A Silicon Carbonitride Ceramic with Anomalously High Piezoresistivity

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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.

1. 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, 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. However, these materials cannot operate in high-temperature environments. On the other hand, high-temperature ceramics typically exhibit low piezoresistive coefficients. 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 a liquid-phase polyurea(methylvinyl) silazane (PUMS) using the method reported previously. 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. 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 Archimeades principle. The composition of the samples was determined, using a combination of elemental analysis and secondary hydrochloric acid ICP, to be SiC0.99N0.85O0.11.

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, Intron 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...
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 exhibit an increase in transverse resistance when loaded under uniaxial compressive stresses.18,19

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

$$K = \frac{\Delta R/R}{\Delta E} = E \frac{\Delta R/R}{\Delta \sigma}$$

(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

$$E = E_o(1 - 1.9p + 0.9p^2)$$

(2)

where $E_o$ is Young’s modulus of the fully dense SiCN material (155 GPa)21 and $p$ is the porosity of the sample measured to be $\sim 26.9$ 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 $\sim 1000$–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

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In polymer-derived ceramics, the free carbon forms a tunneling–percolation system, the gauge factor is related to the piezoresistive coefficient. Stress can lead to a significant change in the resistivity, and thus the change in the concentration of the conducting phase due to the application of pressure is

$$x - x_0 = \frac{x_0 (1 - 2v)}{E}$$

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

$$K = K_0 - B \ln \left( \frac{(1 - 2v)x_0}{E} \right) - B \ln(\sigma)$$

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 microfabrication 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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