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Colossal dielectric constant and interfacial charge polarization in a polymer-derived amorphous silicon carbonitride

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ABSTRACT

The dielectric properties of a polymer-derived amorphous silicon carbonitride were measured at different frequencies and temperatures. The results revealed that the material underwent an interfacial-charge polarization process. This process resulted in an *S*-shaped frequency dependence of the dielectric constant that reached a colossal value of 2×10^4 at room temperature. With regard to the effect of the temperature on the dielectric properties of this material, the dielectric loss peak corresponding to the interfacial-charge polarization process shifted to higher frequencies with temperature by following a 3-dimentional (3D) hopping mechanism. The unique bi-phased amorphous structure of this material accounted for the observed results.

1. Introduction

Polymer-derived ceramics (PDCs) made by direct decomposition of polymer precursors exhibit unique bi-phased structures consisting of amorphous ceramic matrix and free-carbon phases with relatively insulating and conductive properties, respectively [1]. Depending on the chemistry of the precursors and the synthesis conditions, the relative amounts and distribution of the two phases as well as the nature of the interface can be widely tailored. Thus, PDCs represent an ideal system for fundamentally studying structure–property relationships in solid-state amorphous materials, and the functional properties of these materials have attracted considerable attention in the past years. Previous studies primarily focused on the direct current (DC) conduction behavior revealed that the properties of these materials strongly depend on the concentration of the free-carbon phase. Thus, at free-carbon phase concentrations above a critical value, a tunneling-percolation network is formed within the material leading to a high piezoresistive effect [2–4]. On the other hand, at free-carbon phase concentrations lower than the critical value, the conduction nature of the material is determined by the ceramic matrix phase, thereby exhibiting an amorphous semiconducting behavior [5–7]. At these conditions, the conductivity of the materials can be enhanced by the free-carbon phase via the so-called field-concentration effect [8,9]. Despite these extensive efforts, the dielectric behavior of PDCs has not been explored yet.

In this paper, we studied the dielectric behavior of a polymer-derived silicon carbonitride (α-SiCN) ceramic by determining the effect of the temperature and the frequency on its dielectric properties. The α-SiCN ceramic was proved to exhibit a strong interfacial-charge polarization process leading to a colossal dielectric constant. We also demonstrated that this polarization was thermally activated via a 3-dimentional (3D) hopping mechanism.

2. Experimental procedure

2.1. Materials preparation

The α-SiCN material studied herein was prepared by using a commercially available liquid-phased polysilazane as the main precursor [10]. The received precursor was first modified by mixing it with acrylic acid (2 wt%) and phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide (5 wt%) for improving its cross-linking characteristics while increasing its carbon concentration. The modified precursor was solidified upon UV light exposure for 5 min, followed by a heat treatment in a vacuum oven at 120 °C for 7 h. The obtained solid was grinded into a fine powder of ca. 1 µm particle size. The powder was pressed into discs of ca. 12.5 mm in diameter and 1.3 mm in thickness by uniaxial pressing at 50 MPa followed by cold isostatic pressing at 200 MPa. The as-obtained discs were finally pyrolyzed at 1200 °C for 3 h to obtain the ceramic disk samples. The entire process

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was carried out under flowing ultrahigh-purity nitrogen.

2.2. Characterization

The surfaces of the as-received samples were polished to remove possible contaminations before any characterization. X-ray diffraction (XRD) patterns were collected on a D8-Advance Bruker-AXS diffractometer using Cu Ka irradiation. Chemical composition was measured by using a carbon/sulfur analyzer (EMIA-320V, Horiba Co., Hakataku, Japan) for carbon content and an oxygen/nitrogen analyzer (EMGA-620V, Horiba Co., Hakata-ku, Japan) for oxygen and nitrogen contents. Raman spectra were obtained on Renishaw in-Via Raman microscope (Renishaw, London, U.K.) with the 514 nm line of Ar^+ laser as the excitation source. At least ten Raman spectra were obtained from each sample for minimizing the measuring error.

To study dielectric performance of the α-SiCN material, silver paint was pasted on the surface of the disk samples as the electrodes. The dielectric properties were measured as a function of temperature and frequency (f) on a high performance analyzer (Novocontrol Technologies GmbH & Co. KG, Montabaur, German) using the *Cp–D* function.

3. Results

3.1. Materials

XRD pattern was given in Fig. 1, which expectedly revealed its amorphous nature. As determined by carbon/sulfur and oxygen/nitrogen analyzers, the chemical composition of the sample was $SiC_{0.93}N_{0.62}O_{0.48}$, which corresponded to an apparent chemical formula of $0.24SiO_2\cdot0.15Si_3N_4\cdot0.31SiC\cdot0.62\ C$. The volume fraction of the free-carbon phase was subsequently estimated to be 17.6 vol%. Raman analysis (Fig. 2) revealed that the α-SiCN material contained a highly disordered carbon phase. As previously revealed for a polysilazane-derived amorphous SiCN, the free-carbon phase is in form of nanoclusters dispersed within the Si-based ceramic matrix [1,11].

3.2. Dielectric properties

Fig. 3 plots the room temperature dielectric constant (ε') as a function of f for the α-SiCN material. As shown in Fig. 3, α-SiCN showed very high dielectric constant values at low frequencies (i.e., 1.3×10^4 and 2×10^4 at 1 and 0.1 Hz, respectively). The frequency–dielectric constant curve showed an *S*-shape. At both low (< ca. 10 Hz) and medium (> ca. 300 Hz) f ranges, the dielectric constant only slightly changed with f. On the other hand, at middle frequency ranges (10–300 Hz), the dielectric constant steeply decreased by ca. 3 orders of magnitude (from 10^4 to ca. 20) while increasing f. The colossal dielectric constant values and the *S*-shaped f dependence of the dielectric constant have been previously attributed to numerous relaxation mechanisms [12]. However, considering the f range at which the dielectric constant sharply decreased and the bi-phased structure of the α-SiCN material, the colossal dielectric constant and the drastic decrease in the dielectric constant observed in the material are likely produced by space-charge polarization phenomena occurring at the ceramic matrix/free-carbon interphase. According to the Maxwell–Wagner model [13–17], a barrier layer capacitor can be formed upon separation of insulating and conducting phases in the material. Thus, the enormously different conductance characteristics of the two phases favor the accumulation of charge carriers at the interface depletion region upon application of an alternating electric field, thereby forming the so-called interfacial charges. These interfacial charges can significantly contribute to the dielectric behavior of the material by originating a very high dielectric constant. However, the interfacial charges did not form under electric fields oscillating above a critical frequency as these charges were unable to follow the rapid changes of the alternating electric field. At this point, the dielectric constant sharply decreased and remained stable at higher frequencies.

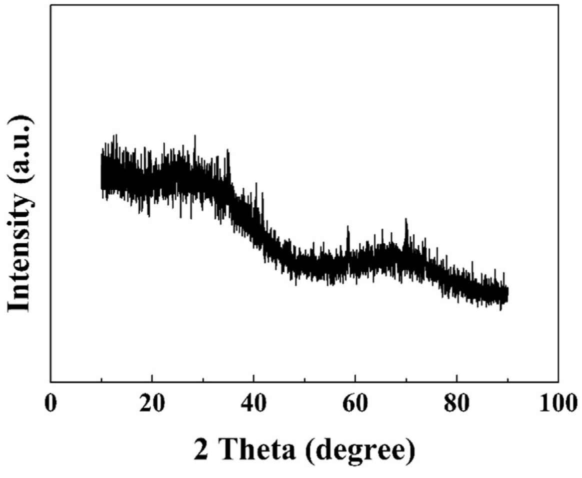

Fig. 1. XRD pattern of the polymer-derived α-SiCN ceramic.

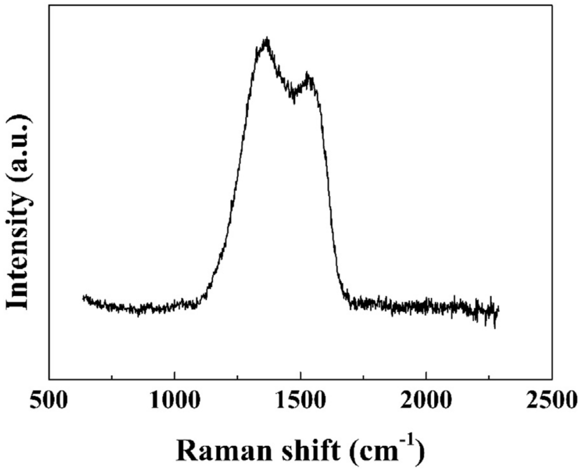

Fig. 2. A typical Raman spectrum recorded from the α-SiCN ceramic.

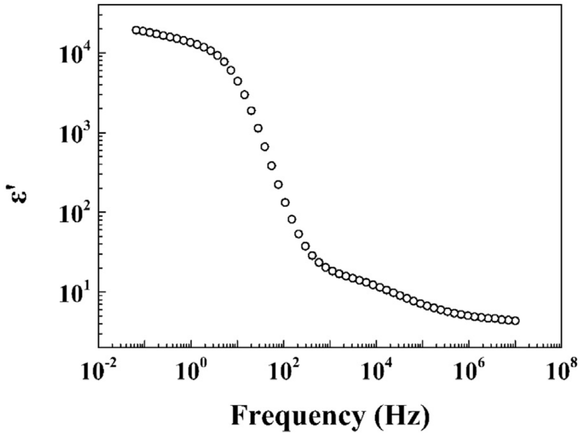

Fig. 3. Dielectric constant as a function of the frequency measured at room temperature.

The dielectric behavior of a material can also be understood by studying its frequency-dependent dielectric loss. Fig. 4 shows the room temperature dielectric loss as a function of f for the α-SiCN material. As shown in Fig. 4, the loss curve showed a peak at middle f ranges and a tail at low f values, thereby revealing the presence of a loss peak and a DC process [12]. The dielectric loss of a bi-phased material can be