field of -10000-10000 Oe ($250/\pi$ A*m^{-1}).

3. Results and discussion

3.1. Morphologies, microstructures of the products

XRD analysis was used to investigate the phase structure of the products. In the XRD patterns (Fig. 1), the peaks centered at 35.6, 41.5, 60.0, 71.8 and 75.6° correspond to the (111), (200), (220), (311) and (222) of 3C-SiC (JCPDS No. 29-1129), respectively. It can be inferred that the as-obtained products were mainly composed of 3C-SiC with low-density stacking faults, since the peak at 33.6° has lower intensity than that of reported SiC nanowires [17,18].

Furthermore, no peaks corresponding to other phases, including retained Si, SiO_x, and graphite can be detected by XRD analysis, indicating that most of the raw materials have been transformed into SiC. The results suggest that, compared with the results of the XRD analysis of SiC nanowires obtained by microwave heating [19], the high-energy ball-milling pre-treatment has the benefit of enhancing the reaction rate of raw materials and the formation of pure-phase SiC products.

As reported in our previous study [19], one-dimensional 3C-SiC can be prepared under microwave irradiation, and the morphologies can be tuned by changing the parameters, such as the reaction activity of the raw materials and the synthesis temperature. Accordingly, as the ball-milling pre-treatment can enhance the reaction activity of the as-utilized raw powders, the as-obtained SiC products may have different morphology compared with one-dimensional 3C-SiC. SEM analysis was thus employed to investigate the morphology of the SiC products, as shown in Fig. 2. The SEM images revealed that the product is mainly composed of micro-sized particles. Regarding the growth mechanism of one-dimensional SiC, relatively larger growth rate along the ⟨111⟩ direction than other crystal directions was commonly believed to be the origin of the formation of one-dimensional SiC products [20]. The formation of SiC particles but not one-dimensional SiC indicates that the ball-milling pre-treatment may result in the high growth rates of SiC along all the crystal directions besides ⟨111⟩.

Besides the higher growth rate along all the crystal directions, another possible mechanism to explain the formation of SiC particles may be the lack of growth space for the linear grow process. Visualization of the interconnected SiC nanoparticles in the TEM images (Fig. 3) reveal that certain portions of the micro-sized SiC particles are composed of several SiC nanoparticles. As mentioned above, the ball-milling pre-treatment may enhance the reaction

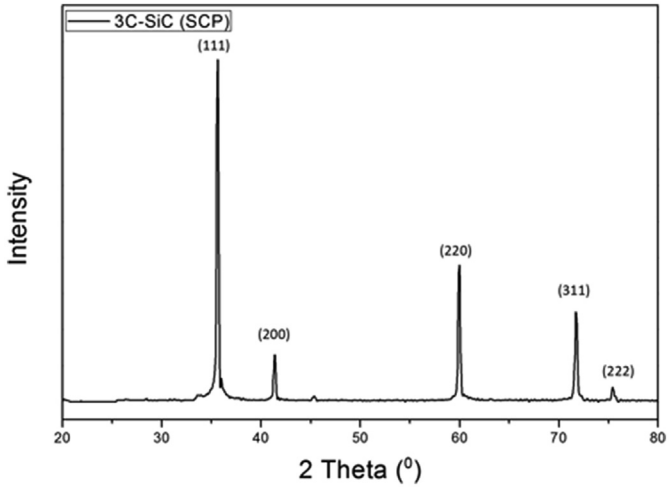

Fig. 1. The XRD pattern of the as-obtained SiC (SCP).