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Frequency-dependent conductive behavior of polymer-derived amorphous silicon carbonitride

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Abstract—The AC conductive behavior of a polymer-derived amorphous silicon carbonitride ceramic was systemically studied. The conductivity exhibited a frequency-dependent switch: at low frequencies, the conductivity is constant and independent of frequency; while at high frequencies, the conductivity increases with frequency, showing a strong relaxation process. Both the frequency-independent conductivity and the characteristic frequency for the relaxation follow the Arrhenius relation with respect to the annealing temperature and follow a band-tail hopping process with respect to the testing temperature. XPS analysis revealed that a sp^3–sp^2 transition took place in the free-carbon phase of the material with increasing annealing temperature. The activation energy of the transition is similar to those for the Arrhenius relations. The following conductive mechanisms were proposed to account for the observed behaviors: the frequency-independent conductivity in the low frequency region is dominated by a long-distance transport of charge carriers via matrix-free carbon path, enhanced by an electric-field concentration effect; while the frequency-dependent conductivity in the high frequency region is dominated by a interfacial polarization process governed by charge carrier relaxation within the free-carbon phase.

Keywords: Frequency-dependent conduction; Polymer-derived ceramics; Amorphous SiCN; Free carbon

1. Introduction

Polymer-derived ceramics (PDCs), synthesized by thermal decomposition of polymeric precursors, are a unique class of covalent amorphous multifunctional materials. Compared to polycrystalline SiC- and Si_3N_4-based ceramics prepared by powder processing, PDCs possess many unusual and superior properties, including excellent stability against high-temperature decomposition and creep [1–3], outstanding oxidation and corrosion resistance [4–6], high temperature semiconducting behavior up to 1300 °C [7,8], and extremely high piezoresistive effect [9–11]. These properties, combined with the direct polymer-to-ceramic process, make PDCs very promising for applications in ceramic fibers [12], ceramic matrix composites [13], energy storage [14], porous components [15], and high-temperature micro-sensors [16,17].

The electrical properties of PDCs have received special attention in recent years, motivated by their potential applications in high-temperature MEMS and micro-sensors, as well as the demands for understanding the structural-property relationships of these covalent amorphous materials. Previous studies, which primarily focused on DC (direct current) behavior, revealed that the conductivity of PDCs could increase by several orders of magnitude with increasing pyrolysis temperature before crystallization [7,18,19]. The increase was believed to be caused by the sp^3–sp^2 transition of the free-carbon phase [17], which was confirmed recently by Chen et al. [20,21] and Wang et al. [22] in different PDC systems. It was also demonstrated that PDCs exhibited a typical amorphous semiconducting behavior [23]. Wang et al. [7] found that PDCs could have three conduction mechanisms in different temperature regimes: conduction in extended states, conduction in band tails, and conduction in localized states. They also found that the

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low-temperature conduction of the materials obeyed band-tail hopping (BTH), rather than variable range hopping (VRH). The AC (alternative current) conductivity of PDCs was also reported occasionally. Haluschka et al. [18] reported a strong frequency-dependent conductivity in polymer-derived silicon carbonitride, and attributed the phenomenon to a large polaron tunneling process [18]. Wang and co-workers [24] reported the complex impedance spectra of the polymer-derived silicon oxycarbide ceramics. However, AC conductive behavior has never been investigated in detail for polymer-derived ceramics. AC-response not only can reveal more structural information of heterogeneous systems such as PDCs studied here; but also will provide useful information for using the material for many applications, such as wireless sensors [17].

In this paper, we present a systemic study on the AC conductive behavior of amorphous silicon carbonitride ceramic (*a*-SiCN) derived from a polysilazane. The effects of annealing temperature and testing temperature on the AC conductivities of the material were measured and analyzed using theoretical models. The microstructure and its evolution with annealing temperature of the material were characterized using X-ray photoelectron spectroscopy (XPS). Conductive mechanisms were proposed by comparing the conductive behaviors and microstructures of the material.

2. Experimental procedure

2.1. Material preparation

The *a*-SiCN studied here was synthesized by thermal decomposition of a commercially available liquid polysilazane (PSN, Institute of Chemistry, Beijing, China). The structure of the PSN is $-[SiNH(CH{=}CH_2)]_x-[NHSiNH(CH_3)]_y-$ ($y/x = 1.2/2$) with a number-average molecular mass of 600–1000, as provided by the manufactory. The as-received precursor was first thermally cross-linked at 350 °C for 2 h under the protection of flowing ultrahigh purity nitrogen in a quartz tube furnace (GSL-1100X, MTI KJ GROUP, Hefei, Anhui, China). The obtained solid was then ground to fine powder of ~1 μm using a high-energy ball miller (QM-3A, Midwest Group, Beijing, China). After sieving, the powder was pressed in a die at a uniaxial pressure of 50 MPa followed by cold isostatic pressing (CHUAN-XI, Sichuan, China) at 200 MPa to produce disks of 16 mm in diameter and ~1.5 mm in thickness. The disks were pyrolyzed at 900 °C for 4 h under a steady flow of N_2 in a quartz tube furnace (GSL-1100X, MTI KJ GROUP, Hefei, Anhui, China). The obtained samples were further annealed at different temperatures between 1000 and 1400 °C for 4 h under a flow of ultrahigh purity N_2 in an alumina tube furnace (GSL-1700X, MTI KJ GROUP, Hefei, Anhui, China).

2.2. Characterization

The surfaces of the as-received samples were polished to remove possible contaminations before any characterization. For X-ray diffraction (XRD) and chemical composition analysis, disc samples were ground into powder manually in an agate mortar. XRD patterns were collected on a D8-Advance Bruker-AXS diffractometer using Cu Kα irradiation. Chemical composition was measured by using a carbon/sulfur analyzer (EMIA-320V, Horiba Co., Hakata-ku, Japan) for carbon content and an oxygen/nitrogen analyzer (EMGA-620V, Horiba Co., Hakata-ku, Japan) for oxygen and nitrogen contents. Silicon content was calculated from the equation of $m_{Si} = 1 - m_C - m_N - m_O$, where m_{Si}, m_C, m_N, and m_O are the mass percentage of silicon, carbon, nitrogen and oxygen, respectively. About 10 mg powder was used for each measurement.

For conductivity measurement, the surfaces of the discs were polished to 1 μm finish. Silver paint (SPI, West Chester, Pennsylvania, USA) was then pasted on the surfaces as the electrodes. The complex impedance (Z^*) spectra of the disk samples were measured on a LCR meter (Agilent 4980A, Agilent Technologies, Santa Clara, California, USA) in the frequency range of 20 Hz to 2 MHz at different temperatures. The AC conductivity (σ' was then calculated using the following equation:

$$\sigma' = \left[\frac{Z'}{Z'^2 + Z''^2}\right] \times \left(\frac{t}{A}\right) \quad (1)$$

where Z' and Z'' are the real and imaginary parts of the complex impedance, respectively; t and A are the thickness and the effective area of the samples, respectively. The spectra were also used to calculate the complex electric modulus (M^*) defined by the following equation:

$$M^* = M' + jM'' = 1/\varepsilon^* = j\omega C_0 Z^*(\omega) \quad (2)$$

where M' and M'' are the real and imaginary parts of the complex electric modulus, respectively, $j = \sqrt{-1}$, ε^* is the complex permittivity, ω is the angular frequency and C_0 is the vacuum capacitance of the cell.

The XPS characterization was carried out on an AXIS ULTRA (Kratos) apparatus (PHI-5400, Perkin Elmer, Waltham, Massachusetts, USA), using monochromatic Al Kα radiation ($hv = 1486.6$ eV) at 150 W. The samples were bombarded by Ar^+ ions for 20 min before data collection to minimize the effects of surface contaminations. The spectra were recorded at room temperature under high vacuum (10^{-9} Torr).

3. Results

3.1. Materials

XRD patterns obtained from the samples annealed at different temperatures are given in Fig. 1. All patterns exhibit no obvious diffraction peaks, indicating that they are all amorphous regardless of annealing temperature. The chemical compositions of the samples annealed at different temperatures are listed in Table 1. It shows that the materials contain silicon, carbon and nitrogen as major components. A small amount of oxygen is also found in all samples, which is likely resulted from the contamination during preparation, especially during the milling step. The chemical formula (Table 1) reveal that the materials contain a fairly large amount of "free carbon" phase, which indicates that similar to other PDCs, the *a*-SiCN samples have two phases: a matrix phase consisting of an amorphous network of SiC_xN_{1-x} ($x = 0$, 1, 2, 3, or 4) tetrahedra and a dispersed "free-carbon" phase consisting of highly disordered carbon. The compositions are essentially the same for the samples annealed at different temperatures,