The study of the microwave absorption property of the Al and N codoped SiC Nanopowders

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Abstract: Nanopowders of aluminum and nitrogen codoped β -silicon carbide (β -SiC) were successfully produced by self-propagating high-temperature synthesis (SHS) in a nitrogen atmosphere. Characterizations by X-ray diffraction and scanning electron microscopy demonstrate the formation of Al-N codoped β -SiC nanopowders. In 1 MPa N₂ atmosphere, the X-ray analysis of the produced powders suggests that Al and N are accommodated in the lattice of SiC, which enlarges with increasing amounts of Al. The electric permittivities of prepared powders have been determined in the frequency range of 8.2-12.4 GHz. Al and N codoping results in the increase of the electric permittivities of SiC, compared to the undoped SiC. With the increasing the amounts of Al, the electric permittivities of the Al and N codoped SiC nanopowders are increased. The paper presents a method to adjust dielectric property of SiC powders in the GHz range. These features confer Al-N codoped β -SiC qualifications of the important microwave absorbing material.

Keywords: β-SiC; Al-N; Nanopowders; electric permittivities

1. INTRODUCTION

For many years, important developments in the growth technique for cubic silicon carbide (3C-SiC) have renewed interest in it for high-temperature structural, electronic device and functional applications [1-3]. Increasing levels of electromagnetic pollution (due to the use of electronic and telecommunication systems) has recently focused attention on the dielectric properties of SiC materials in the microwave range. The n-or p-type doping of SiC can effectively improve the dielectric properties of SiC. Basically in SiC, whatever the polytype, all group III substitutional impurities(like B, Al, Ga) are the potential p-type doping species. Among these impurities, Al gives the shallowest acceptor level for all SiC polytypes when it replaces the Si sites [4-5]. Simultaneously, the group V substitutional impurities (N and P) are the donor species. The N is the most common donor, which substitutes on the carbon sites [6].

P-type doping is difficultly realized for the wide gap semiconductors, while Codoping has been proposed and applied to overcome this difficulty [7]. Meanwhile, it also can effectively improve hole concentrations in wide gap semiconductors, like GaN, ZnO. It is, therefore, reasonable to believe that codoping approach can solve the difficulty of the *p*-doped SiC. Furthermore, Al and N codoping can have a big influence on the dielectric of 3C-SiC powders. According to

the literature, there are few detailed experimental investigations of the Al/N-codoped

3C-SiC powders in N₂ atmosphere. In the present paper, nanosized Al/N codoped SiC powders were produced by the mechanical-activation-assisted self-propagating high temperature synthesis method in N₂ atmosphere, using PTFE (([$-C_2F_4 -]n$) and NH₄Cl as the chemical activators. The features of the produced powders, specifically microstructure, crystalline structure and electric permittivity in the frequency range of 8.2-12.4 GHz, were investigated to evaluate the potential of Al/N-codoped 3C-SiC for consideration in microwave applications

2. EXPERIMENT

Powders of silicon (99.995% pure, mean particle size 10 mm,), carbon black (99.9% pure, mean particle size 2 mm,), PTFE (99.5% pure, mean particle size 0.5 mm, Sinopharm Chemical Reagent Beijing Co., Ltd.), and NH4Cl (99.5% pure, mean particle size 0.5 mm,) were used as starting materials. Aluminum powder (99.5% pure, 325 mesh,) and Nitrogen (99.999%) were used as doping source. In Ar atmosphere, the Al:Si:C molar proportions is 0:1:1, 0.03:0.97:1 (hereafter designated for simplicity as undoped SiC, Al 3%), and in N₂ atmosphere, the Al:Si:C molar proportions is 0.03:0.97:1 and 0.05:0.95:1 (hereafter designated for simplicity as Al 3%-N, Al 5%-N). 1 wt% NH₄Cl and 6 wt% PTFE (with respect to a

100% Al:Si:C powder mixture) were also added to each batch.

The powder mixtures were mechanically dry ball milled for 3 h with SiC balls in a SiC jar. The resultant mixtures were loosely packed into a prismatic graphite crucibl. Then, the loaded crucible was placed into the reaction chamber. The CS reaction was initiated in 3MPa Ar gas or the mixture gas of 1 MPa N₂ gas and 2MPa Ar gas. The crystalline phases in the produced powders were identified using X-ray diffraction analysis (Cu-Ka, Xpert Pro, PANalytical B. V., Almelo, the Netherlands). The microstructures of the powders were observed with a scanning electron microscope (SEM, JSM-6360LV, JEOL, Tokyo, Japan). Complex permittivity was measured using an ANRITSU 37269D vector network analyzer (Kangawa, Japan). The preparation of the samples for the measurement of dielectric parameters was as follows: As-synthesized powders were dispersed in paraffin wax with a weight ratio of powder/paraffin wax of 1/1 by regular stirring at 600 C for 1 h. Samples in the form of rings, with dimensions of 7.0 mm outer diameter, 3.0 mm inner diameter, and 2.0 mm thickness, were solidified at room temperature in air.

3. RESULTS AND DISCUSSION



Fig.1. X-ray diffractograms of the produced Al/N-codoped SiC powders: (b) presents a magnified detail of (a) for the peak corresponding to the plane (1 1 1) of β -SiC (PDF cards β -SiC: 75-0254; a-SiC: 29-1126;).

The crystallographic analysis of the produced powders, presented in Fig.1a, showed that highly crystallized β -SiC pre-dominantly formed in the three kinds of produced powders. There is no evidence of residual silicon and carbon. A small peak of α -SiC phase was also registered, which is consistent with observations reported in earlier study by Song et al [1]. and Su et al [2]. In the Fig. 1a, there is no evidence of residual Al- or N- associated even in the doped samples. Figure 1(b) shows the aforementioned gradual shift of the main peak of β -SiC, which corresponds to the diffraction peak of the plane (111). For Al-N-codoped samples, careful observation reveals that the peaks of the diffractograms are shifted toward higher values of 20 with increasing Al-content.

Table 1 Lattice parameter a and inter-planar space d between the planes (1 1 1) of β -SiC calculated from the diffractograms of Fig. 1 for the produced Al-N-codoped doped SiC powders.

Powder	a (Å)	<i>d</i> (Å)
SiC	4.36341	2.51929
Al 3%-N	4.36466	2.52001
Al 5%-N	4.36582	2.52068

Table 1 presents the variation of the lattice of doped β -SiC (i.e., the lattice con-stant a and the interplanar distance d, calculated by applying the Bragg formula to the results of the diffractograms of Fig. 1). For the Al doping, Al atoms replace atoms of silicon in SiC and introduce some C vacancies in the lattice. Owing to the atomic radius of Al (1.43 Å) is greater than that of Si (1.34 Å), doping Al atoms consequently makes the lattice expand. While, C vacancies will make the lattice shrink. In addition, the N atoms atomic radius is less than that of C. N atoms will substitute for C atoms and form some silicon vacancies, which all can result in shrinkage in the lattice. Meanwhile, It is supposed that the introduction of Al and N atoms can decrease the quantity of the Si and C vacancies, which weaken the influences of Si or C vacancies on the lattice of β -SiC. The doping Al plays the main role in influence on the lattice of SiC. These effects counteract one another, and lattice parameters are expanded at last. With the increase of Al content, the bigger expansion of lattice constants is observed in the Fig. 1b.



Fig.2. Scanning electron microscopicphotographs of the produced powders: (a) SiC; (b) Al 3%-N; (c) Al 5%-N

Fig. 2 shows the SEM photographs of the combustion products of SiC synthesized with Al/N- co-doped SiC. The produced SiC powder has fine spherical particles with a mean size of 350nm. However, the particle size of all doped SiC powders decreases due to Al-N co-doping. The decreasing of particle size is probably due to the fact that Al or N doping will affect the crystallization of SiC and retard the crystalline growth, which is good agreement with the results reported by Su et al [4].

Moreover, the particle size of Al-N- co-doped SiC decreases more than that of undoped SiC with the Al content increasing. And the agglomerates are observed in the Al-Nco-doped powders which are composed of fine particles of ~30nm. The low melting point of Al (660°C)should plausibly result in melting of Al and formation of an Al-rich liquid phase during heating process. That liquid phase likely favored the formation of the agglomerated SiC big particles observed in Fig. 2 b-c. Phenomena such as melting of Al and possible volatilization of volatile compounds absorb heat. Therefore, one might consider them as welcome-phenomena in the process of producing Al-SiC powders since they can potentially reduce the extent of formation of such agglomerates in the produced powder. So no agglomerate is observed in the Al-doped powders. But for Al-N- co-doped powders, the volatilization of Al is suppressed due to the high N pressure and Al also has the large driving force for nitridation of Al-Si (1) phase [5-6]. This may result in the appearance of some agglomerates.



Fig. 3. Frequency dependence of dielectric properties: (a) real part (ϵ ') of the complex permittivity, (b) imaginary part (ϵ '') of the complex permittivity of the doped SiC powders.

The experimental results of the real part (ϵ ') and the imaginary part (ϵ '') of complex permittivity of the doped

powders in the frequency range of X-band are plotted in the diagrams of Fig. 3a and b, respectively. Fig. 5c plots the frequency dependence on loss tangent (where $\tan \overline{\delta} = \epsilon''/\epsilon'$). Generally, it is clearly seen that Al-N- co-doping results in higher values of ϵ' , ϵ'' and $\tan \overline{\delta}$ than the undoped powders of β -SiC over the investigated frequency range between 8.2 and 12.4 GHz. The Al- and N doping have a higher values of ϵ' , ϵ'' and $\tan \overline{\delta}$ than the Al-N- co-doping, whose values of ϵ' , ϵ'' and $\tan \overline{\delta}$ are increasing with the increase of the Al content. While the value of ϵ' for the Al doping is lower than the N doping and Al-N- co-doping.

SiC is a non-magnetic loss material (permeability μ '= 1, μ " = 0), its power dissipation at high frequencies is determined only by dielectric loss. It is reminded that dielectric loss can be either due to ion migration loss, including DC conductivity loss, or ion jump and dipole relaxation losses, or ion vibration and deformation losses, or electron polarization loss [8]. Below about 1010 Hz, DC conductivity loss, ion jump and dipole relaxation losses play crucial role on the dielectric loss. In this study, N-, Al-doping and Al-N- co-doping indicate the formation of defects in the SiC structure (i.e. V_{Si}, V_C, C_{Si}, Si_C) is inevitable. The defects with contrary charges have a strong trend to form pairs because of the static attraction.

These defect pairs are strongly prone to form dipole pairs. Under the alternating electromagnetic field, these dipole pairs will migrate to and fro to form relaxation polarization and loss, thus leading to higher ε ' and ε ", respectively. For Al-Nco-doping, the concentration of carriers will decrease because of the recombination of holes and electrons, which implies the conductivity of Al-N co-doped β -SiC may be a little lower than that of Al-doped β -SiC. However, the drift mobility of carriers is the sum of the mobility of these two carriers. Due to the higher carrier mobility, the conductivity of Al-N- co-doped β -SiC is higher than that of β -SiC. The increase of electrical conductivity would result in rise of the value of ε ". So the value of ε " of doped β -SiC is higher than undoped β -SiC, which suggests better capability of the produced materials for dielectric loss.

Nanopowders of Al and N codoped B-SiC with different amounts of Al were successfully prepared using the SHS in a N₂ atmosphere. By analysing the results of the X-ray diffraction and scanning electron microscopy, it is declared Al-N codoped β-SiC nanopowders are formed. In 1 MPa N₂ atmosphere, the X-ray analysis of the produced nanopowders suggests that Al and N are successfully introduced in the lattice of SiC. The particle size of all doped SiC powders decreases due to Al-N co-doping. Moreover, the particle size of Al-N- co-doped SiC decreases more than that of undoped SiC with the Al content increasing. The electric permittivities of Al-N codoped β-SiC nanopowders have been researched in the frequency range of 8.2-12.4 GHz. The electric permittivities of β-SiC have been increased greatly by doping the Al and N, compared to the undoped SiC. Meanwhile, the electric permittivities of the Al and N codoped SiC nanopowders are further increased with the amounts of Al. These features demonstrate Al-N codoped β -SiC nanopowders are the important microwave absorbing material.

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4. CONCLUSION