Phonon confinement and laser heating effects in Germanium nanowires

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We explore the combined effects of phonon confinement and local heating caused by laser beam absorption on the Raman spectra of Germanium nanowires of different diameters (6 nm, 7 nm, and 12 nm). The asymmetric broadening and downshifting of the first order Raman band is studied as a function of the average wire diameter and the local temperature of the nanowires. The basic phenomenological model with a modified confinement function incorporated with thermal effects is in good agreement with our experimental results. We also show the effects of the nanowire diameter, thermal conductivity of the underlying substrate, and the mediating substance (gallium in this case) on the local temperature of the nanowires.

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I. INTRODUCTION

The research activities done both experimentally and theoretically, on reduced dimensional systems have demonstrated their unique electronic and optical properties[1] and have generated tremendous interest in both scientific and technological communities. Especially, the application of one-dimensional nanostructures such as silicon and Germanium nanowires into integrated optoelectronic devices has triggered immense research pursuits with the expectations of transition from indirect to direct band gap in these materials.[2,3] The importance of quantum confinement effects in low dimensional systems has already been demonstrated with the observance of increase in band gap and the shifting of photoluminescence into visible region in silicon nanowires with sufficiently small diameters. Theoretically, the quantum mechanical effects are expected to dominate in nanowires when the wire diameter approaches the de Broglie wavelength of the carriers. Another equally important and unique quantum mechanical feature of low-dimensional systems is the phonon confinement. Raman spectroscopy can be utilized to study the phonon confinement effects in nanowires.[4,5] In recent years, several papers have reported Raman spectroscopy results on silicon nanowires related to phonon confinement.[6–8] But, most of these results are complicated due to the effects of local heating caused by laser beam absorption,[9,10] wide distribution of nanowire diameters, and unavoidable oxide sheath of the nanowires among other complexities. Here, we report a model of first order Raman excitation that couples the effect of phonon confinement and heating effect on assembly of high density Ge nanowires grown on molten gallium droplets.

II. EXPERIMENT

Ge nanowires were synthesized using bulk nucleation and growth from gallium droplets at temperatures ranging from 200–550 °C using a concept similar to the one described earlier.[11] High densities of crystalline Ge nanowires were grown spontaneously from gallium droplets of sizes ranging from 50 nm to several millimeters, on several different substrates including Germanium and quartz. The results of Ge nanowire synthesis using low-melting metals and the corresponding rationalization about nucleation for nanowire size as a function of synthesis temperature are described in detail elsewhere.[12] Raman scattering measurements on an ensemble of as-synthesized Ge nanowires were performed at room temperature in the backscattering configuration using an in-Via Renishaw micro-Raman system consisting of a cooled CCD detector and a confocal microscope with 50X objective. The spot size at the sample is 1 μm^2. The excitation source was a He:Cd laser with 632.8 nm radiation. Measurements at various laser excitation powers were performed.

III. THEORY

In sufficiently smaller dimensions, the electronic and phonon states are expected to be altered due to quantum confinement. Fundamental studies on confined crystalline nanostructures are being intensively explored and subjected to controversies and inconsistencies. Several groups have reported Raman scattering results on Si and Ge nanowires to confirm the phonon confinement effects by observing the down shifting and asymmetric broadening of the Raman-active optical modes relative to their bulk counterparts.[4–7] The results due to phonon confinement were explained by fitting the experimental line shape with the phenomenological theory first proposed by Richter *et al.*,[4] for spherical nanoparticles and then extended to cylindrical nanostructures by Campbell and Fauchet.[5] According to their model, the plane wave such as bulk phonon wave functions cannot exist inside the nanowires transverse to the wire axis caused by the finite spatial extent and leads to the breakdown of the bulk $q_0=0$ selection rule. Instead, the confined phonons are composed of a sum of bulklike phonons with a range of different wave vectors (q) around the zone center leading to asymmetric broadening and downshifting of the Raman band in nanowires.

The intensity of the first-order Raman spectrum $I_0(\omega)$ (of a single nanostructure) is given by

$$I_0(\omega) \sim \int \frac{|C(0,q)|^2}{\left[[\omega - \omega(q)]^2 + \left(\frac{\Gamma}{2}\right)^2\right]} d^3q, \tag{1}$$

where $C(0,q)$ is the Fourier coefficient[4–6] of the spatial confinement function $W(r)$, $\omega(q)$ is the dispersion relation of Ge, and Γ is the FWHM of the Raman peak of the bulk Ge. The spatial confinement function for the nanowire is assumed to be of the form $W(r)=e^{-(\alpha r/D)2}$ in cylindrical coordinates, where D is the diameter of the nanowire measured radially and perpendicular to the wire axis and α is the confinement parameter. This yields $|C(0,q)|^2=e^{(-q^2D^2/2\alpha^2)}$. For a cylindrical nanowire $d^3q \sim qdq$ with q being perpendicular to the wire axis. The dispersion relationship $\omega(q)$ for the Germanium TO mode is approximated by

$$\omega^2(q) = A + 0.5[A - \cos(\pi q)] + B \tag{2}$$

with $A=45\ 300\ \text{cm}^{-2}$ derived by fitting A to the experimental (neutron scattering) TO branch data[13] for Ge at 300 K and is confirmed by the equation proposed by Kanata *et al.*[7] B is adjusted to match the bulk Ge value measured with our spectrometer. Γ is measured by the convolution of the natural Ge FWHM (Γ_0) and the instrumentation broadening (Γ_i) and is given by

$$\Gamma = \Gamma_0 + \sqrt{\left(\frac{\Gamma_0}{2}\right)^2 + \Gamma_i^2}. \tag{3}$$

In the spectrometer used, bulk Ge has FWHM of $\sim 5\ \text{cm}^{-1}$. By comparing this with the natural FWHM of Ge, the instrumentation broadening $\sim 1.4\ \text{cm}^{-1}$. Since the Raman signal from an individual nanowire is too weak to detect, all our measurements are done on an ensemble of wires. The diameter distribution of the nanowires is determined by Gaussian function

$$P(D) \sim e^{[(D - D_0)^2/2\sigma^2]}, \tag{4}$$

where D_0 is the most probable diameter and σ is the standard deviation of the diameter distribution.

The resulting confinement effect with the diameter distribution included is given by

$$I(\omega) = \int I_0(\omega) P(D) dD. \tag{5}$$

Typically the laser irradiation during Raman measurements can cause sample heating and photon excitation of charge carriers.[7,9,14–16] Down shifting and broadening of Raman band in bulk materials, with increasing laser radiation is typically identified to be due to heating. Poor thermal contact of the nanowires with the substrate and intense focusing of the laser beam in a micro Raman spectrometer can lead to significant heating of the sample. Here, we report results of the temperature dependence of the first-order Raman spectra of Ge nanowires by varying the laser power and thermal conductance of the nanowires and the substrate. In this report, the subtle interplay between quantum phonon confinement, the local heating effect and thermal expansion of the nanowires will be shown to influence both the frequency shift and the asymmetric broadening of the Raman spectra. The Stokes-anti-Stokes intensity ratio of the first order Raman spectra is used to determine the local temperature of the nanowire sample. The intensity ratio is related to the temperature by

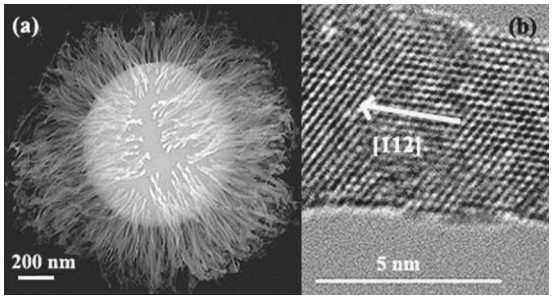

FIG. 1. (a) SEM image of as-synthesized Ge nanowires growing from a single Ga droplet. (b) HRTEM image of a 6 nm Ge nanowire with a growth direction of [211].

$$\frac{I_s}{I_{as}} = K \exp\left(\frac{\hbar\omega_0}{K_B T}\right), \tag{6}$$

where, the prefactor K depends on the absorption constant and the Raman cross section at a given frequency. Typically, the value of K is determined by calculating the Stokes-anti-Stokes intensity ratio (I_s/I_{as}) at a known temperature. In our case, the value for the lowest possible laser power was used to determine K at room temperature assuming no laser induced heating. ω_0 is the phonon frequency.

The phonon confinement function is modified to include the temperature dependence[14–16] as

$$\omega(q,T) = \omega(q) + \Delta\omega_1(T) + \Delta\omega_2(T), \tag{7}$$

$\Delta\omega_1(T)$ is the frequency shift due to phonon decay processes. This phonon-phonon coupling term describes the anharmonic coupling between phonons and is approximated by

$$\Delta\omega_1(T) = A_1\left(1 + \frac{2}{e^{(\hbar\omega_0/2\kappa_B T)} - 1}\right) + A_2\left(1 + \frac{3}{e^{(\hbar\omega_0/2\kappa_B T)} - 1} + \frac{3}{(e^{(\hbar\omega_0/2\kappa_B T)} - 1)^2}\right). \tag{8}$$

Where, the first term describes the coupling of the phonon to decayed low energy two phonons (three phonon coupling) and the second term describes the coupling to three decayed phonons (four phonon coupling). In our analysis, we used only the three phonon coupling term. A_1 is adjusted to match the bulk Ge values.

$\Delta\omega_2(T)$ is the frequency shift due to the thermal expansion of the lattice (interestingly nanowires used in this study exhibit no oxide sheath formation as evidenced by Fig. 1(b), and hence, the compressive stress can be neglected and it is given by

$$\Delta\omega_2(T) = \omega_0[\exp(3\gamma\beta T) - 1], \tag{9}$$

where γ is the Gruneisen parameter and β is the thermal expansion coefficient of Germanium.

The temperature dependence of the FWHM in the formalism[14–16] is

$$\Gamma(T) = \Gamma + \Delta\Gamma(T), \tag{10}$$

where Γ is the FWHM of the bulk Ge including the instrumental broadening, and $\Delta\Gamma(T)$ is given as

$$\Delta\Gamma(T) = B_1\left(1 + \frac{2}{e^{(\hbar\omega_0/2\kappa_B T)} - 1}\right) + B_2\left(1 + \frac{3}{e^{(\hbar\omega_0/2\kappa_B T)} - 1} + \frac{3}{(e^{(\hbar\omega_0/2\kappa_B T)} - 1)^2}\right). \tag{11}$$

The first term is due to the three phonons coupling and the second term resulted by four phonons coupling effect on FWHM of Raman spectrum. Just as before, we neglect the four phonon coupling term, and B_1 is adjusted to match the bulk Ge values.

The asymmetric broadening of the Raman band has been attributed to Fano interference[8] between scattering from the discrete optical phonon and an electronic continuum due to photon-excited charge carriers. At sufficient doping levels, electrons and holes in semiconductors participate in inelastic scattering leading to Fano resonance with optical phonons. An asymmetry on the Fano line shape depends on the electron-phonon coupling strength. Attributable to the observation of asymmetry in low frequency tail, the contribution of Fano resonance for the asymmetric broadening of the Raman spectrum can be ruled out. Since laser excitations generate both holes and electrons in Ge, one should expect some positive asymmetry at least for higher powers as the phonon interact with these hole carriers.

The asymmetric line shape in the phonon mode is also known to be affected by strain caused by oxide layer. But the Ge nanowires used in this investigation were virtually devoid of any oxide sheath.

In this study, the dominant effect depends on the thermal contact of the sample to the substrate and the diameter of the nanowires. A coupled phenomenological model that accounts for both the phonon confinement as well as the temperature effects so as to best describe the observed asymmetry in the phonon line shapes is developed. The first order Raman spectra for the Ge nanowires considering the quantum phonon confinement and the heating effect is expressed as

$$I(\omega, D) = \int_0^1 \int_0^\infty \frac{e^{-(q^2D^2/4\alpha^2)} e^{[(D-D_0)^2/2\sigma^2]}}{\left\{\omega - \left[\omega(q) + A_1\left(1 + \frac{2}{e^{(\hbar\omega_0/2\kappa_B T)} - 1}\right) + \omega_0(e^{-3\gamma\beta T} - 1)\right]\right\}^2 + \frac{1}{4}\left[\Gamma + B_1\left(1 + \frac{2}{e^{(\hbar\omega_0/2\kappa_B T)} - 1}\right)\right]^2} dq dD. \tag{12}$$

IV. RESULTS AND DISCUSSION

Figure 1(a) shows a scanning electron micrograph (SEM) of as-synthesized Ge nanowires grown from a single gallium droplet. Figure 1(b) shows a high resolution transmission electron micrograph (HRTEM) of a Ge nanowire free of any oxide sheath. The diameter of the nanowire is ~6 nm and the growth direction is [211]. The SEM images show that uniform Ge nanowires with small diameter distribution are nucleated from gallium droplets of any size.

In Fig. 2, we display the temperature determined experimentally using Eq. (6) for Ge nanowires with average diameter, $D=12$ nm grown on quartz substrate vs the laser power. The inset of Fig. 2 shows the temperature determined by calculating (I_s/I_{as}) ratio including the estimated error vs. the temperature determined by fitting the data with our model described by Eq. (12). The temperature values determined by either method are in reasonable agreement. It should be emphasized that the accurate temperature determination of an individual nanowires is non-trivial.

Figure 3 shows the Stokes Raman spectrum of the Ge nanowires ($D=12$ nm) using 632.8 nm radiation at 0.85 mW power (circles). The Raman spectrum of the bulk Ge is also shown for comparison (dotted line). It is also shown in Fig. 3 the best fits with systematic inclusion of (i) pure phonon confinement effect (dashed line), (ii) phonon confinement with Gaussian diameter distribution (dotted-dashed line), and (iii) the complete model with the inclusion of temperature effects (solid bright line) given by Eq. (12). The results are in excellent agreement with experimental data. The data collected at the lowest possible laser power in this analysis is used to extract the confinement parameter α assuming no laser heating; The best fit yields $\alpha=1.7\alpha_{CF}$. Previously, Richter *et al.* used $\alpha=1$ in their confinement model while, Campbell and Fauchet have used $\alpha_{CF}=2\pi^2$. The average diameter D and the standard deviation σ are determined using both SEM and TEM analysis. For higher laser powers, these calculated results cannot account for the large down shifting and asymmetric broadening of the experimental data and temperature effects because of inhomogeneous heating were necessary to be incorporated in the analysis. It has been shown that the thermal conductivity of semiconducting nanowires are considerably low compared to their bulk counterparts due to surface scattering of acoustic phonons[17] causing excessive heating. Equation (6) is used to determine the local temperature of the nanowires. Also we determined T by using as a free parameter in Eq. (12) to fit the experimental data.

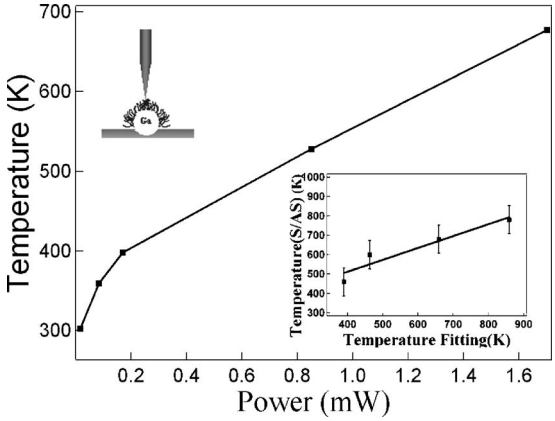

FIG. 2. The temperature determined experimentally using Stokes-anti-Stokes intensity ratio (I_s/I_{as}) for Ge nanowires with average diameter, $D=12$ nm grown on quartz substrate vs. the laser power. The inset is the temperature determined by calculating (I_s/I_{as}) ratio vs. the temperature determined by fitting the data with the model.

Here we discuss the effect of the mediating Ga droplets on the inhomogeneous heating effect of nanowires. Figure 4 shows the Stokes Raman spectra taken at 632.8 nm excitation for Ge nanowire samples with similar sizes (average diameter=7 nm) but grown on two different Ga droplet sizes on Ge substrates with varying laser power levels (circles). Solid lines are the fits to the spectra using modified phonon confinement model including the anharmonic effects and thermal expansion effects using Eq. (12). Smaller Ga droplet (of the order of micrometers), [Fig. 4(a)] resulted in more heating of nanowires compared to the larger Ga droplet (of the order of millimeters), [Fig. 4(b)] for the same average nanowire diameters. This can be attributed to the poor thermal energy transport from smaller Ga droplets to the substrate due to smaller interfacial contact area.

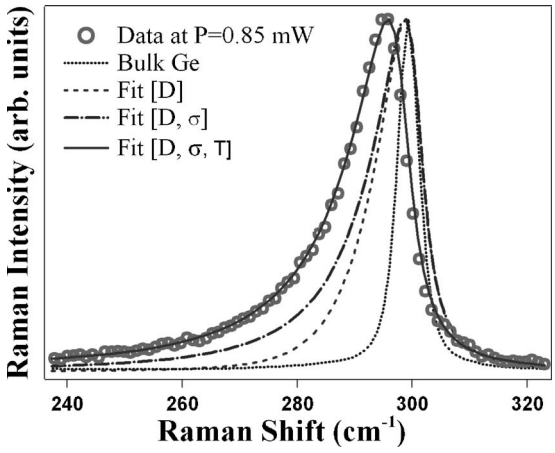

FIG. 3. Stokes Raman spectrum (λ=632.8 nm) of Ge nanowires (12 nm average diameter) at 0.85 mW laser power (circles) and the best fits with systematic inclusion of (i) pure phonon confinement effect only (dashed line), (ii) phonon confinement with Gaussian diameter distribution (dotted-dashed line), and (iii) the complete model with the inclusion of temperature effects (solid line). The Raman spectrum of the bulk Ge is also shown (dotted line) for comparison.

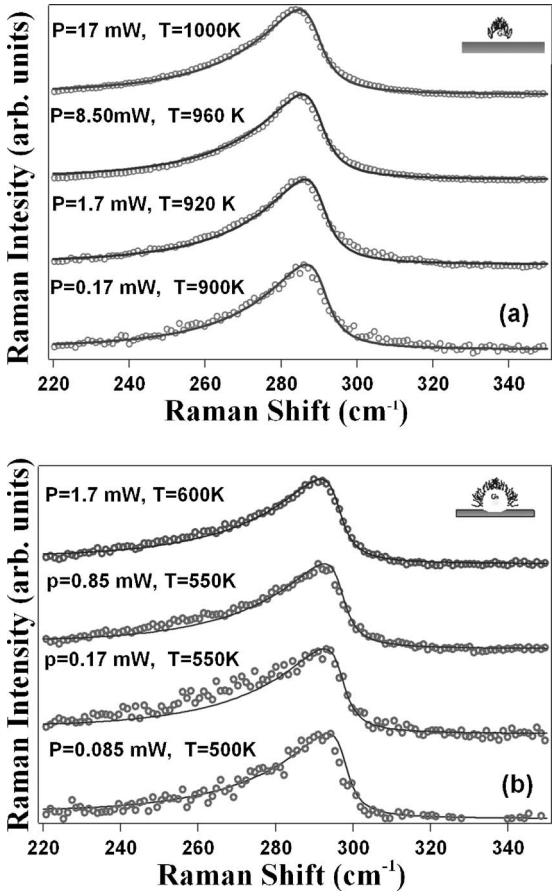

FIG. 4. Raman spectra at 632.8 nm for the Ge nanowire ($D=7$ nm, $\sigma=2$ nm) for varying laser power levels (circles) at two different Ga droplet sizes (a) droplet size ~1 μm and (b) droplet size ~1 mm. The soild lines represent the best fits to Eq. (12).

Next we discuss the effect of the underlying substrate on the inhomogeneous heating effect of nanowires. In Fig. 5, the Raman spectra for two different nanowire samples of similar size (average $D=12$ nm) grown from similar size Ga drop-

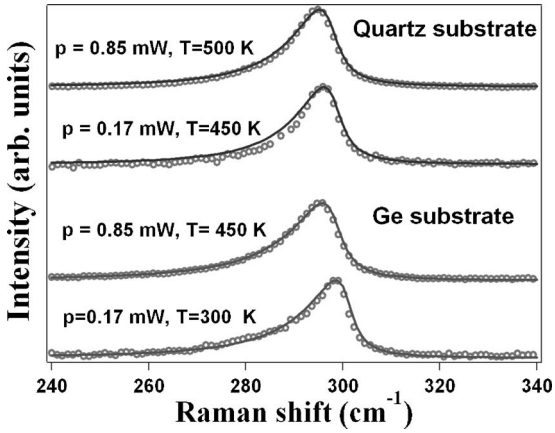

FIG. 5. The Raman spectra for two different nanowire samples of similar size (average $D=12$ nm) grown from similar size Ga droplets on two different substrates, quartz (upper two curves) and Ge (lower two curves) for two different laser power levels.

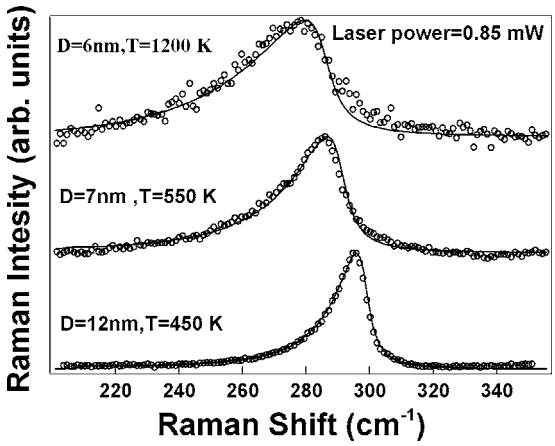

FIG. 6. Raman spectra at 632.8 nm for three different Ge nanowire samples with varying average diameters at the same incident laser power (P=0.85 mW). Solid lines are the best fits to the Eq. (12).

lets on two different substrates, quartz and Germanium, are shown. The upper two curves represent the data for nanowires grown on quartz substrates and the lower two represent that on Germanium substrates for two different laser power levels. Again the circles represent the experimental data and the solid lines represent the best fits to Eq. (12). The heating effect is found to be more pronounced for nanowires grown on quartz substrates for a given laser power level. This can be attributed to the difference in the nature of thermal anchoring of Ge nanowires onto the quartz substrate with poor thermal conduction (thermal conductivity, $\kappa \sim 6$ W/mK) compared to the Germanium substrate with better thermal conduction ($\kappa \sim 60$ W/mK).

Finally, Raman spectrum of Ge nanowire ensembles with three different average diameters, 6 nm, 7 nm, and 12 nm, grown on Ge substrates with similar size Ga droplets were studied as shown in Fig. 6. In each case, the temperature was determined from best fits to Eq. (12) and compared with the values obtained from Eq. (6). The same confinement parameter value for α was used in the entire analysis. For a given power level, the down shifting, broadening, and asymmetry of the Raman line shape increase with decreasing diameter of the nanowires as shown in Fig. 6. These values are displayed in Table I.

The asymmetry is defined as $A=\left(\frac{\omega_m-\omega_-}{\omega_+-\omega_m}\right)$.Where, ω_m is the peak position, ω_- and ω_+ are the frequency at 10% intensity on the low and high frequency sides of the peak maximum. Also the local temperature (as determined by the fits) increases considerably with decreasing diameter of the nanowires. Our model can explain the enhancement of the phonon confinement as well as the suppression of the thermal conductivity with decreasing wire diameter. In order to identify the pure phonon confinement, one has to work at very low laser power levels with nanowires on a substrate with high thermal conductivity or at a lower temperature using a cold stage. The model can be used as a possible tool to determine the diameter and diameter distribution of ensembles of nanowires for a variety of nanowire systems knowing the local temperature of the sample due to laser heating during the spectral measurements. Interestingly, our model can account very well for the larger diameter data for high laser power levels, but excessive heating effects on smaller diameter nanowires prohibit further spectroscopic study at higher Raman laser power.

TABLE I. The peak position, line broadening, and asymmetry for three different samples under the same laser power level.

Ave. diameter (D) (nm)	Peak position (ω_m) (cm^{-1})	FWHM (Γ) (cm^{-1})	Asymmetry (A)
12	301	13	2.58
7	286	22	3.18
6	280	31	3.5

V. CONCLUSIONS

The asymmetric broadening and the down shifting of the Raman line shape in Ge nanowires show complicated dependence on wire diameter and local laser heating. We demonstrated the ability to include the effects of local laser heating and thermal expansion in addition to the pure phonon confinement effects to describe the first order Raman spectra of Ge nanowires. We also observed the effects of thermal conductivity of the underlying substrate and the mediating substance (gallium in this case) on the local temperature of the nanowires. We excluded the effects of Fano resonance arising from interference between photon-excited free carriers and q=0 phonons. This is the first report to address detailed analysis of Raman spectroscopy on Ge nanowires in spite of excellent work on Si nanowires by Piscanec *et al.*[9] and Adu *et al.*[18] Our results support the findings of both groups and confirm the common effect of laser induced heating during micro Raman spectroscopy in addition to phonon confinement at least for polar semiconducting nanowires. In order for one to appreciate phonon confinement effects using micro Raman spectroscopy of semiconducting nanowires it is necessary to use ultra low power laser and high thermal conductivity substrates with good thermal anchoring. Our result should provide good insight into all these factors that have enormous effects on the Raman spectra of Germanium nanowires and any nonpolar semiconductor nanowires.

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