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Core-shell InP–CdS nanowires: fabrication and study

Z Zanolli, B A Wacaser, M-E Pistol, K Deppert and L Samuelson

Solid State Physics/The Nanometer Structure Consortium, Lund University, Box 118, 22100 Lund, Sweden

E-mail: zanolli@pcpm.ucl.ac.be

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Abstract

InP nanowires are fabricated by organo-metallic vapour phase epitaxy and studied via photoluminescence measurements performed on single nanowires, finding evidence of state filling with increasing excitation power density. To increase flexibility in fabrication technology we developed a wet chemical procedure to grow a CdS shell on these wires. In these InP–CdS wires the luminescence efficiency was decreased with respect to the bare wires. The CdS capping procedure needs further investigations to improve the emission properties of nanowires, in order to become technically useful. We suggest as possible improvements of this technique to increase the bath temperature and/or illuminate the sample with UV radiation during the capping procedure.

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

1. Introduction

Semiconductor nanowires (NWs) have recently stimulated wide interest in the scientific community because of their use in studying fundamental physical properties as well as for applications in miniaturized optoelectronic devices and photonic circuits. Nanowires based on many different material systems [1–5] and NWs having heterostructures in the axial and radial direction as well as superlattice NWs [6, 7] have been reported. Concerning the use of NWs in electronic and optical devices we mention nanowires with a built-in p–n junction [8] and that resonant tunnelling diodes [9], single electron transistors [10], LEDs [11] and lasers [12] have been constructed by using NWs. NW-based devices are promising for nanoscale optoelectronic devices with novel functions such as the emission of polarized photons and single-photon pulses. These applications require that the NWs have good electron-to-photon or photon-to-photon luminescence quantum yield. Even though semiconductor nanowires can be grown as nearly defect-free single crystals [13], they suffer limitations due to the relatively large surface-to-volume ratio. As a consequence, excitons can decay nonradiatively via electronic surface states, resulting in poor photoluminescence efficiency. For this reason several attempts to passivate the NW surface have been developed, usually by growing a shell of a semiconductor

having a wider bandgap to cap the nanowire. This shell material has the role of saturating the surface dangling bonds, hence the term ‘passivation’ to describe the process. The reported capping procedures of NWs are typically performed right after the core growth, in the same growth chamber, i.e. by using the same growth technique as already employed for the core [7, 14–17]. Here we report the growth of InP nanowires via organo-metallic chemical vapour phase epitaxy (OMVPE) and the growth of a CdS shell by a chemical bath process. Wet chemical processing allows much more flexible structures to be grown compared with OMVPE alone. This includes organic coatings for biological interfaces.

A direct gap of 1.421 eV at low temperature and 1.344 eV at room temperature characterize bulk InP, the semiconductor chosen for the present study. Therefore, this material system can find applications in fibre optic communications as both source and detector. The use of InP nanowires as polarization sensitive photodetectors [18] has already been demonstrated. The study of radial quantum confinement in small diameter InP single wires has been reported by [19].

The fact that a shell of higher gap semiconductor grown around a nanocrystal can result in a drastic enhancement of the PL efficiency has successfully been demonstrated for CdS nanocrystals with a Zn shell [20] and for InAs nanocrystals with a CdSe or ZnSe shell [21]. In the case of InP, instead, the syntheses of core–shell nanoparticles had only a limited success in the improvement of the luminescence efficiency, for instance in the case of the growth of ZnCdS₂ shells on InP cores [22] and of the growth of ZnS shell followed by aging of the sample for three weeks [23]. The mechanism for an efficient passivation of the InP surface is not completely understood. Besides, the passivation of an NW raises more problematic issues than that of a nanocrystal as a quantum dot (QD). The total number of surface atoms of an NW is higher than in the case of a QD, thus the probability of having a defect on the surface is considerably larger for an NW than for a quantum dot of the same diameter. All excitons located within a distance shorter than their diffusion length (≤ 100 nm) from a surface defect will have a large chance of non-radiative recombination. Therefore, the luminescence properties of an NW can be strongly affected by the presence of a single defect site. We consider this an open question in the investigation of efficient passivation schemes for an NW.

2. Methods of investigation

2.1. Sample fabrication

The InP nanowires were grown by organometallic vapour phase epitaxy (OMVPE) following previously published procedures [24]. In short, Au aerosol nanoparticles of a diameter 20 nm were first deposited on (111) B InP substrates [25]. The substrates were then transferred into the OMVPE reactor, where they were heated to 580 °C for 10 min in a low pressure (10 kPa) H₂/PH₃ atmosphere. After annealing, the temperature was lowered to the growth temperature of 400 °C and trimethylindium was supplied to the reactor for 5 min. The OMVPE reactor that was used has also been used for GaAs growth, hence a background pressure of Ga and As could exist while growing the InP.

The CdS capping of the InP nanowires by an organometallic reaction solution proceeded as follows. A reaction system of air stable reagents was chosen following a procedure for capping CdSe nanocrystals with CdS [26]. The reaction system consists of a 0.04 M Cd and S injection solutions and a reaction bath containing the organic solvents 1-octadecene (ODE), oleic acid (OA), and octadecylamine (ODA), and all reactions were carried out in a N₂ environment low in O₂ and H₂O. The Cd injection solution was prepared by stirring 0.202 g CdO in 4 ml OA and 35.5 ml ODE, while heating to above 150 °C, until the solution became clear. The

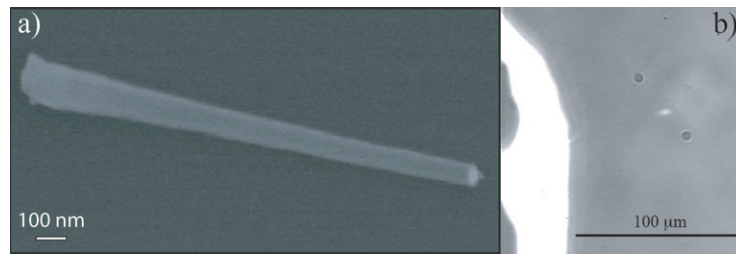


Figure 1. (a) SEM image of the uncapped InP wire (70 nm core diameter), from which the spectra of figure 3(a) were taken. (b) Image of the same NW taken with the imaging set-up. The pattern for the wire location is visible.

S injection solution was prepared similarly by stirring 0.05 g S in 39 g ODE and heating. Substrates with wires attached were secured on a Teflon holder and then transferred into an oxygen free environment. A chemical bath (containing 1.775 g ODA, 7.5 ml ODE, and 4 ml S injection solution) was heated to a constant temperature of 170 °C. The substrate and holder were immersed into this bath and the temperature was allowed to stabilize again to 170 °C. Cadmium injection solution, 4 ml, was then allowed to slowly drip into the chemical bath over the span of 10 min with the temperature being maintained at 170 ± 5 °C. During the dripping of the Cd injection solution the chemical bath turns from clear to a yellow–green colour. After all of the Cd injection solution was introduced, the heating source was switched off and the chemical bath was allowed to cool to 100 °C. After cooling, the substrate and holder were removed from the reaction bath and dipped in clean ODE. The ODE bath with the sample and holder were then removed from the oxygen free environment. The sample and holder were taken out of the bath and rinsed with hexanes, acetone, ethanol, and Milli-Q-water in that order. After rinsing, the sample was blown dry with N₂. For the sample with the thinner shell only half, i.e. 2 ml, of the Cd injection solution was used.

2.2. PL Measurements

Low temperature (~ 5 K) micro-photoluminescence (μ -PL) measurements on single NWs were performed to study their optical properties. The preparation of the samples for the PL measurements consists in the mechanical transfer of the as-grown NWs to a Si/SiO₂ substrate. The substrate is patterned with a coordinate system that allows easy location of the wires. The substrate with the wires is inspected by means of an optical microscope (100 \times objective, dark field) to locate those wires isolated from other wires and/or from any other particle on the substrate by more than ~ 20 μ m. The selected wires were then studied with PL for their optical properties and a scanning electron microscope (SEM) was used after PL to further check the quality of the chosen wires and to measure their diameter (figure 1(a)).

PL images and spectra of single NWs were obtained using a set-up consisting of a long working distance microscope objective, a spectrograph, a nitrogen cooled charge coupled device (CCD) and an imaging camera. The 532 nm line of a frequency doubled Nd–YAG laser was used for the excitation of the NWs. The luminescence from the samples, held on the cold finger of a continuous flow helium cryostat, is collected by the microscope objective and focused onto the entrance slit of the spectrograph and either imaged or spectrally dispersed onto the CCD camera (resolution of 2000 \times 800 pixels). The NWs are first located with the use of the imaging camera (figure 1(b)) and then the spectra are detected with the CCD camera.

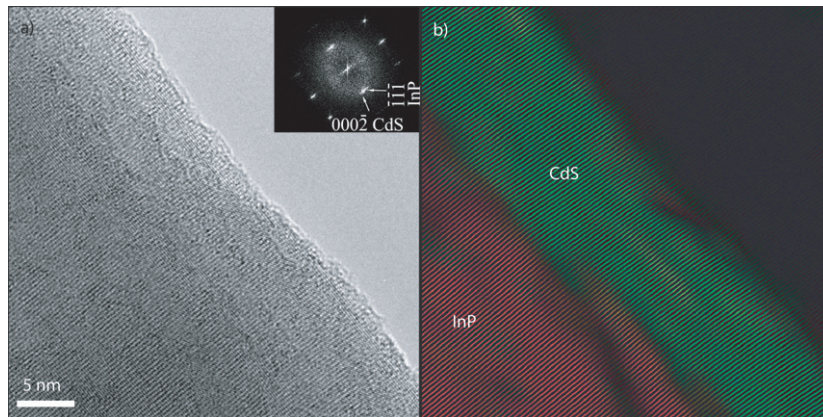


Figure 2. (a) A high resolution TEM image of a sample taken with the beam parallel to the $[11\bar{2}]$ pole. The inset is a Fourier transform of the image. In the Fourier transform two sets of spots are visible. One corresponds to a zinc-blende structure with the same lattice parameters as bulk InP. The other set of spots corresponds to a wurtzite structure with the same lattice constants as CdS. When the first mentioned set of spots is selected with a mask, the red area (grey area on the lower left) in figure (b) is highlighted in the reverse Fourier transform. When the second set of spots is selected, the green area (central grey area) is highlighted instead. This indicates that, as labelled on the image, the green area is CdS and the red is InP. This also reveals that the shell is approximately 10 nm thick.

2.3. TEM analysis

The shape and size of the samples were characterized by transmission electron microscopy (TEM, JEOL 3000F). Samples for TEM were prepared by placing a TEM grid on the same substrate from which the PL samples were taken. The grid was then moved on the surface, scraping nanowires off onto the grid. Images were acquired using a Gatan imaging system. This software allows the generation of the Fourier transform of the TEM image. This transform corresponds to the electron diffraction pattern of the sample under investigation. When a Fourier transform is performed on a high-resolution image of a crystal, the distances between points and special orientations can be analysed to determine the lattice constants and crystal structure of the sample. If more than one set of bright spots appears in the Fourier transform, then more than one crystal structure exists in the sample. One can then analyse the spots to determine a univocal correspondence between bright spots and crystal structures. Indeed, in the Gatan software it is possible to select a single set of spots in the Fourier transform with a mask. When a reverse Fourier transform is calculated from these selected spots one obtains a real space image similar to the original one, with the exception that the parts of the image that have the lattice spacing corresponding to the selected area are highlighted. Selecting the second set of spots by moving the mask can produce a second image where the other structure is highlighted. These two images can be combined in a composite image with different colours corresponding to the different structures in the image. This procedure was employed to analyse the InP–CdS core–shell wires. First a high-resolution TEM image was acquired (figure 2(a)), then Fourier transformed (inset of figure 2(a)) and finally the Fourier mapping led to the two-colour image (figure 2(b)).

3. Results and discussion

Three sets of InP nanowires were grown and studied: without any shell, with a thin ($\sim 2\text{--}3$ nm thick) CdS shell, and with a thicker shell (~ 10 nm). The shell thicknesses were measured with

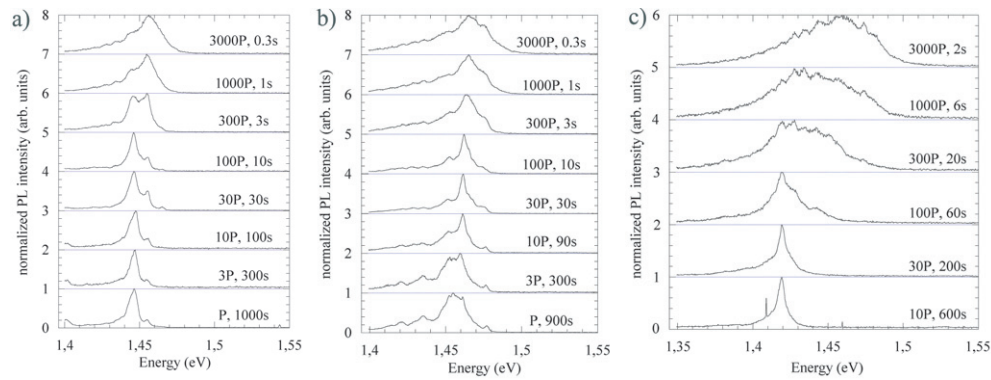


Figure 3. Photoluminescence spectra of InP nanowires at different excitation laser power densities: (a) single uncapped InP NW; (b) two wires with thin (~ 23 nm) CdS shell; (c) four NWs with ~ 10 nm thick CdS shell. The spectra are normalized and shifted in intensity for clarity.

TEM. The wires were about $1.5\text{--}1.8\ \mu\text{m}$ long and the InP core was $50\text{--}70$ nm wide. Since the exciton Bohr radius [27] in bulk InP is ~ 20 nm, quantum confinement effects can be neglected in these NWs. Nevertheless we note that the emission peak at low excitation power density of some of the samples (figures 3(a), (b)) is slightly blue-shifted (25 meV) with respect to the bulk InP emission. This can be due to the incorporation of Ga and/or C during the growth process and consequent alloying with the InP. We can exclude the possibility that the shift originates from wurtzite structure of the wires because the TEM analysis reveals that they are zinc-blende, and also because in the wurtzite case a larger shift of ~ 80 meV is expected [28]. A similar shift in InP wires with ~ 50 nm diameter was also observed by [19], but no explanation was given there for this.

The optical properties of all the studied wires were tested for different excitation power densities. Regardless of the presence and the thickness of the shell material, every sample shows evidence of state filling [29] at high excitation power density. That is, by increasing the power density of the cw excitation laser, the higher energy levels will be progressively populated and will contribute to PL emission. This results in the widening and blue-shifting of the spectra with the increase of the excitation power density. The spectra from the bare InP NW (figure 3(a)) and the NWs capped with the thin (figure 3(b)) and thick (figure 3(c)) shell clearly show this feature.

As concerns the increase in the emission intensity due to the CdS capping procedure we have actually found that the bare InP nanowires have a stronger emission. For the uncapped InP NWs it was possible to detect emission from single NWs but, to obtain comparable emission intensity from the capped wires, we had to average the luminescence collected from several wires, that is from two NWs in the thin shell case (figure 3(b)). The performance of the wires capped with the thicker shell is even worse, since the average luminescence from four NWs (figure 3(c)) provides a luminescence signal one-sixth that of the single uncapped NW at the same excitation power density.

We should stress that the bare InP NWs have a natural capping, i.e. a ~ 3 nm thick layer of native oxide. During the capping procedure, this oxide layer is dissolved and the unsaturated bonds are saturated by the CdS [30]. A reason for the worse performance of the CdS capped wires may reside in the chemical process of breaking some bonds and creating new ones that can leave more dangling bonds on the InP surface with respect to the case when the oxide layer is present. The reaction leading to the formation of the new bonds is a photoelectrochemical

reaction, hence the efficiency of the passivation procedure (i.e. the number of broken surface bonds that are saturated by the CdS) could be improved by increasing the temperature of the chemical bath, the light intensity incident on the semiconductor/electrolyte interface, and the concentration of sulfur atoms in the solution.

4. Conclusion

In summary, we have reported the OMCVD fabrication and PL study of InP nanowires. A passivation procedure of the wires with CdS via a chemical bath was tested. In the NW spectra we have found evidence of state filling at high excitation power density. The luminescence efficiency of the uncapped NWs is actually higher than the capped ones, leading to the conclusion that the chemical reaction to achieve an efficient passivation of the wires needs to be enhanced by increasing the chemical bath temperature and/or by UV radiation.

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