J|A|C|S
COMMUNICATIONS

Resolving Radial Composition Gradients in Polarized Confocal Raman Spectra of Individual 3C-SiC Nanowires

Joëlle Fréchette*[†] and Carlo Carraro

Chemical Engineering Department, University of California, Berkeley, California, 94720

Received August 16, 2006; E-mail: jfrechette@jhu.edu

Silicon carbide nanowires are being actively pursued as components for nanoelectromechanical sensors,[1] nanocatalytic elements,[2] and nano-optical circuits[3] able to operate in harsh environment, high temperature, and high power applications. Notorious challenges accompany the production of high quality SiC (polytypism, micropipes, and inclusions)[4] preventing widespread use in micro- and nanodevices. There is need to establish nondestructive characterization techniques to be employed directly with nanowire-based devices. Confocal polarized Raman spectroscopy, which has recently enabled the interrogation of individual nanometer-size specimens,[5,6] holds the promise to fulfill this need. Previous work has demonstrated the feasibility of generating axial Raman maps of nanowires to screen for crystal structure.[6] Here, we exploit peculiar effects of geometric confinement, in particular the large polarization anisotropy of the Raman signal, to screen individual 3C-SiC nanowires for gradients in chemical composition in the radial as well as axial directions. We illustrate how direct detection of bulk and surface carbonization can be achieved due to both polarization anisotropy and the high surface-to-volume ratio at the nanoscale.

The SiC nanowires were grown on Si(100) substrates. A 50-nm catalyst nickel film was deposited by thermal evaporation on the Si(100) wafer. The substrate was heated resistively in a homemade LPCVD reactor at temperatures varying between 750 and 900 °C. The nanowires were grown from a gas-phase mixture of single precursor 1,1,3,3-tetrachloro-1,3-disilabutane and hydrogen at total pressures varying between 0.5 and 1.0 Torr. After batch synthesis, the wires were dispersed on a flat Au substrate for Raman analysis under a confocal microscope suitable for the acquisition of spectra in backscattering geometry from individual nanowires, such as the specimen shown in Figure 1b (see Methods section for details). Figure 1a displays the unpolarized Raman spectrum of the nanowire shown in Figure 1b. The signal is dominated by the sharp narrow line at 797 cm^{-1}, the zone-center transverse optical phonon (TO) mode characteristic of crystalline cubic SiC. The absence of the corresponding longitudinal optical (LO) mode (expected at 972 cm^{-1}) is indicative of growth along the $\langle 111 \rangle$ direction by the selection rules for zincblende structure polar crystals.[7]

Similar to what is observed in photoluminescence,[8] the Raman signal is highest when the polarizations of both incident and scattered photons are parallel to the wire, and lowest when either (or both) are polarized perpendicular to it. In particular, depolarized Raman intensities are always suppressed by a factor of $\tau \approx (2/(\epsilon + 1))^2$ with respect to polarized Raman intensities (it is understood that the incident light is polarized parallel to the wire). The large suppression of the depolarized signal affords a greatly increased sensitivity to surface modes relative to bulk modes.[9] This happens when the ratio of the number of surface modes to the number of bulk modes per unit length[10] of the wire becomes comparable to τ, i.e. typically for wires of up to 100 nm in diameter (see Supporting Information).

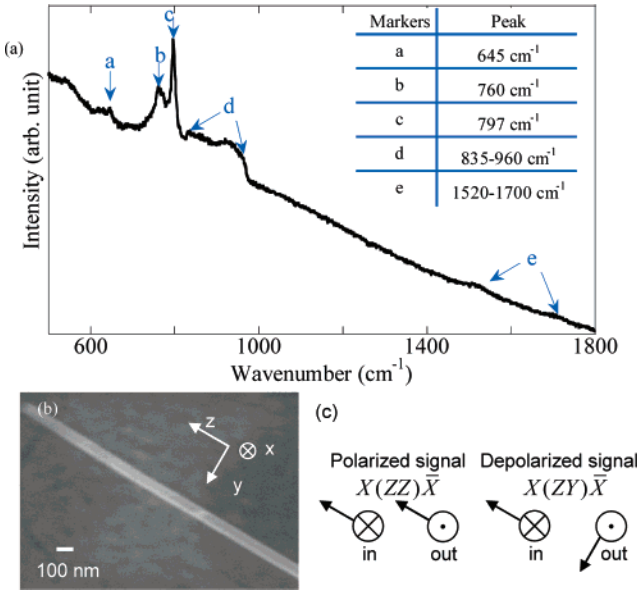

Figure 1. (a) Raman spectrum of the isolated crystalline SiC nanowire shown in (b). (b) Electron micrograph of an isolated SiC nanowire. (c) Illustration of the configuration for the acquisition of polarized and depolarized Raman spectra. The nanowire grows in the $\langle 111 \rangle$ direction.

The exquisite sensitivity of polarized scattering to surface modes allows for the detection of an outermost ordered layer of carbon in some nanowire samples. The presence of carbon is readily detected because of its large Raman cross section. Graphite is characterized by a sharp peak at 1580 cm^{-1} (G-peak), while the diamond degenerate optical phonon occurs at 1330 cm^{-1}. Nanocrystalline graphitic layers also produce a strong, broad signal between 1330 and 1400 cm^{-1} (D-peak), but with frequency that shifts with excitation energy. While most Raman spectra of isolated nanowires do not exhibit any carbon signal (such as in Figure 1a), the presence of carbon appears to be correlated with the hydrogen flow rate during synthesis. Combined with the polarization dependence of the transmission coefficient, Raman scattering can determine whether carbonization has proceeded into the bulk of the nanowire. Parts a and b of Figure 2 show the polarized and depolarized spectra of two nanowires with a strong carbon signal. Due to the sensitivity of polarized scattering to surface modes, the carbon signal in Figure 2a can be identified as being part of the bulk of the wire because the carbon signal is strongly affected by polarization (similar to the carbide signal). On the other hand, the carbon in the wire shown in Figure 2b should be on the surface because its Raman intensity is not substantially diminished in the depolarized spectra.

The presence of carbon in some nanowires (either as a surface layer or as bulk impurity) has been also characterized by spatial mapping along the axial coordinate of the wire. In these experi-

---

[†] Present address: Department of Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, MD.

10.1021/ja0656346 CCC: $33.50 © 2006 American Chemical Society

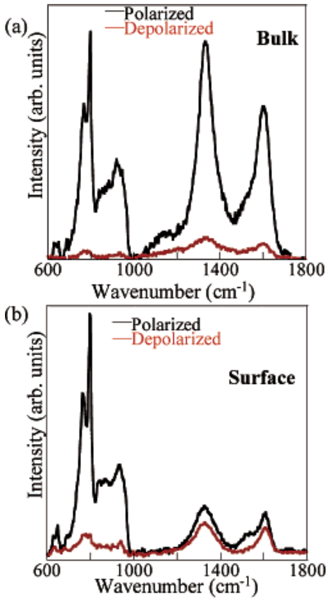

Figure 2. Dependence of the observed carbon signal on polarization in different nanowires. In (a) the carbon signal is strongly affected by polarization, suggesting bulk carbonization. In (b) the carbon signal is nearly unaffected, indicating its presence on the outside of the nanowire.

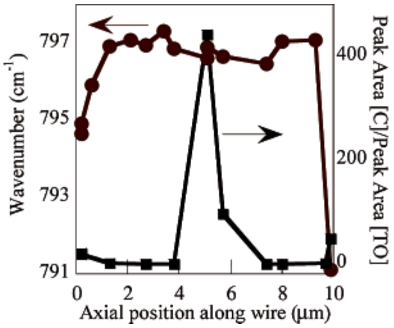

Figure 3. Effect of the carbon content on the position of the TO peak.

ments, we have observed an intriguing correlation between the intensity of the carbon signal and the shift of the SiC TO phonon from its position in an ideal cubic crystalline lattice (797 cm^{-1}) (see Figure 3). Such shift signifies a softening of the Si−C bond and may be brought about either by local lattice disorder or by localized heating of the nanowire as a result of structural disorder (lower local thermal conductivity and higher absorption coefficient). Because the softening of the elastic constants appears larger at the edges of the wire, whereas the carbon signal is higher at the center, we attribute it to thermal effect, which is enhanced at the two ends of the sample because of boundary reflection, consistent with a one dimensional (1-D) model of heat transport.

We conclude by observing that the possibility of tuning growth parameters to encourage or prevent the formation of a nanostructured carbon layer suggests a convenient way of engineering core−shell structures or simply altering the surface properties in a material, which is otherwise extremely inert and thus difficult to functionalize.[11] More generally, this work demonstrates that confocal Raman microscopy can be employed to extract chemical information in the radial direction of an individual nanowire.

Methods. Raman spectra were acquired in backscattering geometry at room temperature with a JY-Horiba Labram spectrometer, equipped with two gratings (low and high resolution, 600 and 1800 grooves/mm respectively; when using the higher resolution grating, care must be taken to correct for the large polarization anisotropy of its response around 633 nm). A HeNe laser (632.8 nm) provided the excitation line through an Olympus BX41 confocal microscope, which was focused on the sample by a 100× long working distance objective. The spot size was less than 1 μm, and the power at the sample, about 13 mW. The laser polarization could be rotated with a half-wave plate. Polarized and depolarized spectra were acquired by placing a polarization analyzer in front of the instrument slit.

Acknowledgment. This work was supported in part by the National Science Foundation.

Supporting Information Available: Detailed calculations of the scattering states of the electromagnetic field in the presence of a dielectric nanowire, showing the importance of polarization analysis; experimental results demonstrating a moderate temperature rise of the SiC nanowires during spectra acquisition. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Yang, Y. T.; Ekinci, K. L.; Huang, X. M. H.; Schiavone, L. M.; Roukes, M. L.; Zorman, C. A.; Mehregany, M. *Appl. Phys. Lett.* **2001**, *78*, 162.
(2) Zhou, W.; Yan, L.; Wang, Y.; Zhang, Y. *Appl. Phys. Lett.* **2006**, *89*, 013105.
(3) Hillenbrand, R.; Taubner, T.; Keilmann, F. *Nature* **2002**, *418*, 159.
(4) Nakamura, D.; Gunjishima, I.; Yamaguchi, S.; Ito, T.; Okamoto, A.; Kondo, H.; Onda, S.; Takatori, K. *Nature* **2004**, *430*, 1009.
(5) Jorio, A.; Pimenta, M. A.; Souza, A. G.; Samsonidze, G. G.; Swan, A. K.; Unlu, M. S.; Goldberg, B. B.; Saito, R.; Dresselhaus, G.; Dresselhaus, M. S. *Phys. Rev. Lett.* **2003**, *90*.
(6) Pauzauskie, P. J.; Talaga, D.; Seo, K.; Yang, P. D.; Lagugne-Labarthet, F. *J. Am. Chem. Soc.* **2005**, *127*, 17146.
(7) Cardona, M. *Light Scattering in Solids II: Basic Concepts and Instrumentation*; Cardona, M., Güntherodt, G., Eds.; Topics in Applied Physics, Vol. 50; Springler-Verlag: Berlin, 1982; pp 19.
(8) Wang, J. F.; Gudiksen, M. S.; Duan, X. F.; Cui, Y.; Lieber, C. M. *Science* **2001**, *293*, 1455.
(9) Fréchette, J.; Carraro, C. *Phys. Rev. B* **2006**, 161404.
(10) Englman, R.; Ruppin, R. *J. Phys. C: Solid State Phys.* **1968**, *1*, 1515.
(11) Ishikawa, T.; Yamaoka, H.; Harada, Y.; Fujii, T.; Nagasawa, T. *Nature* **2002**, *416*, 64.

JA0656346