J. Am. Ceram. Soc., 92 [7] 1603–1606 (2009)
DOI: 10.1111/j.1551-2916.2009.03044.x


journal

# Electron Transport in Polymer-Derived Amorphous Silicon Oxycarbonitride Ceramics

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**The electron transport behavior of polymer-derived amorphous silicon oxycarbonitride ceramics is studied by measuring their temperature-dependent electrical conductivities. The experimental results are analyzed using theoretical models. The results reveal that the materials exhibit three conduction mechanisms: conduction in extended states, conduction in band tails, and conduction in localized states. Particularly, it is found that in a low-temperature regime, the conduction of the materials follows a band tail hopping mechanism, rather than the previously assumed variable range hopping mechanism. The results also reveal that energy gaps such as $E_C - E_F$ and $E_C - E_A$ decrease with increasing pyrolysis temperature.**

## I. Introduction

Recently, a new class of multifunctional high-temperature ceramics has been synthesized by the thermal decomposition of polymeric precursors.[1] The materials, referred as to polymer-derived ceramics (PDCs), exhibit many advantages over traditional ceramics made from powder-based processing. For example, the direct chemical-to-ceramic route of PDCs offers a real opportunity to manipulate the structures and composites, and thereby the properties, of the ceramics at the atomic/nano-scale by tailoring the chemistry of the precursors. PDC processing also leads to a simple, cost-efficient, and near-net shape approach for manufacturing ceramic components and devices with complex shapes. The synthesis of fibers, coatings, composites, micro-electro-mechanical systems, and micro-sensors from PDCs has been demonstrated.[2–5]

Studies on the electrical behavior of PDCs have received extensive attention because not only are the electronic properties important for applications but also such studies can lead to a fundamental understanding of structure–property relationships. Wang *et al.*[6] demonstrated that the conduction mechanisms of the PDCs can be tailored by changing the concentration of free carbon clusters, which are self-formed within disordered matrix phases. The conductivity of PDCs containing a high free-carbon concentration is controlled by a tunneling-percolation process, exhibiting extremely high piezoresistivity,[6,7] while the conductivity of PDCs with a lower free-carbon concentration is determined by the disordered matrix, leading to amorphous semi conducting behavior. While amorphous semiconducting behavior was widely observed in PDCs,[8–11] detailed conduction mechanisms have not been studied yet.

In this paper, we report the study of the electron transport behavior of polymer-derived amorphous silicon oxycarbonitrides (SiOCNs) by measuring their temperature-dependent conductivities. The study is performed on materials obtained at different pyrolysis temperatures. The experimental results are analyzed using existing theoretical models, in order to reveal conduction mechanisms.

## II. Experimental Procedure

The amorphous SiOCNs ceramics used in this study are prepared using a commercially available liquid-phased polysilazane (Ceraset, Kion, Huntingdon Valley, PA), whose chemical structure and physical/chemical properties were reported previously,[12–14] as a precursor. First, Ceraset is mixed with a small amount of phosphonic acid dimethyl ester. The mixed liquid is then photopolymerized to form solid discs with a thickness of 600 μm. The discs are then pyrolyzed in a flow of ultrahigh purity nitrogen in a tube furnace to convert them into fully dense SiOCN ceramics. Four kinds of samples are prepared by using different pyrolysis temperatures of 1000°, 1100°, 1200°, and 1300°C for 4 h, respectively. The obtained samples are examined using X-ray diffraction, which reveals that all samples are amorphous without any diffraction peaks.

To measure the temperature-dependent conductivity of the SiOCNs, the surfaces of the obtained ceramic discs are first polished to a 1 μm finish. Silver paste is applied on these surfaces to form electrodes. The temperature-dependent electrical conductivity of the samples is then measured in a tube furnace under flowing ultrahigh purity nitrogen. To obtain the accurate temperatures, a thermal couple is placed just above the samples. The measurement is conducted in a temperature range of 25°–800°C.

## III. Results and Discussion

Figure 1 plots the electrical conductivity as a function of measuring temperature for the four samples. It is seen that all samples show positive temperature coefficients of the electrical conductivity, indicating that they are semiconductors. The figure also reveals that room temperature conductivities of the materials increase by seven orders of magnitude when pyrolysis temperatures increase from 1000° to 1300°C. In order to understand the electron transport behavior, the experimental data are analyzed using the theoretical models below.

The electronic transport in amorphous semiconductors can be classified into three conduction mechanisms: the conduction in extended states, the conduction in band tails, and the conduction in localized states.[15] Accordingly, the temperature-

P. Greil—contributing editor

Manuscript No. 25719. Received January 11, 2009; approved February 11, 2009.
*Member, The American Ceramic Society.
This work was supported by National Science Foundation of USA (DMR-0706526).
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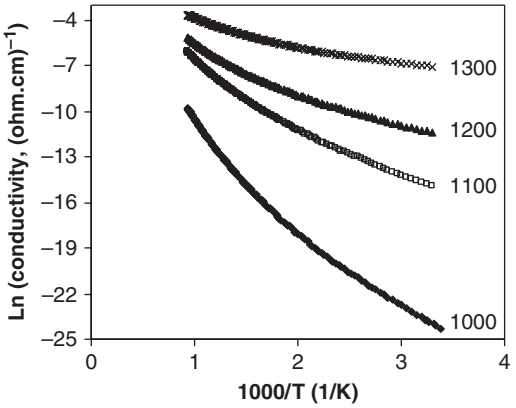


**Fig. 1.** Temperature-dependent conductivities of the silicon oxycarbonitrides samples pyrolyzed at different temperatures, as labeled.

dependent conductivity of amorphous semiconductors can be described by the following equation:

$$\sigma = \sigma_1 e^{-\frac{E_C - E_F}{kT}} + \sigma_2 e^{-\frac{E_A - E_F + w}{kT}} + \sigma_3 e^{-\left(\frac{T_0}{T}\right)^{1/4}} \quad (1)$$

where $E_C$, $E_A$, and $E_F$ are the mobility edge of conduction band, the band tail, and the Fermi level, respectively; $w$ is the thermal activation energy, which is equal to the phonon energy of the material (neglecting the multi-phonon processes); $\sigma_1$, $\sigma_2$, and $\sigma_3$ are prefactors, which have no clear physical significance; and $T_0$ is a characteristic temperature. The first term is the contribution from the conduction in extended states, which occurs at the high-temperature range; the second term is the contribution from the conduction in band tail states, which occurs within the middle temperature range; and the third term is the contribution from the conduction in localized states, which occurs in the low-temperature regime.

The experimental results presented in Fig. 1 are analyzed using Eq. (1). It is seen that the experimental data for all four samples can be well-fitted by the equation (Fig. 2). This suggests that the conduction of the SiOCNs over the entire testing temperature range can be described by the amorphous semiconducting model. The parameters determined by curve fitting are summarized in Table I.

Previous studies assumed that the $T^{1/4}$ dependence of the conduction of PDCs is resulted from the variable range hopping (VRH) mechanism,[8–11] in which electrons transport within the defect energy level close to the Fermi level. According to Mott's model,[16] the prefactor $\sigma_3$ and characteristic temperature $T_0$ should vary in opposite directions for the VRH process

$$T_o \propto 1/N(E_{fn}) \text{ and } \sigma_3 \propto [N(E_{fn})]^{1/2} \quad (2)$$

where $N(E_{fn})$ is the density of the defect state. However, the experimental results shown in Table I suggest that the prefactor $\sigma_3$ and characteristic temperature $T_0$ vary along the same direction. Recent theoretical studies consider a new transport mechanism, in which electrons within the defect level fill empty states near a so-called "transport energy" and then hop back to lower localized states, named the band tail hopping (BTH) conduction mechanism. [17,18] By considering the filling rate and assuming an exponential band tail state distribution, the BTH model also suggests a $T^{-1/4}$ law. Unlike the VRH model, the BTH model predicts that $T_0$ and $\sigma_3$ should follow the following relationship[17,19]:

$$\sigma_3 \propto \exp(T' T_o^{1/4}) \quad (3)$$

Figure 3 plots $\ln(\sigma_3)$ vs. $T_0^{1/4}$. A very good linear fit suggests that the SiOCNs studied here follow the BTH conduction mechanism, rather than the previously assumed VRH mechanism.

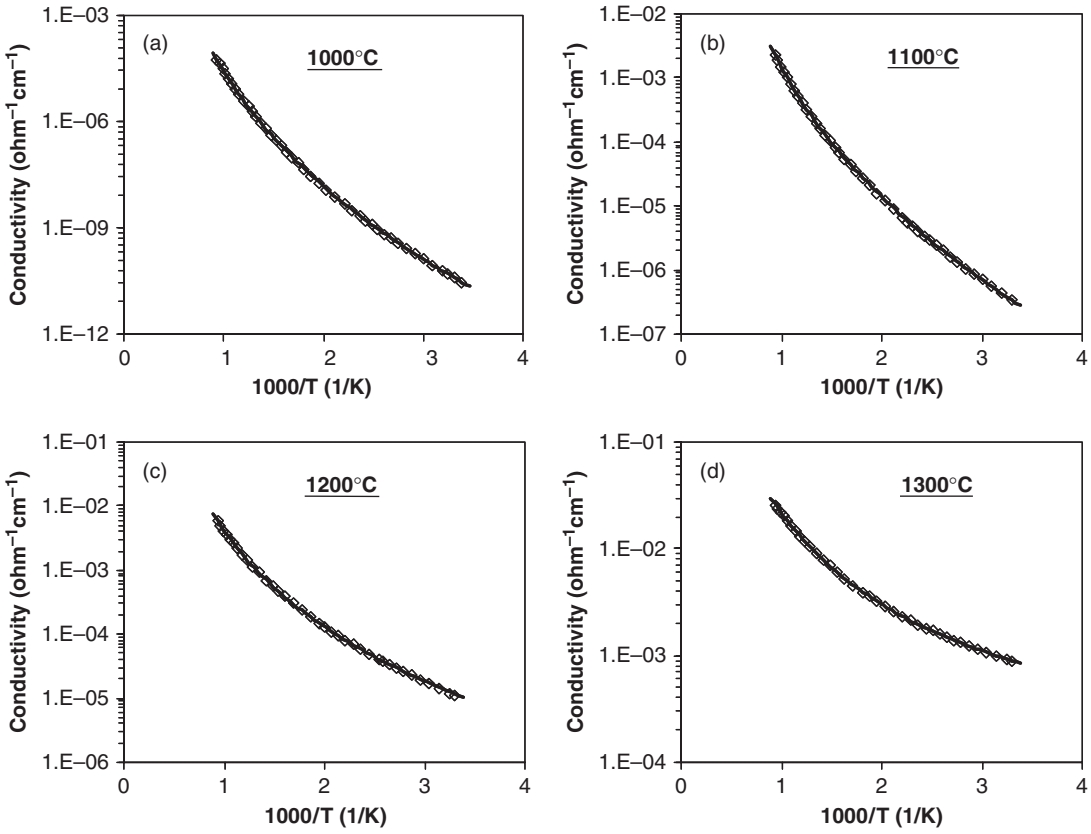


**Fig. 2.** Comparison of experimental results and the theoretical predictions of temperature-dependent conductivity for the samples pyrolyzed at (a) 1000°C, (b) 1100°C, (c) 1200°C and (d) 1300°C. The solid lines are computed from Eq. (1).

**Table I. The Parameters Obtained by Curve Fitting the Temperature-Dependent Conductivity of the SiOCN Samples with Eq. (1)**

| Pyrolysis temperature (°C) | $E_C-E_F$ (eV) | $E_A$-$E_F+w$ (eV) | $T_0$ (K) | $\sigma_3$ ($\Omega^{-1}\cdot cm^{-1}$) |
|---|---|---|---|---|
| 1000 | 1.03 | 0.71 | $1.8\times10^9$ | $1.2\times10^{11}$ |
| 1100 | 0.80 | 0.54 | $2.9\times10^8$ | $0.6\times10^6$ |
| 1200 | 0.75 | 0.52 | $3.5\times10^7$ | $2.4\times10^3$ |
| 1300 | 0.50 | 0.46 | $1.2\times10^6$ | 2.5 |

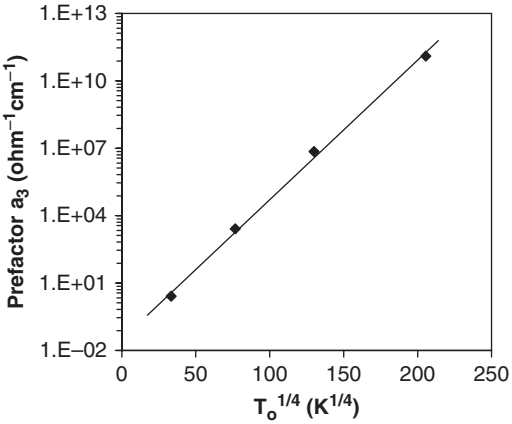


**Fig. 3.** A plot of the prefactor $\sigma_3$ vs. $T_0^{1/4}$ for four silicon oxycarbonitrides samples.

Previous studies on amorphous carbons and carbon nitrides revealed that these covalent glasses followed the BTH mechanism, rather than the VRH mechanism.[20–22]

The results listed in Table I also reveal that the energy differences between the mobility edge ($E_C$) and the Fermi level ($E_F$) decrease with increasing pyrolysis temperature. One explanation for such variation is that the $E_F$ is moving closer to $E_C$ with increasing pyrolysis temperature. Previous studies revealed that SiOCN-based materials consist of carbon-dangling bonds, whose concentration increases with increasing pyrolysis temperature.[23,24] The C-dangling bonds work as donor defects to give electrons and to form defect states within the band gap. Consequently, increase in C-dangling bonds could lead to an increase in the density of the defect states, resulting in the Fermi level moving toward the conduction band and band tail.

The energy difference between the mobility edge and the band tail can be estimated using the data in Table I.[‡] It is seen that $E_C-E_A$ first decreases slowly with increasing the pyrolysis temperature up to 1200°C, then decreases sharply between 1200° and 1300°C (Fig. 4). The existence of a band tail in amorphous semiconductors is due to the structural disorder that destroyed the periodic nature of the crystalline structure.[28] Thus the difference between $E_C$ and $E_A$ is proportional to the degree of structural disorder. The decrease in $E_C-E_A$ suggests that the degree of the structural disorder of the SiOCNs decreases with the pyrolysis temperature. This is consistent with the nuclear magnetic resonance studies, which reveal that the structure of the SiOCNs becomes more ordered with increasing pyrolysis temperature, with a sudden change occurring between 1200° and 1300°C. (T. Jiang, unpublished data).

## IV. Conclusion

The conduction mechanism of polymer-derived amorphous SiOCNs is investigated by measuring their temperature-dependent conductivities. The results show that regardless of pyrolysis temperature, all of the samples exhibit three conduction mechanisms, namely, the conduction in extended states, the conduction in band tails, and the conduction in band tail hopping, which are predominant in different temperature regimes. The results also reveal that the electronic structure of the materials is affected by the pyrolysis temperature.

[‡]The $w$ is the phonon energy of the SiOCNs, which should be in the same range as those of SiC, $SiO_2$, and $Si_3N_4$ phonons; phonon energies are about 100 meV for SiC[25,26] and 120 meV for $Si_3N_4$.[27]

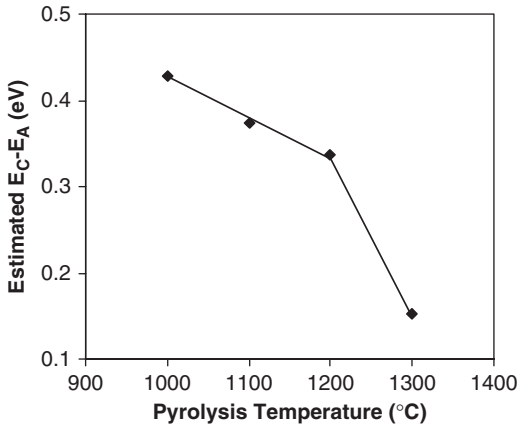


**Fig. 4.** A plot of $E_C-E_A$ as a function of pyrolysis temperature.

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