Nanowires

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Prismatic Quantum Heterostructures Synthesized on Molecular-Beam Epitaxy GaAs Nanowires**

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Semiconductor nanowires have stimulated extensive interest in the last decade because of their potential use as building blocks in future generations of electronic and optoelectronic applications. Equally important, their singular geometry provides an opportunity to test fundamental quantum mechanical concepts and related phenomena.[1–4] Even though significant advances have been made in the synthesis of nanowires and the fabrication of related devices, reproducible fabrication has mainly relied on the use of gold nanoparticles as a seed through the vapor–liquid–solid (VLS) or vapor–solid–solid (VSS) mechanism.[5–7] However, gold is known as a deep-level trap in semiconductors that significantly reduces their optical and electronic transport performance.[8]

More complex structures that enable versatile electronic and photonic functions can be achieved when different materials are combined. Among the possible combinations, coaxial nanostructures synthesized by using the as-made nanowires as a core physical template are particularly interesting.[9] Up to now, coaxial heterostructures have been considered for two main uses: i) the improvement of the performance of nanowire devices, where the shell is responsible for removing the surface states and to confine the carriers at the core, leading to the reduction of surface scattering;[3,10] ii) engineering the optoelectronical properties of the core of a particular device, such as the fabrication of multicolor light-emitting diodes.[5] Little attention has been drawn to the geometry of the deposited shell, as the main functionality continued to be reserved to the core of the nanowire. As in standard semiconductor technology, in principle it should be possible to uniformly coat the nanowires with successive epitaxial layers resulting in multiple quantum heterostructures defining, for example, prismatic quantum wells (p-QW) or a two-dimensional electron gas (p-2DEG). The addition of p-QWs or p-2DEG would constitute an additional functionality to the nanowire and, accordingly, an increased freedom design for nanostructures and devices.

Here we report on a new method for the growth of prismatic quantum heterostructures on GaAs nanowires by using molecular-beam epitaxy (MBE), which has the additional advantage of avoiding the use of gold as the seed for the nanowires. Recently, catalyst-free growth has been achieved both with metal–organic chemical vapor deposition (MOCVD) and molecular-beam epitaxy (MBE).[6–8] The use of molecular-beam epitaxy presents an additional interest as this technique allows us to produce ultrapure nanowires and quantum heterostructures on the nanowire facets with very high crystalline quality and atomically sharp interfaces. This new versatility of MBE in the growth of nanostructures opens great possibility for the generation of novel devices with additional optical and electronic functionalities, as has been previously shown in planar structures.[14–16]

The synthesis was carried out in a Gen-II MBE system. Two-inch (001) and (111)B GaAs wafers coated with a sputtered 10-nm-thick silicon dioxide were used. Special care was taken to ensure a contaminant-free surface.[13] The nanowire growth was carried out at a nominal GaAs growth rate of 0.45 Å s^{-1}, an As_4 partial pressure of 3.5×10^{-6} mbar (Ga-rich conditions), a temperature of 630 °C, and with a rotation of 4 rpm. Typical cross-sectional scanning electron microscopy (SEM) images of a nominal growth of 200 nm of GaAs are shown in Figure 1a and b. The surface is coated with a high density of nanowires. A droplet is observed at the top of each nanowire, suggesting that the Ga droplet has acted as a seed for the nucleation and growth. A detailed analysis of the ensemble reveals that the diameter is 85 ± 10 nm and is uniform along the entire length. The detail of a broken nanowire is shown in the inset of Figure 1a, where the hexagonal cross section of the wires is clearly visible. The nanowires grown on coated (001)GaAs substrates appear at an angle of 35° to the surface, whereas they grow perpendicularly on coated (111)B GaAs wafers; the growth direction thus coincides with one of the ⟨111⟩ directions of the underlying substrate.[14] A detailed cross-sectional transmission electron microscopy (TEM) study of the interface of the nanowire with the oxide indicates the presence of a nanoscopic pinhole that has appeared during the growth process as a consequence of the interaction of Ga and SiO_2 at high temperature.[18] Growth of nanowires has also been achieved on 1-μm-thick oxides (this time randomly oriented), indicating that the presence of the pinhole may only play a role in the selective orientation when contact with the substrate is established through the oxide layer.[20] TEM measurements indicate that the nanowires are single crystalline with a zinc blende structure, and grow along the $[1\bar{1}1]$ direction. The images also indicate a

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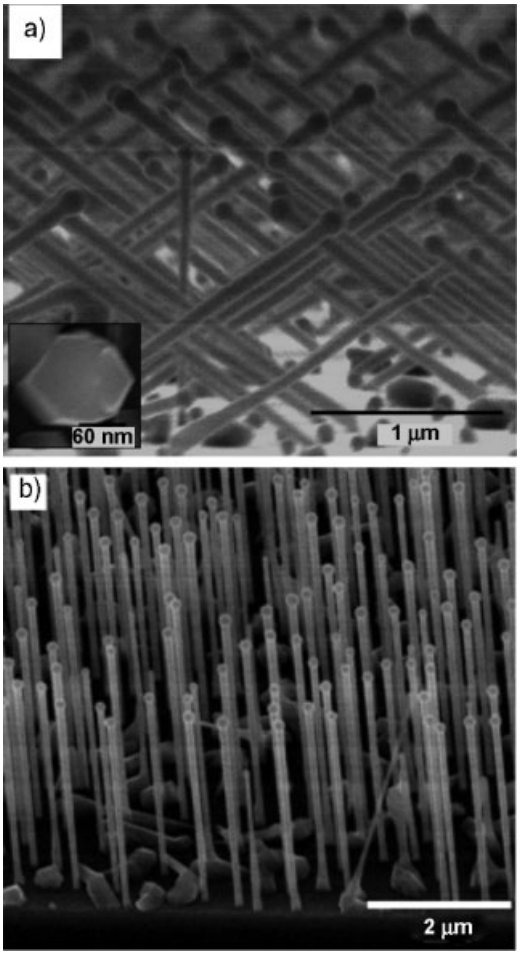

Figure 1. Cross-sectional SEM image of a nominal thickness of 200 nm of GaAs grown on a)10-nm SiO_2-coated (001) GaAs substrates and b) 10-nm SiO_2-coated (111)B GaAs substrates. The inset shows the hexagonal cross section of a wire.

hexagonal prism morphology, with the facets pertaining to the {110} family.[20–24]

With the purpose of adding functionality to the nanowires and taking advantage of the MBE growth capabilities, quantum heterostructures were grown on the {110} facets of the wires. The structure consisted of a quantum well (QW) with a nominal thickness of 4 to 6 nm of GaAs sandwiched between 10-nm $Al_{0.4}Ga_{0.6}As$ barrier layers. For TEM analysis, a GaAs QWs sandwiched between AlAs barrier layers was also fabricated. The whole structure was capped with 8 nm of GaAs. Thanks to the geometry of the nanowires, the deposition resulted in a prismatic configuration of the QWs, which we call p-QWs. Here we would also like to add that the width of the QWs is restricted to the width of the facets of the nanowires, which are of the order of 60 nm, meaning that the QWs can possibly be considered as quasi one-dimensional structures. Selective deposition on the {110} facets of the nanowire was achieved simply by increasing the As_4 beam flux to 1.8×10^{-5} mbar — typical for growth on {110} surfaces. SEM and high-resolution (HR) TEM measurements show a homogeneous increase of the total diameter of the nanowire after growth of the heterostructures. To assess the presence of a prismatic structure, the cross section of the nanowires was measured by TEM (X-TEM).[21] In TEM measurements, GaAs and $Al_xGa_{1-x}As$ layers are typically distinguished by measuring in dark-field mode with the (200) reflections of the GaAs.[22] The prerequisite for this type of imaging is that the zone axis of the sample should be perpendicular to the (200) reflection. If this does not happen, the reflection is completely dark and the dark-field imaging mode cannot be used. As GaAs nanowires grow along the $[1\bar{1}1]$ direction this method cannot be applied for cross-section measurements along this latter zone axis. Pure AlAs and GaAs offer, however, a slightly different contrast in bright-field TEM imaging modus. By using conventional bright-field scanning transmission electron microscopy (STEM) mode, we obtained improved contrast and spatial resolution. In Figure 2a, the cross-section of a nanowire coated with a prismatic QW structure measured by STEM is shown. A GaAs QW embedded in pure AlAs barrier layers on each facet of the nanowire can be distinguished by the different intensities. Interestingly enough, the layers are homogeneous in all facets and do not round up the shape of the nanowire. A closer view of the layers is given in Figure 2b, where the existence of different materials appears more marked. Three layers are clearly observable, thanks to the compositional contrast between pure AlAs and GaAs. In order to check the chemical composition across the layers, an element analysis was realized with electron energy loss spectroscopy (EELS) with a spot-probe size of 0.5 nm. The spectra measured at the center of each of the layers are plotted in Figure 2c. As shown, the EELS responses of the two AlAs layers perfectly overlap and agree with AlAs. Similarly, the EELS spectra obtained on the NW GaAs core and on the GaAs QW also overlap perfectly and agree with pure GaAs.

To further assess the uniformity and quality of the nanowires and p-QWs, photoluminescence spectroscopy (PL) experiments on single nanowires were carried out by the use of a confocal microscope embedded in a He^4 cryostat.[27] The measurements were realized at 4.2 K, using the 632.8-nm line of a HeNe laser as an excitation source. The luminescence was detected and analyzed by the combination of a grating spectrometer and Si charge-coupled device. In order to avoid the interference of the PL signal with the underlying GaAs substrate, the nanowires were first mechanically removed from the initial substrate and transferred in low densities to an oxidized silicon piece. Scanning reflectivity measurements over areas up to 30 μm^2 were first realized to localize the single nanowires at the surface. The PL spectra of four different samples are given in Figure 3a. The samples consist of uncoated nanowires and nanowires with various heterostructures. The PL emission peak of the GaAs nanowires is observed at 1.51 eV with a full width at half-maximum (FWHM) of 6 meV. The position and width of the peak corresponds to undoped bulk GaAs and indicates a high purity and crystalline quality of the core. It should be stressed that the measured FWHM is exceptional and among the narrowest ever obtained in nanowires, further corroborating the advantage of using MBE as a promising synthesis technique. The emission of the p-QWs grown on vertical and angled nanowires was equally investigated at excitation powers from 1 to 50 μW. The PL from the heterostructures

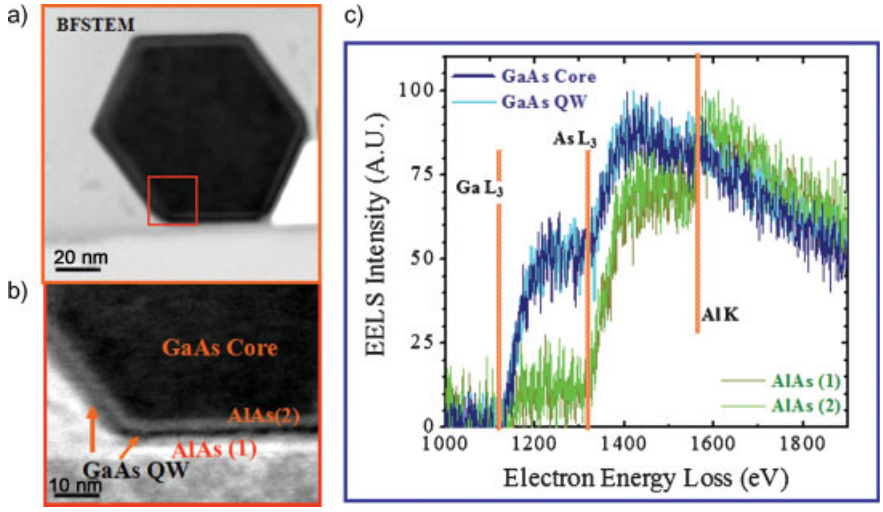

Figure 2. Cross-sectional bright-field scanning (BFS) TEM analysis of the prismatic structure of the nanowire. a) Cross-section BFSTEM micrograph of a prismatic nanowire. The epitaxial layers grown on the facets are observable by the difference in color intensity. b) High-magnification detail of the micrograph in (a), indicating the presence of three epitaxial layers on the facets of the nanowires with a marked contrast. The chemical composition of each layer is indicated. c) EELS of the layers of the p-QW structure. The spectra of the GaAs core and QW are consistent with pure GaAs and overlap. The spectra of the two AlAs barrier layers also overlap and agree with pure AlAs.

respectively. Clearly, only one PL peak appears on the QW corresponding to the vertical wires, in agreement with the quantum wells with equal thickness. Conversely, two clear peaks appear on the QWs of the angled wires. Following the spectra from lower to higher energies, the peaks can be attributed to the PL of a QW with a thickness of 6.5 and 4 nm for the vertical wires and of 5.8 and 5 nm for the angled wires, respectively. The thicknesses are in relatively good agreement with the nominal values that were deposited. The FWHM of the peaks is extremely narrow for nanowire structures (<3 meV), further highlighting the high quality, interface sharpness, and thickness homogeneity of the prismatic quantum structures fabricated with MBE. At this point we should note a slight nuance in regards to what is the effective quantum structure responsible for the photoluminescence. Indeed, at the corner defined by the junction of the quantum wells there is always the formation of a quantum wire (QWR).[29,30] Due to the slightly larger lateral size at the corner, the confinement energy of the QWR is slightly lower. This means that all excited carriers could recombine there. Detailed spatially resolved measurements to investigate this hypothesis are in progress.

is presented on the high-energy side of Figure 3a; the spectra of the vertical wires are shifted up with respect to the angled wires, in order to ease the reading of the figure. Each different sample is labeled on the graph. Spectras (ii) and (iii) correspond to p-QWs grown on vertical nanowires, and spectra (iv) correspond to p-QWs grown on angled wires. From each sample, the low- and high-intensity curves correspond to measurements realized at 8 and 40 μW of excitation power,

Next the growth geometry with respect to the epitaxy process is discussed. A schematic drawing is given in Figure 3c.

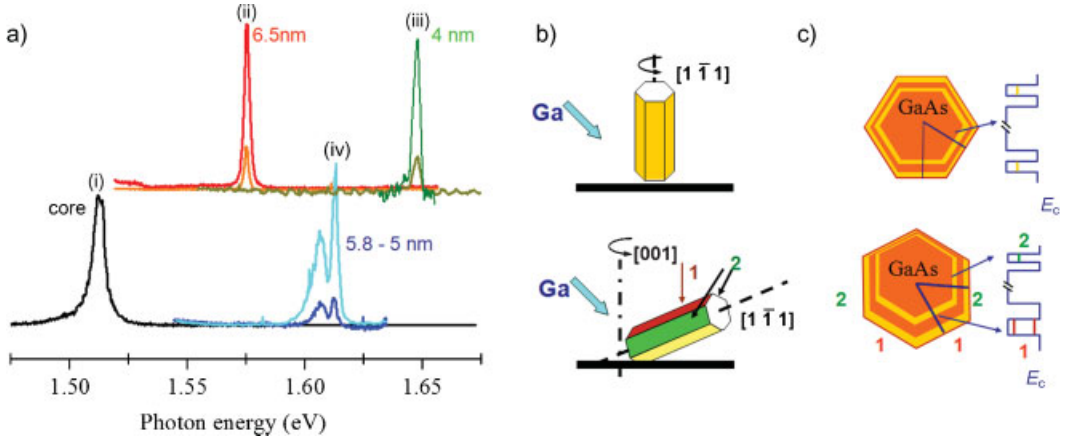

Figure 3. PL spectroscopy and geometry of single nanowires and their prismatic quantum wells. a) Single-wire PL spectra of four different GaAs nanowires: uncoated (i), vertical and p-QWs with thicknesses of 6.5 (ii) and 4nm (iii), and p-QW on angled nanowires with a thickness of 5.8 and 5 nm (iv). All spectra were recorded at 4.2 K. For the p-QWs, the low excitation power corresponds to 8 μW and the large excitation power to 40 μW. b) Schematic image of the growth of the p-QWs in the case of vertical and angled nanowires. The thickness of the quantum wells is larger on side 1 than on side 2, because it is facing the incident Ga beam at a larger angle. c) Representation of the geometry during growth of the quantum heterostructures on the side facets of the nanowires. The incident Ga impinges at a 45° angle on the rotating substrate. The nanowires grow following the [1$\bar{1}$1] direction of the substrate. Facets 1 and 2 of the nanowire are facing the Ga flux at two different angles, leading to two different quantum-well thicknesses. As facets 3 and 4 receive little Ga flux, the thickness of the layers is significantly reduced with respect to facets 1 and 2.

As a result of the geometry of the epitaxy process, the deposition rate on each nanowire facet depends on the orientation. As indicated in the drawing, the Ga flux consists of a directional beam impinging on the surface at an angle of 45°. The effective thickness received by each of the facets depends on the relative angle to the Ga beam, which varies during deposition due to the rotation. In this respect, there are two kinds of nanowire: the ones sticking out of the surface at an angle of 35° and those oriented perpendicularly to the surface. The deposition rate on the facets corresponds to the total flux received, which should be weighted by a factor $\cos\alpha$, where α is the angle between the Ga beam and the normal vector of the nanowire facet. Considering only the geometry, the growth on the facets perpendicular wires should occur at the same rate, while for the angled wires there should be a difference in the growth rate at the facets depending on their orientation. Here it is also important to note that, as the angle with the Ga beam flux is homogeneous along a specific facet, the growth rate there should be spatially isotropic. Following this, the six QWs grown on vertical wires should all have equal thickness. Conversely, QWs grown on angled nanowires should present thicknesses depending on the relative angle of the facet with the flux. In fact, for small nominal QW thicknesses, the deposition on the back facets is so reduced because of the small angle with the impinging Ga beam that it could be ignored. Given the considerations of the growth geometry, the optical measurements are in good agreement. We therefore show that high- quality quantum heterostructures can be grown on the facets of the nanowires in a prismatic way. Additionally, the thickness within the QWs can be modulated by changing the orientation of the nanowires with respect to the MBE beam.

Coaxial-type nanowire heterostructures have been fabricated in the past. The function of the coating layer has been limited to the passivation of the surface states of the nanowires and has been fabricated with an isotropic radial morphology.[12,27] Here we show for the first time that a uniform deposition on each side facet of a nanowire can be added with intrinsic functional purposes. Moreover, the lateral width of the QWs is on the order of 60 nm, meaning that the QWs pertaining to the prismatic structures can be considered as quasi one-dimensional structures. The application of MBE to the fabrication of three-dimensional quantum heterostructures opens a new avenue for a large variety of physical experiments and devices. As an example, and similar to the work presented here, one could realize modulated doped heterostructures on the side facets of the nanowires that would lead to the formation of high-mobility electron (hole) gas systems. These low-dimensional free-carrier systems would be arranged hexagonally in a prismatic configuration, forming quantum wires at the intersections of the QWs.[30–32] Certainly, this may lead to new magneto-resistance properties that would bring even more excitement on the properties of nanostructures.[28] Additionally, other applications such as multijunction solar cells or multi-wavelength nanodetectors could also be envisaged. We have fabricated heterostructures with different thicknesses on the facets of the nanowires up to 30 nm and we have observed the same behavior in the epitaxy. This means that this kind of structure could in principle be extended to many other kinds.

In conclusion, we have presented a novel method for the growth of GaAs nanowires and prismatic quantum heterostructures by molecular-beam epitaxy. The technique avoids the use of gold as a nucleation seed for the wires, solving the key issue of metal contamination. Moreover, we show that the versatility of MBE can be used to selectively grow quantum heterostructures on the facets of the wires, providing a new, large range of functionalities and applications.

Keywords:

molecular beam epitaxy · nanowires · photoluminescence · quantum wells

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