Phys. Status Solidi B **246**, No. 11–12, 2809–2812 (2009) / **DOI** 10.1002/pssb.200982341

physica status solidi b
www.pss-b.com
basic solid state physics

The morphology of silicon nanowire samples: A Raman study

S. Khachadorian*[,1], H. Scheel[1], M. Cantoro[2], A. Colli[3], A. C. Ferrari[2], and C. Thomsen[1]

[1] Institut für Festkörperphysik, Technische Universität Berlin, Berlin, Germany
[2] Department of Engeneering, University of Cambridge, Cambridge, UK
[3] Nokia Research Centre Cambridge UK, c/o Nanoscience Centre, University of Cambridge, Cambridge, UK

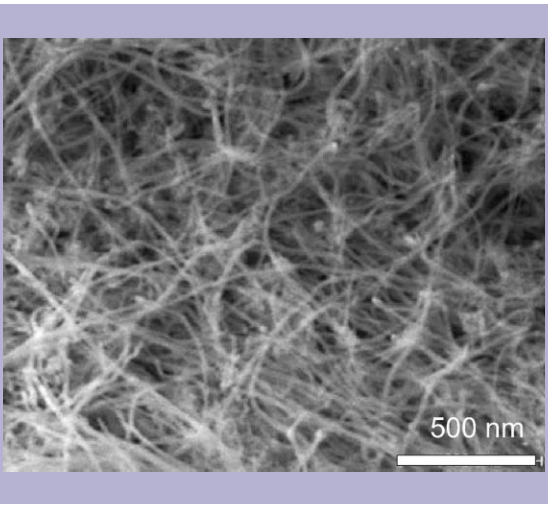
Received 25 May 2009, revised 9 October 2009, accepted 12 October 2009
Published online 18 November 2009

PACS 63.22.Gh, 78.30.Na, 78.67.Lt

---

* Corresponding author: e-mail khachadorian@physik.tu-berlin.de, Phone: +49-30-31422391, Fax: +49-30-31427705

Raman spectra of silicon nanowires (SiNWs) are studied as a function of laser excitation power and temperature. With increase in temperature and power a red-shift of the SiNWs first order optical mode is observed. At ambient conditions, the Raman shift shows a saturated behavior beyond a critical power. Similar measurements, under vacuum, rule out effects due to thermal convection as a reason for the observed saturation. We assign this to a change in sample morphology. A simulation of the SiNW peak position reveals that its temperature behavior can be explained by a four-phonon anharmonic process.



SEM image of a typical SiNWs sample. The SiNW are ~15 nm in diameter and up to a few microns long. The sample is a large bundle of SiNWs (up to 50 μm thick) with strong porosity.

1 Introduction The demand for integration of optoelectronic devices into silicon microelectronics makes the search for Si-based nanostructures, emitting light with good quantum efficiency, promising and interesting. Some initial success in getting over the indirect nature of optical transition in SiNWs encourages this research [1].

Raman spectroscopy has proven as quick nondestructive characterization technique to understand the lattice dynamics of SiNWs [2–4]. In this work we present a detailed study of the Raman spectrum of SiNWs and its dependence on excitation laser power and ambient temperature. We observe a saturation of Raman peak position in power dependent measurements [3]. We do not assign this to a change of laminar to turbulent gas flow in the environment, but we attribute it a morphology variation induced by laser heating, as confirmed by temperature dependent Raman measurements. We compare the experimental temperature-dependent Raman frequencies with those calculated with the model of Ref. [5], and find that these can be explained by four phonons anharmonic processes [2].

2 Experimental details SiNWs are grown by vapor transport [6]. This has high SiNWs yield (up to ~10 mg per run [6]). SiO powder is evaporated at ~1400 °C in a horizontal tube furnace. The Si vapor condenses at ~900 °C on a quartz substrate. The average wire diameter is 15 nm, consisting of an outer SiO_2 shell of 2–3 nm and a crystalline silicon core [6, 7]. The SiNWs are sonicated in isopropanol (IPA) and dispersed on Ag coated Cu substrates, resulting in a small number (2–5) of SiNW aggregates, each 1–2 mm in diameter. The SiNWs are randomly oriented within the aggregate. The macro-Raman-system is a Dilor-XY800 spectrometer with a charge coupled device (CCD) detector. All our data are obtained with the 514.5 nm line of an Ar^+

laser. The focused laser spot has a diameter of about 50 (m. The signal is detected in back-scattering with a spectral resolution of 1.0 cm^{-1}. For the laser power dependent measurements in vacuum and air we use an Oxford Instruments cryostat. A heating-stage cryostat (LINKAM THMS 600) is used for temperature-dependent measurements. The spectra are fitted with a Lorentzian, plus a Gaussian for the low-energy tail [3, 8].

3 Results

In order to distinguish local heating induced by the laser, from global heating due to the environment, we monitor the Raman shift and intensity under two different conditions. We vary the excitation power in the range 1–50 mW. The resulting shifts and signal strengths are plotted in Fig. 1. Starting at $\sim$517.5 cm^{-1}, the phonon frequency decreases initially at a rate ~ -0.5 cm^{-1}/mW with increase in power (black squares). Beyond a critical power $p_c \sim$10–15 mW the slope almost vanishes (0.03 cm^{-1}/mW) and remains slightly positive as reported earlier [3, 8]. In order to investigate the reversibility of this process, we then reduce the power gradually to zero (red circles). Under decreasing power, the phonon frequency returns to its original value at 517 cm^{-1}, having taken, however, a different path in the frequency–excitation power diagram. The hysteretic form is clear from the figure. The normalized Raman intensity, given by the area of the Raman signal divided by the exciting laser power, Fig. 1(b), remains constant up to the critical power when heating. Beyond p_c the intensity drops drastically (by about a factor 7) to $p = 45$ mW. On the returning branch, the intensity remains at this low level, not recovering to its initial value.

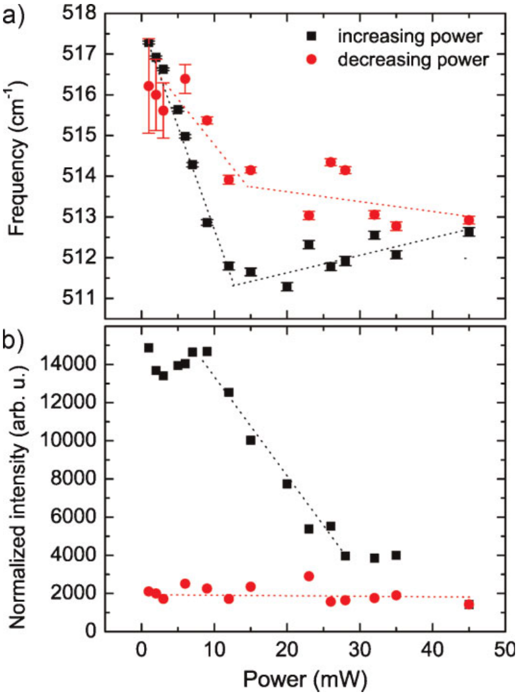


Figure 1 (online color at: www.pss-b.com) (a) SiNWs phonon frequencies as function of excitation power in air. (black solid squares) increasing power, (red solid circles) decreasing power. (b) Normalized intensities as function of power, in air. Normalized intensity is the Raman peak area divided by the laser power.

We can understand this behavior by assuming a change in morphology of the sample. Upon laser heating, the SiNW bundle could contract and move out of focus, explaining the drastic intensity decrease beyond p_c. Correspondingly, the Raman shift ceases to change, remaining at $\sim$512 cm^{-1}. Upon lowering the power, the Raman peak returns to its original frequency, but the signal strength remains weak though due to the loss of focus. The large error bars in Fig. 1(a) for the last four Raman frequencies under decreasing power show the fitting inaccuracy of the Raman frequency. Given that the Raman frequency returns to the original value, we conclude that the microscopic structure, i.e. the SiNWs diameter, remains the same. Melting and re-solidification would lead to a more bulk-like frequency (520 cm^{-1} [9]), which we can exclude. Moreover, as mentioned before, the laser spot diameter on the sample in our macro-Raman-setup is about 50 μm. The power density in this case is about 100 times smaller than in a typical Micro-Raman-setup (spot diameter about 5 μm). A laser induced local heating might also induce stress/strain to the SiNWs due to a temperature gradient. Given that on one hand our SiNWs are only a few micrometers long and on the other hand the diameter of the laser spot on the sample is 50 μm, we do not expect a strong temperature gradient on the SiNWs causing a destruction of our wires. Since the sample is not "refocused" under decreasing power, we conclude that a macroscopic morphology change occurs, which we might imagine as a vertical or sidewise contraction of the SiNW network. To confirm this, we perform power dependent measurements under increasing and decreasing power, where the laser is refocused after every measurement, so that the intensity for increase in power is equal to that under decrease in power (not presented in this paper).

We previously reported that the slope of the Raman shift *vs.* excitation depends on the surrounding gas [3, 8], since this can remove most of the heat by convective conduction, rather than by thermal contact of the SiNWs to the substrate [3]. In order to rule out differences in the gas thermal conductivity in the SiNW environment, e.g. due to onset of turbulent heat conduction, we perform our measurements also in vacuum ($p = 2 \times 10^{-6}$ mbar). Figure 2 shows that the phonon frequency shift is larger in vacuum than in air by about a factor 2, as seen previously [3]. Here, too, we observe hysteresis upon power reduction, when returning to the original Raman shift of 518 cm^{-1} at zero power. We note that the maximum difference in the hysteresis loop is $\sim$2 cm^{-1} for the measurements in air, and approximately four times larger in vacuum. From the occurrence of the hysteresis in vacuum we conclude that the change in Raman slope is not due to a change in heat convection of the surrounding gas, rather, and this is supported by the increase in hysteresis strength, we believe that the sample moves out of focus during the inhomogeneous laser heating process. The

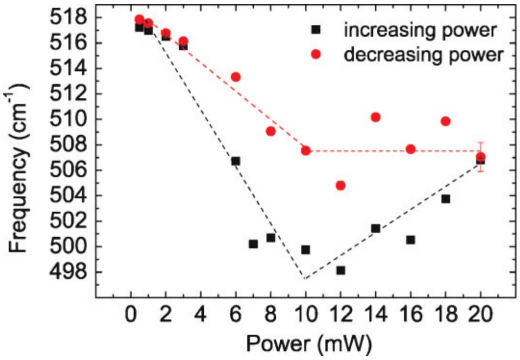


Figure 2 (online color at: www.pss-b.com) SiNWs phonon frequencies as function of excitation power in vacuum for increasing (black solid squares) and decreasing power (red solid circles).

normalized Raman intensity in vacuum, shown in Fig. 3, confirms this interpretation.

In order to further investigate the effects of heating, we place the sample in a heating stage and measure the Raman shift as a function of temperature. In this way we obtain a uniform heating, as compared to the very local laser induced heating. In order to examine the reversibility of the heating process, we measure the Raman shift and intensity for increase and decrease in temperature. Fig. 4(a) plots the peak position as a function of heating stage temperature in the 300–900 K range for increase in (black solid squares) and decrease in temperatures (red solid circles). This decreases at a rate of ~−0.02 cm/K with temperature, with no change of slope. The heating and cooling processes are reversible, when considering the peak position (no hysteresis). Any change of microscopic structure would affect this reversibility. Fig. 4(b) shows the peak intensity as a function of temperature. This decreases for increase in temperature, and the values for decrease in temperature are much lower (about a factor 3) than those for increase in temperature. This cannot be due to a microscopic structural change, given that the intensity drops both during the heating and cooling processes, but we assign this to a macroscopic change of the SiNW network. Since the Raman frequency only depends on the homogeneous temperature, this change in morphology is reflected only in a decreasing Raman intensity. In power-dependent Raman measurements, the local temperature varies, with a consequent change of morphology, resulting in the saturation and hysteresis observed in Fig. 1(a).

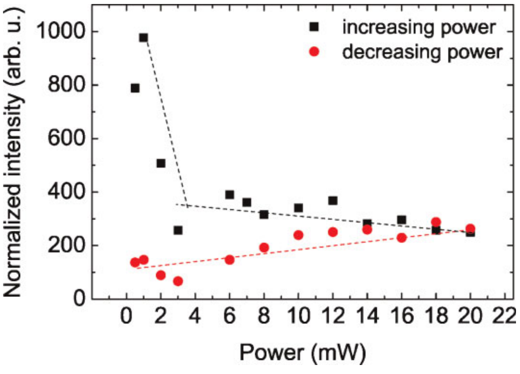


Figure 3 (online color at: www.pss-b.com) SiNWs phonon intensity as function of excitation power in vacuum for increasing (black solid squares) and decreasing power (red solid circles).

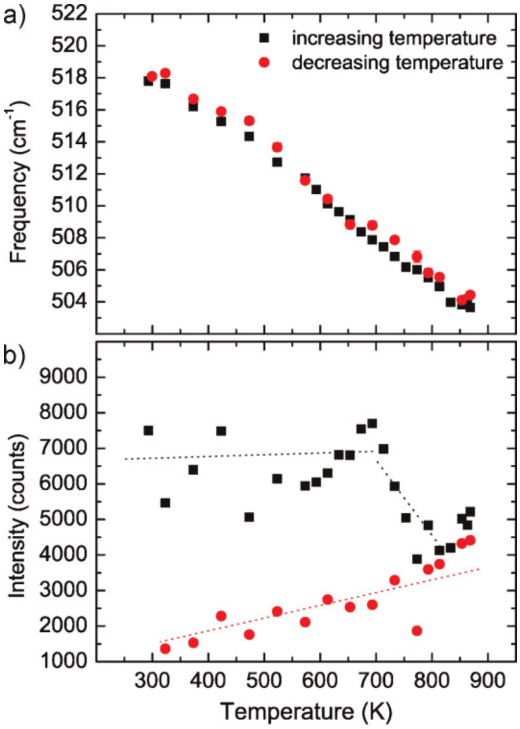


Figure 4 (online color at: www.pss-b.com) (a) SiNW phonon frequencies as function of temperature in air, measured with a heating stage for increasing (black solid squares) and decreasing temperature (red solid circles). (b) Intensity as function of temperature in air.

The temperature dependence of the Raman spectrum of bulk Si was explained by Balkanski et al. [5]. Figure 5 plots the temperature dependence for SiNWs (open circles) and bulk Si (filled black circles). Here, the solid red curves are theoretical fits using three- and four-phonon processes, as for Ref. [5]. These curves are specified by the term

$$\Omega(T) = \omega_0 + \Delta(T), \tag{1}$$

$$\Delta(T) = C\left[1+\frac{2}{e^x-1}\right] + D\left[1+\frac{3}{e^y-1}+\frac{3}{(e^y-1)^2}\right] \tag{2}$$

where $\Omega(T)$ is the peak position for varying temperature (T), ω_0 is the initial peak position, $x = \hbar\omega_0/2k_BT$, $y = \hbar\omega_0/3k_BT$. $C = -2.96$, $D = -0.174$ are constants [5]. We find that for bulk Si $\omega_0 = 526.19\,\mathrm{cm}^{-1}$, while in our SiNWs $\omega_0 = 524.57\,\mathrm{cm}^{-1}$. Indeed, the Raman frequencies of SiNWs in Fig. 5 are $1.5\,\mathrm{cm}^{-1}$ smaller than bulk Si. These are measured with 1 mW laser power, which in

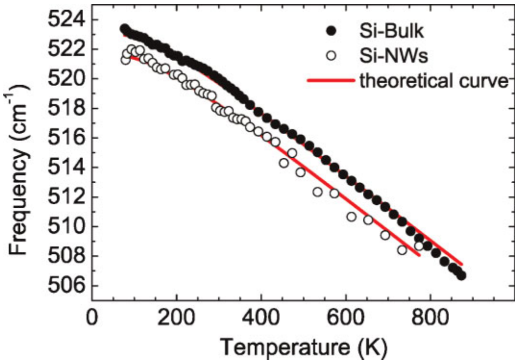


Figure 5 (online color at: www.pss-b.com) Measured and calculated frequencies of SiNWs (black open circles) and bulk Si (black solid circles) as function of temperature, controlled with a heating stage. (red lines) Fit using the Balkanski model.

SiNWs causes a red shift of about 0.5 cm^{-1} due to heating. We assign the remaining difference to an effect of phonon confinement, consistent with what we have previously detected in similar samples [2]. Indeed, by combining phonon confinement with an-harmonicity we can extract a diameter of the SiNW core consistent with that measured by transmission electron microscopy [2, 6, 7].

In conclusion, we showed that the saturation of Raman frequencies measured on a bundle of SiNWs under increasing excitation power is a consequence of morphology changes and not due to a change in convection or sample structure. Thus, using high power we can induce a macroscopic morphology change, while retaining the microscopic structure. The temperature dependence of the Raman spectra can be explained using a four-phonon anharmonic process. Phonon confinement induces a small extra downshift, for the diameters considered here.

Acknowledgements The authors wish to thank Dr.-Ing. D. Berger and Dipl.-Ing. U. Gernert from ZELMI-TU Berlin for the SEM Image. ACF acknowledges funding from the European Research Council NANOPOTS, the Royal Society, the Cambridge Integrated Knowledge Centre (CIKC), and the Cambridge–Nokia partnership.

References

[1] D. D. D. Ma, C. S. Lee, F. C. K. Au, S. Y. Tong, and S. T. Lee, Science **299**, 1874 (2003).

[2] S. Piscanec, M. Cantoro, A. C. Ferrari, A. Zapien, Y. Lifshitz, S. T. Lee, S. Hofmann, and J. Robertson, Phys. Rev. B **68**, 241312 (2004).

[3] H. Scheel, S. Reich, A. C. Ferrari, M. Cantoro, A. Colli, and C. Thomsen, Appl. Phys. Lett. **88**, 233114 (2006).

[4] A. Colli, A. Fasoli, C. Ronning, S. Pisana, S. Piscanec, and A. C. Ferrari, Nano Lett. **8**, 2188 (2008).

[5] M. Balkanski, F. Wallis, and E. Haro, Phys. Rev. B **28**, 1928 (1983).

[6] A. Colli, A. Fasoli, P. Beecher, P. Servati, S. Pisana, Y. Fu, A. J. Flewitt, W. I. Milne, J. Robertson, C. Ducati, S. De Franceschi, S. Hofmann, and A. C. Ferrari, J. Appl. Phys. **102**, 034302 (2007).

[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] H. Scheel, S. Khachadorian, M. Cantoro, A. Colli, A. C. Ferrari, and C. Thomsen, Phys. Status Solidi B **245**, 2090 (2008).

[9] P. A. Temple and C. E. Hathaway, Phys. Rev. B **7**, 3685 (1973).