A metal-free route to synthesize pure-phase 3C-SiC with excellent optical and magnetic properties

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Abstract. Large amount of pure-phase 3C-SiC particles were synthesized via microwave heating, without using any metal catalyst. Ball-milling pre-treatment was employed to enhance reaction activity of raw materials prior to the microwave heating process. The morphology, microstructure of the SiC products were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), and transmission electron microscope (TEM). As the result of SEM, the SiC particles have diameters of 500–2000 nm and smooth surface. TEM image shows that some of the micro-sized SiC particles are composed of agglomerate nano-particles with diameters of 50–200 nm. Photoluminescence and magnetic properties of the SiC products were measured by fluorescence spectrophotometer and vibrating sample magnetometer (VSM), respectively. Ultra-violet emission from the 3C-SiC products can be detected under excitation wavelength of 240 nm. Without any contribution from the magnetic metal ions, the SiC particles can exhibit ferromagnetic properties around room temperature with saturation magnetization (Ms) of 0.9 emu/g, approximately. The excellent optical and magnetic properties of SiC may mainly be attributed to the point defects.

1. Introduction

In current years, compound semiconductors such as ZnO, GaN, and SiC, etc. have draw considerable attentions because their promising applications in optical and electron devices. Many research works have been carried out to synthesize these semiconductors with excellent optical and electrical properties [1-3]. Compared with other compound semiconductors, SiC may be utilized in high-power and high-frequency devices because of the excellent fundamental properties covering high thermal conductivity, high thermal stability, and high mechanical strength [4-6]. Thus, numerous studies on the optical properties of SiC have been made for the practical application in various devices. Photoluminescence properties were commonly measured for evaluating the luminous power of SiC products. Up to now, violet, blue emissions from 3C-SiC products have been found [7-9]. The detected emission peaks of these 3C-SiC products show the blue-shift phenomena compared with the intrinsic luminous peak of bulk 3C-SiC (Eg=2.23 eV). The blue-shift phenomena were always suggested to be attributed to quantum confinement effect [10], oxygen vacancies [11], internal or surface point defects [12] etc. However, the origin of the blue-shift phenomenon is still in debate, and metal impurities which can affect the photoluminescence properties were easily introduced into SiC products in many synthesis processes [13, 14]. Thus, exploitation of metal-free synthesis for preparing pure-phase SiC with excellent photoluminescence properties is still desirable.
Since the proposal of spintronic devices [15], potential application of semiconductors in magnetic devices and fundamental properties of SiC mentioned above lead to larges numbers of studies on the improvement or origin of the magnetic properties of SiC [16-19]. Transition metals including Mn, V, Fe etc. were always introduced into SiC for the preparation of ferromagnetic SiC. However, the precipitation of metal-related secondary phase may limit the understanding of the origin of ferromagnetism of SiC and the application of ferromagnetic SiC at high temperature. Thus, exploration a metal-free route to obtain ferromagnetic SiC have been focused on. The most common methods without any metal impurity is the introduction of Si- or C-related vacancies [20,21], but most of them need complex procedure or strict reaction conditions.

In our previous study [22, 23], we found that the SiC nanowires synthesized via microwave heating exhibit excellent photoluminescence properties or weak room-temperature ferromagnetism. The excellent optical and magnetic property were proposed to be attributed to the surface or internal defects in SiC products. The high reaction rate under microwave heating with high heating rate may benefit the formation of defects covering stacking faults or point defects, further result in excellent functional properties. However, the luminous efficiency and Ms of the SiC products is still need to be enhanced.

In this study, high-energy microwave heating method is also employed to synthesize SiC products because it is a simple and faster process [24]. No metal or other impurity was added in the raw materials. For preparing SiC products with better optical and magnetic properties, ball-milling pre-treatment was employed to enhance the reaction rate. Large amount of micro-sized pure-phase SiC with excellent photoluminescence and magnetic properties were prepared. And also, the origins of the optical and magnetic performance of the obtained SiC products are briefly discussed.

2. Experimental sections

2.1 Synthesis of 3C-SiC products

High-purity silicon (≥99.99%), silica (≥99.0%) and graphite powders (≥99.85%) (mole ratio 1:1:2) were used as raw materials. The mixed powders were ball-milled by 500 agate grinding balls with rotation speed of 400 r/min for 6 h. The crucible together with the specimens was then placed at the center of a commercial microwave vacuum sintering furnace with the type of NJZ10-3 (Nanjing Jiequan Microwave Co. China). Prior to the heating process, the furnace cavity was evacuated below 10⁻⁴ Pa by a watering circulating pump. The employed microwave power was in the range of 3-5 kW. With the use of the microwave heating system, the temperature of the raw powders can be heated over 1500 °C in several minutes. The specimen was kept at the designed temperature (approximately 1350 °C) for 1 h. The temperature was measured by an optical pyrometer (Reytek) on the top of insulation glass. The temperature of the products can be rapidly decreased, and at last light-green powders can be obtained.

2.2 Characterizations

The phase structure of the product were examined by X-ray diffraction (XRD), which were carried out on a D8 ADVANCE X-ray diffractometer (Bruker Co., German) with Cu Kα radiation (λ =1.5418 Å). Morphologies of the product were examined by a field emission scanning electron microscopy (FEI Ltd., Netherlands). Further structural analysis of the products was performed using a FEI Tecnai T20 microscopy (FEI, Eindhoven, Netherlands). The photoluminescence spectra were measured using a Hitachi F-7000 typed fluorescence spectrophotometer at room temperature, with the excitation light of 240 nm from Xe lamp. The magnetization versus magnetic field (M-H) curves were measured using LakeShore 7407 vibrating sample magnetometer (VSM) at room temperature. Data were collected over the magnetic field of -10000—10000 Oe (250/π A*m⁻¹).

3. Results and discussion
3.1 Morphology, microstructure of the as-obtained SiC product

Figure 1. XRD pattern of the light-green products.

The XRD were employed for investigating the phase structure of SiC. In the XRD patterns (figure 1), the peaks 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). From the XRD patterns of the products, it can be found that the product is mainly composed of 3C-SiC. According to the XRD results of our previous study [22], other impurities such as silica and graphite may retained in the SiC products after microwave heating process (1-2 h). Different from the previous results, no other impurity can be found in the XRD patterns, indicating that all the raw materials were completely converted into pure-phase 3C-SiC. The formation of pure-phase 3C-SiC suggest that ball-milling pre-treatment can significantly enlarge the reaction velocity of raw materials in the microwave heating process.

Figure 2. SEM images of the 3C-SiC products with different magnifications.

The morphology and the elemental composition of the SiC products were characterized by SEM and EDS, respectively. Large amount of nano- or micro-sized SiC particles can be found as shown in the SEM images (figure 2a), and the sizes of most SiC particles are in the range of 500-2000 nm. The SEM image with larger magnification (figure 2b) shows that the as-obtained SiC particles have clean and smooth surface. In the previous studies on the synthesis of nano- or micro-sized SiC [7, 10, 25], silica layers could always be found on the surface of SiC core. However, oxygen element can not be detected within the resolution of EDS (figure 3). There are three possible reasons for explaining the absence of oxygen elements: 1) Because of the high formation rate of the SiC, oxidizing atmosphere is rare in the oxidation process, and thus the SiC core can hardly be oxidized; 2) The formed silica layer can easily be reduced in the reducing atmosphere because of the high reaction activity of the ball-milled graphite powders; 3) The oxygen atoms on the surface are rather few, and thus the oxygen element can not be detected by EDS.
Figure 3. EDS spectrum of the as-obtained 3C-SiC particles.

TEM was employed for further information on the microstructures of the SiC particles. From the TEM images (figure 4), it can be found that the micro-sized SiC particles were composed of agglomerate SiC nano-particles. Furthermore, no silica layer can be detected by TEM, and the absence of the silica layer is consistent with the results of the EDS. Selected area electron diffraction (SAED) analyses (inset in figure 4) further confirm that the products are mainly composed of 3C-SiC. The inserted SAED pattern exhibits clear rings corresponding to 3C-SiC {111}, {220} and {311} planes.

Figure 4. TEM image and SAED pattern (inset) of the as-obtained 3C-SiC particles.

3.2 Photoluminescence and magnetism investigations

In this study, ultra-violet emission peak centered at 390 nm are detected under excitation wavelength of 240 nm (figure 5). The broad peak shows a larger emission wavelength compared with the peak under excitation wavelength of 325 nm [22]. It is noteworthy that the broad peak covered the wavelengths corresponding to the E_g of 4H-SiC and 6H-SiC. Besides, the similar ultra-violet emission was also found from 6H-SiC nanowires [7]. Thus, the ultra-violet emission was initially thought to be caused by various polytypes of SiC in the products. However, based on the XRD patterns of the products, the main consistent of the product is 3C-SiC. And also, as the large size of the SiC particles, the size effect or quantum confinement effect can not contribute to the ultra-violet emission from the SiC products.
The oxygen vacancies are also employed to explain the photoluminescence properties of oxide, such as nano-sized SiO$_2$ [26] or ZnO [27]. In these explanations, the oxygen vacancies can provide a site for electron-hole recombination which can cause the blue-shift phenomena compared with well-crystallized bulk materials. However, the oxygen vacancies in the silica layer should not be the single origin of the ultra-violet emission because rare oxygen can be detected by EDS and TEM. Similar to the role of oxygen vacancies in the ultra-violet emission, there may be other point defects which can also provide sites for the electron-hole recombination, such as Si-related or C-related vacancies.

The M-H curve (figure 6) of the obtained 3C-SiC particles exhibit ferromagnetism around room temperature with Ms of 0.9 emu/g and coercivity (Hc) of 70 Oe, approximately. In previous studies, the most effective method to prepare ferromagnetic SiC was reported to be doping transition metal into SiC. For example, the Ms can be enhanced to 0.06, 0.002 and 1.3 emu/g by doping small quantities of Mn, Cr, and Fe, respectively [18, 28, 29]. In our experiment, the magnetic moments of SiC can be significantly enhanced via employing ball-milling pre-treatment and microwave heating method without any metal impurity. It is worth noting that the Ms of the as-prepared SiC is close to the Ni-catalyzed SiC products in our previous study [23]. The ferromagnetic response cannot be attributed to any other impurities since the as-employed raw materials covering silicon, silica and graphite powders did not exhibit ferromagnetism signals.

The origin of ferromagnetic signals from semiconductors without metal impurities is still in debate. Among explanations of the magnetic exhibitions of SiC, the most acceptable contributions are the disorders and point defects covering Si vacancy, C vacancy, and Si-C bi-vacancies in SiC [19-21]. In our previous study [23], high reaction rate under microwave irradiation benefits the formation of point defects which can result in the ferromagnetism exhibition of SiC. And also, ball-milling pre-treatment which can further enhance the growth rate of SiC can be employed to enhancing the Ms of SiC. Thus,
the ferromagnetic signals from the as-obtained 3C-SiC products can be attributed to the internal point defects of SiC. The present work develop a new approach for preparing ferromagnetic SiC without using any transition metals.

4. Conclusions

Pure-phase 3C-SiC can be synthesized by employing ball-milling pre-treatment and microwave heating. The morphology of the SiC products is relative uniform, and the SiC particles have clean and smooth surface. Some of the micro-sized SiC with size of 500-2000 nm are composed of agglomerate SiC nano-particles with size of 50-200 nm. These micro-sized SiC particles can emit ultra-violet light under excitation wavelength of 240 nm. The ultra-violet light may be attributed to the point defects. Without any ferromagnetic metal impurity, the as-obtained SiC exhibit room-temperature ferromagnetism with Ms of 0.9 emu/g and Hc of 70 Oe. The ferromagnetic performance of SiC particles may also mainly be contributed by the internal or surface point defects of SiC.

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