

Size and environment dependence of surface phonon modes of gallium arsenide nanowires as measured by Raman spectroscopy

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Abstract

Gallium arsenide nanowires were synthesized by gallium-assisted molecular beam epitaxy. By varying the growth time, nanowires with diameters ranging from 30 to 160 nm were obtained. Raman spectra of the nanowire ensembles were measured. The small linewidth of the optical phonon modes agree with an excellent crystalline quality. A surface phonon mode was also revealed, as a shoulder at lower frequencies of the longitudinal optical mode. In agreement with the theory, the surface mode shifts to lower wavenumbers when the diameter of the nanowires is decreased or the environment dielectric constant increased.

(Some figures in this article are in colour only in the electronic version)

In the past decade the field of semiconducting nanowires has developed significantly mostly due to the fact that these systems with unique geometry offer great possibilities for further development of optic and electronic devices [1, 2]. Equally important, they offer numerous possibilities for studying exciting physical phenomena arising from carrier confinement and/or the large surface-to-volume ratio [3]. However, the growth of nanowires free of structural defects and contaminants is still one of the key issues.

The vapor–liquid–solid growth method is one of the most common techniques, in which typically gold is used as a catalyst for the nucleation and growth of nanowires [4]. It is widely known that gold introduces deep level traps in the semiconductor bandgap that hinder the optoelectronic properties of the material [5]. By avoiding the use of gold, the properties of the grown nanowires improve significantly. Recently, catalyst-free synthesis of III–V nanowires has been demonstrated by both metal–organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) [6, 7]. From the two techniques, with MBE it is possible to obtain materials with an extremely high purity and good structural properties.

Raman spectroscopy as a non-destructive characterization tool is extensively applied for characterization of low-

dimensional systems such as nanowires and nanocrystals, as it provides valuable information on the structural properties [8, 9].

In this work we present a systematic Raman spectroscopy study of GaAs nanowires grown by MBE without the use of an external catalyst for growth. Nanowires with diameters ranging from 30 nm up to 160 nm were grown. The underlying motivation for the investigation of nanowires with a broad range of diameters was to correlate the features in the Raman spectrum with the change of the surface-to-volume ratio.

The nanowires were grown in a GEN II MBE system. For the growth we have used (001) GaAs wafers covered with a thin layer (approximately 35 nm) of sputtered SiO₂. In order to ensure a clean surface, prior to growth the SiO₂ thin films were etched down to 10 nm by a diluted buffered HF solution. After the etching the substrates were blown dry with nitrogen and immediately transferred into the MBE system. Prior to growth, the substrates were heated to a temperature of 650 °C in order to desorb any remnant molecules on the surface. Then, the temperature was lowered to the growth temperature of 630 °C. For the growth we have used an As beam equivalent pressure (BEP) of 2×10^{-6} mbar and a Ga growth rate of 0.25 \AA s^{-1} , which gives, respectively, longitudinal and radial growth rates of 2 and 0.07 \AA s^{-1} [10]. The nominal thickness of deposited

GaAs was varied for different samples in order to synthesize nanowires with different average diameters. In this way, we have prepared samples with diameters ranging from 30 nm up to 160 nm. Each sample was characterized with a diameter distribution between 10 and 20%.

Transmission electron microscopy (TEM) analysis on the grown wires showed that the wires grow in the [111] B growth direction and have a hexagonal cross section with side facets belonging to the {110} crystalline family [11]. AFM measurements on single nanowires have also shown that the side facets exhibit very small roughness.

The Raman measurements were performed at room temperature by using the 488 nm line from an Ar⁺ laser. A microscope objective (50×) focused the laser on the sample with a spot of several micrometers in size. The same lens collected the scattered light for a triple DILORXY spectrometer and was further analyzed with a nitrogen-cooled Si CCD. The measurements were realized with low excitation power (0.5 mW), with the purpose of avoiding any heating of the sample, which can produce asymmetric broadening and down-shift of the Raman peaks. The sample temperature stayed always below 120 °C, as shown by Stokes/anti-Stokes ratio measurements.

A scanning electron micrograph from the as-grown nanowires is given in figure 1(a). The inset shows the hexagonal cross section of the wires. For the measurements the wires were mechanically removed from the GaAs substrate and transferred onto clean (001) Si pieces by friction between the substrates. The transferred wires were partially oriented along the sliding direction as presented in figure 1(b). Since the laser was focused onto a spot with a diameter of several microns, we estimate that only several nanowires were probed during each measurement. The scattering geometry is presented in figure 1(c). The wires are probed in backscattering geometry with the side facets belonging to the {110} crystalline family. In the backscattering geometry from {110} the longitudinal optical (LO) phonon is forbidden according to the Raman selection rule [12]. In principle, only scattering from the transverse optical phonon (TO) is allowed. As a consequence, the scattering from the top and bottom surfaces of the wires will contribute only in the TO signal in the Raman spectra. On the other hand, the scattering due to LO phonons is not forbidden from the facets painted in blue. The scattering in these facets will contribute to the LO signal in the spectra. As a result, the spectra should present a rather high intensity component of the TO signal and a lower LO signal.

Typical Raman spectrum of the nanowires (with average diameter of 89 nm) is presented in figure 2(a). The solid black line is the recorded data while the green lines are results from a multiple Lorentzian fit. For a comparison in figure 2(b) we have plotted the measured Raman spectrum from bulk (111) GaAs.

On the spectra from the wires two peaks can be clearly observed. The peak positioned at 268.7 cm⁻¹ is due to scattering from the TO phonon and the peak positioned at 292.2 cm⁻¹ is due to scattering from the LO phonon [13]. Both the TO and LO peaks exhibit very small full width at half-maximum (FWHM), around 4 cm⁻¹. By comparing both

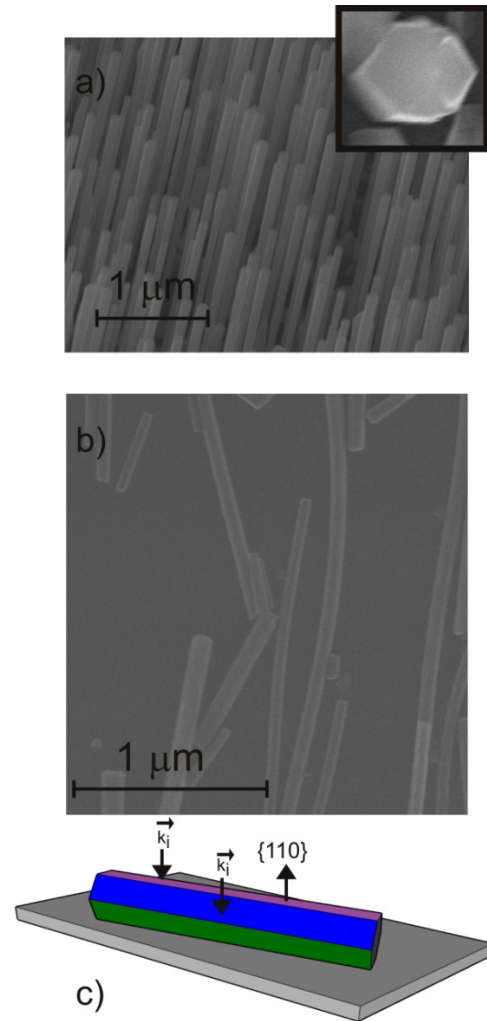


Figure 1. (a) Scanning electron micrograph from the as-grown GaAs nanowires. The hexagonal cross section of the nanowires is presented in the inset. (b) Scanning electron micrograph from GaAs nanowires transferred onto a Si substrate. After the transfer the wires are partially oriented. (c) Schematic drawing of the scattering geometry of the measurements.

graphs one can see that the peak position corresponds very well with the position of the TO and the LO peaks measured on the bulk (111) GaAs. The measured values for the peak positions and FWHM indicate that the synthesized wires have excellent structural quality and are free of defects and stress, which further corroborates the advantage of using MBE.

A third peak positioned on the low frequency side from the LO phonon is also clearly observed. A detailed analysis of this peak, which will be presented in the following, allowed us to attribute it to scattering from surface optical phonons (SO). A simple mathematical expression of the surface modes is given in the case of an infinitely long cylinder [14–16]:

$$\omega_{\text{SO}}^2 = \omega_{\text{TO}}^2 + \frac{\tilde{\omega}_{\text{p}}^2}{\varepsilon_{\infty} + \varepsilon_{\text{m}} \cdot f(q \cdot r)} \quad (1)$$

where

$$f(q \cdot r) = \frac{I_0(q \cdot r)K_1(q \cdot r)}{I_1(q \cdot r)K_0(q \cdot r)} \quad (2)$$

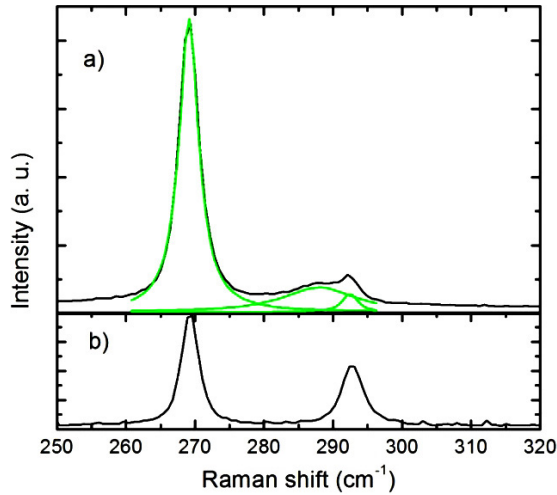


Figure 2. (a) Raman spectra of GaAs nanowires with an average diameter of 89 nm. The black solid line is the recorded data while the lighter coloured (green) lines are results from a multiple Lorentzian fit. (b) Raman spectrum from bulk (111) GaAs.

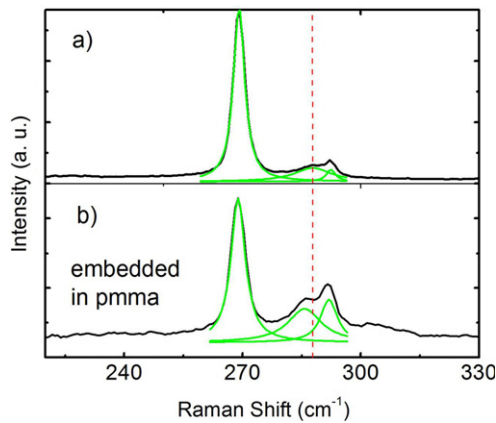


Figure 3. (a) Raman spectra of GaAs nanowires in air. The black solid line is the recorded data while the lighter coloured (green) lines are results from a multiple Lorentzian fit. (b) Raman spectrum from the same sample after covering it with PMMA. The vertical line is a guide to the eye.

with $\tilde{\omega}_p$ the screened ion plasma frequency given by $\omega_{LO}^2 = \omega_{TO}^2 + \tilde{\omega}_p^2/\epsilon_\infty$, $I_j(qr)$ and $K_i(qr)$ being the modified Bessel functions, q is the phonon wavevector, ϵ_∞ is the high frequency dielectric constant of the material while ϵ_m is the dielectric constant of the surrounding medium.

The position of the SO depends on the dielectric constant of the medium that is surrounding the wires as well as on the diameter of the wires. In order to confirm the nature of the third mode as a surface phonon, we have embedded the nanowires with PMMA (polymethyl methacrylate), which has a dielectric constant of 2.8. In figure 3 we have plotted the Raman spectrum from the nanowires in air and the Raman spectrum from the same sample after covering it with a layer of PMMA. The vertical dashed line is a guide to the eye. As can be seen in figure 3(b) there is indeed a shift of 1.8 cm^{-1} of the SO phonon toward lower wavenumbers.

We have measured the Raman spectra of the other samples consisting of nanowires with diameters from 30 to 160 nm.

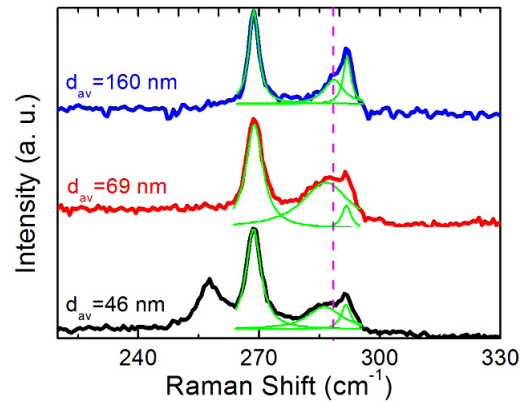


Figure 4. Raman spectra from GaAs nanowires with average diameters from 46 nm (black), 69 nm (red) and 120 nm (blue). The lighter coloured (green) lines are results from a multiple Lorentzian fit. The vertical line is a guide to the eye. The position of the SO phonon down-shifts with the decrease in diameter.

Previous experimental reports on surface phonons in III–V nanowires and nanocolumns showed a down-shift of the position of the SO phonon with a systematic increase in the dielectric function of the environment of the nanowires. However, no systematic study exists as a function of the diameter on ensembles with narrow size distributions [14, 16]. Moreover, no studies exist on nanowires with extremely flat facets. In figure 4 we present representative measurements performed on samples with average diameters of 160, 69 and 46 nm. As shown in the figure, the position of the TO and the LO phonons is independent of the nanowire diameter. However, the SO modes exhibit a down-shift when the diameter decreases. Additionally, for thick nanowires with an average diameter of 160 nm, the SO appears only as a small shoulder on the lower frequency side of the LO peak. However, for nanowires with smaller diameters, meaning a larger surface-to-volume ratio, the SO can be clearly distinguished and it also down-shifts. This trend further proves that the peak located between the TO and the LO peaks can indeed be attributed to scattering from surface phonons.

In the Raman spectra from the wires with the smallest diameter (black curve) another peak appears at around 258 cm^{-1} . The appearance of this peak in Raman spectra of GaAs has been assigned to the presence of As anti-site defects [17]. However, we believe that this peak could also be attributed to the existence of twins in the structure of the nanowires. Indeed, high densities of twins are observed in the nucleation and final stage of growth. As the small diameter wires have a length of 500–800 nm, the twinned region becomes up to 20% of the wire. More detailed investigations on the origin of the peak are currently ongoing.

In order to get a clear overview in figure 5 we have plotted the dependence of the position of the SO phonon from the diameter of the nanowires for several measured samples with different average diameters. For comparison, we have also included the results from the theoretical considerations in cylindrical GaAs wires [14]. Indeed the shift between the samples with different average diameter is not very large, but this can be influenced from the size distribution of the

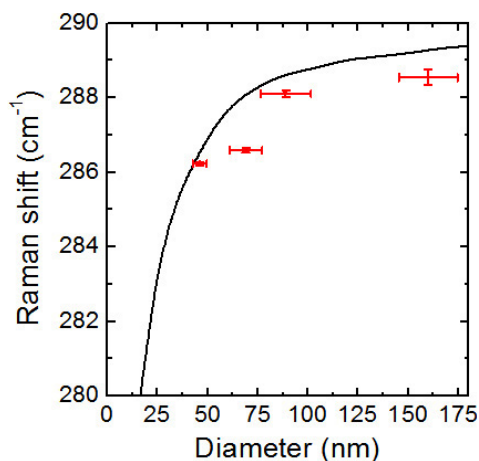


Figure 5. Dependence of the position of the SO phonon from the diameter of the nanowires. The points represent experimental data obtained from several measured samples with different average diameters. The line corresponds to the theoretical prediction for cylindrical GaAs nanowires [14].

diameters in each sample. By comparing our experimental data points with the theoretical curve calculated in [14] according to equation (1) one can see that we observe a larger shift in the SO phonon position, especially for the larger diameters. One possible reason can be the fact that our wires have hexagonal cross section. Lately it was shown that the cross-sectional shape of the nanowires is important when calculating the dispersion curve for the SO phonon [18]. Of course this opens a route for making theoretical calculations for the SO dispersion curve for hexagonal geometry.

In summary we have presented a Raman spectroscopy study of GaAs nanowires synthesized in MBE by the Ga-assisted growth method. We have presented that the nanowires exhibit very good structural quality, shown by the lineshape and position of the peaks. Furthermore we have demonstrated the existence of a surface phonon mode by comparing the spectra of the nanowires in an environment of air and PMMA, which has a higher dielectric constant. By investigating spectra of nanowires as a function of the average diameters, we have

found that the position of the SO phonon down-shifts with the decrease in diameter.

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