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# Raman Spectrum of silicon nanowires

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**Abstract**

We measure the effects of phonon confinement on the Raman spectra of silicon nanowires (SiNWs). We show how previous reports of phonon confinement in SiNWs and nanostructures are actually inconsistent with phonon confinement, but are due to the intense local heating caused by the laser power used for Raman measurements. This is peculiar to nanostructures, and would require orders of magnitude higher power in bulk Si. By varying the temperature, power and excitation energy, we identify the contributions of pure confinement, heating and carrier photo-excitation. After eliminating laser-related effects, the Raman spectra show confinement signatures typical of quantum wires.
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*Keywords:* Raman spectra; Nanostructures; Silicon nanowires

## 1. Introduction

Crystalline nanostructures such as nanotubes and nanowires offer unique access to low dimensional physics, and they can be used, as an alternative system to carbon nanotubes (CNTs), as nanotechnology building blocks to reach higher device integration densities than conventional fabrication methods [1,2]. As for CNTs [3], Raman spectroscopy could become a standard technique for nondestructive characterisation (structural and electronic) of silicon nanowires (SiNWs) and a direct probe of quantum confinement effects [4–7]. Due to the Heisenberg uncertainty principle, the fundamental $q \sim 0$ Raman selection rule is relaxed for a finite size domain, allowing the participation of phonons away from the Brillouin zone centre. The phonon uncertainty goes roughly as $\Delta q \sim 1/d$, where $d$ is the grain dimension or NW diameter. This gives a downshift of the Si peak and an asymmetric broadening. For a SiNW, these features can be calculated by applying the confinement model of Ricther et al. and Campbell and Fauchet (RCF) [4,5].

A number of papers have been published to date [6–13] reporting Raman measurements on SiNW and nanostructures. Peak positions of $\sim 500–510$ cm$^{-1}$ are very commonly reported for wires of $\sim 10–15$ nm diameter [6–13]. However, this contrast with trends calculated within the RCF framework, which predicts shifts not bigger than $\sim 1$ cm$^{-1}$ [7,12]. Some authors try to account for this incompatibility by claiming a size distribution in their samples, necessarily involving extremely thin nanowires or an extremely thin "defect-free" region of their wires. However, even when individual SiNWs, carefully characterised by HRTEM and/or AFM, were measured, the same significantly downshifted and broad Raman peak appeared [6,7,12].

It was also reported [10] that peak position and FWHM of SiNWs depend on the laser excitation wavelength, with peak position decreasing and FWHM increasing for decreasing excitation wavelength, in the 785–488 nm range. This was explained within the RCF model by resonant Raman selection of smaller wires for higher excitation energy [10]. However, again, a close examination of the data in Ref. [10] shows that none of the spectra at any excitation energy matches the measured wire size. Thus, either the RCF model is grossly wrong, or other phenomena, rather than pure confinement, are responsible for previously measured data.

## 2. Results and discussion

Typical effects of laser irradiation during Raman measurements of SiNWs can be sample heating (homogeneous or not) [7,12] and possible photo-excitation of carriers [13]. A

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hot–cold Linkam stage was mounted on our Renishaw 1000 spectrometer, allowing us to heat the SiNWs independently of the laser power, in order to test the effects of homogenous heating. Different excitation wavelengths were used (785, 633 and 514.5 nm) in order to check if, for a given local temperature and wire size, the Raman spectra do actually depend on the excitation wavelength. An important finding of our study is that, for typical excitation wavelength of 514.5 nm, a power as small as 1–2 mW on the sample is enough to significantly modify the SiNW spectra, whilst giving no effect on bulk Si.

The samples considered in this paper were mats of SiNWs produced by oxide-assisted growth [14,15] and PECVD-grown SiNWs deposited on patterned substrates [12]. In both cases, in order to avoid any confusion with the Si signal from the substrate, the wires were placed on Au-coated Si substrates. Details of the deposition process and wire characterisation can be found in Refs. [12,14,15]. The average size of the wires used in this study is about 15 nm, but each wire has a 2–3 nm external oxide layer, resulting in a smaller pure Si wire-core, as experimentally confirmed by removing the oxide by HF [14].

Fig. 1(A) shows the Raman spectrum evolution as a function of the excitation power for 514.5 nm excitation. As the power increases, the peak position moves to lower frequencies and the line broadens. Cycling the power between 0.02 and 2.5 mW produced no significant hysteresis on the spectra, indicating no damage. An estimate of the local temperature can be obtained by considering the peak position, FWHM and the Stokes/anti-Stokes intensity ratio, $I(AS)/I(S)$ [7,12,16–18]. This gives $T\sim 600$–650 K for the wire in Fig 1(A) measured at the maximum power. As a rule of thumb, if we consider to a first approximation the spectral shapes previously reported in literature as result of mere laser heating, a $\sim 10$–15 cm$^{-1}$ downshift of the peak corresponds to a local temperature of $\sim 600$–900 K.

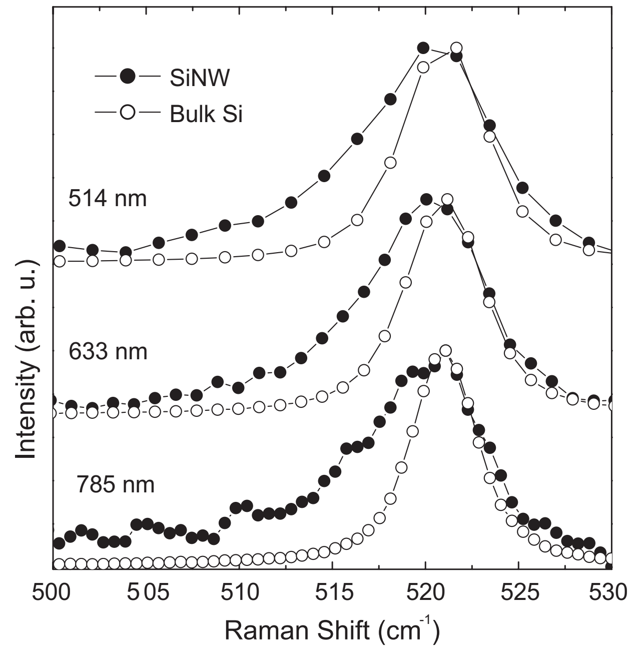


Fig. 2. Comparison of Raman spectra of SiNWs and bulk Si, measured at the same low power ( ~ 0.02 mW) using 514, 633 and 785 nm excitation wavelengths.

Fig. 1(B) compares the Raman spectra taken at a similar maximum power of $\sim 3$ mW for 785, 633 and 514.5 nm excitation. The trend in Fig. 1(B) is remarkably similar to the one presented in Ref. [10] for SiNWs of similar dimensions. Fig. 1(B) shows that 514.5 nm excitation gives much larger downshift and broadening. However, for an extremely low excitation power of $\sim 0.02$ mW, Fig. 2 shows that the spectra converge to the same lineshape and position, independent of excitation energy: an asymmetrically broadened peak. This is demonstrated by the comparison with bulk Si measured in the same conditions at the same excitation

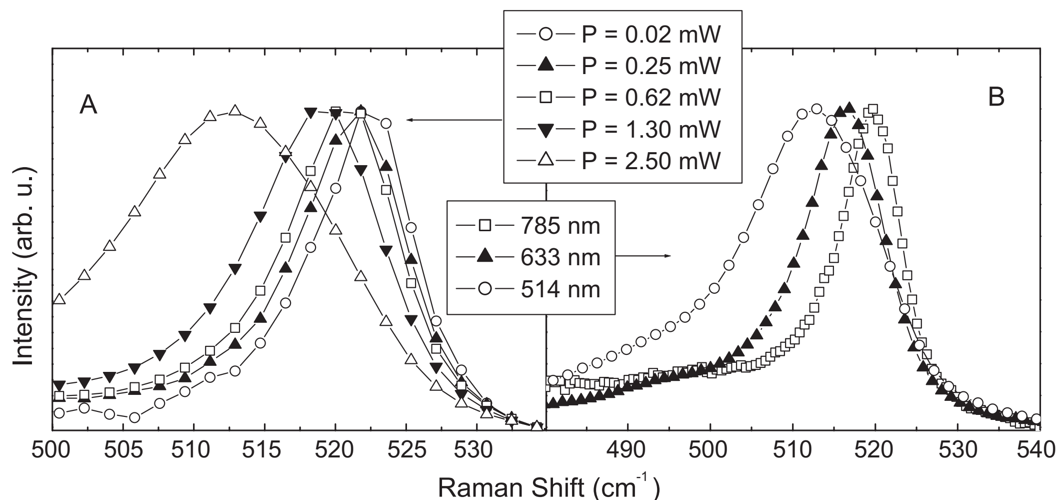


Fig. 1. (A) Raman Spectra of SiNWs measured at 514.5 nm for increasing laser power on the sample. (B) Raman spectra on the same sample as a function of the excitation wavelength for a similar laser power of ~ 3 mW on the sample.

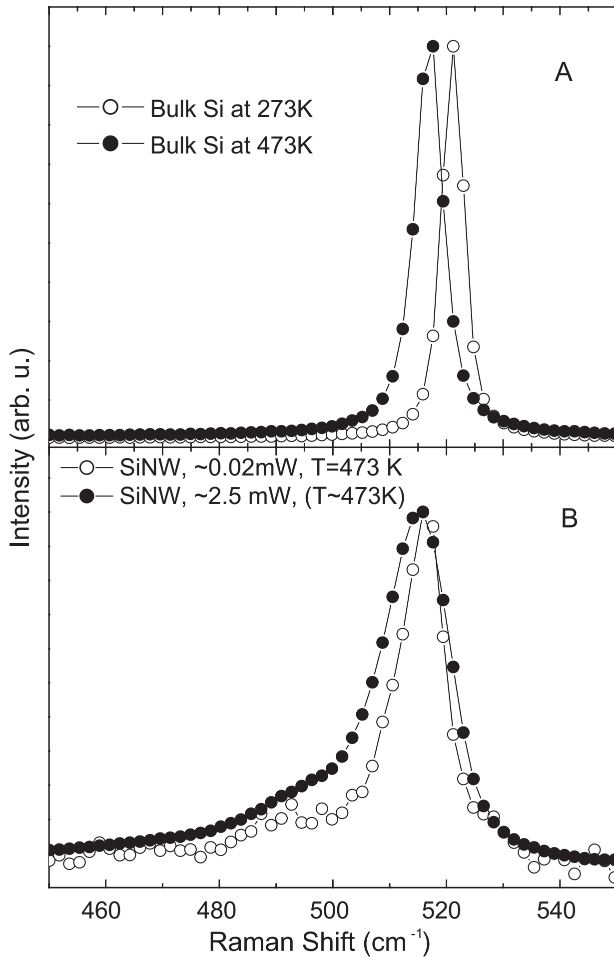


Fig. 3. (A) Comparison of the Raman spectra of bulk Si measured at 514.5 nm at 273 and 473 K. The temperature being defined by a Linkam heating stage. (B) Comparison of the Raman spectrum of SiNWs, measured at 514.5 nm excitation and low power of ~ 0.02 mW at 473 K (as kept by a Linkam heating stage), and the Raman spectrum of the same SiNWs measured at a laser power of ~ 2.5 mW, corresponding to an estimated local temperature of ~ 473 K (resulting from laser irradiation).

energy. Figs. 1 and 2 imply that the spectral changes as a function of excitation wavelength are not due to resonant Raman selection of wires of different sizes, but can be ascribed to the increasing absorption coefficient of Si with increasing excitation energy approaching the Si direct bandgap [19,20]. This results in a higher local temperature for higher excitation energy. The high sensitivity of SiNWs to the laser power, compared to that of bulk Si, could be explained by size effects and poor thermal contact with the substrate. This is not restricted to nanowires, but applies also to nanocrystalline Si and other Si nanostructures [21].

In principle, there is a significant difference between oven annealing of a sample and laser annealing. The first homogeneously heats the sample and gives symmetric broadening and downshift of the main Si line, due to the onset of anharmonic phonon processes [16–18]. Laser annealing can result in temperature inhomogeneity within the sample and, thus, peak broadening [19]. On the other hand, very high power laser annealing in bulk Si can create free carriers [13,19,22]. These excess carriers can interfere with the Si phonon line. An asymmetry toward lower frequency is typical of electrons, whilst a higher frequency asymmetry is indicative of holes [19,22]. A similar effect is observed at room temperature for heavily n- or p-doped Si [23,24]. Furthermore, electronic Raman scattering introduces an extra dependence of the lineshape with the excitation energy, so, for a given carrier density, the asymmetry should decrease going from 514.5 to 785 nm excitation [23]. To summarise, RCF gives a downshift and asymmetric broadening. High power raises the local temperature, which results in further downshift, but adds symmetric broadening. Inhomogenous heating results in further broadening. An excess of photoexcited carriers would give further asymmetric broadening (towards low frequency for electrons and high frequency for holes). Thus, in principle, the high power lineshapes are quite complex to analyse.

These different effects are shown in Fig. 3. Fig. 3(A) compares the spectra taken at 514.5 nm of bulk Si at room temperature and bulk Si at 473 K. Fig. 3(B) compares SiNW measured at ~ 0.02 mW at 473 K and the same SiNW

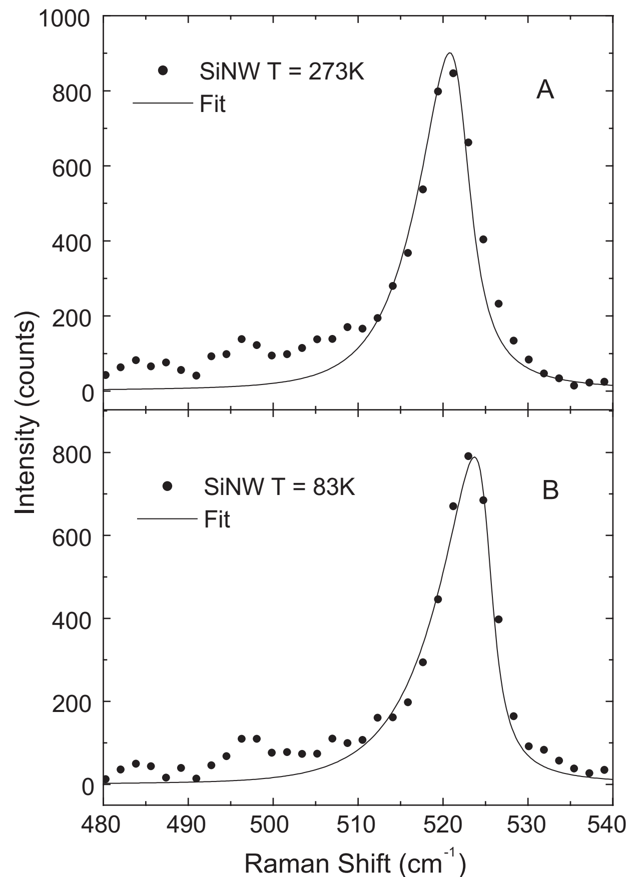


Fig. 4. Dots: Raman spectra of SiNWs spectra measured at (A) 273 and (B) 83 K (as defined by a Linkam cold stage) with low power ( ~ 0.02 mW) at 514 nm. Line: Fit to the measured spectra using the RCF model adapted for nanowires. The diameter of the nanowires is the only fit parameter and is ~ 7 nm, independent of the temperature.

measured at room temperature but at a laser power of ∼ 2.5 mW, so that the local $T$ is ∼ 473 K (as estimated by a combination of peak position, FWHM and I(AS)/I(S) Ref. [18]). Bulk Si at high temperature is downshifted and symmetrically broadened, with respect to room temperature Si, due to pure anharmonicity, Fig. 3(A). The spectrum of SiNW measured at high temperature and low power is broader and more asymmetric than bulk Si at the same temperature, due to phonon confinement. Finally, the spectrum of SiNW measured at high power at room temperature is broader and slightly more asymmetric than the spectrum of SiNWs measured at low power and high temperature, Fig. 3(B). This extra effect can be due to temperature gradients or electronic Raman scattering [13,19,22–24]. To investigate this further, we performed an extensive study of our samples as a function of laser power, excitation energy and temperature in the 83–700 K range. This will be reported in detail elsewhere [18]. Here we want to demonstrate pure confinement effects in our wires.

Fig. 2 compares room temperature spectra taken at 514.5, 633 and 785 nm at the *low power* of ∼ 0.02 mW to the corresponding bulk Si measured at the same wavelengths. $I$(AS)/$I$(S) for the spectra in Fig. 2 is very small, comparable to bulk Si and corresponding to room temperature [7,17–19]. Thus there are no laser heating effects. The shape of the three spectra is exactly the same. This means that no excited carriers were present [23]. Hence we can neglect any electronic Raman scattering. However, all three measurements differ significantly from the reference Si. Even if the peak position looks very similar to bulk Si, the low frequency asymmetry and bigger FWHM are evident by eye inspection. We wrote a least-square fitting software based on RCF model, having as fit parameter the SiNWs diameter [6,18]. By fitting the data in Fig. 2, we get the same diameter of ∼ 7 nm independent of excitation energy, in good agreement with the observed internal core diameter of our SiNWs [12,14,15] (Fig. 4(A)). We then repeated the same measurements at 83 K in order to further dampen any possible residual thermal effect present at room temperature and we fitted the data again. This yields an excellent confinement fit and the same diameter as the room temperature measurements (Fig. 4(B)). This again proves phonon confinement in our SiNWs.

## 3. Conclusions

In conclusion, we showed how the local intense heating caused by the laser power used for Raman measurements heavily affects the spectra of SiNWs. This is peculiar to nanostructures, and would require orders of magnitude higher power in bulk Si. When laser-related effects are duly eliminated, the Raman spectra show confinement signatures typical of quantum wires.

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