



# High-temperature piezoresistive C/SiOC sensors

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**Abstract.** Here we report on the high-temperature piezoresistivity of carbon-containing silicon oxycarbide nanocomposites (C/SiOC). Samples containing 13.5 vol% segregated carbon have been prepared from a polysilsesquioxane via thermal cross-linking, pyrolysis and subsequent hot-pressing. Their electrical resistance was assessed as a function of the mechanical load (1–10 MPa) and temperature (1000–1200 °C). The piezoresistive behavior of the C/SiOC nanocomposites relies on the presence of dispersed nanocrystalline graphite with a lateral size  $\leq 2$  nm and non-crystalline carbon domains, as revealed by Raman spectroscopy. In comparison to highly ordered carbon (graphene, HOPG), C/SiOC exhibits strongly enhanced  $k$  factor values, even upon operation at temperatures beyond 1000 °C. The measured  $k$  values of about  $80 \pm 20$  at the highest temperature reading ( $T = 1200$  °C) reveal that C/SiOC is a primary candidate for high-temperature piezoresistive sensors with high sensitivity.

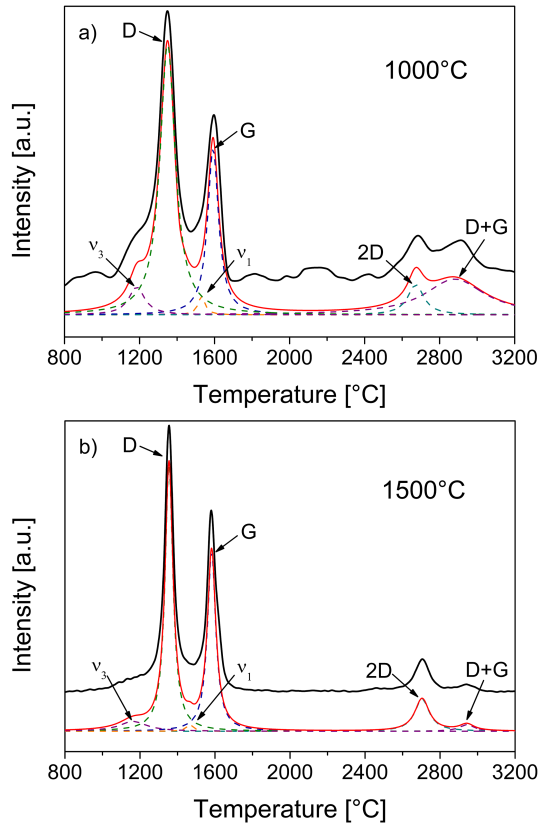
## 1 Introduction

The improvement of combustion processes relies on the exact control of the compression–combustion–exhaust cycles and thus there is a stringent need for pressure sensors with high sensitivity, low response time, high bandwidth of response and outstanding stability at high temperatures and aggressive environments. However, commercially available piezoresistive sensors, which are usually based on semiconductors or polymer composites, are limited by their low thermal stability in air (Kanda and Suzuki, 1991). Recently, polymer-derived ceramics (PDCs) such as silicon oxycarbides (C/SiOC) or silicon carbo(oxy)nitrides (C/SiCN, C/SiOCN) have been shown to combine piezoresistivity (Riedel et al., 2010; Zhang et al., 2008; Terauds et al., 2010) with outstanding temperature and oxidation stability (Riedel et al., 1995, 1996). Hence, they are promising candidates for future high-temperature pressure sensors. Concerning their structural features, PDCs can be described as amorphous and intrinsically nanoheterogeneous materials. The microstructure of C/SiOC with high carbon content has been described as a interpenetrating network of silica and carbon (Papendorf et al., 2013).

In the following, the results of temperature-dependent investigations of the  $k$  factor and of Raman spectroscopic studies are presented for a C/SiOC nanocomposite (13.5 vol% C) as clear experimental evidence for the intimate relationship between the carbon microstructure and the piezoresistive behavior of C/SiOC.

## 2 Experimental procedure

The polymeric precursor (poly(methylsilsesquioxane), PMS MK, Wacker AG, Munich, Germany) was cross-linked at 250 °C for 2 h, pyrolyzed at 900 °C for 2 h under flowing argon and subsequently ball-milled and sieved to a particle size  $< 100 \mu\text{m}$ . The sieved powder was hot-pressed at 1500 °C (30 MPa, Ar atmosphere, dwell 30 min) to obtain dense C/SiOC monoliths. Raman spectra were recorded with a Horiba HR800 micro-Raman spectrometer (Horiba JobinYvon, Bensheim, Germany) equipped with an Ar laser (514.5 nm). The measurements were performed by using a grating of  $600 \text{ g mm}^{-1}$  and a confocal microscope (magnification  $100 \times$  NA 0.9 – numerical aperture) with a  $100 \mu\text{m}$  aperture, giving a resolution of 2–4  $\mu\text{m}$ . The laser power (20 mW) was attenuated by using neutral density filters; thus,



**Figure 1.** Raman spectra of C/SiOC (13.5 vol% C) at 1000 (a) and 1500 °C (b). Dashed lines represent the deconvoluted spectra.

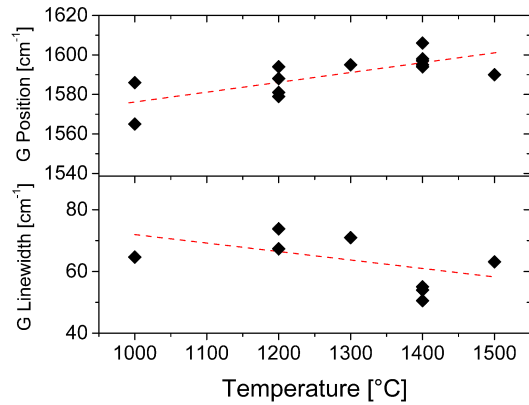
the power on the sample was in the range from 6  $\mu$ W to 2 mW. C/SiOC samples were placed in a cylindrical furnace allowing for resistivity measurements of up to 1500 °C. After achieving the desired temperature, the uniaxial load was applied by a mechanical testing machine (Model 5565, Instron Corp., Canton, MA, USA) using alumina rods as extensions. The resistivities of the loaded and unloaded samples, respectively, were calculated from the observed voltage changes and the applied currents.

### 3 Results and discussion

Piezoresistive materials are commonly classified by their  $k$  factor (gauge factor), which is defined as the change of the sample resistivity with applied stress:

$$k = \frac{Y}{R_0} \cdot \frac{\Delta R}{\Delta \sigma}, \quad (1)$$

with  $Y$  being the Young modulus ( $Y = 85$  GPa for C/SiOC; Papendorf et al., 2013),  $R_0$  the resistivity of the stress-free sample,  $\Delta \sigma$  the applied mechanical load and  $\Delta R$  the change in the resistivity upon applying the mechanical load. As shown below, C/SiOC containing 13.5 vol% of dispersed carbon exhibits  $k$  values of  $\approx 10^2$  in the temperature range

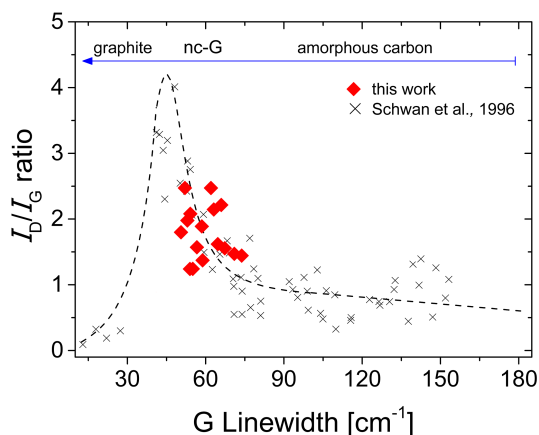


**Figure 2.** G position and linewidth as a function of sample preparation temperature.

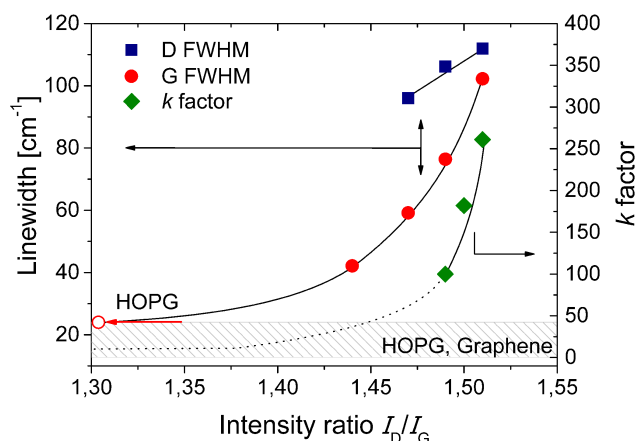
from 1000 to 1200 °C. The  $k$  factor decreases with increasing temperature, indicating a direct correlation with activated electronic transport. The Arrhenius plot provides an activation energy of  $\geq 0.3$  eV for  $k$ . A similar behavior has been observed for C/SiOCN nanocomposites containing 8.5 vol% segregated carbon (Terauds et al., 2010). However, the two composites differ with respect to the magnitude of  $k$ . Rather high  $k$  values ( $k \approx 10^3$ ) have been reported for C/SiOCN in the temperature range  $700 < T < 1000$  °C. We note that the C/SiOCN composite has a lower carbon content than our sample and, accordingly, a higher resistivity and a higher  $k$ . In the following we present Raman data of the carbon phase of C/SiOC and combine them with the piezoresistivity results to provide evidence that the piezoresistive effect is linked to the microstructure of the carbon phase, notably its disordered non-crystalline part.

#### 3.1 Raman spectroscopy

Raman spectroscopy is a powerful method to characterize the various types of carbon, providing information about the degree of ordering of the carbon atoms, ranging from perfectly ordered  $sp^2$ -bonded carbon to less ordered non-crystalline carbon (Ferrari and Robertson, 2000; Dresselhaus et al., 2008; Pimenta et al., 2007). In graphitic materials, the Raman spectrum is dominated by two strong features: the G mode at  $1581 \text{ cm}^{-1}$  and the D mode at  $1350 \text{ cm}^{-1}$ . The G mode involves in-plane bond-stretching of  $sp^2$  carbon ( $E_{2g}$ -symmetry) and is, together with its second harmonic mode (2-D), the only mode with significant intensity in graphene (two-dimensional single layer of graphite). Disordered carbon materials contain additional bands in their first-order Raman spectrum whose origin is still debated in literature. For example, the D band has been recently attributed to double resonant Raman scattering, questioning the assumption that it is strictly related to aromatic rings (Thomsen and Reich, 2000; Saito et al., 2001).



**Figure 3.** Ratio  $I_D / I_G$  vs. linewidth of G. The dashed line is a guideline for the eye taken from literature (Schwan et al., 1996). Increasing graphitization from amorphous carbon to nanocrystalline graphite (nc-G) and graphite is indicated by the arrow at the top.



**Figure 4.** Correlation of Raman and piezoresistivity data for C/SiOC (13.5 vol% C). The dashed area represents literature values for  $k$  and Raman linewidth of highly ordered carbon (HOPG, graphene).

An often used method to determine the degree of order in graphitic-like materials is to assess the intensity ratio  $I_D / I_G$  of the D and G bands. The Raman spectra of C/SiOC samples prepared at 1000 and 1500 °C and rapidly cooled down to freeze the microstructure are shown in Fig. 1. The spectrum for C/SiOC at 1000 °C reveals high-intensity D and G bands, less intense 2-D and D + G bands (the second harmonics), and weak  $\nu_3$  and  $\nu_1$  bands at 1180 and 1520  $\text{cm}^{-1}$ . We assign the latter peaks to polyolefinic chains following Ferrari and Robertson (2004). With increasing temperature, the  $\nu_1$  peak is shifted to lower wave lengths, induced through chain growth. A comparison of the spectra recorded for the samples prepared at 1000 and 1500 °C indicates a clear tendency of ordering of the segregated carbon with increasing temperature, as  $I_D / I_G$  decreases. In line with this result, the

linewidth (full width at half maximum, FWHM) of G narrows by  $\approx 15 \text{ cm}^{-1}$  and the G position shifts by  $\approx 25 \text{ cm}^{-1}$  (Fig. 2). The Raman data suggests that  $\text{sp}^2$  domains associated with the G band are progressively aligned yielding nanocrystalline graphite. Similarly, the polyolefinic structures represented by the  $\nu_3$  and  $\nu_1$  bands may be integrated into the aromatic domains by, e.g., a Diels–Alder reaction, explaining the observed decrease of the  $\nu_3$  and  $\nu_1$  bands (see Fig. 1). However, a non-crystalline part still remains, since we do not see a substantial change in the intensity of the D line. Thus, carbon appears to remain dispersed in C/SiOC, the main change in the microstructure being the progressive formation of nanocrystalline graphite.

The assignment to nanocrystalline graphite is confirmed by the observed range of  $I_D / I_G$  values ( $1.2 < I_D / I_G < 2.5$ ) for all samples prepared at 1000–1500 °C. According to Ferrari and Robertson (2000) the lateral domain size can be derived from  $I_D / I_G$  by the following equation:

$$\lambda \frac{I_D}{I_G} = C'(\lambda) \cdot L_a^2, \quad (2)$$

yielding domain sizes of 1.5–2.0 nm for C/SiOC (13.5 vol% C). The Raman data of the graphitization process of carbon materials (amorphous carbon  $\rightarrow$  graphite) has been summarized in literature (Schwan et al., 1996). Figure 3 presents the comparison of our data with literature. Evidently, the Raman features of carbon in C/SiOC correspond to those of the nanocrystalline carbon.

### 3.2 Piezoresistivity

The Raman data presented above have shown that both crystalline and non-crystalline carbon exists in C/SiOC and that their fractions depend on the preparation conditions. Considering carbon being primarily responsible for the piezoresistive behavior of C/SiOC, a close correlation between the Raman data and the gauge factor should be observable. We therefore perform piezoresistive measurements on samples with the same  $I_D / I_G$ , i.e., samples with the same carbon microstructure.

Figure 4 summarizes the results of the Raman and piezoresistivity measurements. As it can be seen in Fig. 4, the  $k$  factor and the linewidths of D and G follow the same trend, i.e., both increase with increasing  $I_D / I_G$ . For the sake of comparison, the Raman linewidths and  $k$  factors of HOPG and graphene available in the literature have been included (shaded area). HOPG and graphene are extended, highly ordered  $\text{sp}^2$  materials with narrow linewidth and low  $k$  values due to small amounts of defects (grain boundaries dislocations, dangling bonds, etc.). C/SiOC is far less ordered. The non-crystalline carbon content appears to determine the  $k$  factor enhancement. Values of  $k > 100$  mark C/SiOC as a promising piezoresistive sensor material. Its most important advantage relies on its very high temperature stability in air because of the frozen-in microstructure. To our knowledge,

only very few piezoresistive materials are available for elevated temperature ( $250 < T < 1000^\circ\text{C}$ ) (Fraga et al., 2012; Gregory et al., 2002). Piezoresistive sensors for operations at temperatures even above  $1000^\circ\text{C}$  may be realized with composites C/SiOX ( $X = \text{O}, \text{N}$ ). However, their feasibility as piezoresistive sensors for the daily use has to be proven by further work.

#### 4 Conclusions

C/SiOC nanocomposite materials have been investigated by Raman spectroscopy of quenched samples ( $1000 < T < 1500^\circ\text{C}$ ) and stress-dependent resistivity measurements (1–10 MPa) in the temperature range of  $1000 < T < 1200^\circ\text{C}$ . The observed values of the  $k$  factor (of the order of  $10^2$ ) are significantly higher than those of well-ordered carbon and decrease with increasing temperature, indicating a direct correlation with activated electronic transport ( $E_A \geq 0.3 \text{ eV}$  for  $k$ ). The comparison of the Raman and piezoresistivity data reveals that the piezoresistive effect in C/SiOC (13.5 vol% C) is mainly determined by the non-crystalline/defective carbon content.

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