A luminescence study of doping effects in InP-based radial nanowire structures

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Abstract. We have used micro-photo- and cathodo-luminescence at low temperatures to study the effects of sulphur doping in InP and radial InP/InAs/InP structured nanowires. Samples with pure wurtzite crystal structure, with modulated wurtzite/zincblende crystal structure and with different radial InAs growth times were investigated. We observed a doping concentration gradient along the nanowires, the location of segments of different crystal structure and thickness fluctuations on the monolayer scale of the InAs layer.

1. Introduction
Nanowires (NWs) have been predicted to play a significant role in future electro-optical devices [1]. In order to realize devices, many parameters must be controlled simultaneously. One crucial parameter is the doping, which can have an effect on the crystal structure of the NWs. For instance, if InP NWs are doped with sulphur during growth, an otherwise mixed zincblende (ZB)/wurtzite (WZ) crystal structure can be turned into pure WZ [2]. When the doping is interrupted for specific time periods, the length and location of segments with the mixed crystal structure can be controlled along the NW [3]. These segments are referred to as stacking fault (SF) segments. The surface of the side facets of WZ NWs tend to be smooth, whereas for ZB they are corrugated. Any subsequent radial layer growth will consequently be influenced by the surface and therefore by the crystal structure.

In this work we show optical properties of InP NWs with pure WZ and with a modulated crystal structure, as well as InP/InAs/InP core/shell/cap NWs. For the latter, samples with radial InAs layers grown on both pure WZ and modulated crystal structure InP NW cores have been studied. The studies were done by micro-photoluminescence (µPL) spectroscopy and cathodoluminescence (CL) imaging.

2. Experimental details
The NW samples were grown using metal-organic vapour phase epitaxy (MOVPE). Two types of InP NW cores were prepared, one with pure WZ and one with a modulated crystal structure. The cores were about 2 microns long and about 60 nm in diameter. The modulated structures contained a number of roughly 100 nm long SF segments. For all InP NW core samples a second batch of samples with subsequent radial InP underlayer, InAs shell and InP cap growth were prepared. A series of samples using different InAs growth times on each type of NW core were also made. A more detailed description of the growth can be found elsewhere [3].
Optical measurements were performed on both NWs standing on their growth substrate (as-grown) and single NWs broken off and re-deposited on a gold-coated Si-substrate. The latter contains alignment marks, which facilitates CL and PL correlation measurements. The as-grown samples were studied both in top and side view. In side view the sample was cleaved through the middle along the NW length and mounted with the cleaved surface facing the laser or electron beam. This geometry is important especially for CL, as it allows studies on the full length of the NWs, the substrate, and the interface between them at the same time. The PL measurements were carried out at 4 K using the 532 nm line from a frequency doubled Nd-YAG laser as the excitation source using an excitation density of about 0.1 W/cm$^2$ and the spectral resolution below 1 meV. The CL measurements were carried out in an SEM operating at 5 kV and a probe current of 10-50 pA, with the sample at 7 K.

3. Results and discussion

3.1. PL of InP NW cores with and without SFs

The doping to achieve the pure WZ structure is often so high that it leads to degenerate doping, which broadens the emission above the 1.49 eV bandgap energy of the WZ InP. This is known as a Burstein-Moss shift [4]. The emission is also broadened to lower energies below the bandgap. Similar observations have previously been reported on a nearly identical structure by Wallentin et al. [5]. In our case we observe emission from single NWs ranging from below 1.4 eV up to about 2 eV, shown in blue in Figure 1.

The band alignment of InP WZ/ZB heterostructures is of type II, with the WZ conduction band (CB) edge above the CB of ZB. The extensions of the individual phases in the SF segments are thin enough to confine electrons in the ZB phase and holes in the WZ phase. This results in spatially indirect transitions, i.e. type II transitions. Such emission can be observed in the single NW spectrum shown in red, Figure 1, at 1.42-1.48 eV. For thin ZB sections in a predominantly WZ InP NW, this range correspond to extensions of 2-8 monolayers (MLs) according to Jancu et al. [6]. In addition, similar emission in the range up to 2 eV due to the doping is also present in this sample.

![Figure 1. µPL spectra of a single InP NW with pure WZ crystal structure (blue) and with multiple SF segments (magenta). For comparison the spectrum of the pure WZ NW (and of the NW with SFs at energies above 1.51 eV) has been magnified.](image)

3.2. PL of InP/InAs/InP Core/Shell/Cap with and without SFs

Radial growth of thin layers of InAs on pure WZ NW cores of InP leads to the formation of smooth quantum wells (QW). By varying the growth time of these thin layers, it is possible to shift the emission energy of the QWs. The QWs are well defined and the thickness varies in steps of single MLs in the radial direction. As the QWs are thin, the difference in quantization introduced by one ML is significant, and the thickness variations in single NWs lead to several emission peaks. In a series of NW growth runs with different growth times for the radial layer, we identified the emission peaks...
from QW thicknesses ranging from one to twelve MLs, measured on ensembles of NWs on as-grown samples [7]. Figure 2a shows an example of µPL spectra from single NWs with three different InAs growth times, 10 (black), 5 (blue) and 2 s (magenta).

![Figure 2. Single NW µPL spectra of InAs between InAs growth times. In a) the number of radial InAs MLs are indicated at the corresponding peak.](Image)

When the doping of the core is interrupted in short segments, we observe that the smooth QW breaks up into island formation at the SF segments. These islands form quantum dots (QDs) of various sizes and shapes and their emission is red-shifted, mainly due to the increased radial thickness. In Figure 2b, µPL spectra from a series of single NWs with multiple SF segments equally distributed along the NW and with three different InAs growth times are shown.

3.2.1. Identifying the location of the QDs. Using monochromatic CL imaging, the location of the QDs can be identified. Figure 3a shows an SEM image of an as-grown SF sample in side-view. The corresponding monochromatic CL images recorded at 0.95 and 0.87 eV are shown in (b) and (c), respectively. 0.95 eV corresponds to five MLs, the dominating thickness of the QWs in between the SF segments. This is supported by the PL spectrum in Figure 2a. By varying the detection energy (not shown here), different segments light up. At 0.87 eV the origin of the luminescence is less localized, but it is mainly found at the SF segments.

![Figure 3. a) SEM image of as-grown samples with five SF segments and a 5 s InAs growth time seen in side-view. CL image recorded at b) 0.95 eV and c) 0.87 eV.](Image)

3.2.2. Identifying the location of the SF segments. The location of the SF segments has already been identified indirectly as the regions in between the QWs, Figure 3b. However, there is a second way to do this with CL imaging. Figure 4b shows a CL image recorded at 1.55 eV of an as-grown sample with one SF segment near the top of the NWs. This energy is above the bandgap of WZ InP, and
related to the doping, as shown in Figure 1. The SF segments show up as dark regions in CL images recorded at energies above 1.49 eV. In addition, the main peak in Figure 4c is from the QW on the WZ parts of the NW. This peak corresponds to a one ML thick QW.

A feature that can be observed in the CL image is a doping concentration gradient going from high to low from the top to the bottom of the NW. This can be seen for all energies above 1.49 eV, as the CL images look similar, with the brightest luminescence at the top of the NWs. Interestingly we have previously seen the opposite behaviour when using S as dopant in ZB InP/InP Core/Shell NWs [8].

![Figure 4](image)

**Figure 4.** a) SEM image of as-grown samples with one SF segment and a 2 s InAs growth time seen in side-view. b) CL image recorded at 1.55 eV and c) CL spectra of the same region seen in a).

4. Summary

We have reported on µPL and CL measurements on InP based NW samples with pure WZ and modulated WZ/ZB crystal structure. The origin of the luminescence as well as the location of quantized structures and SF segments have been shown by CL imaging.

Acknowledgements

This work was performed within the Nanometer Structure Consortium at Lund University (nmC@LU), supported by the Swedish Research Council, by the Swedish Foundation for Strategic Research, by the Knut and Alice Wallenberg Foundation, by the Top-level Research Initiative “Nanotechnology and Energy Efficiency”, and by the EU program AMON-RA (214812). This project is based on a project that was funded by E·ON AG as part of the E·ON International Research Initiative as well as by VINNOVA.

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