Correlated micro-photoluminescence and electron microscopy study of a heterostructured semiconductor nanowire

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Abstract. Correlation between the optical and the structural properties of an individual heterostructured nanowire (NW) is crucial for optimising the NW synthesis and device design. In this work, low temperature (10 K) micro-photoluminescence (\(\mu\)-PL), low and high voltage scanning transmission electron microscopy and conventional transmission electron microscopy are applied to the same individual NWs. The studied NWs, grown by Au-assisted molecular beam epitaxy, have a wurtzite GaAs core with a zincblende GaAsSb axial insert, enclosed with an AlGaAs radial shell and a GaAs capping layer. By subsequent analysis of one and the same NW by \(\mu\)-PL and several electron microscopy techniques in different microscopes, we can relate the spectral features of a single NW to the structural features, such as different crystal phases, lattice defects and composition.

1. Introduction

III-V semiconductor nanowires (NWs) are attractive for a broad range of applications as for example solar cells, lasers, single photon sources and sensors. The electro-optical properties of III-V NWs are directly related to the crystal phase (zincblende (ZB) or wurtzite (WZ)), lattice defects and the composition. In practice, NWs from the same batch can differ for example by dimensions or defect configuration. Therefore structural and electro-optical properties of the same NW have to be investigated. Direct correlation between the optical properties and the structural characteristics of an individual NW is crucial for understanding band alignments and quantum confinement effects as well as for optimizing the NW synthesis and device design for future applications. Transmission electron microscopy (TEM) based techniques are commonly used to fully characterize structural elements of NWs. However, conventional TEM specimens are not well suited for micro-photoluminescence (\(\mu\)-PL) studies. So far, only a few correlated PL-TEM studies of the same NW have been reported [1,2].

In this work, low temperature (\(~10\) K) \(\mu\)-PL, scanning (transmission) electron microscopy (S(T)EM) at 30 kV and 200 kV and conventional transmission electron microscopy (TEM) at 200 kV are applied on the same WZ GaAs/AlGaAs core-shell NWs with ZB GaAsSb core inserts. Due to the complexity of this particular heterostructure, a range of different electron microscopy techniques were required to understand which structural features actually affected the optical properties. By detailed correlated study of one NW, particular structural characteristics are directly connected with the observed PL features.

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2. Experimental details
The NWs were grown by Au-assisted molecular beam epitaxy [3,4]. The heterostructure consists of WZ GaAs core with ZB GaAsSb axial insert, AlGaAs radial shell, and GaAs cap. In addition, an axial WZ AlGaAs segment forms on top of the WZ GaAs core during AlGaAs radial shell growth [4]. NWs were ultrasonically dispersed in isopropanol and drops of the solution were transferred onto a Si TEM grid with a 50 nm thick amorphous silicon nitride support film (ThinWindows Inc.). For safe handling and good heat conduction in the µ-PL experiments, the TEM grid was sealed between two Mo washers with central holes of 2 mm [5].

µ-PL was performed in a Janis ST-500 cryostat at ~10 K, using continuous laser excitation at the wavelength of 532 nm. The power density at the specimen was varied from 1 W/cm² to about 50 W/cm². The detection system included a Horiba Jobin Yvon iHR500 spectrometer with a 300 grooves/mm grating and an Andor Newton EM Si electron multiplying charge-coupled device (EMCCD). The spectral resolution of the system is about 200 µeV.

Structural characterization was performed on a Hitachi S-5500 S(T)EM (30kV, cold field emission gun) for low magnification bright field (BF) STEM and on a Philips CM30 TEM (200 kV, LaB₆) for BF TEM, dark field (DF) TEM, and selected area electron diffraction (SAED). A JEOL 2010F TEM/STEM (200 kV, Schottky field emission gun) was used for lattice imaging (HREM) and high angle annular DF (HAADF) STEM (probe size approx. 0.5 nm, 49-120 mrad collection angle range).

3. Results and discussion
A NW, containing all structural elements of the studied heterostructure after breaking off from the substrate, was selected from the PL-TEM dataset of about 30 NWs for a more detailed TEM and STEM characterization. Figure 1 shows that the PL spectra of the NW contain three bands, designated as A (1.35-1.45 eV), B (1.50-1.55 eV) and C (1.58-1.65 eV), which are characteristic for this NW heterostructure. The BF STEM (30 kV) image in the inset of figure 1 presents an overview of the NW divided into regions I (containing ZB GaAsSb insert surrounded by the WZ GaAs core and the AlGaAs shell, full line box), CS (WZ GaAs/AlGaAs core-shell, dashed line box) and AS (WZ AlGaAs axial segment, dotted line box) which are the origins of the characteristic PL emissions A, B and C respectively [2,4,5]. Low voltage STEM provides quick insight into morphology and size of the NW and can be performed before µ-PL as well [5].

The ground state of GaAsSb related PL emission (band A) is observed at 1.39 eV (figure 1) for this NW. No blue shift of this PL band can be observed with increase of excitation power. Such behavior indicates that both electrons and holes are confined within the GaAsSb insert (i.e. type I band alignment between ZB GaAsSb insert and WZ GaAs core) [6]. At higher excitation powers a PL peak at 1.42 eV appears (figure 1). The origin of this PL transition is not clear at present.
Region I of the NW is shown in detail in figure 2. DF TEM (figure 2(a)) visualizes the different crystal phases present with the highest contrast: the ZB insert (dark) in the WZ NW (bright) with some stacking faults (SFs). The NW has a diameter of 76 nm in region I, just above the fracture, and a 38 nm long ZB GaAsSb insert. There are two adjacent SFs in the WZ GaAs core starting at about 21 nm above the insert (figure 2(a,b)). The crystal phases were confirmed by SAED (not shown). Note that the crystal phases and the SFs can be identified by lattice imaging (HREM) on the 50 nm thick SiN support film. Type I behavior of GaAsSb related PL emission (figure 1) indicates that the two SFs (figure 2(a,b)) are far enough away from the insert not to affect carrier recombination within the insert.

Figure 2 shows that the fracture of the NW occurred within ZB and WZ sections in region I, which might have impact on the PL emission from the ZB GaAsSb insert. HAADF STEM was used to visualize the difference between the WZ GaAs core and the WZ AlGaAs shell, or the ZB GaAsSb insert and the ZB AlGaAs shell. The HAADF STEM image in figure 2(d) and area intensity profile in the inset show the core-shell structure of regions I and CS with a core diameter of 27 nm. The shell is about 25 nm thick, whereas the width of the NW at the lower ZB-WZ interface is 49 nm as viewed in a <110> projection. This indicates that the fracture of the ZB section occurred mostly within the ZB AlGaAs shell. Since the insert is mostly intact and almost completely passivated by ZB AlGaAs shell and WZ GaAs core, the GaAsSb related PL emission (band A in figure 1) remains observable.

![Figure 2](image.png)

**Figure 2.** Detailed TEM characterization of the region I: (a) DF TEM image on a <110> zone. (b) HREM image. (c) HREM image of the upper ZB-WZ interface. (d) HAADF STEM image few degrees off a <110> zone with 100 nm area intensity profile (inset). Diameter of the core is 27 nm.

The upper part of the NW (regions CS and AS) is shown in figure 3. HAADF STEM shows where the transition between the core-shell structure and the axial WZ AlGaAs segment occurs (figure 3(a)). The WZ GaAs/AlGaAs core-shell segment above the two SFs in region I (figure 2(a,b,d)) is SF free for about 0.7 μm, which is the estimated core length above the insert based on the growth parameters [3]. The WZ region with high SF density (about 0.3 μm long) follows as observed in HAADF STEM and BF TEM (figure 3(a,b)). The gradual transition from WZ GaAs/AlGaAs core-shell to axial WZ AlGaAs segment starts in this region. In the axial AlGaAs segment, the SF density is reduced (figure 3(a,c)) compared to the core-shell transition region. The area intensity profiles (figure 3(d)) of the HAADF STEM image (figure 3(a)) show the core-shell structure in area 1 and the axial AlGaAs segment (no core-shell structure) in area 2. The anti-tapering shape of the NW (inset of figure 1) explains the higher intensity of the axial AlGaAs area profile (profile 2, figure 3(d)).

In the PL spectra (figure 1), band B (GaAs related PL emission) is broad and weak compared to bands A and C. The B-band is related to a mixture of various type II recombinations due to the SFs in the WZ GaAs core [5]. The peak at 1.55 eV that appears at higher excitation powers is not completely understood at present.
The AlGaAs related PL emission is coming from the axial AlGaAs segment and not from radial AlGaAs shell [4,5]. The significant volume of the axial AlGaAs segment (40% of the total NW length of 2.2 μm), the presence of SFs in the axial AlGaAs and the high SF density in the WZ GaAs/AlGaAs core-shell transition region can partly account for the strong AlGaAs PL emission compared to GaAsSb and GaAs PL emissions since SFs act as carrier traps. SFs here seem to prevent carrier diffusion from their origin, within the axial AlGaAs segment, through the WZ GaAs core towards the ZB GaAsSb insert.

4. Conclusions
One single NW has been studied by μ-PL and in three different electron microscopes to directly correlate the structural features to the optical properties. ZB GaAsSb related PL emission exhibits type I band alignment when the SFs in surrounding WZ GaAs core are far away (about 21 nm) from the ZB GaAsSb insert. By combining HREM and HAADF STEM, it was determined that the fracture within the ZB phase occurred mainly within the AlGaAs shell. Such fracture still allows PL emission from the ZB GaAsSb insert. The GaAs related PL emission, at about 1.52 eV, originates from type II recombination between SFs and the WZ GaAs core with varying distribution of SFs in the region of transition from core-shell to axial AlGaAs segment. The AlGaAs related PL emission originates from the WZ AlGaAs axial segment and is most prominent in the PL spectra of this NW due to the presence and distribution of SFs in the axial segment and in the transition region from core-shell to the axial segment.

Acknowledgment
This work was supported by “RENERGI” program (Grant No. 190871) of the Research Council of Norway.

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