NANO LETTERS

2003
Vol. 3, No. 12
1745−1750

Surface Optical Phonons in Gallium Phosphide Nanowires

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Received September 29, 2003; Revised Manuscript Received October 15, 2003

ABSTRACT

Raman scattering studies of crystalline GaP nanowires reveal a strong additional peak in the first order spectrum that can be clearly assigned to surface optical (SO) phonons. The frequency of this SO peak is found to be sensitive to the dielectric constant of the surrounding medium in which the nanowire is embedded. A theory for the SO phonons in cylindrical wires is presented, the SO mode dispersion ω(q) and the experimental peak frequency are then used to predict the wavelength of the dominant Fourier component of the surface potential responsible for activating the SO mode. Interestingly, this SO phonon wavelength is found to agree with the wavelength of diameter modulation observed for some nanowires.

Semiconducting nanowires represent interesting solid state systems that have shown promise recently for new electronic devices, electrooptic devices, and sensors.[1−4] Measurements of their fundamental physical properties are starting to appear in the literature.[5−7] In particular, there have been reports of Raman scattering studies in polar semiconducting nanowires in which peaks in the Raman spectra have been identified with the TO and LO phonon modes at zero wavevector ($q = 0$). The frequencies of these peaks are similar to that reported for the bulk. However, a "shape effect" for polar semiconducting nanowires has also been reported that stems from the long-range nature of the electromagnetic fields associated with these phonons.[7] The shape effect has been reported to lead to new optic modes whose frequency should differ by 2−10 cm^{-1} from that of the $q = 0$ optic mode in bulk.[7] In this paper, we present results on surface optical (SO) phonons in GaP nanowires. In the perfect nanowire, these modes should not be observable by Raman scattering. However, we observe strong scattering from these modes, and it appears likely that they are activated by periodic oscillations in the wire cross section (or diameter) along its length. An additional Raman peak identified with SO modes in core−shell GaP@GaN nanowires has been reported previously.[8] However, the present work, we believe, is the first to definitively make the SO assignment by virtue of the effect of the overlaying dielectric medium. A theory for the SO modes in a cylindrical polar semiconducting nanowire is also presented here which can explain qualitatively the experimental observations, such as the shift in the SO band frequency with (1) the value of the dielectric constant of the surrounding optical medium, and (2) the period of the diameter oscillation along the wire. Thus, SO modes may be quite useful in detecting small diameter oscillations in the nanowires.

The modes at the surface of a nonmagnetic object are determined by the dielectric properties of the materials on both sides of the surface and also by the shape of the object. For a recent review of these SO modes, the reader is referred to ref 9. Fuchs and Kliewer first predicted surface optical phonons in 1965.[10] Ibach, using inelastic electron scattering, observed them for the first time.[11] Since then, they have been observed by a variety of other methods (e.g., Raman scattering, attenuated total reflection (ATR), and infrared transmission measurements) on planar surfaces and on the curved or faceted surfaces of small particles.[12−15] Using a perfect surface, the SO modes cannot be observed optically due to momentum conservation constraints. In this case, optical detection of the surface modes is possible only if a source of wave vector is supplied through strong Fourier components of the surface potential.[9] This can be accomplished in different ways, i.e., surface roughness, or by construction of a grating along the surface, which will cause the surface to absorb the phonon momentum in units of $2\pi/L$, where L is the spacing between grating elements. Yet another method for detecting SO modes involves placing a prism at the surface of the sample. The evanescent wave from the prism−sample interface can probe the surface.[12]

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10.1021/nl034842i CCC: $25.00 © 2003 American Chemical Society
Published on Web 11/05/2003

In our case, we believe that the periodic oscillations of the nanowire cross section provide the "grating" necessary to overcome momentum conservation and observe the modes by Raman scattering.

The highly crystalline GaP nanowires used for our measurements were synthesized using pulsed laser vaporization of a GaP/5%Au target in a flow of ~100 sccm of Ar/5%H_2 at a pressure of 100 Torr. The details of the growth apparatus, sample preparation, and characterization have been published elsewhere.[16] The as-grown GaP nanowires exhibit a light yellow color. Our electron microscopy data indicate that the growth proceeds along the ⟨111⟩ direction by the vapor−liquid−solid (VLS)[1] growth mechanism, i.e., the nanowires are observed by TEM to have a Au particle at one end. Using high-resolution transmission electron microscopy (JEOL 2010F at 200 kV), lattice fringes were observed extending to the surface of the nanowire. Furthermore, it was difficult to observe any amorphous layer on the surface of the wires. We have also used TEM to determine the diameter distribution and growth direction of the two batches of nanowires studied here. The most probable diameter of the two sets of nanowires was found to be ~ 20 and 50 nm, respectively, by fitting a log-normal function to the diameter distribution obtained from atomic force microscopy images.[16]

Raman spectra were collected at room temperature with a JY−Horiba T64000 Raman microprobe spectrometer in a backscattering configuration (laser spot diameter ~1 micron). Our samples were in the form of thin films of tangled nanowires deposited on a crystalline silicon substrate by placing a drop of GaP/ethanol solution fresh from agitation in an ultrasonic bath onto the substrate and spinning the sample at ~500 rpm. The spectra were collected with the films in air or under solvents of various refractive indices. The power at the sample was about 1 mW, and care was taken to avoid any effects due to laser heating.

Figure 1a shows an SEM image of GaP nanowires. Figure 1b shows a high-resolution TEM image (JEOL 2010F at 200 kV) of a small section of a GaP nanowire. The clear contrast of the lattice fringes out to the surface of the nanowire indicates that the wire is highly crystalline. The growth direction is seen to be ⟨111⟩, and the spacing between lattice fringes is 0.315 nm, which is in good agreement with the spacing between ⟨111⟩ planes in GaP data (powder diffraction data: 32−397). The ⟨111⟩ growth direction dominates; occasionally we can observe wires with a ⟨110⟩ growth direction.

Figures 2 and 3 show, respectively, the Raman spectra of GaP nanowires with most probable diameter $\bar{d} = 20$ and 50 nm. The spectra were collected with the wires in air, dichloromethane, and aniline. The data are represented by the solid squares, and the thin lines are the results of a Lorentzian line shape analysis. There are three prominent features in each spectrum. The lowest and highest frequency bands, respectively, are identified with the $q = 0$ TO mode and $q = 0$ LO mode, in reasonable agreement with bulk crystalline GaP (LO: 367 cm^{-1}, TO: 403 cm^{-1}[17]). The difference in the peak position of the LO band in bulk and

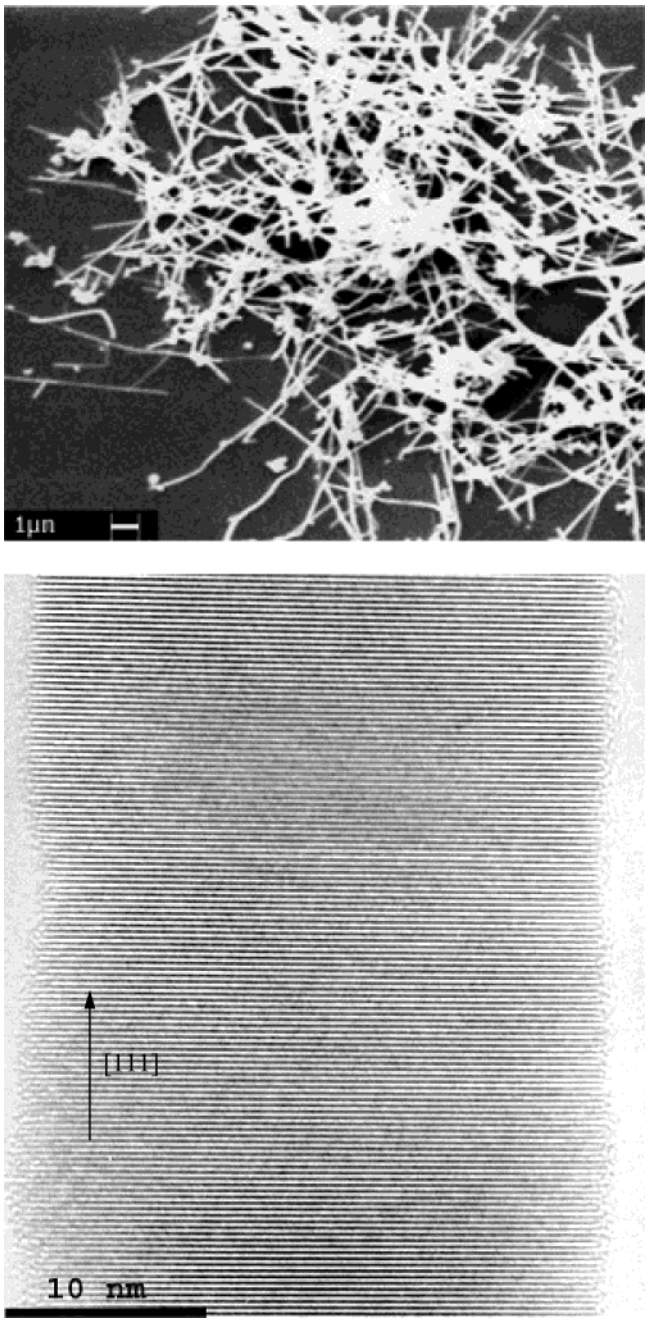

Figure 1. (a) SEM image of GaP nanowires deposited on a silicon substrate. A thin layer of Au was coated to decrease charging effect. (b) High-resolution TEM image of a gallium phosphide nanowire. The spacing between adjacent lattice fringes is 0.315 nm, which confirms that the growth direction is ⟨111⟩.

our nanowires (~2 cm^{-1}) has been recently suggested to be due to a "shape" effect arising from the high aspect ratio of the polar semiconducting nanowires that truncates the dipolar sum in a nanowire as a result of the boundary.[7] As shown in Figures 2 and 3, there is a third Raman band lying between the TO and the LO bands. We can positively identify this band with SO modes because of its sensitivity to the dielectric constant of an external medium (ϵ_m) in contact with the nanowire, e.g., air ($\epsilon_m = 1$) or dichloromethane ($\epsilon_m = 2$) or aniline ($\epsilon_m = 2.56$). Furthermore, in polar semiconductors, the surface modes usually appear between the TO and

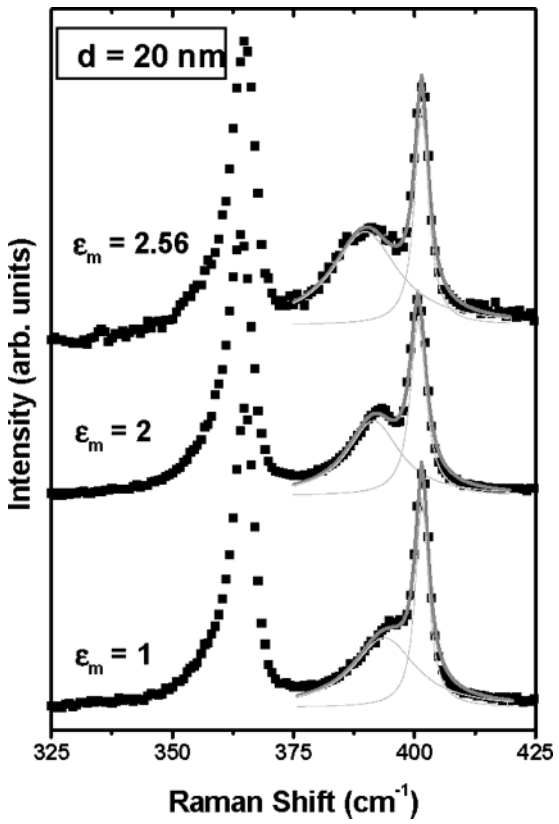

Figure 2. Raman spectra of GaP nanowires with most probable diameter $\bar{d} = 20$ nm recorded in three different media with different dielectric constant (ϵ_m). The low, middle and high frequency bands are identified respectively with the TO, SO, and LO phonons. The solid lines represent Lorentzian line shapes used to fit the SO and LO band.

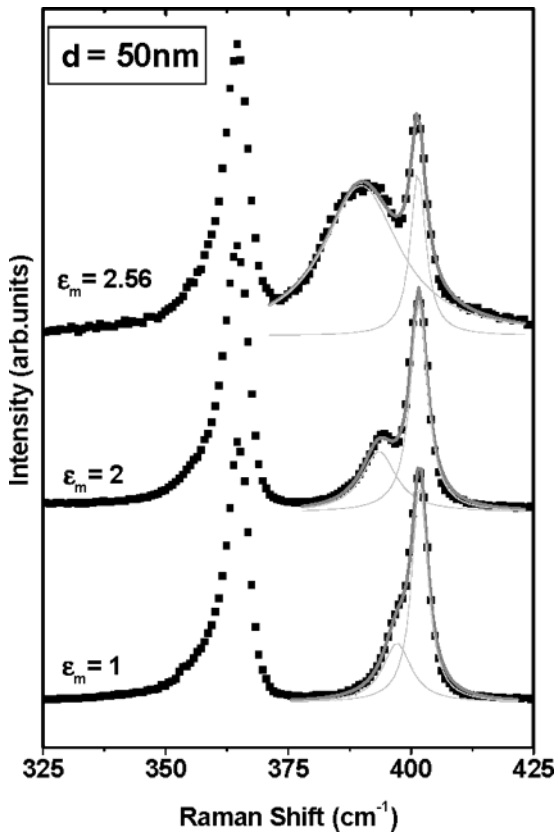

Figure 3. Raman spectra of GaP nanowires with most probable diameter $\bar{d} = 50$ nm recorded in three different media with different dielectric constant (ϵ_m). (Also see caption to Figure 2.)

LO bands, although, in most cases the SO modes are difficult to observe. As can be seen by comparing the spectra for $\bar{d} = 20$ nm (Figure 2) and $\bar{d} = 50$ nm (Figure 3) wires, the scattering from the surface mode is quite prominent in both cases, with comparable integrated intensity to the LO and TO bands. It might be argued that the additional band located between the LO and TO bands in Figures 2 and 3 is similar to the mode seen in earlier studies on doped bulk GaP by Galtier and Martinez who identified it as a bound impurity phonon band.[18] They found that in S- or Te-doped GaP, the LO mode downshifts (<1 cm^{-1}) and an additional weak band appears on the low frequency side of the LO mode. However, the spectra in Figures 2 and 3 show that the intermediate frequency band softens as the dielectric constant of the suspension medium is increased, whereas the LO and TO bands do not change position. Based on this observation, we can unambiguously assign the intermediate frequency band to SO modes.

In earlier studies on porous and nanoparticle GaP, SO bands were observed using Raman and infrared spectroscopy.[13−15] Most of the analyses were based on a continuum model. The frequencies of the TO and the SO modes were used to estimate the particle size of the nano- or microcrystals, and the particle size was found to correlate with that obtained by TEM or SEM. In some of this previous work, the calculated frequency of the SO mode was found to be in poor agreement with experiment.[14] However, the large discrepancy was attributed to the (simplistic) assumption that the crystallites were spherical. In another recent work on infrared transmission of GaP nanoparticles, the discrepancy between theory and experiment for the SO band position was attributed to contributions from higher frequency surface modes.[15]

To quantitatively understand the variation of the line shape parameters of the SO band in our nanowires, we have made a least-squares fit to the spectrum, as shown in Figures 2 and 3, to a sum of two Lorentzians (indicated by the thin line). For simplicity, and to avoid possible complications from the asymmetric TO band, only the part of the spectrum close to the LO and the SO band was fit. Figure 4 shows the dependence of the surface band line shape parameters, peak position, and line widths plotted as a function of the dielectric constant ϵ_m of the overlaying media.

The dispersion relation $\omega_{SO}(q)$ for a SO mode in an infinite long cylindrical wire, in the limit where the phonon wavevector $q \gg \omega/c$, can be written as[9]

$$\omega_{SO}^2 = \omega_{TO}^2 + \frac{\tilde{\omega}_p^2}{\epsilon_\infty + \epsilon_m f(x)}; \quad x = qr \tag{1}$$

where ω_{TO} is the TO mode frequency at zone center, $\tilde{\omega}_p$ is the screened ion plasma frequency given by $\omega_{LO}^2 = \omega_{TO}^2 + \tilde{\omega}_p^2/\epsilon_\infty$, ϵ_∞ is the high-frequency dielectric constant of bulk

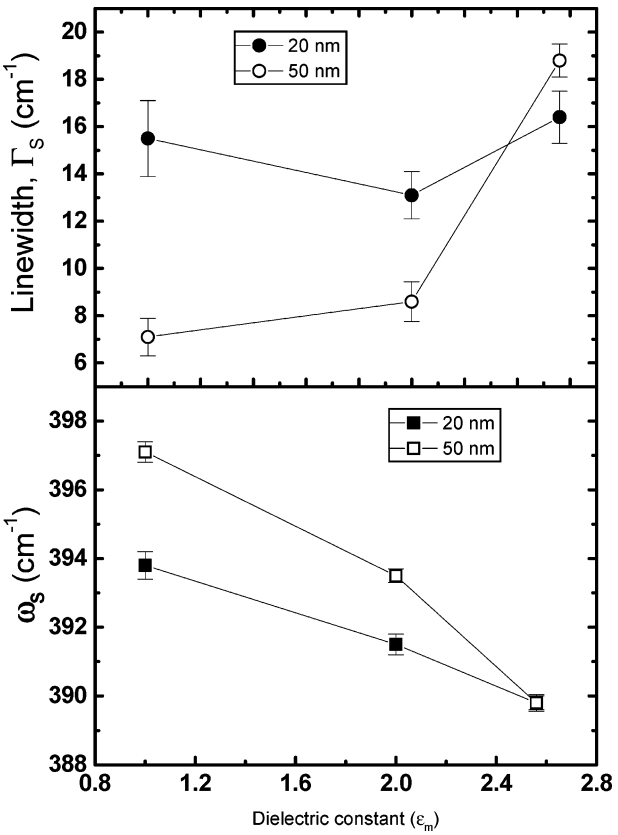

Figure 4. Variation of the line shape parameters for the SO band (peak position and line width) as a function of the dielectric constant of the overlaying medium. The lines are guides to the eye.

GaP, $d = 2r$ is the wire diameter, and $f(x)$ is obtained from the eigenvalue equation

$$f(x) = \frac{I_0(x)K_1(x)}{I_1(x)K_0(x)} \tag{2}$$

Here $I_j(x)$ and $K_j(x)$ are Bessel functions. In Figure 5 we plot the ω_{SO} vs qr given by eq 1 for $\epsilon_\infty = 9.075$, $\tilde{\omega}_p = 501.5$ cm^{-1}, $\omega_{LO} = 403$ cm^{-1}, $\omega_{TO} = 367$ cm^{-1} for $\epsilon_m = 1$. If we were to plot the SO dispersion for a $d = 20$ nm wire vs q (not vs qr) and compare it to that of plane surface (i.e., $d = \infty$), we would find very different characteristics. The maximum dispersion takes place, for a $d = 20$ nm wire, at $q^*_{wire} \sim 2 \times 10^7$/m. This q^* value marking maximum dispersion is much larger than its counterpart for SO modes at a plane surface (i.e., $q^*_{plane} \sim \omega_{LO}/c \sim 2.5 \times 10^5$/m). Thus, it is clearly important to use the correct (cylindrical) geometry when describing the SO phonons in small diameter nanowires. We can also use eqs 1 and 2 to calculate the frequency of the SO phonon band as a function of ϵ_m. Results for the three experimental ϵ_m and $x = 1$, 1.5, 2, 3, 4 are shown in Table 1, and the parameter values for the quantities used are the same as used to compute the dispersion curve in Figure 5. To observe the SO mode using Raman scattering, we presume that the surface potential along the axis of the nanowire is perturbed by a strong component with wavevector q, i.e., inelastic light scattering via SO phonons with this

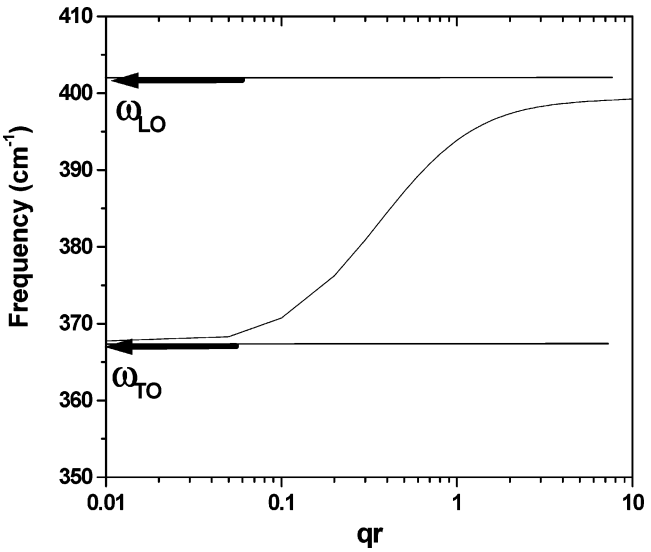

Figure 5. Calculated dispersion of the SO mode for a GaP nanowire ($\epsilon_m = 1$). The arrows indicate the $q = 0$ LO and TO phonon frequencies. We assume that the LO and TO phonon branches are dispersion less as shown by horizontal lines. The nanowire diameter is given by $2r$.

Table 1. Calculated Surface Optical Phonon Frequencies[a]

x	$f(x)$	ω_{SO} (x, $\epsilon_m = 1$) (cm^{-1})	ω_{SO} (x, $\epsilon_m = 2$) (cm^{-1})	ω_{SO} (x, $\epsilon_m = 2.56$) (cm^{-1})
1.0	3.203	392.4	387.2	385.2
1.5	2.176	394.6	390.2	388.4
2.0	1.760	395.6	391.7	390.0
3.0	1.427	396.5	393.1	391.5
4.0	1.295	396.9	393.7	392.1

[a] As a function of $x = qr$, where r is the wire radius and ϵ_m is the dielectric constant of the medium; cf., eqs 1 and 2.

average wavevector is particularly important. If we compare the computed SO frequencies $\omega_{SO}(q)$ to those obtained experimentally, we can deduce values for the important wavevector q responsible for the observation of the SO band. It appears that values of the SO band frequency calculated for $x \approx 4$ are close to the experimentally obtained values for the sample of $\bar{d} = 50$ nm, while $x \approx 1.5$ values correspond to those SO mode observed for the sample with most probable diameter, $\bar{d} = 20$ nm. Since $q = x/r$, we can obtain the value of q for the different diameter nanowire samples. We find approximately the same value of q for the two sets of wires, i.e., for $\bar{d} = 20$ or $\bar{d} = 50$ nm, $q \approx 1.5 \times 10^8$/m. Therefore, the length scale which is responsible for excitation of the SO mode is given by $2\pi/q \approx 40$ nm. Since this length scale is similar in both cases, there must be an inherent length scale in the nanowires responsible for the activation and observation of the SO band. We believe that the symmetry breaking mechanism responsible for the observation of the SO band is the presence of the wire diameter modulation along the nanowire growth direction. This modulation can indeed be observed in TEM images, as presented in Figure 6, where we show four different images with different wire diameters. The diameter modulation

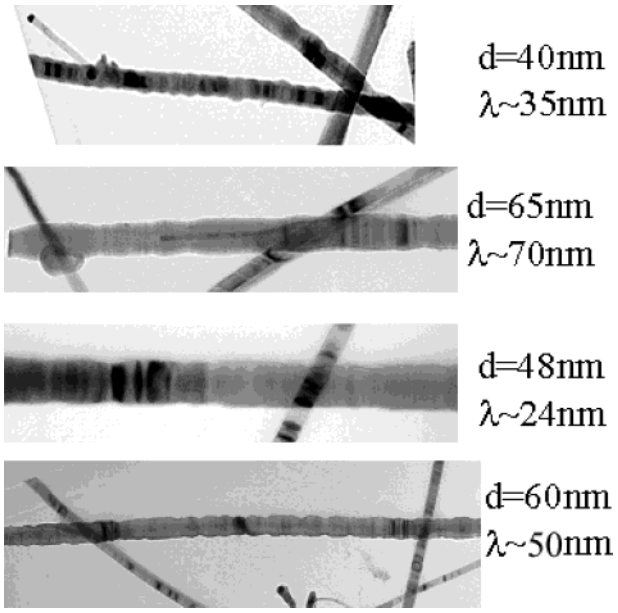

Figure 6. Bright field TEM images of GaP nanowires showing nearly periodic modulation of wire diameter. The diameter and the modulation wavelength for each image appear to the right. Diameter oscillations were observed to be more prominent in larger diameter nanowires.

wavelength λ, listed on the right of the image, was calculated using commercially available image analysis software.[19] The diameter modulation wavelengths we found, λ ($\sim$ 30−70 nm), for the small subset of nanowires measured (Figure 5) is consistent with the length scale ($\sim$40 nm) we have calculated. Again, it is important to point out that the dispersion for an SO mode calculated in a cylindrical geometry is crucial for estimating the wavelength of the important Fourier component of the surface potential that breaks the symmetry and "activates" the SO modes in a Raman scattering event. It is also possible that SO Raman scattering from larger nanowires (d > 40 nm) in the log-normal diameter distribution with a more prominent diameter modulation (Figure 6) might dominate the SO spectrum for the nanowire ensemble. This proposal might be proved if one can measure SO mode frequency from individual wires with known diameter modulation wavelength.

The above formulation to understand the SO band position does not include any dynamics of the SO phonons, and therefore is inadequate to describe the variation of the SO mode line width as a function of ϵ_m as shown in Figure 4 (top panel). Even though the line widths of the LO mode in the two nanowire samples with different diameter distributions are comparable to within 10% in all overlaying media, the line width of the surface band in the 20 nm diameter sample is twice (in air) of that observed in the 50 nm sample (in air). This implies that the surface phonons in the 20 nm nanowires have a lifetime that is half of the 50 nm nanowire batch. We believe that one of the reasons for such a large difference in the two line widths is due to the difference in the decay channel phase space available to the SO phonons for the two samples. As the SO phonon frequency decreases, the difference between the TO band and the SO decreases. It is well-known from earlier experiments that the TO line widths are much larger than the LO line widths. In earlier studies on bulk GaP, this large width is attributed to anharmonic interaction of the TO phonon with a nearly degenerate band of combined transverse and longitudinal acoustic modes near the X and K points of the Brillouin zone.[20] This result was reconfirmed by careful isotope substitution experiments by Widulle et al.[21] Therefore, it is likely that as the dielectric constant increases there are additional decay channels available for the SO mode, which were available only to the TO mode at lower values of ϵ_m. This might also explain that the fact that the line width of the SO band for the 20 nm sample is even larger in air because the SO band position is lower compared to the 50 nm sample.

It is interesting to consider the origin for the diameter modulation in a nanowire. As early as the 1970s, Givargizov et al. reported similar periodic instabilities in the cross section of submicron-diameter silicon whiskers grown by chemical vapor deposition via VLS mechanism.[22] It was proposed that the self-oscillating nature of the filament cross section stemmed from the instability of the diameter of the liquid droplet during the growth process.[22] The model involves the idea that the contact angel of the droplet (i.e., wetting of the growing surface) depends on the roughness on the interface, which, in turn, depends on supersaturation, and hence, on the curvature of the droplet.[22,23] The occurrence of the diameter modulation was related to growth conditions, such as temperature, supersaturation, and impurities.[22] Another possible reason offered to explain the diameter modulation is polynuclear growth.[23] The stacking roughness of ⟨111⟩ GaP nanowire surface may form preferential nucleation sites for precipitation of Ga and P vapor and grow into periodic convexities via ledge mechanism.[24]

In conclusion, we have carried out detailed Raman measurements on the SO modes for two sets of GaP nanowires with two different most probable diameters. The SO mode is clearly identified by its movement in the Raman spectrum as the overlaying medium dielectric constant is varied. Based on a theoretical formulation for SO modes in a cylindrical wire, we have estimated the range of phonon wavevector q over which the SO mode should be observed. Using this range of q we have also estimated the characteristic wavelength of the perturbation of the surface potential that activates the Raman scattering process for the SO modes. We found this wavelength is $\sim$30−70 nm, in good agreement with the wavelength of very obvious diameter modulations in our sample.

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NL034842I