

Laser-Induced Fano Resonance Scattering in Silicon Nanowires

R. Gupta,^{*,†} Q. Xiong,^{†,‡} C. K. Adu,[†] U. J. Kim,[†] and P. C. Eklund^{†,‡}

Departments of Physics and Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802

Received February 26, 2003; Revised Manuscript Received March 25, 2003

ABSTRACT

We have studied the impact of excitation laser power density on the Raman spectrum of small-diameter (5–15 nm) silicon nanowires. At low power densities, a Lorentzian line is observed at 520 cm^{-1} , the same value as that of the zone center LO (TO) phonon in bulk silicon. With increasing laser illumination, the Raman band downshifts and asymmetrically broadens on the low-frequency side. Our results contradict the traditionally accepted notion that a downshifted and asymmetrically broadened line in Si nanowires is due to quantum confinement effects. Rather, we suggest that the downshifting can be due to a laser heating effect of the nanowire and that the asymmetric line shape is due to a Fano interference between scattering from the $k = 0$ optic phonon and electronic continuum scattering from laser-induced electrons in the conduction band.

The growth and physical properties of semiconducting nanowires are being intensively investigated in response to recent reports of new devices such as nanowire field-effect transistors,¹ lasers,² light-emitting diodes,³ chemical sensors,⁴ and logic gate circuits.⁵ Fundamental studies on constrained crystalline systems are ongoing in order to understand the impact of quantum confinement on many of the key physical properties (e.g., charge and heat transport down the wire and optical emission).

For example, several groups have reported the observation of phonon confinement in Si nanowires using Raman scattering.⁶ They observed an asymmetric band downshifted by a few wavenumbers relative to the frequency of the Raman-active optic mode in bulk Si and have identified this line shape with a phonon confinement phenomenon, fitting the experimental line shape to an analytical expression first proposed by Richter.⁷ In Richter's model, the confinement of the phonon wave function transverse to the wire axis leads to a breakdown of the bulk ($k = 0$) Raman selection rule. As a result, other phonons (with different frequencies) in the same branch are "activated", leading to an asymmetric broadening and shifting of the Raman band in the confined nanowire. Of course, for phonon confinement to be observed, it is required that the phonon mean free path be greater than the nanowire diameter. The one-phonon Raman band in bulk Si is at 520 cm^{-1} , and it is Lorentzian.

Similar to previous reports on small-diameter Si nanowires,⁶ we also observe an asymmetric broadening and downshifting of the one-phonon Raman band relative to that of the bulk. The most probable diameter of our nanowires

is ~ 9 nm (including an ~ 1 nm oxide layer). However, we can correlate the observed difference between the nanowire and the bulk (infinite crystal) spectrum with the incident laser power. For our samples, we conclude that the observed line asymmetry in Si nanowires is *not* connected with phonon confinement. At our lowest laser powers, we indeed find a symmetric (Lorentzian) line shape for the nanowire with a frequency equal to that of bulk Si and with a line width about twice that of the bulk. Below, we show that the asymmetric Raman band we observe at powers above ~ 1 $\text{mW } \mu\text{m}^{-2}$ is due to Fano resonance scattering between the ($k = 0$) LO (TO) phonon and conduction-band electrons. We use the notation LO (TO) for the zone center Raman-active mode in Si because the mode is triply degenerate at the center of the Brillouin zone. However, later in the paper, to calculate the line shape for a quantum-confined nanowire, we use the dispersion of the LO mode of Si. We believe that the error due to this approximation is not significant.

The silicon nanowires (Si NWs) used for our work were prepared by pulsed laser vaporization (PLV) of a Si target containing ~ 10 at. % Fe.⁸ Details about the nanowire synthesis and characterization have been published elsewhere.⁸ The diameter distribution of the nanowires was determined using AFM and TEM. Both diameter distributions were in agreement and could be well fit to a log-normal distribution with a most probable Si core diameter, $d = 6.7$ nm.¹⁰ HRTEM showed that the growth axis was $\langle 111 \rangle$. The Raman spectra were collected in the backscattering direction using a JY-Horiba T64000 micro-Raman spectrometer with an Olympus BX40 confocal microscope (100 \times objective with 0.95 NA). The sample was illuminated in air using 568.2-nm radiation, and the laser spot diameter was ~ 1 μm . The laser power at the sample was measured using a

* Corresponding author. E-mail: rug4@psu.edu.

[†] Department of Physics.

[‡] Department of Materials Science and Engineering.

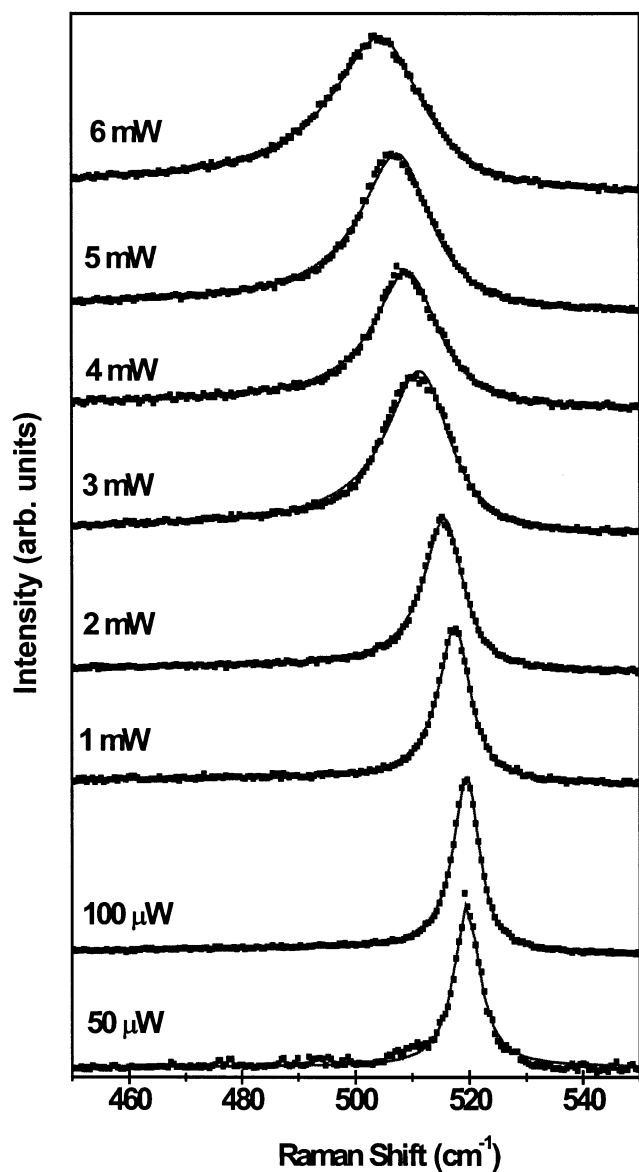


Figure 1. Stokes Raman spectra of $d \approx 8$ -nm-diameter silicon nanowires on a quartz substrate in air. The spectra were collected with a $100\times$ objective as a function of the incident laser power (568.2-nm radiation). The Raman band downshifts and asymmetrically broadens as the laser power increases. The solid lines are fits of the spectra to a Fano resonance line shape; the line-shape parameters are plotted vs laser power in Figure 3.

miniature power meter. At each laser power, both the Stokes and anti-Stokes spectra were recorded.

In Figure 1, we display the Stokes Raman spectra of our Si nanowires collected at successively higher laser powers using 568.2-nm radiation. As seen in the Figure, the phonon band downshifts with increasing laser power. Furthermore, the asymmetry of the band also increases with increasing laser power. It should be noted that at the lowest power (50 μ W) we observe that the Raman band of the Si nanowires is symmetric and located at the same position as that in bulk crystalline silicon. However, the full width at half maximum (fwhm) of this low-power Si nanowire Raman line is broader (by a factor of ~ 2) than that observed in bulk Si at room temperature. The solid curves overlaying the upper seven

spectra in the Figure are from a Fano line-shape analysis, as discussed below. Similar to the behavior of the Stokes Raman spectra displayed in Figure 1, the related Si NW Raman band in the anti-Stokes spectrum also downshifts and asymmetrically broadens to a lower-frequency shift as the laser power density is increased. For brevity, these spectra are not shown.

A downshifting and broadening of a Raman line with increasing laser irradiation is usually identified with a heating phenomenon. This is certainly the case here, as will be seen shortly. As the temperature of the sample increases, the lattice constant increases, and the bonds between atoms weaken. The homogeneous (symmetric) broadening with temperature of the Lorentzian line shape of the LO (TO) mode in bulk silicon is well known and can be understood in terms of the lattice anharmonic effects. What is unusual about the Si NW spectra observed here is that the line broadens *asymmetrically*; it can be well fit by a Fano resonance line shape that is associated with an interfering continuum scattering process—in this case, activated by the incident laser irradiation.

It should be noted that many of the nanowires in our thin film are probably not in good thermal contact with the quartz substrate but are, in fact, suspended by other nanowires. Thus, we have taken Stokes and anti-Stokes spectra to compute the local temperature in the scattering volume. We have also estimated the local temperature in the Si NWs from the peak position of the Raman line using the third-order anharmonicity parameters for bulk crystalline silicon reported earlier.¹¹ Of course, we are assuming that the variation of the peak position with temperature in our Si nanowires and bulk silicon is approximately the same. Both methods of estimating the local temperature versus the incident laser power can be compared in Figure 2. The circles and squares in the Figure represent the temperature determined from the band position and the Stokes/anti-Stokes intensity ratio, I_S/I_{AS} , respectively. In the latter, the temperature T is computed from

$$\frac{I_S}{I_{AS}} = A' e^{\hbar\omega_0/kT} \quad (1)$$

where I_S and I_{AS} refer to the integrated area of the Stokes and anti-Stokes bands at the same laser power. A' depends on the optical absorption constant, scattering cross section, and Raleigh factor at Stokes and anti-Stokes frequencies. Assuming that the optical absorption constant and the scattering cross section are the same for both processes, we obtain a value of ~ 0.8 for the lowest (room) temperature data.^{11,12} This value is also consistent with the value of A' obtained by normalizing the lowest power data to 300 K (ambient). As can be seen in Figure 2, there is reasonable agreement between the temperatures determined by both methods, with the exception of one data point. The solid line in the Figure is a guide to the eye and indicates that the local temperature in the Si NWs is approximately linear in the incident laser power. Local temperatures as high as ~ 600 °C were reached with laser powers of ~ 6 mW. Because these measurements were made in air, it might be suggested that laser-induced oxidation of the NWs has taken place. However, the heating effects we have observed are completely

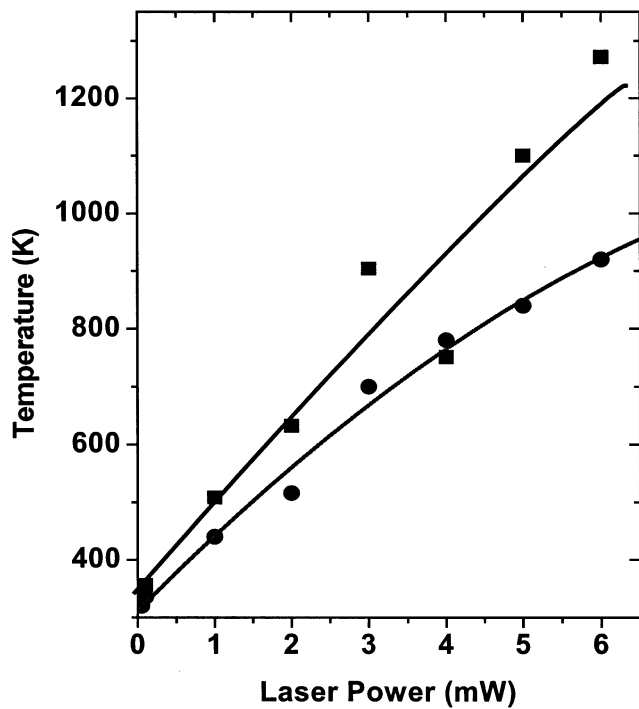


Figure 2. Dependence of the local temperature on the incident laser power. The solid squares show the temperatures obtained from the ratio of the Stokes/anti-Stokes intensity ratio, and the solid circles represent the temperatures obtained from the Raman peak position (assuming that the anharmonicity of bulk Si applies to the nanowires).

reversible (i.e., a narrow Lorentzian line shape can be recovered at low laser power after exposure to high laser powers). Dry oxidation of Si substrates is normally carried out above $\sim 900^\circ\text{C}$.

The effect of high laser power on the Raman scattering from the optic phonon in bulk Si has been studied using an amplified, frequency-doubled pulsed (Nd:YAG) laser pumped dye laser (pump 565 nm ; probe 532 nm).¹³ The band was also observed to broaden to lower frequency at high intensity, and the line shape was fit to a Fano resonance and was identified with interference between scattering from the optic phonon ($k = 0$) and continuum scattering from the laser-excited electron–hole plasma. In a recent paper, the effect of continuous-wave laser irradiation density at 514.5 , 600 , 650 , and 708 nm on the Raman spectrum of bulk silicon was reported.¹⁴ In contrast to the results found previously using pulsed Nd:YAG radiation, beyond a particular threshold irradiation intensity, the Raman band upshifted a little and broadened asymmetrically to higher frequency. This behavior was also attributed to a Fano interference between scattering from the discrete optic phonon and an electronic continuum, but in this case, the continuum was assigned to photoexcited holes.¹⁴ Comparing their spectra for different laser powers with those on boron-doped p-type silicon, they managed to extract the hole density at different laser powers.

Fano interference scattering in doped bulk silicon has been extensively dealt with in earlier Raman studies.^{15–19} The interference causes an asymmetric line shape described by eq 2 below. It has been observed in both n-type^{17,18} and p-type^{15,16} Si. At sufficiently high doping levels, holes or

electrons are free to participate in an inelastic light-scattering process exciting the free carriers to the next higher conduction or valence band. It is the scattering from this continuum channel that can participate in a Fano resonance with the LO (TO) phonon scattering. An asymmetric “Fano” line shape that depends on the electron–phonon coupling strength is the result. It has been reported that a doping of at least $4 \times 10^{19}\text{ cm}^{-3}$ is required to observe the Fano line shape in n-type silicon.¹⁹ However, in p-type silicon, there appears to be no such lower bound on doping.¹⁶ It therefore seems that the electronic continuum scattering in p-Si is relatively much stronger than in n-Si. Considering these studies and the asymmetric line shape observed in our spectra, we have fit our data to the Fano line shape given by

$$I(\omega) = A \frac{(q + \epsilon)^2}{(1 + \epsilon^2)} \quad \epsilon = \frac{(\omega - \omega_0)}{\Gamma} \quad (2)$$

where ω_0 is the renormalized or “dressed” phonon frequency in the presence of the coupled scattering, q is the asymmetry parameter ($1/q$ is sometimes referred to as the coupling strength), and Γ is the line-width parameter and is related to the phonon lifetime. The influence of the electronic Raman scattering on the phonon scattering is determined by q . A small value of q implies that the interference is strong. The strength of the interference increases with increasing wavelength of the exciting laser. It is convenient to work in units of $1/q$ because in the limit of $1/q \rightarrow 0$ the Fano line shape reduces to a Lorentzian. It has been generally found in bulk Si that $1/q$ is proportional to the free carrier concentration.^{15,16} The thick solid lines in Figure 1 are the fits of our Stokes spectra to the Fano line shape given by eq 2. The data at the lowest laser power ($50\text{ }\mu\text{W}$) exhibits a symmetric line shape that is well fit by a Lorentzian with $\text{fwhm} = 5.4\text{ cm}^{-1}$ and includes the experimental resolution of $\sim 1\text{ cm}^{-1}$. In Figure 3, we summarize the laser-power dependence of the Stokes Fano line-shape parameters (ω_0 , $1/q$, Γ) for our Si NWs. As can be seen from the top panel (Figure 3c), the coupling parameter $1/q$ increases with increasing laser power P and the local temperature T (Figure 2). $1/q$ depends on the strength of the continuum scattering. The negative value of $1/q$ implies that there is constructive interference between the discrete phonon and electronic continuum on the low-wavenumber side and destructive interference on the high-wavenumber side. It is also worth noting that the magnitude of $1/q$ that we find for Si NWs at high laser power is much larger than that reported in bulk Si; this could possibly stem from confined electronic states. We should also mention that to determine the local temperature T (Figure 2) from the peak position data we have assumed that the difference between the bare discrete phonon frequency (i.e., the frequency of the nanowire in the absence of interference effects) is approximately the same as that in the presence of the Fano interference. This is acceptable because experimental and theoretical results on degenerately doped n-type silicon¹⁷ ($n = 1.5 \times 10^{20}\text{ cm}^{-3}$) show that this difference is only $\sim 0.5\text{--}0.6\text{ cm}^{-1}$. By viewing increasing laser power P as driving an increase in the local nanowire temperature and

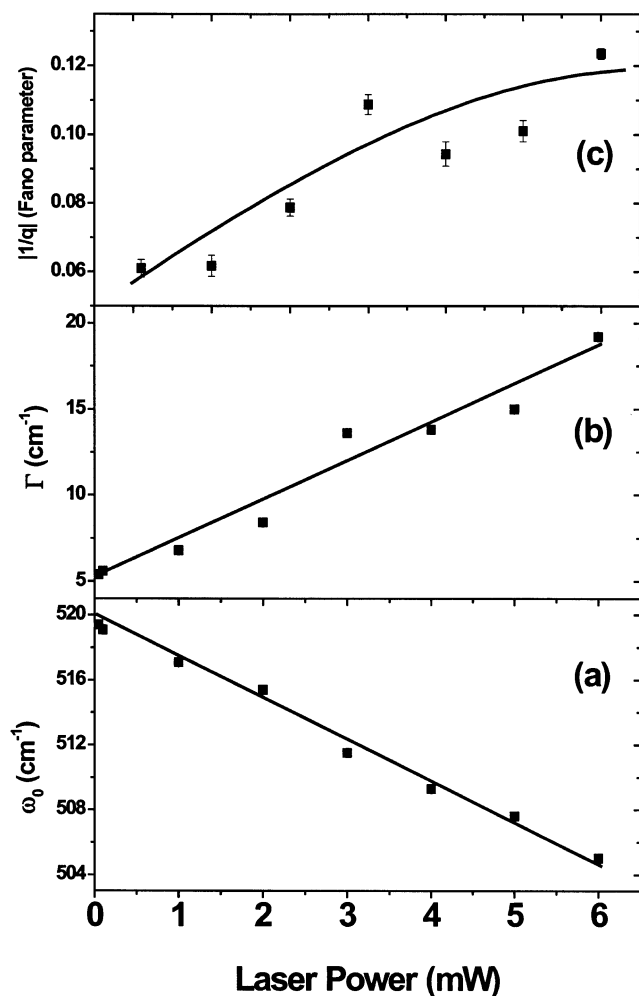


Figure 3. Variation of the Fano line-shape parameters with incident laser power. The Fano line shape, eq 2 (solid line), was fit to the spectra (dots) in Figure 1. Peak position (ω_0), line width (Γ), and the coupling parameter ($|1/q|$) are plotted in the three panels as a function of the laser power. Lines are guides to the eye.

therefore an expansion of the lattice constant, it is also expected that (1) the phonon lifetime parameter $1/\Gamma$ will decrease with increasing P and (2) the phonon frequency ω_0 will decrease with P , as observed.

We next make contact with Raman scattering results on doped bulk n-type silicon.^{17,18} In this case, it has been noted that the continuum Raman scattering must arise from electronic transitions between the Δ_1 and Δ'_2 conduction bands along the X direction in the Brillouin zone.^{17,18} These low-energy transitions are Raman-allowed but infrared-forbidden. In the case of p-type silicon, the electronic scattering is a result of transitions between heavy and light hole valence bands at the Brillouin zone center (Γ point).^{14,16} However, in the case of small-diameter nanowires, it should be considered that these optical transitions might be altered by quantum confinement. Effects of confinement on the electronic states have been proposed in Si NWs. For example, photoluminescence spectra on 15-nm diameter Si NWs were found to exhibit a strong peak at 2.4 eV.²⁰ This luminescence was assigned to new direct optical transitions across the semiconducting gap, in agreement with theoretical calculations on much smaller diameter Si nanowires. However, it

is also possible that the reported 2.4-eV luminescence in Si nanowires may be associated with SiO_2/Si interface states as, for example, was proposed in porous Si.²¹

In earlier reports^{6,22} on Raman scattering from Si NWs of a mean diameter of 10–20 nm, it was found that the one-phonon peak was significantly downshifted and broadened on the low-wavenumber side. This behavior was explained in terms of the phonon confinement model of Richter et al. developed for small crystalline spherical particles⁷ and extended by Campbell and Fauchet (C–F) to the geometry of small-diameter wires.²³ According to this model, the confinement of the phonon wave function perpendicular to the wire axis leads to a breakdown of the $k = 0$ Raman selection rule and activates scattering from nearby k -vector phonons in the same branch. Since the phonon dispersion curves of bulk silicon have a negative slope away from the Brillouin zone center, the sampling of a continuum of phonon wave vectors should cause a downshifting and an asymmetrical broadening of the one-phonon line. However, contrary to earlier reports,^{6,22} our Si NWs exhibit a symmetric one-phonon Raman band at low excitation intensity. This observation indicates that in our nanowire samples (most probable core diameter ~ 7 nm) either the phonon mean free path is too short to support quantum confinement or that earlier micro-Raman studies of other Si nanowire samples had elevated the local sample temperature such that an extrinsic Fano broadening was observed, as reported here. As pointed out by Campbell and Fauchet (C–F), there are two necessary requirements to observe quantum confinement effects (i.e., phonon dispersion and phonon lifetime). The line width of the Raman band in Si nanowires (fwhm nanowire = 5.4 cm^{-1}) is nearly twice that observed in bulk Si (fwhm bulk = 3.2 cm^{-1}). Therefore, the phonon mean free path is roughly half of that of bulk silicon. This could be the reason for not observing phonon quantum confinement in our nanowires.

In light of this result, it is of interest to compare the theoretical line shape for $d = 4$ - and 7-nm-diameter Si NWs calculated according to the C–F phonon confinement model (dashed curves) to a Fano line shape (solid curves). This comparison is shown in Figure 4. For the C–F line shape, we have described the phonon dispersion by a parametrization of the bulk Si LO²⁴ ($\omega^2 = A + B \cos(\pi k/2k_{\text{max}})$, $A = 1.714 \times 10^5 \text{ cm}^{-2}$, and $B = 1 \times 10^5 \text{ cm}^{-2}$). For comparison, the Fano line shape (eq 2) is least-squares fit to the calculated C–F result for 4- and 7-nm wires. As can be seen in the Figure, the calculated line shapes cannot be fit to a Fano line profile. The mismatch between the two different line shapes increases as the mean wire diameter becomes smaller. This inequivalence of line shape further shows that confinement effects are not significant in our nanowires. Although not shown in Figure 4, as the mean diameter increases (> 10 nm), it is possible to fit the calculated C–F result with the Fano line shape. However, in these cases, the value of $1/q$ is very small, and the line shape is very close to that of a Lorentzian, as is a C–F line shape for a large-diameter wire. This indicates that due caution is necessary in assigning the origin of the Raman line shape to quantum confinement. Furthermore, in another recent report on Si NWs,²⁵ the one-

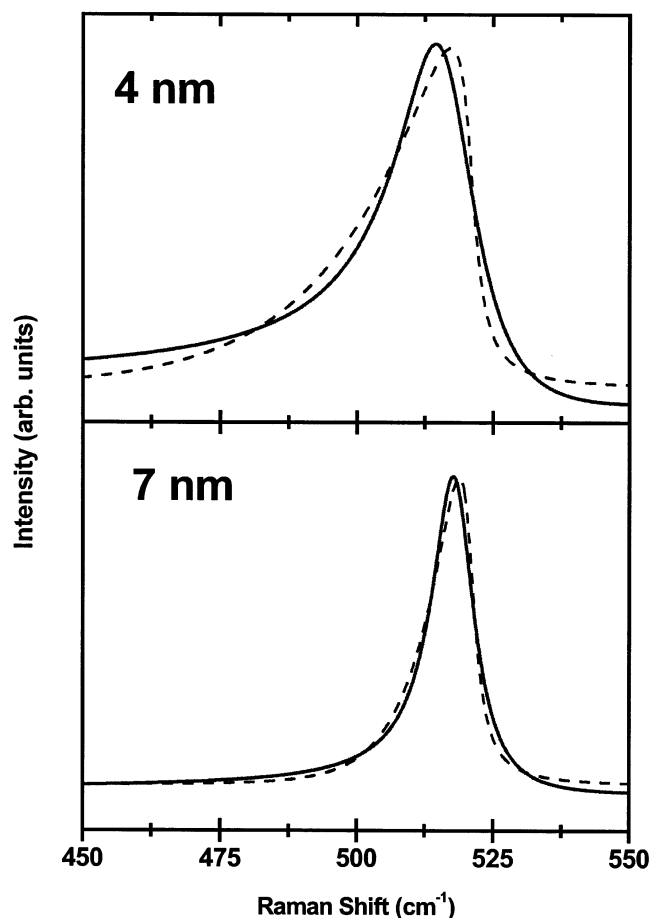


Figure 4. Comparison of the Campbell–Fauchet (C–F) phonon confinement line shape (dashed line) to that of a Fano resonance. The C–F line shapes are for long $d = 4$ - and 7-nm nanowires using the LO phonon dispersion of bulk Si. In each case, the Fano line shape is the result of a least-squares fit to the C–F line shape.

phonon Raman peak position was reported to exhibit a small shift as a function of the excitation laser wavelength. This was attributed to a size-selective resonance enhancement mechanism in which the longer wavelengths excite the larger-diameter nanowires preferentially. Conversely, the smaller-diameter wires were proposed to be resonantly selected by shorter-wavelength excitation, thus they exhibit a larger downshift of the Raman band. In the context of the present results, we believe that laser heating should also be considered to be a possible explanation for these reported wavelength-dependent excitation effects. Perhaps the spectra were collected at different powers or the nanowires had different thermal anchoring.

In conclusion, we have presented experimental evidence that shows that the asymmetric broadening to lower frequency of the one-phonon Raman band of small-diameter Si nanowires can be due to a Fano resonance driven by a laser-induced phenomenon and need not be the result of phonon confinement. The heating of the nanowire can be exaggerated by (1) poor thermal coupling of the nanowires to a heat sink (substrate) and (2) tight focusing of the incident laser beam (as can be the case in micro-Raman spectrometers). As the laser power is increased, we observe that the line shape changes from a symmetric Lorentzian to a

downshifted and asymmetrically broadened Fano. The C–F phonon confinement model cannot explain these data. Our analysis shows that the downshifting and broadening probably arises as a result of laser heating. We suggest that the line asymmetry at higher laser powers is due to Fano interference between scattering from free carriers and the discrete LO (TO) $k = 0$ phonon. A comparison of our results to those from bulk Si suggests that the carriers in our Si NWs are in the conduction band. Further experiments as a function of excitation wavelength combined with theoretical modeling would perhaps help in pinpointing the exact nature of the electronic continuum and hence the band structure of small silicon nanowires.

Acknowledgment. This work was financially supported by NSF-NIRT, grant no. DMR-0103585 and the NSF-MRSEC program at U-Penn, grant no. DMR00-79909. R.G. was supported by UPenn-MRSEC (DMR00-79909). Q.X. acknowledges support by NSF-NIRT (DMR-0103585). We acknowledge helpful discussions with Professor G. D. Mahan at Pennsylvania State University.

References

- (1) Cui, Y.; Lieber, C. M. *Science (Washington, D.C.)* **2001**, *291*, 851.
- (2) Mao Huang, M. A.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. *Science (Washington, D.C.)* **2001**, *292*, 1897.
- (3) Haoquan Yan, J. C.; Schaller Johnson, R. D.; Haber, L. H.; Saykally, R. J.; Peidong, Y. *J. Phys. Chem. B* **2001**, *105*, 11378.
- (4) Duan, X. F.; Huang, Y.; Cui, Y. et al. *Nature (London)* **2001**, *409*, 66.
- (5) Cui, Y.; Wei, Q. Q.; Park, H. K. et al. *Science (Washington, D.C.)* **2001**, *293* (5533), 1289.
- (6) Huang, Y.; Duan, X. F.; Cui, Y. et al. *Science (Washington, D.C.)* **2001**, *294*, 1313.
- (7) Li, B. B.; Yu, D. P.; Zhang, S. L. *Phys. Rev. B* **1999**, *59*, 1645.
- (8) Wang, R. P.; Zhou, G. W.; Liu, Y. L. et al. *Phys. Rev. B* **2000**, *61*, 16827.
- (9) Richter, H.; Wang, Z. P.; Ley, L. *Solid State Commun.* **1981**, *39*, 625.
- (10) Adu, C. K. W.; Bhattacharyya, S.; Sumanasekera, G. U. et al. *J. Nanosci. Nanotechnol.* Submitted for publication, 2003.
- (11) Ellis, R. S.; Wagner, W. C. *Appl. Phys. Lett.* **1964**, *4*, 89.
- (12) Bevington, P. R.; Robinson, D. K. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 2003.
- (13) Balkanski, M.; Wallis, R. F.; Haro, E. *Phys. Rev. B* **1983**, *28*, 1928.
- (14) Konstantinovic, M. J.; Bersier, S.; Wang, X. et al. *Phys. Rev. B* **2002**, *66*.
- (15) Compaan, A.; Lee, M. C.; Trott, G. J. *Phys. Rev. B* **1985**, *32*, 6731.
- (16) Magidson, V.; Beserman, R. *Phys. Rev. B* **2002**, *66*, 195206.
- (17) Balkanski, M.; Jain, K. P.; Beserman, R. et al. *Phys. Rev. B* **1975**, *12*, 4328.
- (18) Cerdeira, F.; Cardona, M. *Phys. Rev. B* **1972**, *5*, 1440.
- (19) Chandrasekhar, M.; Renucci, J. B.; Cardona, M. *Phys. Rev. B* **1978**, *17*, 1623.
- (20) Jouanne, M.; Beserman, R.; Ipatova, I. et al. *Solid State Commun.* **1975**, *16*, 1047.
- (21) Nickel, N. H.; Lengsfeld, P.; Sieber, I. *Phys. Rev. B* **2000**, *61*, 15558.
- (22) Yu, D. P.; Bai, Z. G.; Ding, Y. et al. *Appl. Phys. Lett.* **1998**, *72*, 3458.
- (23) Kanemitsu, Y.; Ogawa, T.; Shiraishi, K. et al. *Phys. Rev. B* **1993**, *48*, 4883.
- (24) Feng, S. Q.; Yu, D. P.; Zhang, H. Z. et al. *J. Cryst. Growth* **2000**, *209*, 513.
- (25) Campbell, I. H.; Fauchet, P. M. *Solid State Commun.* **1986**, *58*, 739.
- (26) Kanemitsu, Y.; Uto, H.; Masumoto, Y. et al. *Phys. Rev. B* **1993**, *48*, 2827.
- (27) Mishra, P.; Jain, K. P. *Phys. Rev. B* **2000**, *62*, 14790.
- (28) Zhang, S. L.; Ding, W.; Yan, Y. et al. *Appl. Phys. Lett.* **2002**, *81*, 4446.

NL0341133