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Synthesis and dielectric properties of nano Si/C/N powders

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Nano Si/C/N powders with different configurations were prepared by Chemical Vapor Deposition (CVD). The crystallinity of the products increased with increasing reaction temperature. The powder prepared at 1200 °C consisted of amorphous spherical particles with a particle size of 20 to 50 nm. The nanocrystalline particles produced at 1400 °C, with a mean size from 50 to 100 nm, were also spherical. The powder prepared at 1600 °C consisted of whiskers with a diameter from 20 to 50 nm, and the length ranged from 100 to 200 μm. XRD results indicated the whisker sample was mainly β-SiC, which was in good agreement with the SAED pattern. The permittivity of the powders was measured in the frequency range from 8.2 GHz to 12.4 GHz and loss tangents were calculated also. The permittivity and loss tangent of the amorphous Si/C/N nano powder were the lowest of the three samples studied. The ε', ε'' and $\tan\delta$ of the Si/C/N powders all decreased with increasing frequency. Impurity conduction, charged defects, quasi-free electrons, and π-bonds caused by nitrogen dissolved in the SiC lattice were the reasons for the dielectric loss of the Si/C/N powders.

Introduction

Nano-materials are increasingly receiving recognition and have been developing extensively in recent years. Nano-composites find important applications in electrics and structural components, because these materials exhibit improved mechanical,[1] electrical[2] and magnetic[3] properties. Within the nano-material family, Si/C/N is one of the most common and widely studied materials.[4] This nano-material exhibits excellent mechanical properties at both room temperature and elevated temperatures.[5] The characteristics of Si/C/N nano-composite powders, such as chemical and phase composition, particle size, grain size, grain morphology, defects, specific surface area, lattice constant, and local structure of microcrystallites, have been studied in detail. Much work has been reported on the synthesis, sinterability and heat-treatment of the nano-powder. However, only few data concerning the electrical characterization of this novel class of materials are presently available. Haluschka *et al.*[6,7] found the change of the microstructure correlated with the results of the d.c.-conductivity measurements which were carried out between room temperature and 400 °C. Nevertheless, the dielectric properties of Si/C/N nano-composite powders have hardly been reported, especially at high frequency.

This paper focuses on the Si/C/N formation behavior from the CVD process by XRD analysis and the dielectric properties of the powder. It is evident that the electrical properties are controlled by the synthesis conditions, particularly by the heat-treatment atmosphere as well as by the annealing time and temperature and can be adjusted over a wide range. The measurements are correlated with the solid state reactions and phase transformations which take place during synthesis. Furthermore, information on the mechanisms which are responsible for the high loss tangent in the materials, can be derived.

Experimental procedure

Preparation of Si/C/N nano-composite powder

The original nano-powders used in this work were prepared from CH_3SiCl_3, NH_3, H_2 and N_2 by the Chemical Vapor Deposition (CVD) method.[8–10] Adjusting the flow rate of reaction gases, reaction temperature and vacuum degree resulted in the formation of Si/C/N nano-composite powders with different compositions and configurations. The chemical composition of the Si/C/N powder was determined with a nitrogen analyzer (LECO-TN14) for the nitrogen content, with an oxygen analyzer (LECO-RO316) for the oxygen content, and with a carbon analyzer (LECO-CS344) for the carbon content. The silicon content was calculated as remaining. The crystalline phase of the powder was analyzed by XRD (Cu Kα) using X-ray powder diffraction on a powder diffractmeter (Riguku, Japan). Transmission electron microscopy (TEM) images were produced using a JEM-2000CX (Japan).

Microwave permittivity measurement

The permittivity of the Si/C/N nano-composite powders was measured by a method based on the measurements of the reflection and transmission modes between 8.2 GHz and 12.4 GHz, in the fundamental wave-guide mode TE_{10}, using rectangular samples ($10.16 \times 22.86 \times 2.00$ mm^3). After calibration with an intermediate of short circuit and blank holder, reflection and transmission coefficients were obtained with the help of an automated measuring system (HP8510B network analyzer). Both the real and imaginary parts of the permittivity and permeability were calculated. For dielectric materials ($\mu' = 1$, $\mu'' = 0$) the relative error varies between 1% (pure dielectric) and 10% (highly conductive materials). The Si/C/N nano-composite powders were dispersed in melting paraffin wax, which consisted of 10 wt% Si/C/N nano-composite powder and 90 wt% paraffin wax, and then the mixtures were cast into the brass holder ($10.16 \times 22.86 \times 2.00$ mm^3).

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Table 1 Nano-powder chemical compositions and synthesis conditions

Synthesis temperature/°C	Chemical composition (wt%)				Flow rate of reaction gase/ml min^{-1}		
	Si	C	N	O	NH_3	H_2	N_2
1200	48.82	30.38	9.66	11.05	200	200	400
1400	50.88	32.49	10.09	6.47	160	200	400
1600	49.66	33.91	11.61	4.82	100	150	100

Result

Configuration and phase composition of Si/C/N nano-composite powders

The synthesis conditions and chemical compositions of the studied powders are reported in Table 1. It is illustrated in Table 1 that the synthesis conditions determine the chemical composition of the nano-powders. The nitrogen content of the nano-powders is decided by both the flow rate of NH_3 and the synthesis temperature. The retention times of different powders were different. The higher the synthesis temperature, the shorter the retention time.

Fig. 1 shows the TEM micrographs and SAED patterns of Si/C/N nano-composite powders prepared at different temperatures. They reveal that the powders are in different configurations. For (a) and (b), which prepared at 1200 °C and 1400 °C respectively, two kinds of particles are found: nearly spherical and having a smooth morphology, and loosely agglomerated. The average particle diameter was in the range 20–50 nm. The diameter of the powder prepared at 1400 °C is slightly larger than that prepared at 1200 °C. The electron diffraction pattern of the particles produced at 1200 °C shows very blurred diffraction rings, indicating an amorphous structure. The electron diffraction pattern of the particles produced at 1400 °C showed Debye rings overlapped by several spots, indicating the co-existence of crystalline and amorphous structures. For (c), the powder prepared at 1600 °C, it can be seen that whiskers and spherical particles co-exist. The length of the whiskers increased from 100 to 200 μm with diameters increasing from 20 to 50 nm. The length and radius of the whiskers are dependent on the reaction conditions. The slower the flow rate of gases through the furnace tube, the larger the length and diameter of whiskers. During the preparation at 1600 °C, the quantity of powder decreased with the growth of whiskers, in the meantime the particle size decreased also. No Debye ring could be found in the whisker's SAED pattern, only spots arranged regularly. This indicates that this powder is completely crystalline. From Fig. 1, we can deduce that the crystallinity of the powders produced by vapor phase reactions increased with increasing reaction temperature.

The crystalline phase are identified by X-ray diffraction (Fig. 2). The powders produced at different temperatures exhibited very different XRD patterns. The powder produced at 1200 °C showed only a broad hump, which indicated that the powder is amorphous and this is in good agreement with the SAED result. The XRD pattern of the powder prepared at 1400 °C shows a broad hump overlapped with several weak

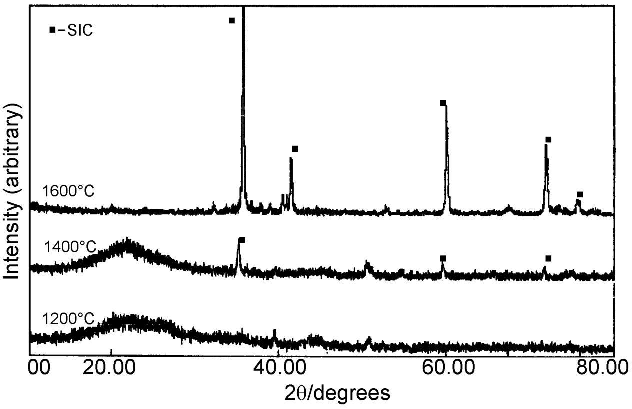
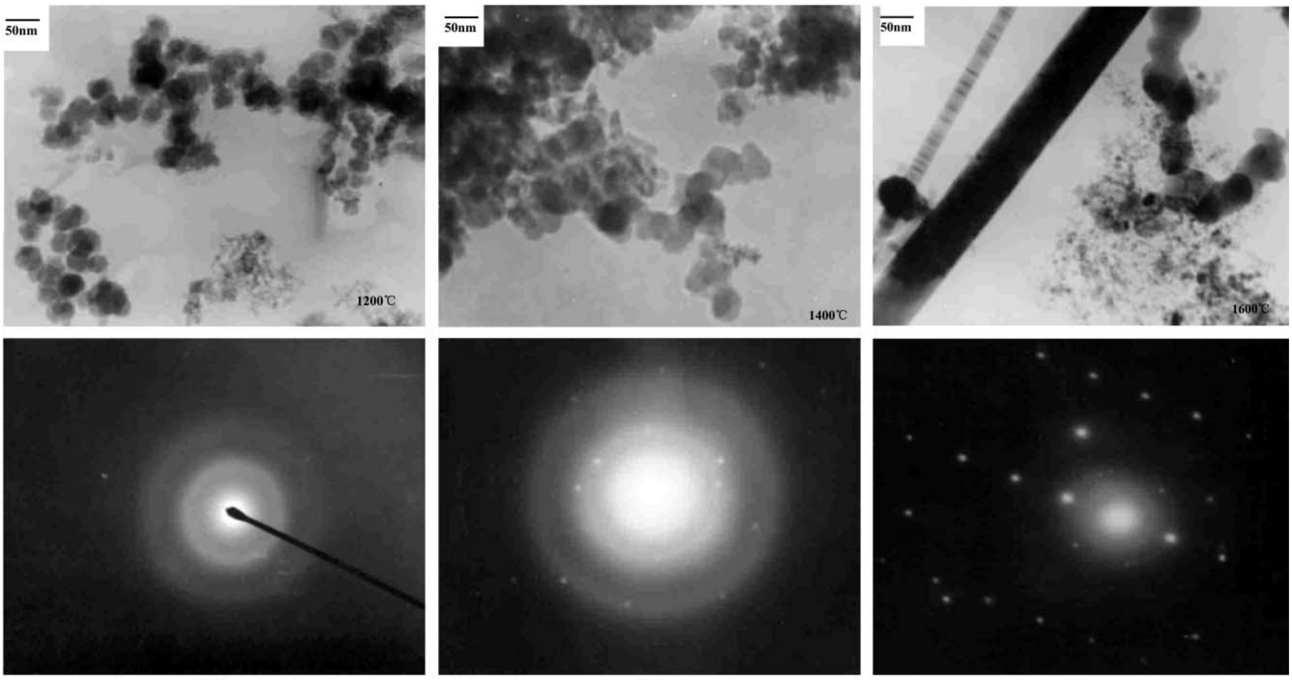


Fig. 2 XRD patterns of Si/C/N nano-powders.



(a) (b) (c)

Fig. 1 TEM micrographs and SAED patterns of Si/C/N nano-composite powders.

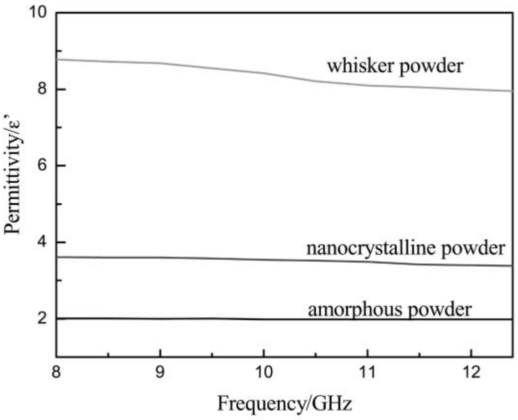


Fig. 3 The frequency dependence of ε' of Si/C/N nano-powders.

peaks. The weak intensities can be associated with the small grain size of the SiC particles, and the limit of 5 to 10 vol%. The crystalline fraction of powder prepared at 1400 °C is rather small. The powder produced at 1600 °C exhibited fairly sharp peaks at $2\theta = 35^\circ$, 58° and 73°, corresponding to the β-SiC structure.

The mean crystalline size of β-SiC in the nano-crystalline Si/C/N powder calculated from the full width at half maximum of the (111) peak using Scherrer's method was approximately 6.1 nm. The lattice constant of β-SiC, measured from the β-SiC (311) line, was 4.356 Å. The corresponding data of Si/C/N powder is 4.329 Å.The difference of lattice constants between β-SiC in nano-crystalline Si/C/N powder and β-SiC was attributed to the presence of nitrogen atoms in Si/C/N powder. XRD results indicate that β-SiC is the exclusive phase of the powder, so it can be deduced that part of N is dissolved in the SiC lattice. The amount of dissolved nitrogen in SiC–N solid solution has not been studied precisely; Komath[11] has reported that the nitrogen content of the solid solution is at most about 0.3 wt%. But considering the total amount of nitrogen in the Si/C/N powder, a large amount of nitrogen is still in the amorphous phase. Suzuki *et al.*[12] found that the lattice constant of the crystalline SiC phase drastically decreased with nitrogen content which is in good agreement with our experiment result. It is well known that nitrogen can exist in SiC as a solid solution, and nitrogen atoms are considered to occupy carbon sites.[12] Nitrogen atoms dissolved in SiC could exist in both SiC crystals and grain boundaries. No matter what form nitrogen takes, the charge equilibrium in SiC is broken, due to the difference of atom diameter and valence of the two kinds of atoms.

Electrical properties of Si/C/N nano-composite

Electrical properties of Si/C/N nano-powders can be determined at various frequencies.[13–16] The interaction between electromagnetic waves and condensed matter can be described by using complex permittivity, ε ($\varepsilon = \varepsilon' + i\varepsilon''$, where ε' is the real part, ε'' the imaginary part), and conductivity σ. The relation between the real part of the (polarization) conductivity $\sigma'(\omega)$ and the imaginary part of the permittivity $\varepsilon''(\omega)$ is $\sigma'(\omega) = \omega\varepsilon''(\omega)$, where ω is the angular frequency.

Fig. 3 shows the real part of the complex permittivity of Si/C/N nano-powders with the paraffin wax matrix *versus* the frequency. Fig. 4 indicates the imaginary part of the complex permittivity of Si/C/N nano-powders with the paraffin wax matrix *versus* the frequency. Fig. 5 gives the frequency dependency of loss tangents tanδ ($\tan\delta = \varepsilon''/\varepsilon'$) for the powders.

In Fig. 3, 4 and 5, the complex permittivity and loss tangent of the amorphous powder are $\varepsilon' = 2.01$–1.98, $\varepsilon'' = 0.10$–0.06 and $\tan\delta = 0.05$–0.03. The loss tangent of nano-crystalline Si/C/N powder ranges from 0.31 to 0.27. The ε' and ε'' of nano-crystalline Si/C/N powder range from 3.61 to 3.38, 1.10 to 0.89 at the frequency range of 8.2–12.4 GHz respectively. The corresponding dates of Si/C/N nano-whiskers are $\tan\delta = 0.41$ to 0.40, $\varepsilon' = 8.78$ to 7.95, and $\varepsilon'' = 3.55$ to 3.40. An almost frequency dispersion behavior is evident for all of the various types of powders. The complex permittivity and loss tangents decreased with increasing frequency.

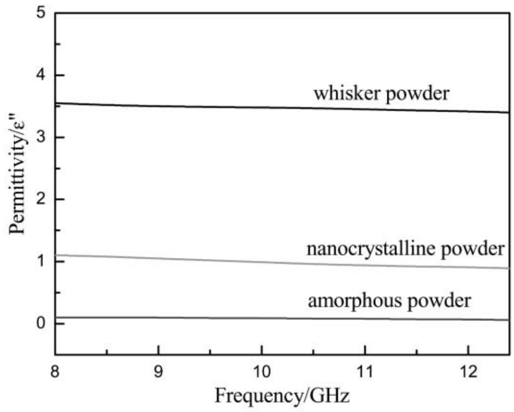


Fig. 4 The frequency dependence of ε'' of Si/C/N nano-powders.

It is clear from Fig. 3 to Fig. 5 that the complex permittivity changes with crystallinity of Si/C/N nano-composite powders. A comparison among different samples shows that the complex permittivity and loss tangent of amorphous powder are considerably lower than those of the nano-crystalline and whisker powders. Crystallinity of nano-powders would cause both complex permittivity and loss tangent increases to a certain degree. It is interesting to note that ε', ε'' and tanδ show maxima for the powder prepared at 1600 °C. It can be inferred that the crystallinity of powders plays an important role in the variation of the loss tangent and complex permittivity. The change of microstructure correlates with the results of measured ε'' and tanδ.

Discussion

Many reasons such as the grain size can cause the variation of dielectric properties of Si/C/N powders. The dielectric properties are strongly dependent on the microstructure and the morphology of powders.[17]

The increase in ε', ε'' and tanδ with increased crystallinity may be understood in terms of the formation of a solid solution. During the preparation of Si/C/N powders, nitrogen dissolved in the SiC and occupied carbon positions. As it is known, nitrogen atom and carbon atom differ in valence. The

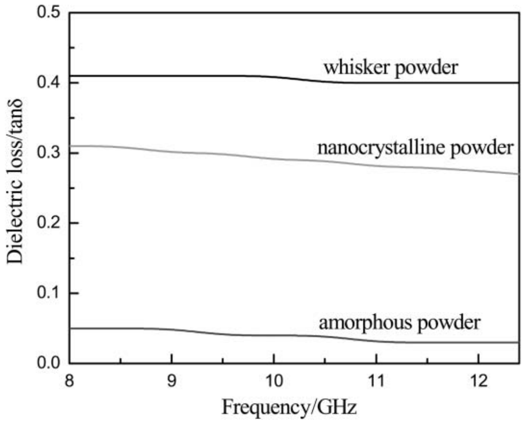


Fig. 5 The frequency dependence of tanδ of Si/C/N nano-powders.

difference of valence between N and C would cause a single or a pair of charged defects.[15] There are two possible nonparamagnetic N forms in Si/C/N nano-powders.[12] One is a trivalent N bonded to three Si atoms ($SiC_{3/4}N_{1/3}$), another possible form is a positively charged N atom bonded to four Si atoms ($^{+}N(Si)_4$) which cause a pairs of negatively charged defects. In both possible forms that nitrogen takes, negatively or positively charged defects occur. The expelled electrons may exist in the form of π-bonds in the SiC skeleton. In an alternating electric field, conjugated π electrons would oriented repeatedly. So as a resonance of the electric field, a dielectric relaxation process that is due to the orientation of conjugated π-electrons of Si/C/N is observed.

Impurities at interfaces is another important factor that intensifies the loss tangent in Si/C/N nano-powders. High surface area is one of the typical characteristics of nanostructures,[16] which supply opportunities for impurities to be distributed. In crystal materials the additives are mostly positioned at grain boundaries or crystal surfaces. In Si/C/N nano-powder prepared at 1400 °C, nitrogen and other impurity atoms congregated near the grain boundary also, which may cause impurity conduction. Interfacial conduction, impurities and additives play a crucial role in intensifying the ε'' and tanδ of the powders.

Maxwell–Wagner effects, which are the interfacial polarization due to the contributions of charge accumulation at material interfaces, may partly explain the phenomena observed above. Interfacial polarity causes a build-up of charges near heterogeneities and grain boundaries in polycrystalline materials.[18] This kind of polarity may also contribute to loss tangent.

On the other hand, amorphous carbon in nano-powders also contributes to the dielectric loss and tanδ. As the chemical compositions of these three powders are similar, more nitrogen dissolved in SiC implies that more carbon has to be combined with Si in the form of a dangling bond, which is just a loose force. Therefore, the carbon can very easily escape from the SiC lattice and become amorphous component.

The charged defects and quasi-free electrons would move in response to an electric field, and a diffusion or polarization current results from the field propagation. The relaxation drastically increased the ε'' and tanδ.

Conclusion

The investigations reported here reveal that the dielectric properties of Si/C/N nano-powders strongly depend on the crystallinity and configurations. The relationship between properties and structure can be summarized as follows:

1) Si/C/N nano-composite powders with different configurations but similar chemical compositions are synthesized by Chemical Vapor Deposition (CVD). XRD results revealed the powders are amorphous, nanocrystalline and whiskers. The whisker powders are mainly SiC in which a great deal of nitrogen atoms are dissolved.

2) The dielectric properties of the Si/C/N nano-composite powder were measured in the frequency range from 8.2 GHz to 12.4 GHz. The real and imaginary parts and loss tangent of the amorphous Si/C/N nano-powder are much lower than those of the other two kinds of powders. The ε', ε'' and tanδ of microcrystalline and whisker Si/C/N nano-powders all decreased with increasing frequency. The ε'' and tanδ increased with increasing crystallinity of the powders. The change of the microstructure correlates with the results of dielectric properties.

3) The microcrystalline SiC in the nano-composite powder dissolved a great deal of nitrogen. So abundant impurity congregates near the grain boundary and impurity conductance is then caused. In an alternating electric field these would increase the loss tangent of the powders.

4) Charged defects and quasi-free electrons are introduced due to the valence difference between nitrogen atoms and carbon atoms. They moved in response to the alternating electric field, and a diffusion or interfacial polarization current results from the electric field propagation. The ε'' and tanδ of the powders are due to the dielectric relaxation.

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