Radial composition variations in the shells of GaAs/AlGaAs core-shell nanowires

J S Nilsen[1], J F Reinertsen[2], A Mosberg[1], V T Fauske[1], A M Munshi[3], D L Dheeraj[3], B O Fimland[2,3], H Weman[2,3] and A T J van Helvoort[1]

[1]Department of Physics & [2]Department of Electronics and Telecommunications, Norwegian University of Science and Technology (NTNU), NO-7491, Trondheim, Norway.
[3]CrayoNano AS, Otto Nielsens vei 12, NO-7052, Trondheim, Norway.

E-mail: julie.s.nilsen@ntnu.no

Abstract. GaAs nanowires (NWs) are seen as promising building blocks for future optoelectronic devices. To ensure reproducible properties, a high NW uniformity is required. Here, a substantial number of both position-controlled and randomly grown self-catalyzed GaAs/AlGaAs core-shell NWs are compared. Single NWs are characterized by correlated micro-photoluminescence (μ-PL) spectroscopy and transmission electron microscopy (TEM). TEM is done in the ⟨110⟩- and ⟨112⟩-projections, and on the ⟨111⟩-cross-section of the NWs. The position-control grown NWs showed a higher degree of uniformity in morphology. All NWs on both samples had a predominantly stacking fault free zinc blende structure, with a main optical response around the GaAs free exciton energy. However, NW-to-NW structural variations in the tip region and radial compositional variations in the shell are present in both samples. These structural features could be the origin of variations in the optical response just below and above the free exciton energy. This correlated study demonstrates that the observed distinct, sharp PL peaks in the 1.6 - 1.8 eV energy range present in several NWs, are possibly related to radial compositional variations in the AlGaAs shell rather than the structural defects in the tip region.

1. Introduction

For the development of future optoelectronic devices based on NWs, self-catalyzed GaAs/AlGaAs core-shell NWs are an attractive model system [1]. The NWs are easily grown using a vapor-liquid-solid (VLS) mechanism, even on different types of lattice mismatched substrates due to the strain relaxation on the NW surface. However, the correlation between structural defects and the optoelectronic properties is still debated. One reason for this is that the NWs are subject to large NW-to-NW variations within a growth batch. Therefore, a significant sampling set combined with correlated optical and structural analysis of the same single NWs is required. To reduce the NW-to-NW variations for fundamental studies and more importantly for the smooth integration into larger scale devices, position-controlled growth has attracted quite some attention recently [2, 3]. Here we compare the structure of random and positioned-control grown NWs.

2. Experimental

The NWs in this study are grown on a Si(111) substrate both randomly and with position-control. The latter is achieved by covering the substrate with a 40 nm thick thermal SiO_2 film. Holes in the film about 100 nm in diameter and 1 μm apart were made by nanoimprint lithography [3]. The GaAs cores are grown through a self-catalyzed VLS mechanism using molecular beam epitaxy. Growth parameters for the two samples can be found in table 1.

Table 1. Growth parameters for the two samples. Shell growth is initiated before Ga droplet consumption and goes via a vapor-solid mechanism. Notation: Random/positon-controlled.

	Ga [ML/s]	As [Torr]	Al [ML/s]	[min]	[°C]
GaAs core	0.7/0.6	$8.0 \times 10^{-6}/5.5 \times 10^{-6}$	-/-	20/25	630
$Al_{0.33}Ga_{0.67}As$ shell	0.2/0.3	$9.0 \times 10^{-6}/1.0 \times 10^{-5}$	0.10/0.15	30/20	630
GaAs cap	0.2/0.3	$9.0 \times 10^{-6}/1.0 \times 10^{-5}$	-/-	15/8	630

For characterization, the NWs were dispersed on a 50 nm thick SiN support. The study was performed in a correlated manner, meaning the same individual NWs were studied first in μ-PL at 12 K and subsequently by TEM [4]. For each growth batch at least 15 NWs were studied. In addition to conventional TEM techniques, selected NWs were studied in the ⟨112⟩-projection as well as in the ⟨111⟩-cross-section (the latter made using focused ion beam (FIB)) using high angular annular dark field scanning TEM (HAADF STEM).

3. Results and discussion

Scanning electron microscopy (SEM) of as-grown samples (fig. 1(a, d)) illustrates the difference in morphology between random and position-controlled growth of NWs.

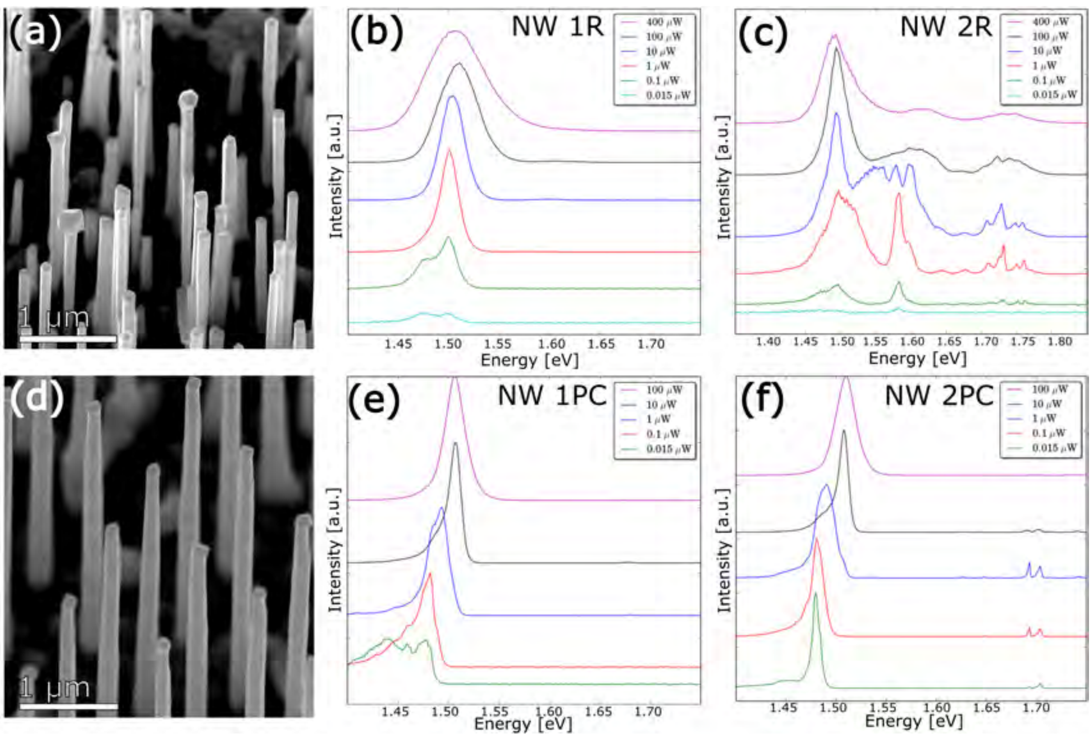

Figure 1. (a) and (d): Tilted SEM images of as-grown samples. Power-dependent PL spectra at 12 K are seen in (b, c) for two randomly and (e, f) for two position-control grown NWs.

Journal of Physics: Conference Series **644** (2015) 012007 doi:10.1088/1742-6596/644/1/012007

The spacing between the NWs in the randomly grown sample is varying, giving local variations in the growth conditions for the cores and for the different facets during shell and cap growth.

The PL spectra show that there are differences in the optical properties between the two samples, but more pronounced are the NW-to-NW differences within each sample. PL spectra from four NWs are presented in fig. 1(b, c) and (e, f). All the spectra have a peak around 1.51 eV, assigned to the recombination of the GaAs free exciton [5]. The shoulder peak just below this energy seen for some NWs is most likely related to different types of defects [6]. The presence of peaks with energy above that of the free exciton (fig. 1(c, f)) are uncommon and previously not seen when the shell is thin and grown at lower temperature. These peaks are present in about 30% of the position-control grown NWs and in 70% of the randomly grown NWs studied. The energy range in which these peaks are found is 1.6 - 1.8 eV. To better understand the origin of this high-energy emission, structural characterization by TEM of the same NWs was performed. Stacked dark-field (DF) TEM images in the ⟨110⟩-projection from the tip region of the NWs in fig. 1(b, c) and (e, f) are shown in fig. 2(a-d), respectively.

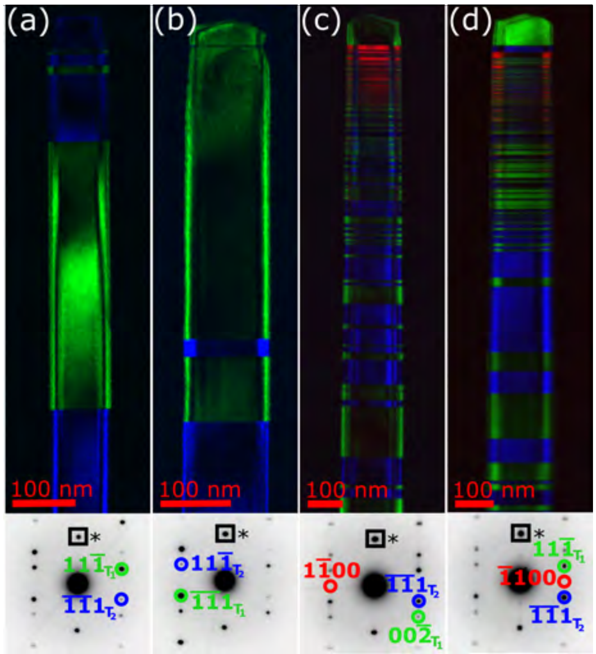

Figure 2. Stacked DF TEM images with the corresponding inverted diffraction patterns of the top part of the same NWs as characterized by PL. (a) NW 1R, (b) NW 2R, (c) NW 1PC and (d) NW 2PC. $[111_{T_1,T_2}]$ and WZ [0002] are marked with *.

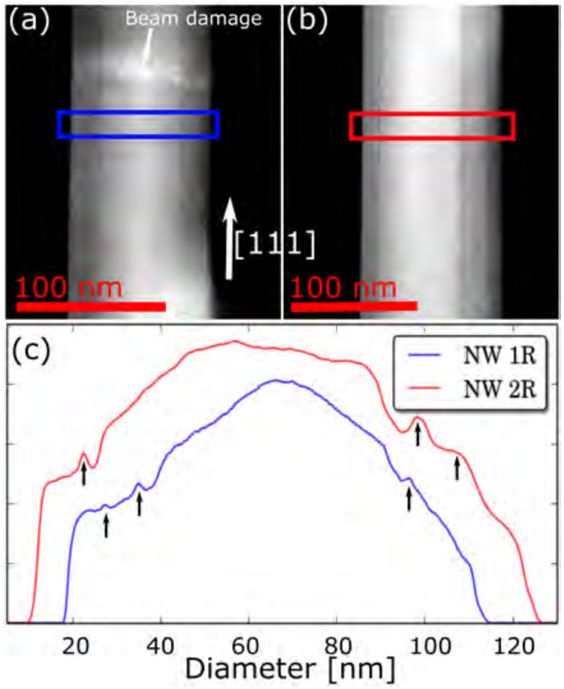

Figure 3. HAADF STEM images of (a) NW 1R and (b) NW 2R, taken in ⟨112⟩. (c) Intensity profiles from the areas marked in (a) and (b). Arrows mark peaks in HAADF STEM intensity.

For the NWs shown here, the position-control grown NWs have considerably more lattice defects than the randomly grown NWs, despite the more homogeneous morphology (fig. 1). On the other hand, the randomly grown sample has far more NW-to-NW variations in the morphology and defect structure considering the whole set of NWs studied. Most NWs in both samples had some wurtzite (WZ) phase present, which forms during Ga droplet consumption [7]. However, no relation between high-energy peaks and lattice defects in this correlated study could be identified. HAADF STEM characterization of several NWs tilted onto a ⟨112⟩-direction, revealed that the NWs had a line structure in the AlGaAs shell running along the length of the NWs (fig. 3). To study the shell structure more closely, cross-sectional FIB samples were prepared from the middle of these NWs, and their HAADF STEM images are given in fig. 4.

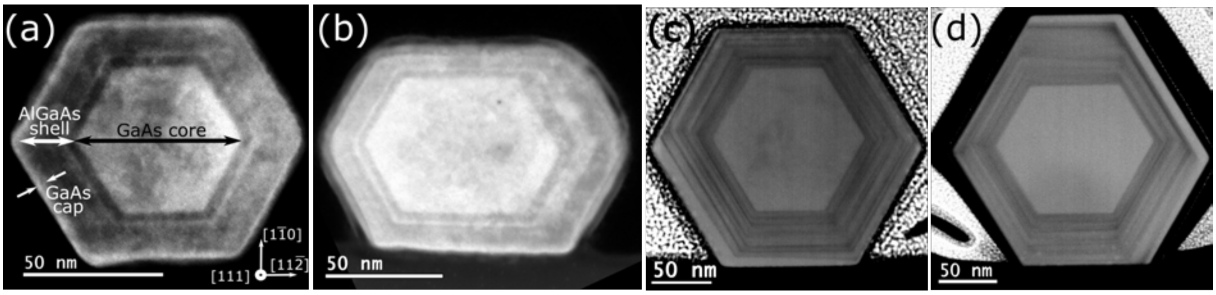

Figure 4. (a-d) HAADF STEM of the cross-sections of the NWs in fig. 2(a-d), respectively.

The cross-sections with an even specimen thickness revealed the presence of compositional variations in all six segments of the AlGaAs shell, matching the line structure in the HAADF STEM images of whole NWs in the [21$\bar{1}$]-projection (fig. 3). These lines are Al-deficient and Al-rich radial bands, and they vary in thickness both within and between each shell segment. Such bands are not commonly seen in this type of core-shell NWs. Instead, Al-enrichment in the ⟨112⟩-direction has been reported in NWs grown at low temperature shell growth [8]. It is possible that in some shell segments, the formation of an Al-deficient layer between two Al-rich barriers could lead to confinement of carriers, which could explain the high-energy features seen in the PL spectra of several NWs. However, the energies are higher than one would expect assuming a pure GaAs well, considering the thickness of the Al-deficient layers [9] .

4. Conclusions

By using correlated PL-TEM on a relatively large number of randomly and position-control grown GaAs/AlGaAs core-shell NWs, it is demonstrated that both growth methods have pronounced NW-to-NW variations within one batch. In addition to conventional TEM to study lattice defects, HAADF STEM in two different directions (⟨112⟩ and ⟨111⟩) on the same NWs showed the presence of fine-spaced radial compositional variation along the entire AlGaAs shell on both samples. These variations are different for every shell segment. Further work is needed to confirm if these radial compositional variations could be the sole explanation for the observed sharp high-energy (1.6 - 1.8 eV) PL emission present in several of the here studied NWs.

Acknowledgments

The Research Council of Norway is acknowledged for the support to the NorFab (197411/V30) and the NORTEM (197405) facilities, as well funding the projects 239206/O70 and 214235/F20.

References

[1] Fontcuberta i Morral A 2011 *IEEE J. Sel. Top. Quant.* **17** 819
[2] Gibson S J, Boulanger J P and LaPierre R R 2013 *Semicond. Sci. Tech.* **28** 105025
[3] Munshi A M *et al.* 2014 *Nano Lett.* **14** 960–966
[4] Todorovic J, Moses A, Karlberg T, Olk P, Dheeraj D L, Fimland B O, Weman H and van Helvoort A T J 2011 *Nanotechnology* **22** 325707
[5] Ahtapodov L *et al.* 2012 *Nano Lett.* **12** 6090–6095
[6] Spirkoska D *et al.* 2009 *Phys. Rev. B* **80** 245325
[7] Krogstrup P, Curiotto S, Johnson E, Aagesen M, Nygård J and Chatain D 2011 *Phys. Rev. Lett.* **106** 125505
[8] Kauko H, Zheng C L, Zhu Y, Glanvill S, Dwyer C, Munshi A M, Fimland B O, van Helvoort A T J and Etheridge J 2013 *Appl. Phys. Lett.* **103** 232111
[9] Shi T *et al.* 2015 *Nano Lett.* **15** 1876–1882