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Nitrogen content dependent microwave absorption property of nitrogen-doped SiC materials annealed in N_2: Opposing trends for microparticles and nanowires

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ABSTRACT

Nitrogen-doped SiC microparticles (SiCp) and SiC nanowries (SiCNWs) with different nitrogen contents were successfully synthesized by a simple and effective method, in which SiCp and SiCNWs were directly annealed in N_2 at 1500 °C with different holding times to adjust the contents of nitrogen for the first time. The nitrogen content of N-doped SiCp and SiCNWs increased with holding time, from 2.91 at.% and 3.05 at.% for 1 h to 5.05 at.% and 5.25 at.% for 4 h. The size of N-doped SiCp and SiCNWs was larger than that of pristine SiCp and SiCNWs, while the size tended to increase firstly and then decrease. The results of dielectric parameters showed that both real part ε' and imaginary part ε'' of permittivity of the samples increased greatly with increasing N contents in most frequency range, while two opposing trends for nitrogen content dependent microwave absorption property of N-doped SiCp and SiCNWs were observed. The electromagnetic (EM) wave absorption capability of N-doped SiCp was significantly improved with increasing nitrogen content compared with fully permeable wave pristine SiCp, and the minimum reflection loss (RL_m) and maximum effective absorption bandwidth (EAB) could be up to −33.5 dB and 4.4 GHz, respectively. The EM wave absorption performance of N-doped SiCNWs exhibited a decreasing tendency with increasing nitrogen content, and the RL_m was decreased from −57 dB for pristine SiCNWs, to −51.2 dB for SiCNWs with 3.05 at.% N, and to −29.3 dB for SiCNWs with 5.25 at.% N. Moreover, if the experimental process in present study was decomposed into heat-treatment and N-doping, the heat-treatment played extremely negative effect on the EM wave absorption performance of samples, while N-doping still had positive impact on the EM wave absorption performance. It is believed that the current work will provide a new insight into the fabrication of SiC materials with fascinating properties by doping.

1. Introduction

With the rapid development of wireless communications and electronics industry, the EM wave generated by these devices has become a serious concern for human life, and then EM absorption materials have aroused worldwide attention to protect human being from the harm of EM wave [1–4]. Great efforts have been made to develop high performance EM wave absorption materials for the use in the GHz range, in which EM absorbers could reduce EM radiation by absorbing EM waves and converting them into other kinds of energy [5–7]. Generally, an ideal EM absorber should not only exhibit strong absorption property, low cost, light weight, thinner and antioxidation capability, but also possess flexibility, hydrophobicity, corrosion resistance, and high temperature stability when it is used in a harsh environment, such as in the aerospace [8–10].

To date, lots of EM wave absorbers have been explored, including graphene, carbon nanotubes (CNTs), Fe_3O_4, ZnO, SiC, and so on [4,7,10–13]. It is worth noting that SiC with a wide band gap has been considered to be a promising candidate due to its high

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mechanical strength, good high temperature stability, excellent resistance to oxidation and corrosion [4,7,10]. According to our survey, the dielectric and microwave absorption properties of SiC in different forms have been widely studied, such as SiC powders, SiC foam, SiC whiskers (SiCw) and SiCNWs [4,7,10,14–16]. The dielectric loss of pure SiC is not desirable and numerous efforts have been made to improve dielectric properties of SiC through different methods [17]. One common means is to prepare nano-structural SiC materials with special dielectric and electrical properties, and the other one is doping to tune dielectric properties (e.g., Fe-, Al-, Ni-, B- and N-doping) [17–24]. For example, Li et al. reported that SiCNWs might own high performance of EM wave absorption because of their high surface-to-volume ratio and quantum size effects compared to SiCp, short fibers, and SiC-based ceramic, which was confirmed by the contrast experiments conducted between the SiCNWs and SiCp [18]. Cao et al. prepared the Fe-doped SiCw with stacking faults, showing a higher dielectric permittivity than that of undoped SiCw with stacking faults. Both dielectric permittivity and microwave absorption properties of Fe-doped SiCw increased significantly with the increase in dopant concentration [19]. Al-doped SiCw were also synthesized, in which both the dielectric loss and microwave absorption of SiCw increased with the increase in dopant concentration [20]. Ni-doped SiC powders with improved dielectric and microwave absorption properties were fabricated, whose RL_m were from −13.34 to −22.57 dB [21]. Su et al. found that the dielectric real part ε' and dielectric loss tanδe of undoped SiC powder decreased with boron content [22], while Li et al. found that real part ε' and imaginary part ε'' of complex permittivity of SiC powders decreased firstly, and then increased for the same variable parament [23]. Nitrogen-doped SiC powders were synthesized by combustion synthesis using α-Si_3N_4 as solid nitrogen dopant, and the real part ε' and imaginary part ε'' of the complex permittivity of doped SiC powder were greatly increased compared to undoped ones [24]. Given the above, it is reasonable to believe that doping is an effective method to adjust the dielectric properties of SiC by the content of doping element. Recently, many approaches have been adopted to realize N-doping, including in-situ synthesis RF magnetron sputtering, chemical vapor deposition (CVD) and pyrolysis of a polymer precursor [25–27], while the above methods might all require burdensome equipment and complicated operation. Therefore, it is urgently needed to develop a simple method to against these drawbacks. In spite of series of research about N-doped SiC nanostructures, no relativity between the dielectric and microwave absorption properties of SiCNWs and N dopants has been reported to the best of our knowledge.

In present study, N-doped SiCp and SiCNWs with different nitrogen contents were successfully prepared by a simple and effective method, in which SiCp and SiCNWs were directly annealed in N_2 with different holding times at high temperature to introduce different nitrogen contents for the first time. The effects of different contents of N-doping on the microstructure, dielectric property and microwave absorption property of SiCp and SiCNWs were studied systematically.

2. Experimental

2.1. Preparation of nitrogen-doped SiCp and SiCNWs

During the experiment, all of the chemical reagents without further purification were analytical grade. SiCp (99% pure, particle size about 1 μm; CAS No: 409-21-2, Aladdin Chemistry Co. Ltd, Shanghai) and SiCNWs with a diameter of 200–500 nm and a length of 10–50 μm (3C-SiC, 99% in purity, Changsha Sinet Advanced Materials Co., Ltd. China) were used as raw materials. The doping process was conducted under the flowing nitrogen atmosphere, in which the nitrogen content of N-doped SiC could be controlled by the holding time at 1500 °C (1 and 4 h). The SiCp and SiCNWs were poured into a graphite crucible, respectively, and the graphite crucible was sent into the quartz tube. The furnace was heated up from room temperature to 1500 °C at a rate of 3 °C min^{-1} for different holding hours in N_2. After the heating was terminated, the furnace was first cooled to 800 °C at a rate of 3 °C min^{-1} and then naturally cooled to room temperature. The as-prepared products corresponding to the holding time at 1500 °C were designated as SiCp-1-N_2, SiCp-4-N_2, SiCNWs-1-N_2 and SiCNWs-4-N_2, respectively.

2.2. Morphology, microstructure and compositional characterization

The morphology of the SiCp and SiCNWs was observed using scanning electron microscopy (SEM, HELIOS NanoLab 600i, USA) and transmission electron microscopy (TEM and HRTEM, Tecnai G^2-F30, USA). The phase and elemental compositions, and chemical binding states of products were analyzed by X-ray diffraction (XRD, X'PERT PRO MPD, Holland) using Cu Ka radiation (40 kV, 30 mA), Raman spectra collected on a confocal Raman spectroscopic system (Renishaw, In Via) using a 532-nm laser, and X-ray photoelectron spectroscopy (XPS, Escalab 250, USA). The static light scattering measurements were performed on a particle size distribution analyzer (Horiba LA-920).

2.3. The dielectric and microwave absorption properties characterization

Owing to the low dielectric loss of paraffin, the samples for dielectric parameters measurement at room temperature were prepared by mixing the products with paraffin in a mass ratio of 1:1 at about 85 °C, and then pressed into a ring with an outer diameter of 7 mm and an inner diameter of 3 mm, which was tested by a vector network analyzer (Agilent N5230A, coaxial line method) to give the real and imaginary parts of the permittivity [4,7,10,28]. Furthermore, the reflection loss (RL) curves of the products could be calculated by the following equations based on the line theory [4,7,10,28]:

$$RL(dB) = 20\lg\left|\frac{Z_{in}-1}{Z_{in}+1}\right| \quad (1)$$

$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left[j\frac{2\pi fd}{c}\sqrt{\mu_r\varepsilon_r}\right] \quad (2)$$

where Z_{in} represents the normalized input impedance of the material, f is the frequency of microwave, d is the thickness of the material and c is the velocity of EM wave in free space [4,7,10,28].

3. Results and discussion

Different holding times at 1500 °C with 1 and 4 h in N_2 were selected with a flowing rate of 60 ml/min to control the doping levels of SiCp and SiCNWs during the heat-treatment. The as-synthesized samples, SiCp-1-N_2, SiCp-4-N_2, SiCNWs-1-N_2 and SiCNWs-4-N_2, refer to the samples prepared with different holding times of 1 h, 4 h, 1 h and 4 h, respectively.

Fig. 1a–c and d–f show representative SEM images of pristine SiCp, SiCp-1-N_2, SiCp-4-N_2, pristine SiCNWs, SiCNWs-1-N_2 and SiCNWs-4-N_2. Compared with that of the pristine microparticles, the sizes of SiCp-1-N_2 and SiCp-4-N_2 exhibited the tendency to