Structural Properties of GaN Nanowires and GaN/AlN Insertions Grown by Molecular Beam Epitaxy

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Abstract
The microstructure of GaN nanowires (NWs) at the Si(111) substrate interface and the strain state of GaN insertions in GaN/AlN nanowire heterostructures have been studied by high resolution transmission electron microscopy. We have found that GaN NWs are relaxed from the beginning of the growth, due to a plastic relaxation mechanism. Concerning the GaN insertions in AlN, the presence of dislocations in the AlN capping layer can explain their partially relaxed state and the apparent discrepancies between experimental results and theoretical modelling.

1. Introduction
It is well known that the efficiency of nitride-based optoelectronic devices is limited by the high densities of threading dislocations (TDs), typically up to $10^9 - 10^{10}$ cm$^{-2}$, generated by the use of highly mismatched substrates. Therefore, the growth of nanowires (NWs), which can be considered as a juxtaposition of non-coalesced grains, appears very promising since TDs formed by the coalescence of adjacent grains in the usual 2D layer growth should be suppressed. Furthermore, in case of axial heterostructures, such as AlN/GaN, the presence of free surfaces at the side should allow lateral relaxation and consequently prevent the formation of misfit dislocations at the interfaces. These two characteristics make nitride wire-like heterostructures potentially very interesting for the realization of efficient light emitting devices (LEDs) in the visible and UV range [1,2]. However, the details of the NWs’ growth and especially their nucleation are still far from being clear. Moreover, due to the reduced diffusion length of Al compared to Ga and to its enhanced incorporation probability on the NWs’ sides, the formation of AlN/GaN wire-like heterostructures is accompanied by the growth of a thin AlN shell around the GaN insertions [3-5]. This experimental feature raises the issue of strain relaxation in GaN/AlN core-shell heterostructures through dislocation formation beyond a given critical thickness, which has recently been addressed from a theoretical point of view [6,7].

This has motivated us to investigate by TEM the microstructure of nitride NWs, and especially the strain state, directly related to the optical properties. We have focused on two main points which are reported in the following, namely the interface with the substrate and the AlN/GaN insertions.

2. Experimental
Samples were grown catalyst-free by plasma-assisted molecular beam epitaxy (PA-MBE) on a thin (0001) AlN buffer layer deposited on (111) Si. After a base of standard GaN NWs, between 500 and
700 nm thick [8], several tens of nm of AlN containing insertions of GaN were grown according to the procedure described in [5]. The nanowires were either scrapped off the substrate and dispersed on a Cu microscope grid covered with a lacy carbon film, or covered with glue and then prepared in cross-sectional orientation by mechanical polishing followed by Ar-ion milling. During this last process, the top part of the NWs was often removed. The TEM investigations were performed on a Jeol 4000EX microscope operated at 400kV (Cs=1nm). For strain maps determination by the Geometrical Phase Method (GPA) [9], off-axis high resolution images, i.e. tilted from the main [11-20] zone axis, were recorded. This configuration was chosen in order to enhance the signal to noise ratio [10,11] and therefore increase the reliability of the analysis.

3. Nanowire/substrate interface
A typical HREM image of a NW base, taken along the [11-20] zone axis, shows the Si/AlN and AlN/GaN interfaces (Figure 1a). No amorphous layer is present at these interfaces, contrary to the case of direct growth of GaN NWs on Si [12]. We observe a coincidence relationship between Si and AlN (4 to 5 interplanar distances (inset)) as already reported in [13]. An almost complete strain relaxation in AlN grown on Si is therefore expected.

![Figure 1](image1.png)

Figure 1. (a) HREM image of a NW base taken along the [11-20] zone axis. The inset shows the coincidence between Si and AlN
(b) c-tilt off-axis HREM image of the same NW
(c) corresponding map of the c lattice parameter and profile from Si to GaN (inset)
(d) a-tilt off-axis image showing the presence of dislocations at the AlN/GaN interface

The NW was then tilted around the c and a axes successively in order to get off-axis images. The c-tilted image (Figure 1b) has been analyzed by the GPA method to obtain a map of the c/2 lattice parameter (Figure 1c). Si was chosen as the reference region. The inset represents a profile from Si to GaN integrated over the black rectangle area. Surprisingly, the c/2 values of AlN and GaN correspond to almost fully relaxed material (0.249 and 0.259 nm respectively). On the other hand, the a-tilted image, figure 1d, clearly reveals the presence of two misfit dislocations at the AlN/GaN interface.
This indicates that a plastic relaxation mechanism occurs in the present case, which is markedly different from what is observed in the case of Stranski-Krastanow (SK) QDs where elastic relaxation takes place. We can therefore conclude that the thin AlN buffer layer behaves as a compliant substrate. These results confirm that GaN grown on AlN is fully relaxed from the beginning and are in total agreement with those recently obtained from in-situ grazing incidence synchrotron X-ray diffraction experiments [14].

4. AlN/GaN insertions

The investigated sample consisted of successive GaN inclusions, 30 nm in diameter and 2.5 nm in height, separated by 12 nm high AlN regions, as shown in figure 2a. The presence of a thin AlN shell around the wire should be noticed. The strain component along the nanowire axis, $\varepsilon_{zz}$, was obtained by applying the GPA method, the reference region being chosen as the AlN side part and taken as fully relaxed. $\varepsilon_{zz}$ was calculated as $\varepsilon_{zz} = (d_{002} - d_{002\text{ref}}) / d_{002\text{ref}}$ with $d_{002\text{ref}} = 0.5c_{\text{AlN\text{bulk}}}$, and is given in figure 3b. Concerning AlN, we note an in-plane tensile strain in the central part with respect to the reference side, leading to a decrease of the AlN c-lattice spacing ($\approx -1\%$) with respect to the reference region. Concerning the GaN inclusions, we notice that $\varepsilon_{zz}$ is maximal in the central part where it reaches about 6% and that it remains almost constant along the growth direction (Figure 2b). On the other hand, a lateral gradient is observed, with a decrease from the central part to the side where it reaches about 4%, a value close to the GaN relaxed one. This behaviour is different from the case of SK QDs, for which the highest strain is localized at the bottom of the QD and in the wetting layer as well [11].

![Figure 2](image)

**Figure 2.** (a) HREM showing the GaN insertions in AlN 
(b) Mapping of strain component $\varepsilon_{zz}$ obtained from GPA. The reference region was taken in the AlN side part 
(c) Mapping of $\varepsilon_{zz}$ computed with a valence force field model

These experimental results were compared with computed ones obtained by using a nearest neighbour valence force field based on Keating’s model [15]. We considered {0001} oriented AlN nanowires with hexagonal cross section (radius $R \approx 15$ nm) and {1-100} facets. The GaN insertion was modelled as a slice of a sphere. Periodic boundary conditions were applied along the c axis on a supercell of height $L \approx 13$ nm. The elastic energy of the nanowire was minimized assuming coherent growth (no dislocation). In order to make the calculation easily comparable to HRTEM results, the atomic columns were then projected in a (1-100) plane, and the deformation $\varepsilon_{zz}$ was computed from the average column positions using a finite difference scheme, taking AlN as the reference material. The $\varepsilon_{zz}$ map in a 2.5 nm thick GaN insertion with radius $R_{\text{GaN}} = 30$ nm is plotted in figure 2c. As expected, the GaN layer mostly undergoes biaxial compressive strain from the AlN nanowire and therefore tends to be dilated along the c axis ($\varepsilon_{zz} > 4\%$) despite the AlN shell [16]. The strain appears to be maximal at the basis of the GaN layer where it peaks in the corners. The decrease of $\varepsilon_{zz}$ toward the upper edge results from strain relaxation and from the increase of the AlN content in each projected atomic column. As a whole, this feature deviates markedly from the GPA results, especially in the vicinity of the corners of GaN insertions.
These discrepancies could be explained by the presence of a relaxation mechanism not taken into account in the calculations, such as the presence of dislocations. In fact, the appearance of dislocations in nanowires has been theoretically predicted in either axial [6] or coaxial heterostructures [7], depending on the lattice mismatch and wire radius, or core radius and shell thickness, respectively. We indeed observed the insertion of an extra (0002) plane at the GaN/AlN interface, as illustrated in figure 3 for three successive inclusions. Furthermore, from this image, one can point out that the dislocations occur at the same position along the oblique side of the three inclusions, corresponding to the same AlN shell thickness, namely about 3 nm. This is in qualitative agreement with what has been predicted [7] for coaxial nanowire heterostructures.

Figure 3. (a) HREM image showing a dislocation at the AlN/GaN interface for three successive inclusions. (b) enlargement showing the insertion of an extra (0002) plane in AlN

5. Conclusion
Our TEM studies have shown that the GaN NWs are relaxed from the beginning of the growth, which has been assigned to the compliant role of the thin AlN buffer layer grown on the Si substrate and the presence of dislocations at the AlN/GaN interface. This is markedly different from the classical case of QDs. We have also found that GaN insertions in AlN are partially relaxed, the strain release occurring through the formation of misfit dislocations during the capping process by AlN. This is probably due to the rounded shape of the GaN insertions which leads to a local radial thickening of the AlN capping layer beyond the critical thickness.

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