Raman scattering on silicon nanowires: The thermal conductivity of the environment determines the optical phonon frequency

H. Scheel[a)]
Institut für Festkörperphysik, Technische Universität Berlin, 10623 Berlin, Germany

S. Reich
Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307

A. C. Ferrari, M. Cantoro, and A. Colli
Department of Engineering, University of Cambridge, Cambridge CB3 OFA, United Kingdom

C. Thomsen
Institut für Festkörperphysik, Technische Universität Berlin, 10623 Berlin, Germany

(Received 28 November 2005; accepted 26 April 2006; published online 8 June 2006)

We studied the Raman spectra of silicon nanowires as a function of excitation power for various ambient gases. For a given excitation power, we find that the gas thermal conductivity determines the wire temperature, which can be detected by a change in phonon frequency. This shows that the redshift of the optical phonon in silicon nanowires compared to bulk silicon is mainly due to the lower thermal conductivity of nanowires and an increase in laser heating. The spectra of nanowires allow distinguishing gases on the basis of their thermal conductivity. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2210292]

Nanostructures made from various materials and in various shapes (wells, wires, and dots) have attracted continuous interest for decades. The unique properties of carbon nanotubes have led to a research focus on one-dimensional systems such as nanotubes and nanowires.[1,2] Silicon is particularly interesting for nanomaterials because of our present-day technology. Despite the growing interest in Si nanowires (SiNWs) their properties are not very well understood and we lack quick, nondestructive characterization techniques. The frequency of the main Raman line of Si nanowires, for example, has been attributed to quantum confinement, laser heating, or Fano interferences.[3,4] An experiment to discriminate between these effects is still missing.

In this work we present a detailed analysis of the Raman spectrum of SiNWs and its dependence on excitation laser power. Using different ambient gases we demonstrate a direct connection between the Raman frequency shift and the thermal conductivity of the embedding gas. The exciting laser heats the wire; the steady state temperature is given by the thermal conductance of the surrounding gas. The dependence of the phonon frequency on the surrounding medium shows that local heating is responsible for a strong redshift compared to bulk Si. Moreover, gases can be distinguished by their thermal conductance.

The SiNWs used for this study were produced by vapor transport growth,[5,6] which allows high yield SiNW production. Si/SiO_2 powders are evaporated at $\sim 1200\,^{\circ}C$ in a horizontal tube furnace. The Si vapor then condenses at $\sim 800\,^{\circ}C$ on a substrate (average production ~ 10 mg per run). The average wire diameter is 15 nm, consisting of an outer SiO_2 shell of 2–3 nm and a crystalline core.[6,7] For Raman measurements the SiNWs are sonicated in isopropanol (IPA) and dispersed on Ag coated Cu substrates, establishing a small number (2–5) of SiNW spots. Each sample spot is 1–2 mm in diameter and approximately 20–50 μm thick, as observed by atomic force microscopy. Within the SiNW spot the wires are randomly arranged, most likely together with other silicon-oxide nanoparticles. A cryostat sample chamber was flushed with He, air, or Ne to measure the nanowires in different gases; we also performed low-temperature measurements using liquid He.

Macro-Raman spectra were excited with the 514 nm line of an Ar-ion laser, dispersed by a Dilor-XY800 Raman spectrometer, and detected with a charge coupled device (CCD). The exciting laser power P was measured in front of the cryostat window; ~25% laser power is lost at the windows. The nanowire Raman spectra were fitted by a Lorentzian plus a Gaussian for the low-energy tail. Phonon frequency shifts $\Delta\omega$ are determined with respect to the TO of a reference bulk silicon sample, measured under the same experimental conditions. Note that our laser power densities are one to two orders of magnitude smaller than in previous Raman studies on Si nanowires because of the macro-Raman setup.

Figure 1 shows a power series of SiNW spectra measured in 0.1 mbar of air. We observe an asymmetric Raman peak in silicon nanowires, which is redshifted and broadened compared to the optical phonon of bulk silicon.[3,4,8] Shifting and broadening increase with increasing laser power, which has been attributed to heating.[3] We confirmed an increase in temperature T by measuring the ratio between the intensities of the anti-Stokes I_{aS} and Stokes I_S Raman spectra, $I_{aS}/I_S = e^{-\hbar\omega_0/k_BT}$, where $\hbar\omega_0 = 64.6$ meV is the phonon energy and k_B is Boltzmann's constant. We corrected the Raman intensities for spectrometer sensitivity and the ω^4 dependence of the cross section.[9,10] The other corrections (absorption, refractive index, transmission, and Raman susceptibility) cancel in the investigated spectral region for bulk silicon.[11]

Figure 2(a) shows the anti-Stokes/Stokes (aS/S) ratio of SiNWs (crosses) and of bulk silicon (circles). In bulk silicon

[a)]Electronic mail: harald.scheel@physik.tu-berlin.de

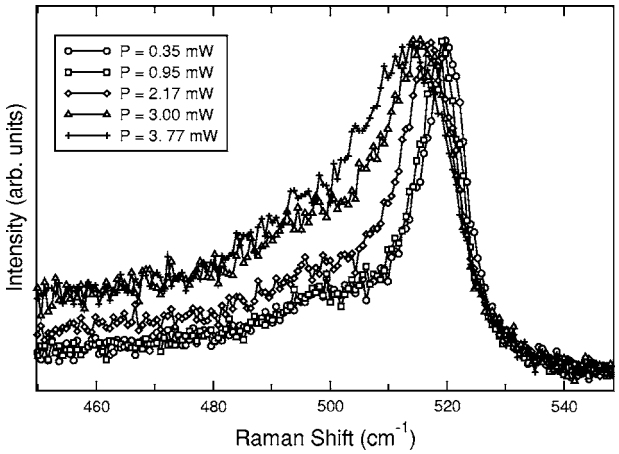

FIG. 1. Raman spectra of Si nanowires as a function of excitation power, see legend. The spectra were measured in air at a pressure $p=0.1$ mbar.

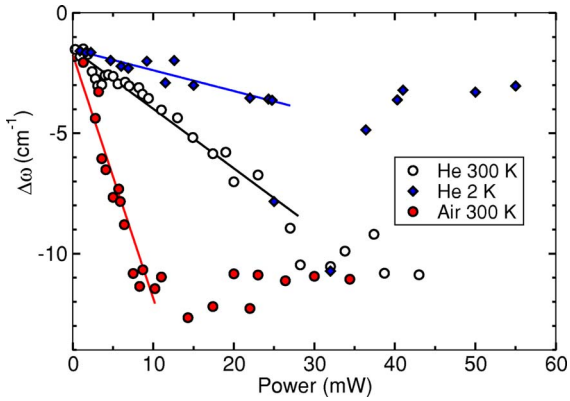

FIG. 3. (Color online) Phonon frequencies of SiNWs as a function of excitation power in He gas, air, and superfluid He. The lines are fits in the power ranges of linear frequency shift.

the ratio is constant because of the large thermal conductance of the bulk. In SiNWs, in contrast, the aS/S ratio increases with excitation power, Fig. 2(a), and the phonon frequency decreases, Fig. 2(b). Both observations agree nicely with an increase in nanowire temperature and the low thermal conductivity of silicon nanostructures.[12–14] The aS/S ratio in Fig. 2(a) changes slope around 1.5 mW, accompanied by a decrease in temperature.

The aS/S ratios lead to relatively large temperatures, compared to other methods.[3,15] For example, the aS/S ratio yields a temperature of 1750 K at $P=3.8$ mW, whereas we find $T\approx 600$ K from the phonon frequency shift in Fig. 2(b).[15] In the following we determine the temperature from the phonon frequency of silicon (Fig. 7 in Ref. 15). Phonon frequencies measured under increasing power [triangles in Fig. 2(b)] are systematically lower than the frequencies under decreasing power (crosses). Changes in slope and smaller redshifts when decreasing power were observed on all samples and for all gases. A smaller redshift after excessive heating, when returning to lower laser powers, indicates a reduced nanowire temperature. The approximate temperature

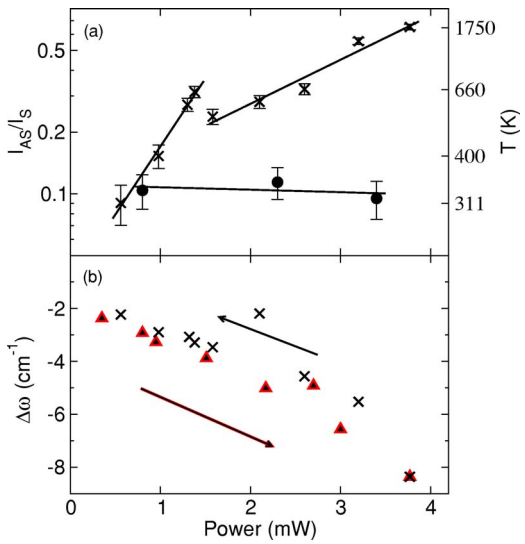

FIG. 2. (Color online) (a) Anti-Stokes/Stokes ratio of SiNWs (crosses) and bulk Si (circles). (b) Shift of the phonon frequency with respect to bulk silicon. Triangles (crosses) are peak positions for increasing (decreasing) laser power, see also arrows. The spectra were measured in air ($p=0.1$ mbar).

for a redshift of 4 cm^{-1} is 500 K, while a redshift of 2 cm^{-1} is generated by a local temperature of 400 K (Ref. 15). A lower local temperature can result from a change in thermal contact or from a reduced absorbed power. Both effects are hard to differentiate, and it is difficult to rule out one or the other. A more detailed account will be published elsewhere.

In Fig. 3 we show the SiNW phonon frequency as a function of laser power for wires in air, helium gas (300 K), and superfluid helium (2 K). Clearly, the shift in phonon frequency with laser power depends strongly on the ambient gas. We argue that this comes from local heating by the laser and the thermal conductivities of the gas or liquid. Air, with the lowest thermal conductivity, produces the strongest changes in phonon frequency for a given laser power. For helium gas the slope reduces by a factor of 4. And finally, the large thermal conductivity of liquid He results in only small changes of the phonon frequency with laser power.

The strong dependence of the phonon frequency on the surrounding gas shows that a large fraction of the heat generated by the laser dissipates through the wire surface. This is consistent with a typical wire length ~ 1 μm, which is much shorter than the diameter of the laser spot. Conductance from wire to wire is small because of the small contact areas between the wires in our unoriented sample of isolated wires.[16] Finally, only a tiny fraction of the sample is in direct contact with the substrate, since the sample thickness (20–50 μm) is again large compared to the wire length. Thus, we expect dissipation through the surrounding gas to be an important contribution to the total thermal conductivity. This is in excellent agreement with the strongly varying slopes in Fig. 3.

Above a critical power P_c the shift of the Raman peak position saturates. This is best seen in Fig. 3 for wires in air. For laser powers above $P_c=10$ mW the phonon redshift $\Delta\omega=-12$ cm^{-1} remains approximately constant. This redshift corresponds to a local temperature of ≈ 750 K. There is some statistical scatter in the measured peak positions by up to 1 cm^{-1}. P_c depends on the thermal conductivity of the gas; the higher the conductivity, the larger the critical power. Neglecting the liquid He measurements, we always observed the saturation of the redshift for comparable temperatures or redshifts.

The reduced slope for $P>P_c$ in Fig. 3 can either be due to an increase in the thermal conductivity of the Si nanowires

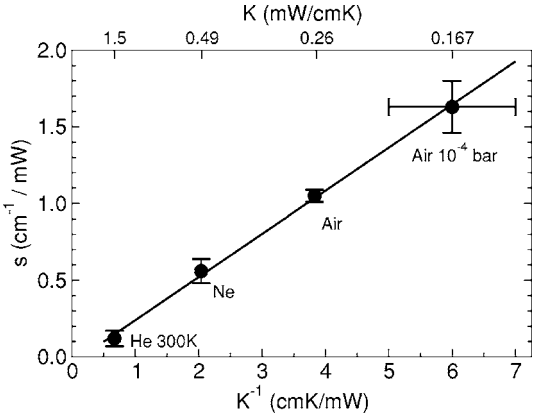

FIG. 4. Slope s of the SiNW frequency shift with excitation power vs inverse of the thermal conductivity K^{-1} of He, Ne, and air at 300 K (see labels). Thermal conductivities were taken from Ref. 19. Error bars are standard deviations when determining s from a linear regression.

or a more effective heat transport away from the wires. We assume that the morphology of our sample is not drastically changed at high laser power, because all changes are fully reversible in the power range shown in Fig. 3. Lysenko *et al.*[17] reported an increasing thermal conductivity in mesoporous silicon films with increased oxidization. A similar laser-induced oxidation of our nanowires could lead to a change in slope in Fig. 3. An increased oxidation at higher laser powers is unlikely to be the origin of the observed saturation, though, because we also observe it in helium atmosphere, see Fig. 3 (open black circles). Another possible origin of the saturation in Fig. 3 is a change of laminar to turbulent gas flow, which is more effective in heat transport. However, the amount of heat carried away by convection must still be proportional to the temperature gradient between the wire and the surrounding gas, i.e., we expect a change in slope, but not a vanishing slope. In order to understand the saturation above P_c further investigations will be performed.

We now evaluate the power dependence of the phonon frequency in the low-power region (<4 mW), where the frequency shift is proportional to the incident laser power. Around 300 K, the slope s of the Raman frequency versus power is proportional to the change in temperature.[15] Using the steady state solution[18] for the temperature difference ΔT between a heat source (laser heated wire) and a drain (gas) the slope s can be written as

$$s \propto -\frac{\Delta T}{\eta} \propto \frac{1}{K}, \tag{1}$$

where η is the generated heat energy per unit volume and time, and K is the thermal conductivity. Thus, the slopes s in Fig. 3 are expected to be proportional to the inverse of the thermal conductivities K^{-1}. In Fig. 4 we plot s over K^{-1} and find a linear dependence in excellent agreement with our model. For a given laser power $P<P_c$, the nanowire temperature and Raman peak position are determined by the thermal conductivity of the gas surrounding the wire. The dependence of the Raman frequency on excitation power could be used to measure K and hence identify different gases, as it is done in thermal conductivity gas sensors.

In conclusion, we demonstrated that the Raman spectrum of Si nanowires depends on the medium around the wires, which is a consequence of the low thermal conductivity of Si nanostructures. We showed that the measured phonon frequency is related to the thermal conductivity of the gas around the wire. Our findings are important for characterizing nanowires and provide a way for measuring the thermal conductivity by Raman scattering.

A.C.F. acknowledges funding from The Royal Society and The Leverhulme Trust.

[1] S. Reich, C. Thomsen, and J. Maultzsch, *Carbon Nanotubes: Basic Concepts and Physical Properties* (Wiley, New York, 2004).
[2] D. D. D. Ma, C. S. Lee, F. C. K. Au, S. Y. Tong, and S. T. Lee, Science **299**, 1874 (2003).
[3] S. Piscanec, M. Cantoro, A. C. Ferrari, J. A. Zapien, Y. Lifshitz, S. T. Lee, S. Hoffmann, and J. Robertson, Phys. Rev. B **68**, 241312(R) (2003).
[4] R. Gupta, Q. Xiong, C. K. Adu, U. J. Kim, and P. C. Eklund, Nano Lett. **3**, 627 (2003).
[5] R. Q. Zhang, Y. Lifshitz, and S.-T. Lee, Adv. Mater. (Weinheim, Ger.) **15**, 635 (2003).
[6] A. Colli, A. C. Ferrari, S. Hofmann, J. A. Zapien, Y. Lifshitz, S. T. Lee, S. Piscanec, M. Cantoro, and J. Robertson, AIP Conf. Proc. **723**, 445 (2004).
[7] S. Hofmann, C. Ducati, R. J. Neill, S. Piscanec, A. C. Ferrari, J. Geng, R. E. Dunin-Borkowski, and J. Robertson, J. Appl. Phys. **94**, 6005 (2003).
[8] N. Fukata, T. Oshima, K. Murakami, T. Kizuka, T. Tsurui, and S. Ito, Appl. Phys. Lett. **86**, 213112 (2005).
[9] M. Cardona, *Light Scattering in Solids II* (Springer, Berlin, 1982).
[10] S. Reich, A. C. Ferrari, R. Arenal, A. Loisea, I. Bello, and J. Robertson, Phys. Rev. B **71**, 205201 (2005).
[11] A. Compaan and H. J. Trodahl, Phys. Rev. B **29**, 793 (1984).
[12] N. Mingo, Phys. Rev. B **68**, 113308 (2003).
[13] D. Li, Y. Wu, P. Kim, L. Shi, P. Yang, and A. Majumdar, Appl. Phys. Lett. **83**, 2934 (2003).
[14] M. J. Kostantinovic, S. Bersier, X. Wang, M. Hayne, P. Lievens, R. E. Silverans, and V. V. Moshchalkov, Phys. Rev. B **66**, 161311 (2002).
[15] M. Balkanski, R. F. Wallis, and E. Haro, Phys. Rev. B **28**, 1928 (1983).
[16] To estimate an upper boundary for the fraction of the nanowire surface in contact with other wires we consider a 1 μm long wire with a diameter of 15 nm. We assume the wire to be in contact with 20 other wires (one contacting wire of 15 nm diameter every 50 nm) and a contact area $(15\ \text{nm})^2$. This yields a ratio ~ 10 between the free surface area of the cylinder and the area in contact with other wires.
[17] V. Lysenko, L. Boarino, M. Bertola, B. Remaki, A. Dittmar, G. Amato, and D. Barbier, Microelectron. J. **30**, 1141 (1999).
[18] H. B. Calen, *Thermodynamics* (Wiley, New York, 1960).
[19] *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill, New York, 1972).