

# Size effects on phonon localization and Raman enhancement in silicon nanotips

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**Silicon nanotip arrays exhibit a wide variety of interesting optical and electronic properties associated with their dimensionality. We here investigate the effect of size-induced changes on phonon localization and explain the enhanced Raman response. The occurrence of normally forbidden transitions in the photoluminescence spectra provides evidence for the predicted localization effect. Spatially resolved Raman spectroscopy reveals a continuous change of the silicon Raman peak position and peak width along the nanotip that is attributed to a smooth change between bulk properties at the base to size-induced phonon confinement in the apex of the nanotip. This approach allows to exclude heating effects that normally overwhelm the phonon confinement signature. The Raman spectra are in excellent agreement with the spatial correlation model and the extracted correlation length is comparable to the tip dimensions. The observed phonon confinement coincides with an enhancement of the Raman scattering efficiency at the tip apex and results in a 40-fold increase of the sample's Raman intensity compared with bulk silicon. These results provide a step toward the integration of Si based optoelectronic devices. Copyright © 2012 John Wiley & Sons, Ltd.**

**Keywords:** phonon localization; Raman spectroscopy; silicon nanotips; Raman enhancement

## Introduction

Nanostructured materials have attracted significant interest in the last decade because their properties can be fundamentally altered through control of their dimensions. Especially large effort has been devoted into research of nanostructuring silicon because of the material's immense commercial importance. It is expected that confinement effects as encountered in nano-objects can help improve the light emission efficiency of this material and open new areas of application such as high efficiency photovoltaics or LEDs. Phonon localization in nanostructured materials,<sup>[1]</sup> for example, can provide a route to relax the phonon-selection rules associated with photon emission from indirect band-gap materials and has thus been found to lead to an increase of the luminescence efficiency of silicon.<sup>[2]</sup> Raman technology has emerged as an important tool to study phonon confinement in nanostructured silicon and other materials.<sup>[3]</sup> Analyzing the effect of phonon confinement on Raman spectra quantitatively, however, is challenging because other experimental factors, such as heating or doping, usually have larger contributions to changes of the Raman response. A model system is needed that allows the comparison of nanostructured and bulk silicon to isolate the effect of size constraints on Raman spectra without interference from other parameters and thus provide a basis for a more detailed understanding.

Here we present silicon nanotips (SiNTs) as such a model system for nanostructured silicon. By dry etching high aspect ratio tips into a silicon wafer, bulk and nanoscopic properties are combined within one physical system. This combination results in unique properties such as broadband absorption<sup>[4]</sup> and high efficiency light emission.<sup>[5]</sup> We here investigate these SiNT structures by Raman spectroscopy, high resolution electron microscopy and photoluminescence spectroscopy. First, the existence of phonon localization due to size effects in the SiNTs is established. Spatially resolved Raman spectroscopy is then utilized to localize the source of phonon confinement and the contribution of the

confinement effect on the Raman response is determined experimentally. Finally, a continuous transition in optical properties from bulk to nanostructured silicon as a function of tip dimension is demonstrated. This variation in confinement is correlated with a large enhancement of the Raman intensity and results in a 40-fold enhancement of the Raman response.

## Experiment

A high-density electron cyclotron resonance plasma discharge of a silane (SiH<sub>4</sub>), methane (CH<sub>4</sub>), hydrogen (H<sub>2</sub>), and argon (Ar) gas mixture was used to etch out silicon nanotips from a bare untreated crystalline silicon wafer. First, SiC clusters were formed by the reaction of CH<sub>4</sub> and SiH<sub>4</sub> plasma. These particles were found to be uniformly distributed on the surface of the substrate and were subsequently used as etch masks. The unmasked regions were etched by Ar and H<sub>2</sub> plasma to generate nanotips. This self-masked dry etching technique was successfully applied to fabricate high-density and uniform nanotip arrays over a large area. A detailed description of the synthesis and properties of the SiNTs can be found elsewhere.<sup>[6]</sup>

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The high-resolution scanning electron microscope image shown in Fig. 1 was taken using a JEOL JSM-6500 field emission scanning electron microscope. Arrays of aligned SiNTs with a tip diameter in the range of  $\sim 5$  nm, a taper length of  $\sim 500$  nm, a base diameter of  $\sim 100$  nm, and an overall length of  $\sim 1$   $\mu\text{m}$  can be observed. Further high-resolution transmission electron microscope (HRTEM) analysis (Fig. 1(b)) showed that the surface of the as-grown nanotips is very smooth and free of nanoscale Si-particles. This indicates that any observed phonon confinement indeed originates from the Si-nanotips and not from nanocrystallites as found previously.<sup>[7]</sup>

Raman spectra were taken in a homebuilt confocal microscope setup with a 532 nm excitation source that was introduced in a Carl Zeiss Axioplan 2 microscope. Using an Epiplan Neofluar 100 $\times$  objective with a depth of focus of 0.6  $\mu\text{m}$ , the laser beam waist diameter was measured to be 1  $\mu\text{m}$ .

## Results and discussion

A first evidence for phonon confinement in the investigated sample can be found in the photoluminescence spectrum of SiNTs as shown in Fig. 2(a). The majority of peaks are also present in bulk Si and could be assigned to transverse optical and zone center ( $O_{\Gamma}$ ) phonons following Dean *et al.*<sup>[8]</sup> Another peak at 1.18 eV may be due to the absorption of an intervalley phonon

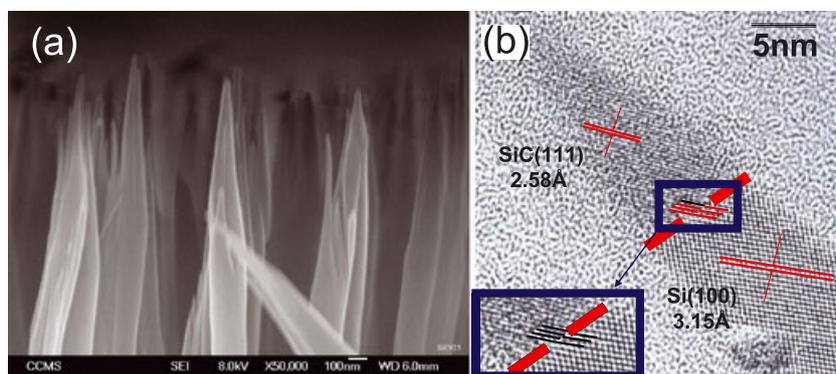
(IV<sup>a</sup>).<sup>[8]</sup> However, the exact mechanism involved in these emissions requires further examination.

The relaxation of the momentum selection rules associated with the phonon confinement will not only result in a higher photoluminescence intensity than Si bulk as reported previously<sup>[2,5]</sup> but also promote no-phonon transitions that are normally forbidden in intrinsic silicon wafer because of momentum conservation requirements. One no-phonon transition can be seen in Fig. 2(a) around 1.15 eV, which provides an indication for the occurrence of phonon confinement.

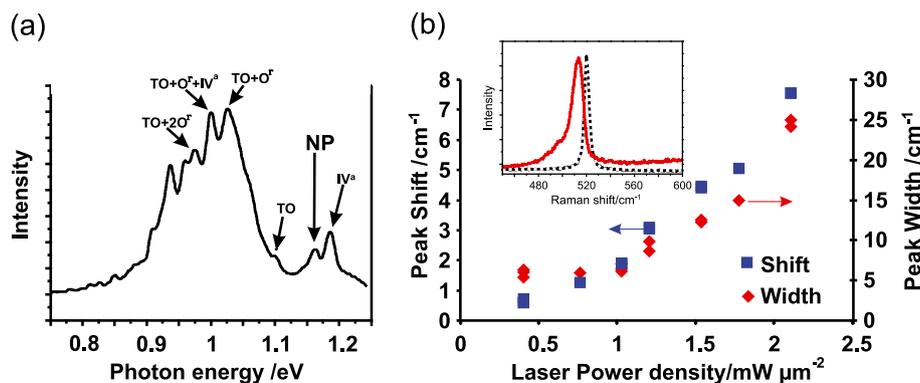
The inset of Fig. 2(b) shows the downshift and asymmetric broadening of the Si F2g Raman peak of the SiNTs (dashed line) in comparison with Si bulk (solid line). It has been demonstrated that such a downshifted phonon line may be due to the partial breakdown of the Raman selection rule attributed to phonon localization effects.<sup>[7]</sup>

This result is indicative of the effect of phonon localization only if other factors can be ruled out. Some effects like strain, high density of photogenerated electrons, or Fano resonances are not considered in the subsequent analysis because the shape of the asymmetric phonon peak does not agree with results from those experiments or the electron concentration required to justify such a shift would be unreasonably high.<sup>[9]</sup>

Another reason for the downshift, however, might be the intense local heating caused by the laser excitation.<sup>[10]</sup> To further clarify this fact shift and FWHM of the Raman silicon optical



**Figure 1.** (a) Cross-sectional SEM image of Si nanotips (SiNTs). (b) HRTEM image of a SiNT. (inset) Magnified HRTEM image of the interface between Si and SiC cap on which the lattice mismatch of Si/SiC = 4:5 can be observed.



**Figure 2.** (a) Photoluminescence spectrum of SiNT sample (514.5 nm laser excitation at 20 K), (b) downshift and broadening of the Raman F2g Si-peak as a function of incident laser power (inset) Raman spectra measured from bulk silicon (dashed line) and from the cross section of SiNTs (solid line).

phonon peak at  $520\text{ cm}^{-1}$  is plotted as a function of incident laser power in Fig. 2(b). There is a clear dependence between laser power and change to the Raman spectra. Especially for high laser powers the shift and broadening of the Raman feature vary linearly with the laser power indicating a heating-induced effect. The observed heating effect in SiNTs is significantly pronounced in Si nanostructures because they are more sensitive to laser-induced heating because of their lower thermal conductivity, bad thermal contact with the substrate and smaller thermal mass than Si-bulk. A deviation from this linear relationship in the low power region of Fig. 2(b) indicates that broadening and shift are also affected by other factors than heating. This behavior reveals an important signature of the phonon-localization effect in accordance with previous reports.<sup>[11]</sup> Hence, the contribution of the effect of phonon confinement to the Raman spectra has to be isolated from changes caused by laser-induced heating.

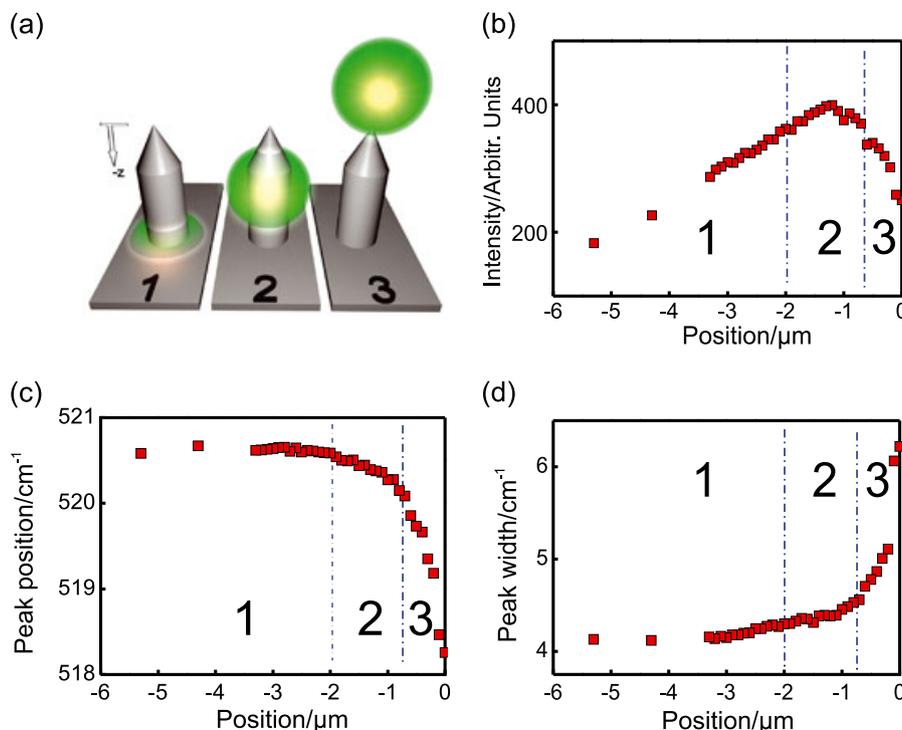
Subsequently measurements of the Raman response of a sample with homogeneous composition but spatially varying dimensions are presented that can provide a clear signature of the size effect on the phonon confinement of silicon. The investigated SiNTs increase in diameter in vertical direction from the base ( $d=100\text{ nm}$ ) to the apex ( $d=5\text{ nm}$ ) (as shown in Fig. 3(a)). Considering this geometry, the phonon confinement effect should be strongest close to the apex of the nanotips where the dimensions are significantly restricted. To isolate the source of the phonon confinement signature we collected spatially resolved Raman spectra as a function of the vertical focal position of the confocal microscope.

Figure 3(a) shows the position of the laser spot with respect to the nanotip. Because the laser spot is focused to  $\sim 1\text{ }\mu\text{m}$  it is of similar dimension as the SiNT height and the Raman intensity obtained from the sample is a convolution of the SiNT shape and the focal spot. The Raman intensity *versus* focal position as shown in Fig. 3(b) can thus be divided into three parts. In region

1 (from  $-6\text{ }\mu\text{m}$  to  $-2\text{ }\mu\text{m}$ ), the Raman intensity is determined by an increasing response from the underlying silicon substrate as the focus moves towards the substrate surface. Region 2 ( $-2\text{ }\mu\text{m}$  to  $-0.8\text{ }\mu\text{m}$ ) contains the Raman signal from the whole nanotip and the Raman intensity increases until the laser spot is overlapping with the entire nanotip before it decreases again. The final region (3) ( $-0.8\text{ }\mu\text{m}$  to  $0\text{ }\mu\text{m}$ ) is characterized by a decreasing Raman signal as the laser spot leaves the nanotip. (The smooth transitions between the regions in Fig. 3 are thought to be caused by variations in the taper length of SiNTs across the sample and the non-negligible focal spot size). Region 3 is expected to provide the most insight into the size dependence of the phonon localization because there is a gradual change in critical dimension with focal length. As the overlap between sample and laser spot decreases the largest diameter of the illuminated nanotip part shrinks continuously while the focus moves towards the top and the effect of phonon confinement on the Raman spectrum becomes more pronounced.

The different response from these three regions can be discriminated in the position of the silicon peak (Fig. 3(c)) where a constant peak position in region 1 can be seen as expected from the bulk silicon substrate. A weak downshift in region 2 is observed as the laser spot overlaps with the apex of the SiNT. Finally, a strong downshift in region 3 occurs and gets more pronounced as the laser spot interacts with a smaller and smaller part of the apex. This strong downshift in region 3 is accompanied by a broadening of the silicon peak as seen in Fig. 3(d). From this behavior, it can be inferred that the size constrictions of the nanotip apex is indeed the source of the phonon localization because the characteristic downshift and broadening is largest just before the laser spot leaves the apex.

Furthermore, when comparing region 3 in Figs 3(c) and (d) and Fig. 3(b) it can be seen that the downshift and broadening is



**Figure 3.** (a) Sketch of nanotip with indication of focal points according to positions 1,2,3 in plots (b-c), (b) integrated intensity of Raman Si-peak *versus* focal position, (c) position of Si-peak *versus* focal position, (d) peak width of Si-peak *versus* focal position.

accompanied by a decrease in Raman intensity. The variation of intensity can be explained by a reduced interaction volume of laser spot and nanotip resulting in a lower laser power across the nanotip. Thus, the change of Raman peak position and width occurs despite a lower laser power on the nanotip and is thus not caused by heating of the sample. This provides further evidence that phonon localization is indeed causing the observed changes to the Raman spectra. We thus experimentally confirm that the maximum Raman shift induced by phonon confinement in nanometer sized structures is only about  $2.5 \text{ cm}^{-1}$  as calculated before<sup>[10]</sup> and is easily overshadowed by the heating-induced shift.

To quantify the effect of the phonon confinement, we fit the Raman spectra to the spatial correlation model. The Raman intensity,  $I(\omega)$ , at a frequency  $\omega$ , can be expressed by the following three-dimensional integral over all momentum values  $q$ :

$$I(\omega) = \int d^3q \frac{|C(0,q)|^2}{(\omega - \omega(q))^2 + (\Gamma_0/2)^2}$$

where  $\omega(q)$  is the phonon dispersion curve,  $\Gamma_0 = 3.5 \text{ cm}^{-1}$  is the width (full-width at half-maximum) of the intrinsic Raman lineshape of a silicon single crystal, and  $C(0,q)$  is the Fourier coefficient of the phonon confinement function. Because the partially illuminated apex is treated as a 0D object, the phonon confinement function for a sphere is assumed

$$|C(0,q)|^2 \cong e^{-q^2 L^2 / 16\pi^2}$$

where  $L$  is the extracted confinement length for the 0D case. For the dispersion relation, we use the analytical model relationship based on a one-dimensional linear-chain model,<sup>[12]</sup>

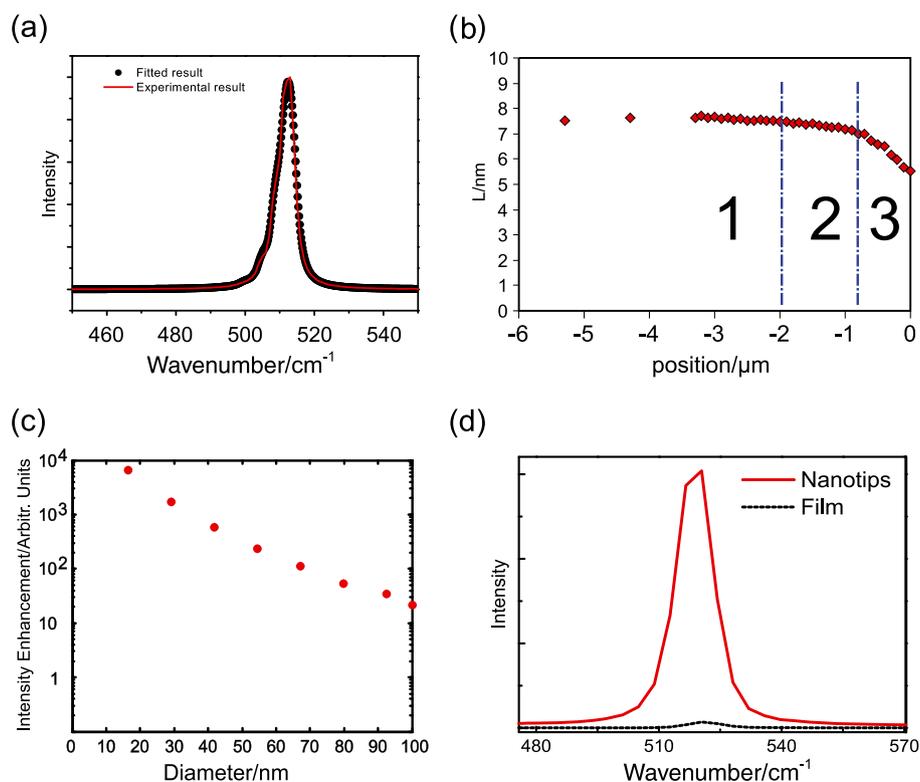
$$\omega(q) = \left[ A + B \cos\left(\frac{q}{2\pi}\right) \right]^{0.5} + D$$

where  $A$  and  $B$  are related to the atomic masses of the constituent atoms and the force constant between nearest-neighbor planes.  $A = 1.714 \times 10^5 \text{ cm}^{-2}$  and  $B = 1 \times 10^5 \text{ cm}^{-2}$  for Si single crystal.<sup>[10]</sup>  $D$  is an adjusting parameter that contains the spectrometer response but also the effect of heating-induced shifting.

Figure 4(a) shows a Raman spectrum obtained from the apex of the SiNTs at high laser power and an excellent agreement between fitting function (dot) and experimental data (solid line) is observed. The extracted confinement length  $L$  is about 6 nm, which correlates well with the apex diameter of the SiNTs as shown in Fig. 1(b).

When fitting all the Raman spectra obtained as a function of focal position, one can extract the spatial evolution of phonon confinement length  $L$  and heating-induced shifting  $D$ . From the absence of variation in  $D$  we infer that the temperature is constant along the nanotip. The change of  $L$  versus focal position is shown in Fig. 4(b). Although the confinement length  $L$  at the apex is in good agreement with the physical dimensions of the tip,  $L$  reaches only 7.5 nm away from the apex, which is smaller than expected for bulk silicon. This is attributed to an asymptotic approach of the Raman peak shift and broadening towards bulk values.<sup>[10]</sup> Thus, a small experimental error in the Raman spectra will have a significant effect on the calculation of  $L$  for small shifts. We thus have to consider this value of  $L = 7.5 \text{ nm}$  as the bulk equivalent within the experimental error.

The continuous decrease in the correlation length as seen in region 3 represents the smooth transition from the bulk optical properties of the SiNT base towards nanosize effects along a nanotip. It has to be emphasized that these measurements are



**Figure 4.** (a) Fit of spatial correlation model to experimental Raman spectra of SiNTs; (b) extracted correlation length  $L$  versus focal position; (c) Raman enhancement as function of illuminated tip diameter; and (d) comparison of Raman intensity of nanotip and bulk Si samples.

conducted on a sample of homogenous composition and height and changes to the Raman characteristics are expected to be solely due to size effects. This demonstrates the usefulness of SiNTs as model systems for size-induced property changes and will hopefully encourage more research in this direction.

To illustrate the potential of this model system, the Raman intensity of Si in the presence of phonon confinement was investigated. The Raman scattering cross section as a function of lateral dimension can be obtained by deconvolution of the SiNT volume illuminated by the laser from the Raman intensity distribution shown in Fig. 3(b). Figure 4(c) shows the enhancement of the Raman intensity normalized to the bulk portion of the tip as a function of SiNT diameter, which was estimated from scanning electron microscopy images. Despite the large error margin caused by the estimation of nanotip parameters the enhancement follows a similar trend as obtained by Cao *et al.*<sup>[13]</sup> More detailed studies of the correlation of phonon confinement and Raman enhancement in the SiNTs are underway and will elucidate if large internal fields obtained at the apex or relaxed phonon selection rules associated with the size constrictions are responsible for the enhancement. The Raman enhancement caused by the nanotip's apex consequently originates only from a small portion of the sample. The enhancement effect, however, causes a disproportional contribution to the overall Raman signal and results in a 40-fold increase of the Raman response of the silicon nanotip sample compared with the unpatterned silicon wafer (Fig. 4(d)).

## Conclusions

In summary, the effect of size constraints on the phonon-localization effect and the Raman scattering efficiency in SiNTs has been investigated. No-phonon transitions in the photoluminescence spectra indicate that phonon confinement occurs in our sample. Spatially resolved Raman spectroscopy provides a clear signature of phonon confinement without interference from laser-induced heating. The source of the asymmetric broadening and downshift is found to be localized at the apex of the SiNTs. The Raman spectra can be well fitted with the spatial correlation model, and the obtained correlation length is in good agreement with the diameter of the apex of

the SiNTs. The transition of optical properties between bulk and nanostructured silicon that occurs along the nanotip was correlated with a large enhancement of the Raman scattering efficiency at the nanotip's apex. Our results thus demonstrate the potential of using SiNTs as both a model system to study the size-dependent properties of silicon and as a route to controlling the fundamental properties of Si. The observed large enhancement of the Raman signal shows the potential of using nanostructures to enhance optical properties and is an important step towards realizing the integration of Si-based optoelectronic devices.

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