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# Quantitative Raman Analysis of Free Carbon in Polymer-Derived Ceramics

Tao Jiang,[*,‡] Yansong Wang,[§] Yiguang Wang,[*,¶] Nina Orlovskaya,[*,‖] and Linan An[*,†,‡,‖]

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

[§]Optical Tech Research Center, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science, Changchun 130032, China

[¶]National Key Laboratory of Thermostructure Composite Materials, Northwestern Polytechnical University, Xi'an, China

[‖]Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, Florida 32816, USA

**Nanosized carbon clusters self-formed in polymer-derived ceramics (named free carbon) play a key role in determining the properties of the materials. However, it is difficult to quantitatively measure the concentration of the free carbon. Lack of this information restricts the understanding of the properties of the materials. In this paper, we report a Raman spectroscopy-based quantitative method to measure the free carbon concentration by using silicon as an external reference. We demonstrate that the technique provides a simple and reliable way for the carbon content quantification.**

## I. Introduction

Recently, amorphous silicon-based ceramics were synthesized by thermal decomposition of polymeric precursors.[1] This new class of materials, named polymer-derived ceramics (PDCs), has attracted extensive attention due to their unusual structures/properties and potential applications.[2–5] One unique structural feature of PDCs is that they always contain a certain amount of free carbon, formed spontaneously during pyrolysis.[6] Previous studies suggested that these nanoscaled free carbon clusters play a key role in determining the properties of PDCs. For example, the conduction mechanism of PDCs strongly depends on the concentration of the carbon clusters,[7–9] varying from a tunneling percolation mechanism for materials with a high free carbon concentration to an amorphous semiconducting mechanism for materials with a low free carbon concentration. The free carbon is also responsible for the high-temperature thermal stability of the materials.[10]

While free carbon clusters were widely observed in PDCs, quantitatively measuring their concentration has not been reported. Transmission electron microscopy (TEM) can only be used to observe these carbon clusters within relatively small areas,[11] but is not suitable for large-scale quantitative measurements. X-ray diffraction is also not suitable for such measurements due to the amorphous nature of the materials. Electron paramagnetic resonance has been used to determine the concentration of the free carbon by measuring the carbon-dangling bond concentration.[12] However, the two concentrations have no direct relationship. The lack of quantitative information on the free carbon concentrations drastically limits the understanding of the properties of PDCs in detail.

In this paper, we report a Raman spectroscopy-based method for quantitative measurements of free carbon concentrations within PDCs. The method uses silicon as an external reference. First, a calibration curve is obtained by measuring the relationship between the concentration ratio of silicon to carbon and the Raman band intensity ratio of the two materials. The calibration curve is then used to obtain free carbon concentrations in PDCs by analyzing the Raman band intensity ratio of silicon to PDCs. The average size of the free carbons is also estimated from the Raman intensity ratio of D to G bands.

## II. Quantitative Raman Analysis

The intensity of the Raman band, $I$, of a given species can be expressed as[13]

$$I = k(v)A(v)J(v)CI_o(v)^4 \quad (1)$$

where $k(v)$ is a constant related to the spectrometer, $A(v)$ the self-absorption of the medium, $J(v)$ a molar scattering parameter, $C$ the concentration of the species responsible for the scattering, $I_o$ the intensity of the incident beam, and $v$ the frequency of the incident radiation. Equation (1) cannot be directly used to measure the concentration of the species because the constants associated with the materials are usually difficult to obtain. More importantly, Raman intensity is sensitive to the surface conditions of the sample; thus it can vary significantly from sample to sample, even when they share the same composition.

However, quantitative Raman analysis can be performed by using an external reference. From Eq. (1), Raman signals obtained from the sample containing the external reference can be expressed as

$$\frac{I_r}{I_s} = K\frac{C_r}{C_s} \quad (2)$$

where $I_r$ and $I_s$ are respective Raman band intensities of the reference and the species to be measured; $C_r$ and $C_s$ are re-

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*Member, The American Ceramic Society.
†Author to whom correspondence should be addressed. e-mail: lan@mail.ucf.edu

spective concentrations of the reference and the species. The prefactor $K$ is only related to the properties of the species and the reference; thus it should be a constant for a given species–reference system. Note that because both the species and the reference are in the same sample, $K$ is no longer affected by the surface conditions of the sample. It is seen from Eq. (2) that if $K$ is known, the concentration of the species can be calculated by measuring the relative Raman band intensities from a sample containing a known amount of reference.

For a given species–reference system, $K$ can be determined experimentally. This can be simply done by measuring the relative Raman band intensities from the sample of the known species-to-reference ratio. $K$ can also be determined graphically based on Eq. (2) by measuring relative Raman band intensities from a set of samples with different species-to-reference ratios.

## III. Experimental Procedure

In this study, we use silicon powder (NP-Si-P50, MTI Corporation, Richmond, CA) as the external reference because it has a strong and sharp Raman signal. In order to obtain the calibration curves, the silicon powder is mixed with pure carbon (graphite) powder (633100, Sigma-Aldrich Corp., St. Louis, MO) at different volume ratios using high-energy ball milling (8000M-115, Spex Certiprep Group, Metuchen, NJ) for 40 min. The obtained powder mixtures are then pressed into disks of 12.5 mm in diameter and 3 mm in thickness. The Raman spectra are obtained for the disks using Renishaw invia Raman microscopy (Renishaw Inc., Gloucestershire, UK). The excitation source used is the 532 nm line of a silicon-solid laser, and the size of the focused laser beam is $\sim$10 μm. In order to minimize the measurement error as a result of a possible nonhomogeneous mixture, at least 20 Raman spectra are obtained for each disk from sites randomly selected.

The PDC tested in this study is synthesized using a commercially available liquid-phase polysilazane (Ceraset, Kion, Huntingdon Valley, PA) as a precursor. First, Ceraset is mixed with 4 wt% of dicumyl peroxide. The mixture is then solidified by heat treatment at 150°C for 30 min in pure $N_2$. The solid is crushed into powder using high-energy ball milling for 40 min, and then pyrolyzed in a flow of ultrahigh-purity nitrogen at 1300°C for 4 h to convert it into an amorphous silicon carbonitride (SiCN) ceramic powder of $\sim$1 μm in diameter.[14] The obtained ceramic powder is mixed with the silicon powder at different volume ratios using high-energy ball milling for 40 min. The mixtures are then pressed into disks. Raman spectra are then obtained for these disks using the same procedure and parameters described above.

## IV. Results and Discussion

Figure 1 shows typical Raman spectra obtained for the pure silicon powder, the pure carbon powder, and the mixture of the silicon and carbon powders. As is expected, the positions and curve shapes of Raman signals for both silicon and carbon in the mixture remain the same, as they are in free-stand forms. This is the first sign that the silicon could be a good reference for measuring the concentration of free carbons.

The intensities of Raman signals are represented by the area underneath the bands (Fig. 1). For carbons, the intensity is the sum of the area underneath both the G and D bands. Figure 2 shows the intensity ratio of silicon to carbon Raman bands as a function of the volume ratio of the two materials (because silicon and carbon are the only two components of the mixture, the volume ratio of the two is equal to their volume fraction ratio). It is not a surprise that the signal ratio and the volume fraction ratio exhibit a well-defined linear relationship, as predicted by Eq. (2). Such a well-defined linear relationship is also indicative that our measurements are accurate. The $K$ factor for the silicon–carbon system is equal to 0.0164, as calculated from the data presented in Fig. 2.

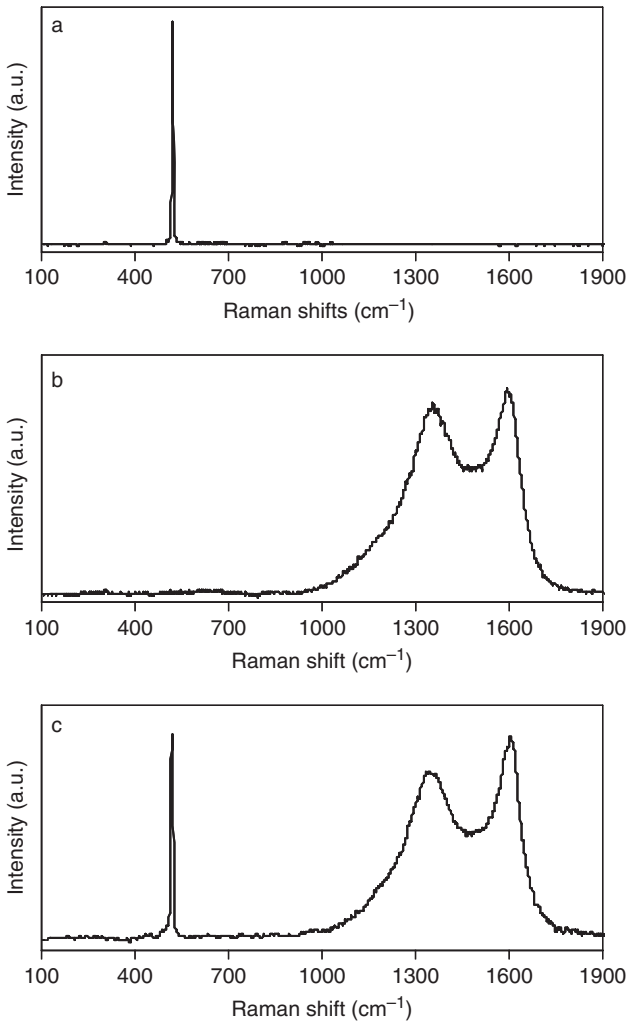


**Fig. 1.** Raman spectra of (a) the pure silicon reference, (b) pure graphite powder, and (c) the silicon–carbon mixture with a volume ratio of 2:1.

To measure the free carbon concentration in amorphous SiCN, silicon powder is mixed with the SiCN powder in known proportions. The typical Raman spectra of the SiCN powder and the mixture are shown in Figs. 3(a) and (b), respectively. The spectrum of the SiCN contains only two bands, belonging to the D and G bands of free carbon. The position and shape of the Raman bands for the SiCN powder in the mixture are the same as for pure SiCN.

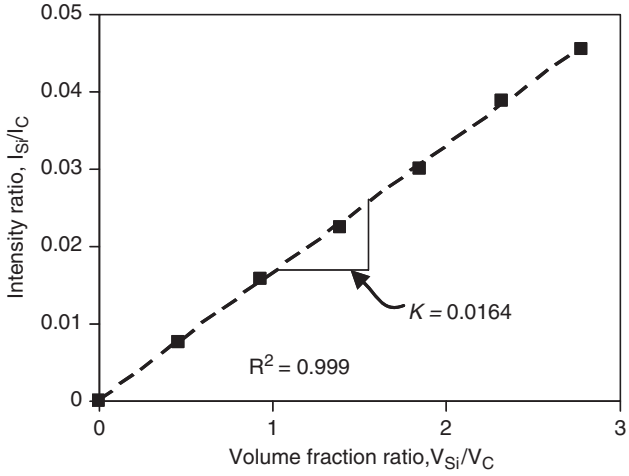


**Fig. 2.** A plot of the Raman band intensity ratio of Si to C as a function of the volume ratio of Si to C.

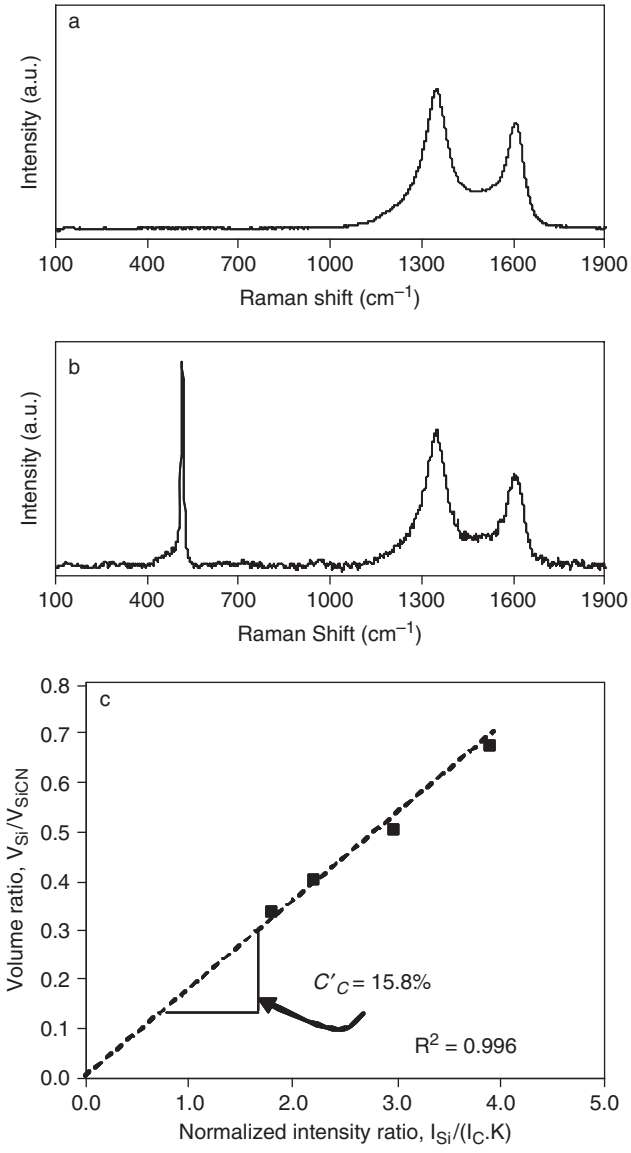


**Fig. 3.** (a, b) Typical Raman spectra obtained from the silicon carbonitride (SiCN) powder and the silicon–SiCN mixture with a volume ratio of 1:1. (c) Plot of the silicon to SiCN volume ratio as a function of the normalized silicon to SiCN Raman intensity ratio.

The SiCN contains a certain amount of the free carbon, in which the volume fraction, $C'_C$, is

$$C'_C = \frac{V}{V_{SiCN}} \tag{3}$$

where $V_C$ is the volume of the free carbon in the SiCN and the $V_{SiCN}$ volume of the SiCN (including that of the free carbon). The respective volume fractions of the free carbon and the silicon powder in the silicon–SiCN mixture are

$$C_C = \frac{V_C}{V_{SiCN} + V_{Si}} \tag{4a}$$

$$C_{Si} = \frac{V_{Si}}{V_{SiCN} + V_{Si}} \tag{4b}$$

where $V_{Si}$ is the volume of the reference silicon within the mixture. According to Eqs. (2) and (4), we have

$$\frac{I_{Si}}{I_C} = K\frac{C_{Si}}{C_C} = K\frac{V_{Si}}{V_C} \tag{5}$$

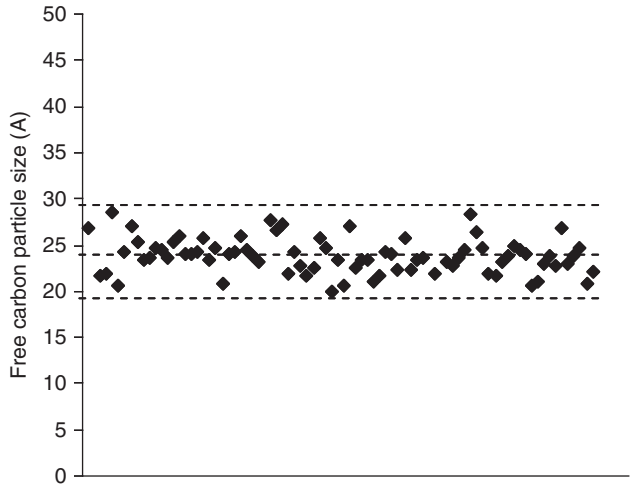


**Fig. 4.** Free carbon sizes measured in the polymer-derived ceramic.

Combining Eqs. (3) and (5), we obtain

$$\frac{I_{Si}}{I_C}\frac{1}{K} = \frac{V_{Si}/V_{SiCN}}{V_C/V_{SiCN}} = \frac{1}{C'_C}\frac{V_{Si}}{V_{SiCN}} \tag{6a}$$

Rearranging Eq. (6a), we obtain that

$$\frac{V_{Si}}{V_{SiCN}} = C'_C\frac{I_{Si}}{I_C K} \tag{6b}$$

Equation (6b) suggests that the volume ratio of silicon to SiCN ($V_{Si}/V_{SiCN}$) should exhibit a linear relationship with the normalized intensity ratio $\left(\frac{I_{Si}}{I_C K}\right)$, and the slope of the curve is the free carbon concentration in SiCN to be measured. Figure 3(c) plots the $V_{Si}/V_{SiCN}$ as a function of the normalized intensity ratio. A well-defined linear relationship is obtained, as predicted by Eq. (6b). Again, such a well-defined linear relationship suggests that the measurement is highly accurate. The free carbon concentration of the SiCN is measured from the curve to be 15.8 vol%. A previous study[8] showed that this material possesses a tunneling-percolation behavior, suggesting a high free carbon concentration, which is in conformity with the current results.

The Raman spectra can also be used to estimate the diameter, $L_a$, of the carbon clusters. Tuinstra and Koening suggested that the $L_a$ is related to the relative intensity of the G and D, according to following equation[15]:

$$\frac{I_D}{I_G} = \frac{C(\lambda)}{L_a} \tag{7}$$

where $I_D$ and $I_G$ are the intensities of D and G bands, respectively; $C(\lambda)$ is a constant that depends on the wavelength of the incident beam. For the beam used in this study ($\lambda = 532$ nm), $C$ is $\sim$4.95 nm.[15–18] Figure 4 plots the diameters of the free carbon from 80 measurements. The average size of the carbon cluster is $24 \pm 2$ Å. This value is consistent with the TEM results.[11]

## V. Summary

We report a simple Raman spectroscopy-based technique to quantitatively measure the concentration of the free carbon within PDCs. Silicon powder is used as the external reference. Our results suggest that the technique is highly accurate.

## References

[1]E. Kroke, Y. L. Li, C. Konetschny, E. Lecomte, C. Fasel, and R. Riedel, "Silazane Derived Ceramics and Related Materials," *Mater. Sci. Eng.*, **26**, 97–199 (2000).

[2]S. Yajima, Y. Hasegawa, K. Okamura, and T. Matsuzawa, "Development of High-Tensile-Strength Silicon Carbide Fiber Using an Organosilicon Polymer Precursor," *Nature*, **273**, 525–7 (1978).

[3]L. An, W. Xu, S. Rajagopalan, C. Wang, H. Wang, J. Kapat, L. Chow, Y. Fan, L. Zhang, D. Jiang, B. Guo, J. Liang, and R. Vaidyanathan, "Carbon Nanotube Reinforced Polymer-Derived Ceramic Composites," *Adv. Mater.*, **16** [22] 2036–40 (2004).

[4]P. Greil, "Polymer-Derived Engineering Ceramics," *Adv. Eng. Mater.*, **2** [6] 339–48 (2000).

[5]L. Liew, W. Zhang, L. An, S. Shah, R. Lou, Y. Liu, T. Cross, K. Anseth, V. Bright, and R. Raj, "Ceramic MEMS — New Materials, Innovative Processing and Futuristic Applications," *Am. Ceram. Soc. Bull.*, **80** [5] 25–30 (2001).

[6]R. Raj, R. Riedel, and G. D. Soraru, "Introduction to the Special Topical Issue on Ultrahigh-Temperature Polymer-Derived Ceramics," *J. Am. Ceram. Soc.*, **84**, 2158–9 (2001).

[7]Y. Wang, L. Zhang, W. Xu, T. Jiang, Y. Fan, D. Jiang, and L. An, "Effect of Thermal Initiator Concentration on Electrical Behavior of Polymer-Derived Amorphous SiCN Ceramics," *J. Am. Ceram. Soc.*, **91**, 3971–5 (2008).

[8]L. Zhang, Y. Wang, Y. Wei, W. Xu, D. Fang, L. Zhai, K. Lin, and L. An, "A Silicon Carbonitride Ceramic with Anomalously High Piezoresistivity," *J. Am. Ceram. Soc.*, **91**, 1346–9 (2008).

[9]J. Cordelair and P. Greil, "Electrical Conductivity Measurements as a Microprobe for Structure Transitions in Polysiloxane Derived Si–O–C Ceramics," *J. Eur. Ceram. Soc.*, **20**, 1947–57 (2000).

[10]T. Varga, A. Navrotsky, J. L. Moats, R. M. Morcos, F. Poli, K. Müller, A. Saha, and R. Raj, "Thermodynamically Stable $Si_xO_yC_z$ Polymer-Like Amorphous Ceramics," *J. Am. Ceram. Soc.*, **90**, 3213–9 (2007).

[11]N. Janakiraman and F. Aldinger, "Fabrication and Characterization of Fully Dense Si–C–N Ceramics from a poly(ureamethylvinyl)silazane Precursor," *J. Eur. Ceram. Soc.*, **29**, 163–73 (2009).

[12]B. Hahn, R. Weissmann, and P. Greil, "Electron Paramagnetic Resonance Investigation of Carbon Distribution in SiOC Glasses," *J. Mater. Sci. Lett.*, **15**, 1243–4 (1996).

[13]J. R. Ferraro, K. Nakamoto, and C. W. Brown, *Introductory Raman Spectroscopy*, 2nd edition, Elsevier, Amsterdam, 2003.

[14]A. Dhamne, W. Xu, B. Fookes, Y. Fan, L. Zhang, S. Burton, J. Hu, J. Ford, and L. An, "Polymer–Ceramic Conversion of Liquid Polyaluminasilazanes for SiAlCN Ceramics," *J. Am. Ceram. Soc.*, **88**, 2415–9 (2005).

[15]F. Tuinstra and J. L. Koening, "Raman Spectra of Graphite," *J. Chem. Phys.*, **53**, 1126–30 (1970).

[16]A. C. Ferrari and J. Robertson, "Interpretation of Raman Spectra of Disordered and Amorphous Carbon," *Phys. Rev. B*, **61**, 14095–107 (2000).

[17]D. S. Knight and W. B. White, "Characterization of Diamond Films by Raman Spectroscopy," *J. Mater. Res.*, **4**, 385–93 (1989).

[18]M. J. Mathews, M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, and M. Endo, "Origin of Dispersive Effects of the Raman *D* Band in Carbon Materials," *Phys. Rev. B*, **59**, R6585–8 (1999). □