Raman Spectroscopy and Structure of Crystalline Gallium Phosphide Nanowires

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Gallium phosphide nanowires with a most probable diameter of ~20.0 nm and more than 10 μm in length have been synthesized by pulsed laser vaporization of a heated GaP/5% Au target. The morphology and microstructure of GaP nanowires have been investigated by scanning electron microscopy and transmission electron microscopy. Twins have been observed along the crystalline nanowires, which have a growth direction of [111]. Raman scattering shows a 4 cm⁻¹ downshift of the longitudinal optical phonon peak in the nanowire with respect to the bulk; the transverse optical phonon frequency and line width are, however, the same as in the bulk. The quantum confinement model first proposed by Richter et al. cannot explain the observed behavior of the Raman modes.

Keywords: Pulsed Laser Vaporization, Gallium Phosphide Nanowires, Raman Scattering.

Successful synthesis of long silicon nanowires by pulsed laser vaporization (PLV)¹ has driven recent attempts to synthesize compound semiconductor nanowires such as GaAs, GaN, InP, etc.,² and to understand the physical properties of these quasi-one-dimensional systems.³ Semiconductor nanowires with diameters, d, in the range 10 nm < d < 50 nm and lengths exceeding several micrometers have intriguing optical and electronic properties that may be distinct from those of bulk semiconductors and may find applications in future optoelectronic devices. Gallium phosphide (GaP) is a very important semiconductor material because of its wide indirect band gap (~2.3 eV) and potential applications in optoelectronics.³ Some theoretical calculations have predicted that fundamental physical properties, such as the band gap of the semiconductor, will change because of quantum confinement.³ For Si nanowires, phonon quantum confinement effects have been observed by Raman scattering⁶ and electron confinement by photoluminescence.⁷ Several methods have been reported recently to produce GaP nanowires, such as carbon nanotube template-confined growth,⁸ oxide-assisted growth with excimer laser ablation of a GaP and Ga₂O₃ mixture,⁹ vapor-liquid-solid (VLS)¹⁰ growth with pulsed laser vaporization (PLV) of a GaP target and monodisperse Au nanoparticles deposited on a silicon substrate.¹¹

Here we report on the synthesis of highly crystalline GaP nanowires by PLV of a GaP/5% Au target and studies of phonon confinement by Raman scattering. Our electron microscopy data indicate that the growth proceeds by the VLS mechanism.¹⁰ The morphology and structure of the nanowires have been investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Our PLV apparatus is shown schematically in Figure 1. A pulsed Nd:YAG laser (Telescopie Series SL803, Spectron Laser Systems) with a pulse width of 15 ns and a repetition rate of 10 Hz was used to vaporize the Au/GaP target. Both the fundamental (1064 nm at 850 mJ/pulse, delayed by ~40 ns) and first harmonic (532 nm at 450 mJ/pulse) lines were present. The target was made by pressing GaP (99.99%) powder (Aldrich Inc.) mixed with 5 mol% gold (99.96%) powder (Alfa-Aesar Inc.). The target was centered in a ~1-m-long quartz tube with an inner diameter of 25 mm (Fig. 1). A tube furnace was used to control the target temperature at ~870 °C, which was monitored by an inconel-sheathed thermocouple (type K) placed just above the target. The nanowires were found on the wall of the quartz tube ~30 cm behind the target as a result of a small Ar/5% H₂ flow (100 sccm) in the inner tube. After the system was pumped down to 20 mTorr and flushed several times with Ar gas, the temperature was increased to 850–890 °C and the Ar/5% H₂ flow was initiated at a pressure of 100 torr. The laser beam was focused on the target to a spot size of ~2 mm and rastered slowly across the target surface. The ablation or vaporization process was carried out for 2 h. The laser was then shut down and the power to the furnace turned off,
allowing the system to cool slowly to room temperature in ~3 h under flowing Ar/H₂.

The as-grown GaP nanowires exhibit a light yellow color. The sample was first dispersed in ethanol with an ultrasonic horn (Misonix Inc., XL2010) operated at 100 W, and then the suspension was spin-coated onto silicon substrates. A Leica LEO 400 SEM was used to study the morphology of the GaP nanowires. SEM images were collected with an acceleration voltage of 5 kV; a thin Au overlayer was deposited on the nanowires to decrease the charge accumulation. TEM images were collected with a FEI-Philips 420ST TEM operated at 120 kV. High-resolution transmission electron microscopy (HRTEM) images, energy-dispersive X-ray (EDX) spectroscopy, and scanning transmission electron microscopy (STEM) data were collected on a JOEL 2010F microscope operated at 200 kV. The sample for these studies was prepared by depositing a drop of the nanowire/ethanol suspension on the copper grid. We have used TEM to determine the diameter distribution and growth direction of our nanowires. The instrument magnification was calibrated with the use of a standard grating replica, and the rotation was calibrated with a α-MoO₃ platelet. Raman spectra were collected with a JY-Horiba T64000 micro-Raman spectrometer in a backscattering configuration at room temperature. The sample was illuminated with 514.5-nm radiation with a laser spot diameter of ~1 μm, with a 100 x objective on an Olympus BX40 confocal microscope. The power at the sample was about 10 mW. For Raman measurements, a thin film of tangled nanowires was prepared by putting a few drops of the suspension on a piece of indium foil and allowing the ethanol to evaporate.

Figure 2 shows a typical SEM image of the as-prepared GaP nanowires. The wires appear to be straight and entangled with each other. Most of the wires are longer than 10 μm. Figure 3 shows a bright-field TEM image of GaP nanowires. In the VLS mechanism, a small metal particle serves as a solvent for the vapor reactant (GaP). The filament grows from the surface of the particle and can be viewed as a solid phase coexisting with a liquid pseudobinary alloy (e.g., Au-GaP) in the droplet.¹⁻² Inset (1) to Figure 3 shows a small solidified metal particle at the end of a nanowire, consistent with the VLS mechanism. We have used STEM (Fig. 4a) to map the Au concentration along the nanowire from the droplet. It was found that the droplet has an abrupt change in Au concentration. Only a
trace of Au was found within 1 nm of the droplet in one wire (out of five). We believe this is due to Au diffusion during the growth. No Au was found in the body of the wires; this is desirable for future investigation of transport and optical properties. We also checked the composition of the droplet by energy dispersive X-ray spectroscopy (EDX) (Fig. 4b). It was found that the droplet contains mainly Au, Ga, and P, which support the VLS mechanism. Figure 4c shows an EDX spectrum of a nanowire; it contains Ga and P. The tiny amount of oxygen might come from the solvent or surface adsorption contamination from the atmosphere, since no appreciable amorphous layer was observed on the surface of the wires in HRTEM (Fig. 5).

The TEM images (Fig. 3a) also show some segmental contrast features (arrow), which are attributed to twins. Inset (2) to Figure 3a shows a selected-area diffraction (SAD) pattern from an individual GaP nanowire. The growth direction has been determined to be (111), as shown in Fig. 3a and 5. GaP exhibits a zincblende structure with space group $F\overline{4}3m$. The diffraction pattern in Fig. 3a was indexed as two superimposed $\{110\}$ zone axis patterns that have a $\sim$110° (or 70°) rotation with respect to each other. This can be attributed to twins with two equivalent (111) directions along the wire axis. Twin boundaries have also been observed in Si and Ge nanowires, although the origin of the twins in nanowires is still not understood. This type of rotational twin with a (111) twin axis has also been observed in GaAs and InAs whiskers grown by metal-organic vapor phase epitaxy (MOVPE). It has been suggested that this defect strongly depends on the growth conditions (e.g., temperature, pressure, and gas flow). The diameter distribution, as shown in Figure 3b, has been calculated from several TEM images. The distribution has been fitted to a log-normal distribution function (log-normal function: $A\exp[-(\ln(x_{0})/w)^2]$, where $x_{0}$ is the peak position in nanometers and $w$ is the full width at half-maximum in nanometers); the peak in Fig. 3b is located at 20.3 ($\pm$1.8) nm with the log-normal tail extending to larger diameters ($\sim$70–80 nm). It should be noted that the growth conditions had not been optimized to produce smaller-diameter nanowires or a tighter diameter distribution. This diameter distribution can be controlled to some extent by the growth conditions, such as gas pressure and choice of gas (nitrogen, argon, or helium). Figure 5 shows an HRTEM image of a GaP nanowire with a diameter of about 25 nm. The image shows that the wire is highly crystalline and...
that no appreciable oxide layer was found, which is supported by EDX data (Fig. 4c).

Raman scattering is a powerful tool for characterizing the quality of materials. It is sensitive to composition, presence of disorder, impurities, and the size of the system under investigation. The downshifting and broadening of Raman bands in nanostructured semiconductors have been qualitatively explained in terms of a phonon confinement model of Richter. The first quantitative attempt to understand these effects was made by Fauchet and Campbell, who used Richter’s phenomenological phonon confinement model. The physics underlying the phonon confinement effect can be understood as follows: In a nanowire, because of the dimensional constraint along the directions perpendicular to the wire axis, a range of phonon wave vectors, $0 < q < 1/d$, is required to describe the Raman-active phonon in the nanowire. Since for most semiconductors, the optical-mode frequencies in the bulk decrease away from the Brillouin zone center, the Raman-active mode in the nanowire broadens to lower frequency and downshifts. This effect is larger in smaller-diameter wires. Thus, confinement leads to a breakdown in the $q = 0$ Raman selection rule applied to crystalline bulk materials.

Figure 6 shows a typical Raman spectrum of our GaP nanowires; polycrystalline bulk GaP is measured under the same optical conditions; and the spectrum is included for comparison. Each spectrum consists of two peaks that we identify with first-order scattering from longitudinal optical (LO) and transverse optical (TO) phonons. We presume that in the nanowires we have $\omega(LO) > \omega(TO)$, as in the bulk. Therefore, for GaP nanowires, the LO phonon mode is seen to be downshifted by $\sim 4$ cm$^{-1}$ with respect to its position in the bulk. Also, the nanowire LO mode exhibits a noticeable asymmetric broadening of the LO band not seen in the bulk material. However, the TO phonon peak in the nanowire remains almost the same as that observed in the bulk GaP. It should be also noted that the full width at half-maximum (FWHM) of the TO band of our nanowires is the same as that of the bulk. This is additional proof of the structural quality of these nanowires. The observations of the LO and TO modes are notably different from that reported by Shi et al. for oxide-assisted growth of GaP nanowires. In the Raman measurements of Shi et al., the LO and TO bands in the nanowire downshifted by 8 and 5 cm$^{-1}$, respectively, and both broadened. They attributed this to combined effects of confinement, planar defects, and stress within the GaP nanowires arising because of lattice distortion.

We have carried out a simple calculation of the Raman lineshape for our nanowires, using the model of Richter extended by Fauchet and Campbell. The Raman intensity for the “confined” TO or LO phonon in a nanowire of radius $r_0$ is written as

$$I_{NW}(\omega) = \int_0^{q_{max}} \frac{|C(q)|^2}{(\omega - \omega(q))^2 + (\Gamma/2)^2} 2\pi q dq$$  \hspace{1cm} (1)

where $\omega(q)$ is the phonon dispersion of the LO or TO Raman mode, $\Gamma$ is the natural linewidth, and the wave vector $q$ is perpendicular to the wire axis (111). $C(q)$ is the Fourier coefficient of the phonon confinement function and depends on $r_0$. We assume that the phonon dispersion in the nanowires is the same as that of bulk GaP, and we take an approximate isotropic dispersion given by $\omega(q) = [A + B \cos(q/(\pi/a))]^{1/2}$, where $A = 137,670$ cm$^{-1}$, $B = 21,155$ cm$^{-1}$ for the LO branch and $A = 126,025$ cm$^{-1}$, $B = 7,200$ cm$^{-1}$ for the TO branch, fit to the neutron scattering data. In Figure 7 we

Fig. 6. Raman spectra of GaP nanowires and polycrystalline GaP materials. For nanowires, the first-order LO phonon band is downshifted and broadened by $\sim 4$ cm$^{-1}$ with respect to the bulk, whereas the first-order TO band remains the same as that observed in bulk GaP.

Fig. 7. Calculated LO (a) and TO (b) Raman band line shape in the Fauchet-Campbell model as a function of wire diameter $d$ ($d = \infty$ represents the bulk GaP).
show the calculated Raman lineshape for both the LO and TO modes for nanowires with different diameters. There are two points of significance in Figure 7. First, it would be very difficult to observe any confinement effects on the LO or TO Raman bands for nanowires with \( d \geq 10 \) nm. Second, the confinement effect for the LO mode at \( d = 5 \) nm is stronger than for the TO mode. This stems from the stronger LO phonon dispersion. Returning to our experimental data (Fig. 6), we see that only the LO mode is appreciably different from its counterpart in the bulk. If this shift were a simple consequence of phonon confinement, then we would expect a similar shift in the TO mode. Secondly, the Richter-Fauchet-Campbell model predicts almost no shift for 20-nm-diameter GaP nanowires, which is the most probable diameter for our sample obtained from a log-normal fit to the measured distribution. We do not expect the small-diameter wires (<4 nm) in the sample to cause only the LO nanowire band downshift. Therefore we have not carried out the above calculation incorporating the diameter distribution of the nanowires. In an earlier work on bulk crystalline GaP doped with sulfur or tellurium impurities by Galtier and Martinez,\(^1\) it was found that in the presence of impurities only the LO mode downshifts. However, the downshifts observed in their experiments were small (\( \sim 1 \) cm\(^{-1}\)), even for degenerately doped GaP. In our experiments the downshifting of the LO band is large, <4 cm\(^{-1}\). We also believe that if the downshifting is due to the screening of the LO mode in the presence of impurities, then it should lead to broadening of both the LO and TO modes in the nanowires. In our experiments, we observe that the line widths of the TO mode in bulk and nanowires are nearly the same. In a recent work, Mahan et al.\(^18\) have shown that the long-range dipolar interactions in a polar semiconductor responsible for the splitting of the LO-TO modes in the bulk give rise to a different splitting in the nanowire. Their study shows that the LO-TO splitting depends on the aspect ratio of the sample; it is a “shape” effect rather than a “size” effect. Preliminary analysis seems to indicate that our data are consistent with this model. However, it is important to point out that further polarization-dependent measurements on single nanowires are needed to see if the character of the LO (TO) mode in a nanowire is different from that in the bulk. The FWHM of the LO mode in the nanowire is much larger than that in the bulk. Part of the reason for this is that a slightly lower frequency surface mode is present and overlaps the LO band. A paper on these surface modes will be submitted.\(^19\) Further work is in progress to understand the surface-mode properties in GaP nanowires.

In summary, highly crystalline GaP nanowires have been successfully synthesized by pulsed laser ablation of a target made of \((\text{GaP})_{0.95}\text{Au}_{0.05}\) powders. The nanowire diameter distribution is well described by a log-normal distribution with a most probable diameter of \( \sim 20.0 \) nm, and wire lengths of about 10 \( \mu \)m are typical. The wires grow by the VLS mechanism. TEM images and the selected-area diffraction pattern show that some of the nanowires are twinned along the [111] growth direction. An asymmetrical broadening of only the first-order longitudinal optical phonon is observed; the transverse optical phonon is unaffected. This observation cannot be accounted for by the phonon confinement model of Richter-Fauchet-Campbell, and an alternative explanation is needed to account for the experimentally observed behavior of the Raman bands in GaP nanowires.

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References and Notes


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