GaN, AlGaN, HfO$_2$ based radial heterostructure nanowires

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Abstract. Gallium nitride based core/shell nanowire heterostructures are promising components for UV optoelectronic nanodevices. A better understanding of their growth mechanisms is required to tailor the growth and the properties of these structures. We report an investigation of GaN-based radial nanowire heterostructures grown by Molecular Beam Epitaxy combined with Atomic Layer Deposition of HfO$_2$ dielectric cladding. The structural quality of GaN nanowire samples coated with different materials, the elemental distribution along the nanowires’ length, as well as the elemental incorporation mechanism are discussed.

1. Introduction
In the last few decades research in the field of nitride materials has been focused towards controlling the growth and morphology of structures at the nano-scale. The combination of GaN, Al$_x$Ga$_{1-x}$N, and AlN in various heterostructures has potential applications in optoelectronic devices in the far ultraviolet and in high frequency devices [1]. In addition, the performance of AlGaN / GaN high electron mobility transistors has been found to improve using HfO$_2$ to passivate surface states [2]. It has been demonstrated previously that Plasma Assisted - Molecular Beam Epitaxy (PA-MBE) is a promising technique for the growth of free-standing GaN nanowire (NW) structures [3] that can be used as components of nano-scale devices. One of the next challenges is to control the growth of NW radial heterostructures incorporating cores of GaN and shells of different materials whose device structure and physical properties can be appropriately tailored. A critical issue is the control of the uniformity of the coating material. In this contribution, we present a study of nanowire samples with GaN cores coated with a single shell of either AlGaN or HfO$_2$ or a double shell of AlGaN-GaN.

2. Experimental
Two samples which consist of core/single-shell (sample A) and core/double-shell (sample B) nanowire structures were grown on $\alpha$-sapphire substrates using plasma assisted MBE. GaN cores of the NWs of both samples were obtained using Ni catalyst seeds to promote NW columnar growth under group V-rich conditions (N:Ga ratios of 9:2 for 1h 15min at 730 °C). For sample A, an Al$_{0.2}$Ga$_{0.8}$N shell was deposited for 3.5 minutes at 730 °C after switching to group III-rich conditions (N : Ga flux ratio 7:10 and Al : Ga flux ratio of 1:4). Details and mechanisms of NW growth by PA-MBE under different conditions are described in [2]. For sample B, an additional deposition of GaN followed the preparation of the GaN/AlGaN structure (as for sample A) to form an outer shell under Ga-rich conditions (N:Ga ratio of 7:10 for 3.5 minutes). A third sample, C, was obtained through a combination of PA-MBE growth followed by Atomic Layer Deposition (ALD). For sample C the first step involved GaN NWs growth on silicon (001) under the group-V rich conditions used for sample A. The second step consisted of depositing a coating of HfO$_2$ using [(MeCp)$_2$HfMe(OMe)] (MeCp =
CH(C₅H₅) precursor in toluene (0.05M) using water vapour as the oxidant. 150 cycles of atomic layer deposition were used to obtain a 6 nm thick coating.

Samples A and B were analysed using a HB601VG cold-FEG STEM microscope operating at 100kV (minimum probe size ~1nm), which is equipped with a windowless Si(Li) EDX spectrometer. Sample C was analysed using a 2010F FEG-TEM operating at 197kV, equipped with a scanning unit and an EDX detector. TEM samples A and B were prepared by mechanically scraping the NWs from the substrate surface into an ultrasonic bath of iso-propanol before depositing the NWs in suspension on a lacey carbon film supported by a TEM Cu grid. Samples B and C were prepared with the classic sandwich technique followed by mechanical polishing and Ar⁺ ion milling to electron transparency.

3. Results and discussion
Energy-dispersive X-ray (EDX) point analyses and line scans were performed on sample A, to spatially quantify the Al concentration and distribution along the width and length of the NWs. Figure 1a) shows a typical EDX point analysis. The Al concentration was quantified using K-factors calculated with the Zaluzec and Mott-Massey atomic models assuming the thin film approximation. A general decrease of the Al : Ga ratio is observed from the NW growth tip (~6 at% Al) towards the root end (~1 at% Al) in the NWs analysed.

![Figure 1](image.png)

Transverse EDX Al line-profiles were obtained from several NWs by integrating the X-ray counts within a 100 eV wide energy window centred on the Al-K peak at 1.56 keV. It was not feasible to reliably eliminate the background contribution using the EDAX software automatic background subtraction routine because of the very low count rates. The small excitation volumes and the short acquisition times, required to avoid beam damage to the sample, generate particularly low count rates for the Al signal. To assess the background component of the Al profile a second acquisition, with a 100eV wide window, was set just above the Al peak and acquired simultaneously. As shown in Figure 1(b) the resultant Al profile is above the background only near the NW tip (linescan L1) with lateral maxima compatible with a projected volume of a shell containing Al. Near the substrate end of the NW (linescan L2) the Al and background signals are similar, indicating a decrease in shell thickness along the NWs length. A general enlargement in diameter of the NW growth tip is observed similar to pure GaN NWs grown with the same growth sequence (group-V rich followed by group-III rich conditions) [3]. The Al distribution (decreasing from the tip downwards) follows a reverse trend with respect to the group-V rich growth of pure AlGaN [4] NWs. This observation is attributed to the different growth mechanism of the NW under group-III growth conditions [3] combined with the
lower mobility of Al under group-III rich growth conditions with respect to Ga [5]. A shadowing effect of neighbouring wires of the incoming atomic fluxes might also play a role.

Figure 2. (a), (b) TEM bright field (BF) cross section images of sample B (GaN/AlGaN/GaN core/inner shell/outer shell structure) showing NW coalescence and ‘hat’ structures. (c) STEM secondary electron image of a NW tip and EDX maps corresponding to Al-K, Ga-L, N-K X-rays. Al is at background level in the upper part of the ‘hat’ structure.

The NW tip broadening effect is more drastic for sample B. Bright field images of a TEM cross-section (Figures 2a, b) show a non-uniformity of the NW diameters that often coalesce especially near the top of the wires where large “hat” structures tend to form. NW coalescence can be attributed to a progressive and uneven deposition of material particularly during the last two stages of radial growth (shell formation under group-III rich conditions). EDX maps of harvested nanowires show that the Al distribution stops abruptly at the ‘hat’ structure (Figure 2c).

Figure 3. (a) STEM HAADF image of sample C with insets showing the line scan positions of Figure 4. (b) HREM image of the NW tip imaged along [11-20] zone axis with diffractogram. The lattice planes visible are \( d_{0002} = 0.26 \) nm (horizontal fringes) and \( d_{1-100} = 0.27 \) nm (vertical fringes).

Al appears here at background level suggesting that the ‘hat’ formation mainly takes place during the growth of the outer GaN shell. Point analysis along the NWs (not shown here) indicates an increase of the Al : Ga ratio from the substrate towards the NW growth tip confirming an Al distribution similar to that in sample A. To overcome this limitation of the MBE growth mechanism,
ALD has been used as an alternative technique to deposit HfO$_2$ on GaN NWs. HREM images (Figure 4b), taken along [11-20] wurtzite direction, show a single crystalline NW with sharp lateral walls.

The core/shell structure is not visible from the high-angle annular dark field (HAADF) image (Figure 3b) but a small EDX Hf signal was observed above the background along the whole length of the wires, which is shown in the line scans of Figure 4. For these EDX analyses the Hf signal was obtained integrating over a 300 eV wide window centred on the Hf-L$_{\alpha 1}$ peak, and the background was evaluated averaging a pre-peak and a post-peak window of roughly the same size. The thickness of HfO$_2$ deposited (~1nm) was thinner than a thin film (~ 6nm) grown under the same conditions. Although ALD is a ‘saturative’ cyclic growth process, the difference in deposition rates is probably due to limited adatom surface diffusion and the higher surface-to-volume ratio of NWs compared with planar 2D layers. Further investigation and tuning of the ALD growth process is needed to obtain a thicker and uniform radial coverage of NWs but, as a preliminary result, it suggests a possible way of producing free standing dielectric-semiconductor heterostructures.

4. Conclusions
Core/single shell GaN/AlGaN NWs showed a partial coverage of AlGaN with a thickness of the Al-rich shell decreasing toward the growth substrate. A similar Al distribution was found for core/double shell GaN/AlGaN/GaN radial NW structures and attributed to an Al incorporation mechanism dominated by a decreased diffusion along the NW walls, with a shadowing effect from neighbouring NWs. During the growth of the outer GaN shell, the deposition of material at the NW tip formed “hat”-like structures. HfO$_2$ deposited onto GaN NWs was found to be uniformly distributed along the NW length but with a lower thickness than expected. This preliminary observation suggests that ALD is potentially a complementary deposition method to provide uniform dielectric isolation of MBE grown NWs.

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