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# A Silicon Carbonitride Ceramic with Anomalously High Piezoresistivity

Ligong Zhang,[‡] Yansong Wang,[§] Yun Wei,[‡] Weixing Xu,[‡] Danjie Fang,[‡,††] Lei Zhai,[¶] Kuo-Chi Lin,[||] and Linan An*,[†,‡]

[‡]Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, Florida 32816

[§]Laboratory of Excited State Process, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science, and the Graduate school of Chinese academy of Sciences, Changchun, Jilin 130032, China

[¶]NanoScience Technology Center, University of Central Florida, Orlando, Florida 32816

[||]Institute of Simulation and Training, University of Central Florida, Orlando, Florida 32826

**The piezoresistive behavior of a silicon carbonitride ceramic derived from a polymer precursor is investigated under a uniaxial compressive loading condition. The electric conductivity has been measured as a function of the applied stress along both longitudinal and transverse directions. The gauge factor of the materials was then calculated from the data at different stress levels. The results show that the material exhibits an extremely high piezoresistive coefficient along both directions, ranging from 1000 to 4000, which are much higher than any existing ceramic material. The results also reveal that the gauge factor decreases significantly with increasing applied stress. A theoretical model based on the tunneling–percolation mechanism has been developed to explain the stress dependence of the gauge factor. The unique piezoresistive behavior is attributed to the unique self-assembled nanodomain structure of the material.**

## I. Introduction

The electrical resistivity of a material can change when a stress is applied onto it. This phenomenon, which is referred to as the piezoresistive effect, has widespread applications in a variety of sensors for sensing pressure, vibration, and acceleration,[1] and has been used to understand the conducting mechanism of materials. From the applications point of view, higher sensing accuracies and wider sensing ranges require materials with higher piezoresistive coefficients. Existing materials that exhibit high piezoresistive coefficients are well-doped semiconductors, diamond films, and polymer-based composites.[2–5] However, these materials cannot operate in high-temperature environments. On the other hand, high-temperature ceramics typically exhibit low piezoresistive coefficients.[6,7] The development and applications of high-temperature sensors are extremely limited due to the lack of suitable materials.

Recently, a new class of materials, known as polymer-derived ceramics (PDCs), has been synthesized by thermal decomposition of polymeric precursors.[8,9] The materials as obtained are X-ray amorphous (no diffraction peaks), consisting of silicon, carbon, nitrogen as well as a small amount of oxygen. PDCs possess excellent thermo-mechanical properties that are retained up to very high temperatures, such as excellent thermal stability,[10] high oxidation/corrosion resistance,[11] and creep resistance,[12] thus making them suitable for high-temperature applications. Because of the direct polymer-to-ceramic processing of PDCs, the materials can be used easily to fabricate ceramic-based micro-electro-mechanical systems and microsensors.[13] However, few studies have focused on the electronic behavior of the materials.[14,15]

In this paper, we report the piezoresistive behavior of a polymer-derived silicon carbonitride (SiCN). We find that the material exhibits extremely high piezoresistive coefficients of ~1000–4000, which are much higher than that of any existing ceramic.

## II. Experimental Procedure

The SiCN ceramic reported here is synthesized by the thermal decomposition of a liquid-phase polyurea(methylvinyl) silazane (PUMS) using the method reported previously.[8,9,11] First, commercially available PUMS is mixed with ~4 wt% dicumyl peroxide, which acts as the thermal initiator to lower the solidification temperature of the PUMS.[16,17] The liquid mixture is then solidified at 150°C for 0.5 h in ultrahigh-purity nitrogen, followed by heat treatment at 350°C for 4 h in ultrahigh-purity nitrogen. The obtained solid is then crushed and ball milled into fine powders using high-energy ball milling. The powder is then compressed into disks and pyrolyzed at 1400°C for 4 h in a tube furnace under ultrahigh-purity nitrogen to convert the precursor into SiCN ceramics. The density of the obtained specimens was measured using the Archimedes principle. The composition of the samples was determined, using a combination of elemental analysis and secondary hydrochloric acid ICP, to be $SiC_{0.99}N_{0.85}O_{0.11}$.

For measuring the piezoresistive coefficients, the obtained specimens were cut into a rectangular shape of 5 mm × 5 mm cross section and 3 mm thickness. Silver paste was painted on the surfaces of the specimens and dried in air for a day to form electrodes. The specimens were then tested under uniaxial compressive stresses using a universal testing system (Instron 3369, Instron industrial, Norwood, MA). To measure the resistance, a constant DC voltage of 0.75 V was applied on the specimen using the Keithley 230 programmable voltage source (Keithley Instruments, Cleveland, OH) and the current was measured using a digital multimeter with an accuracy of 0.1 mA (DM-5300, Sperry, Milwaukee, WI). The resistance was then calculated by $R = V/I$, where $R$ is the resistance, $V$ is the applied voltage, and $I$ is the measured current. The resistance of the sample was measured as a function of applied stress along both longitudinal

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*Member, The American Ceramic Society.
[†]Author to whom correspondence should be addressed. e-mail: lan@mail.ucf.edu
[††]D. Fang is a summer student from Oviedo High School, Oviedo, Florida 32766.

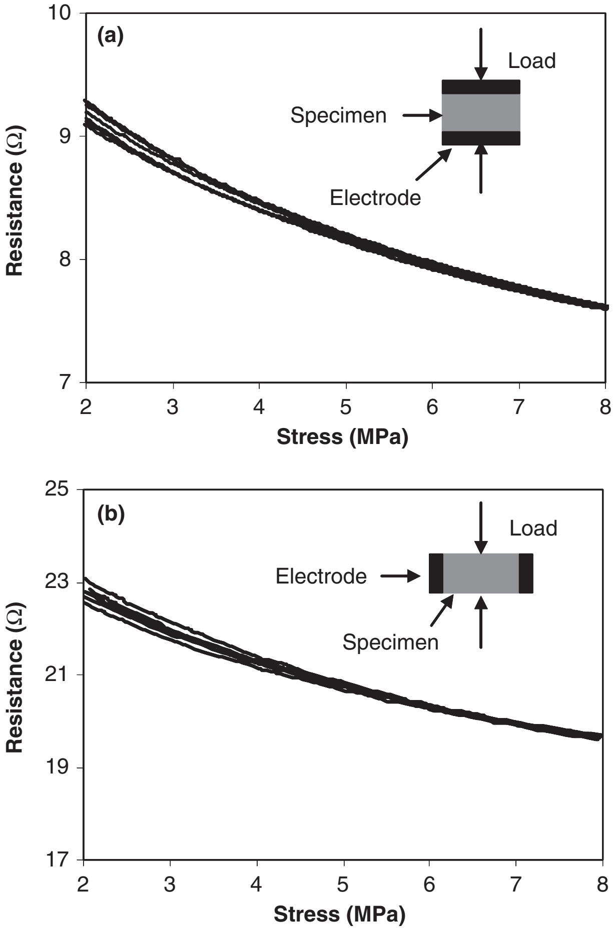

**Fig. 1.** Longitudinal (a) and transverse (b) resistances of the SiCN as a function of the applied pressure for three loading–unloading cycles, illustrating the high reproducibility of the data. The insets show schematics showing the testing geometries.

(parallel to the loading direction) and transverse (perpendicular to the loading direction) directions (insets in Fig. 1).

## III. Results and Discussion

Figure 1(a) plots the longitudinal resistance of the SiCN sample as a function of the applied stress for three loading–unloading cycles. In order to avoid any uncertainty that could occur at low stresses, the experiments were performed with applied stresses ranging from 2 to 8 MPa. It could be seen that the resistance–stress curves were highly reproducible during the three loading–unloading cycles, indicating that the change in resistance is a result of the elastic deformation. The resistance of the sample decreases significantly with increasing stress, suggesting that the material should have a high piezoresistive coefficient. The transverse resistance of the sample versus the applied pressure is plotted in Fig. 1(b). Again, the resistance shows excellent reproducibility during three loading–unloading cycles. It is interesting that the transverse resistance also decreases with the applied pressure, unlike semiconductors, which exhibited an increase in transverse resistance when loaded under uniaxial compressive stresses.[18,19]

The piezoresistive coefficient, $K$ (also known as gauge factor), of a material is defined as

$$K = \frac{\mathrm{d}R/R}{\mathrm{d}\varepsilon} = E\frac{\mathrm{d}R/R}{\mathrm{d}\sigma} \quad (1)$$

where $R$ is the electric resistance, $E$ is the Young's modulus of the material, and $\sigma$ is the applied stress. To calculate the gauge factor of the SiCN, the Young's modulus of the material is estimated using the following equation,[20]

$$E = E_\mathrm{o}(1 - 1.9p + 0.9p^2) \quad (2)$$

where $E_\mathrm{o}$ is Young's modulus of the fully dense SiCN material (155 GPa)[21] and $p$ is the porosity of the sample measured to be ~26.9 vol% (measured using the Archimedes principle). The calculated Young's modulus of the SiCN sample reported here is 86 GPa. The gauge factor of the SiCN is then calculated from the curves presented in Fig. 1 using Eq. (1) and is plotted in Fig. 2 as a function of applied stress. It is surprising that the SiCN exhibits an extremely high gauge factor in the range of ~1000–4000, which is much higher than that of any existing high-temperature material. Typically, such a high gauge factor has only been observed in conductor-filled insulating polymer composites.[5]

The piezoresistive behavior of SiCN as shown in Fig. 2 is quite unique as compared with conventional crystalline semiconductors. First, the gauge factor of the SiCN decreases nonlinearly with increasing stress, while semiconductors like silicon and silicon carbide exhibit a constant gauge factor within the pressure range used here.[2,6] The longitudinal and transverse gauge factors of the SiCN have the same sign, but those of semiconductors usually have opposite signs. The SiCN behaves in a manner similar to conductor-filled insulating polymer composites and thick-film resistors, which also have the same-signed longitudinal and transverse gauge factors that decrease with increasing stress.[5,22,23] It has been demonstrated that in these

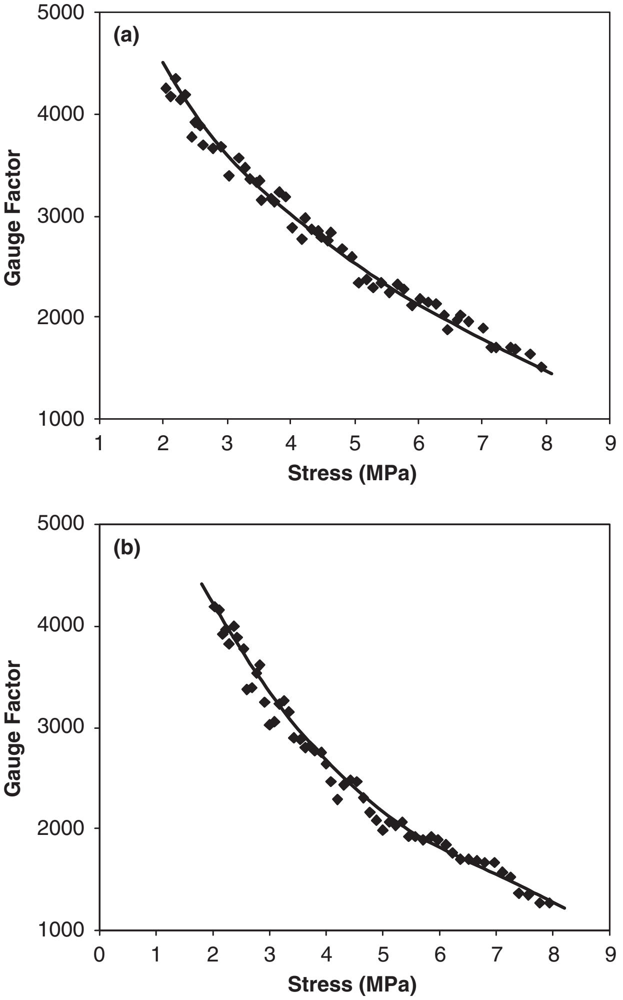

**Fig. 2.** Plots of gauge factors as a function of the applied pressure for (a) longitudinal and (b) transverse directions.

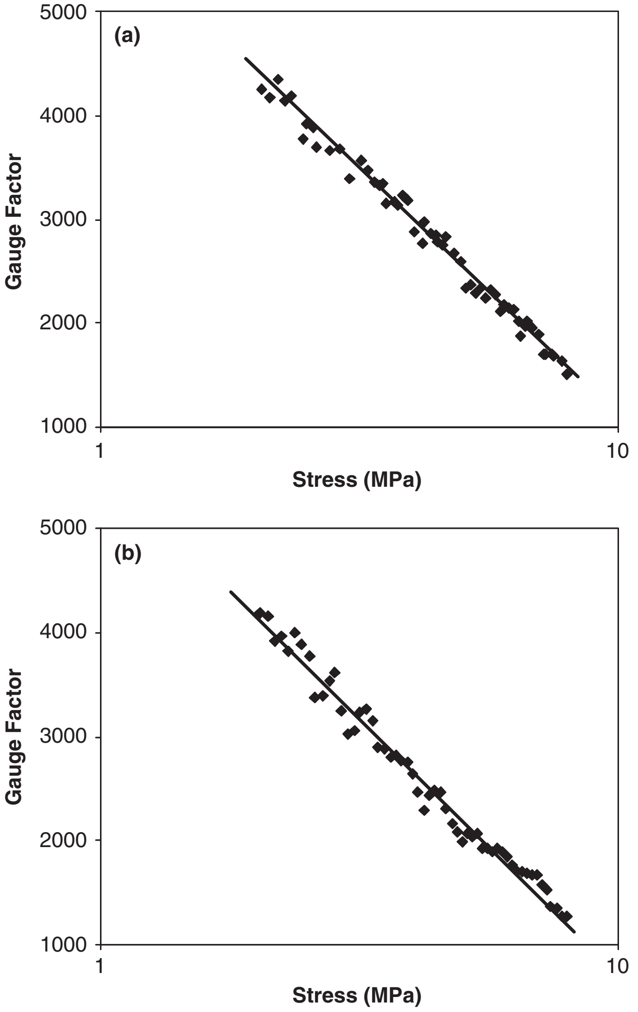

**Fig. 3.** Plots of gauge factor as a function of the logarithm of the applied pressure for (a) longitudinal and (b) transverse directions. The dots represent the experimental results, while the solid lines represent the theoretical trend predicted using Eq. (5).

latter materials, the piezoresistivity results from the tunneling–percolation mechanism.

The unusual piezoresistive behavior of the SiCN ceramic could be related to its unique microstructure. Previous studies revealed that polymer-derived SiCN ceramics are comprised of $SiC_xN_{4-x}$ ($x = 0$–4) building units and free carbons (C–C bonds), as summarized in Raj *et al.*[24] Recently, it was observed that in polymer-derived ceramics, the free carbon forms graphene sheets that divide the materials into nanoscale domains.[25] Such a nanodomain structure was also observed from the SiCN studied here.[26] This unique microstructure of the SiCN, which is formed during pyrolysis via a self-assembly process, could be used to explain the observed piezoresistive behavior. We believed that the conducting graphene sheets in the SiCN form a tunneling–percolation structure. The resistivity of the material is then determined by a tunneling process and is sensitive to the distance between the graphene sheets. The slight decrease in the distance between the graphene sheets caused by the applied stress can lead to a significant change in the resistivity, and thus a high piezoresistive coefficient.

To further examine this assumption, here, we compare the experimental data with the tunneling–percolation model. For a tunneling–percolation system, the gauge factor is related to the concentration of the conducting phase through the following equation:[27]

$$K = K_o - B\ln(x - x_o) \tag{3}$$

where $K_o$ and $B$ are material-dependent constants, $x_o$ is the original concentration of the conducting phase without applied stress, and $x$ is the concentration of the conducting phase under the applied stress. The concentration of the conducting phase can be related to the applied stress by assuming that the graphene sheets are not compressible, but the total volume decreases with the applied pressure. For isotropic materials, the change in volume can be calculated by $\frac{\Delta V}{V_o} = \frac{1-2\nu}{E}\sigma$, where $\Delta V$ is the change in volume, $V_o$ is the original volume, and $\nu$ is Poisson's ratio. Thus, the change in the concentration of the conducting phase due to the application of pressure is

$$x - x_o = x_o\frac{(1-2\nu)}{E}\sigma \tag{4}$$

The combination of Eqs. (3) and (4) leads to

$$K = K_o - B\ln\left(\frac{(1-2\nu)x_o}{E}\right) - B\ln(\sigma) \tag{5}$$

Equation (5) suggests that the gauge factor should be a logarithmic function of the applied stress. Figure 3 plots the experimentally measured gauge factors (dots) as the logarithm of the applied stress. It is apparent that the experimental data follow the trend predicted by Eq. (5) very well (solid line), supporting that the SiCN exhibits the tunneling–percolation conducting mechanism.

## IV. Conclusion

In summary, we report a polymer-derived SiCN that exhibits an extremely high piezoresistive coefficient ranging between 1000 and 4000. We demonstrate that this piezoresistive behavior of the material follows the tunneling–percolation model. The results provide strong evidence supporting a recently proposed nanodomain structural model of polymer-derived ceramics. The high piezoresistivity, together with the micro fabrication capability and excellent high-temperature thermal–mechanical properties of polymer-derived ceramics, makes the SiCN an excellent candidate material for high-temperature sensors.

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