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Report on the experiment performed at the ESRF after the proposal n° 02-02-745

The proposal 02-02-745 concerned the study by resonant XRD of AlGaN nanowires. However, these samples being unavailable at the beginning of the first shift, we decided to investigate GaN/AlN core-shell nanowires instead.

Investigation of GaN/AlN core-shell nanowires by Multiwavelength Anomalous Diffraction.

III-Nitride semiconductor materials are of great interest for optoelectronic applications due to the large range of wavelengths covered by the band gaps of their different alloys, spanning over the whole visible spectrum down to UV light. Thanks to their exceptional crystalline quality, defect-free GaN nanowires (NWs) grown by MBE are especially considered as a building block for the creation of high-efficiency devices. Promising heterostructures based on GaN NWs such as AlN dot in GaN NWs [1] are currently raising interest. However, the optical properties of such nitride nanowire heterostructures are governed to a large extent by the presence of the internal electric field built-in along the *c*-axis, a combination of spontaneous polarization and piezoelectric components. An alternative to this problem, is the fabrication of radial nanowire heterostructures. Yet, the realization of such heterostructures requires a mastering of their structural properties. In particular, the issue of strain relaxation of their core/shell nucleus is still largely unexplored, although being of primary importance. Our work at the ESRF focused on the study of the strain properties of these heterostructures, namely GaN/AlN core-shell NWs.

Our samples were grown by plasma-assisted molecular beam epitaxy on Si(111) substrates at INAC/SP2M/NPSC (CEA-Grenoble). The GaN NW cores were first grown under N-rich atmosphere and high substrate temperature conditions corresponding to a Ga desorption time of 6 s ± 0.2 s (about 850°C) [2]. Their typical length is 250 nm, for a diameter of about 20 nm. Following the growth of the GaN cores, AlN was deposited on their top, which simultaneously resulted in the formation of an AlN shell around the GaN core, due to the significant lateral growth of AlN assigned to the limited diffusion of Al on the NW facets [3]. It has actually been checked that in our experimental conditions, the ratio between the vertical and lateral growth rates of AlN (v_v/v_l) was about 30 (figures (a) and (b)). Based on this calibration, several samples with nominal shell thicknesses ranging from 1 to 12 nm were grown.

The samples were investigated by resonant X-Ray diffraction (XRD) performed on the BM02 beamline with the eight-circle diffractometer equipment. hkl scans were measured with a Vantec linear detector around both the (10-15) and the (30-32) Bragg reflection of the relaxed AlN at different energies close to the Ga K edge (10.367 keV). Reciprocal space maps were taken large enough to cover also the Bragg reflection of the GaN core. It was then possible to extract the Ga scattering contribution (modulus of the Ga partial structure factor) and the Al and N scattering contribution (modulus of the Al and N partial structure factor) through the analysis of MAD measurements [4].

Focusing on the Ga contribution, we pointed out the position of the spot in the reciprocal space and determined the *a* and *c* lattice parameters of the GaN core. (10-15) reflections being more sensitive to the out-of-plane parameter *c*, they were used to extract the strain ε_c expressed as:

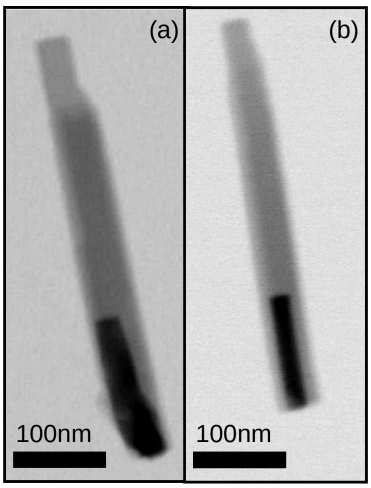
$$\varepsilon_c = \frac{c_{GaN} - c^0_{GaN}}{c^0_{GaN}} = \frac{l^0_{GaN} - l_{GaN}}{l_{GaN}}$$

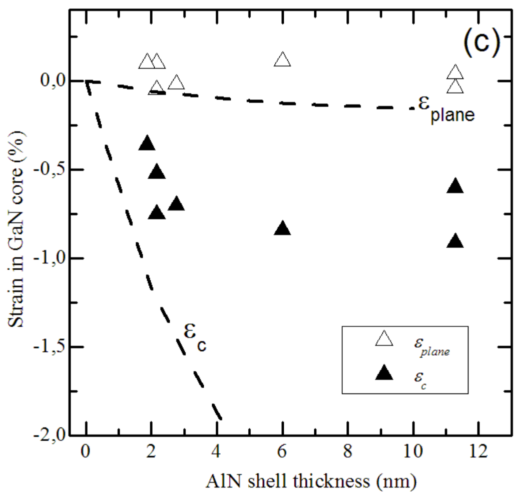
where c_{GaN}^0 is the relaxed c parameter of GaN, c_{GaN} is the strained one, $l_{GaN}^0 = 4.80$ is the value of the Miller index l of relaxed GaN in the relaxed AlN reciprocal space and l_{GaN} is the value obtained from the (10-15) reciprocal space maps of the strained GaN core.

Similarly, the (30-32) reflections were used to determine the in-plane strain ε_{plane} through an equivalent expression relating the *a* lattice parameter to the Miller index *h*. These strains ε_{plane} and ε_c are plotted in figure (c) as a function of the shell thickness (open and full triangles respectively) and compared to the value of strain calculated theoretically from an atomistic valence force field model (dashed lines on figure (c))

Despite small fluctuations, the in-plane strain $\varepsilon_{\mathrm{plane}}$ is close to zero which means that the *a* lattice parameter of the GaN core is not or very weakly strained by the AlN shell. On the other hand, ε_{c} increases with increasing shell thickness up to about 3 nm, following the theoretical trend. However, for AlN shells thicker than 3 nm, the out of plane strain obtained from resonant XRD drastically differs from the theoretical calculations. Our attention was therefore drawn by the fact that while XRD technique provides an averaged information on an ensemble of NWs, calculations were performed for ideal (perfect) NW heterostructures. Yet, Scanning Electron Microscopy (SEM) in transmission mode revealed that the wires often exhibit an asymmetrical AlN shell and a bent GaN core (figure (a)).

These results together with further investigations of the NWs performed by Raman measurements and HRTEM (paper submitted to *Nanotechnology*) let us think that asymmetry in the AlN shell plays a determinant role in the structural properties of the core-shell NWs. On the one hand, when the shell grows homogeneously, the system responds elastically, which results in a large out-of-plane strain within the GaN core. This strain increases as a function of the shell thickness without plastic relaxation and in the absence of significant in-plane strain. The extrapolation of the results of reference 5 for a 10 nm radius GaN core and an AlN shell actually suggests that plastic relaxation would occur even for a shell as thin as 1 nm through the introduction of line dislocations. Nevertheless, the HRTEM analysis performed on our NWs did not allow us to observe such dislocations and their presence is still under questioning. We however presume that their existence at the GaN/AlN interface could partly account for the GaN in-plane relaxation put in evidence by the XRD data. Concerning the out-of-plane relaxation mechanism, the possibility of the formation of loop dislocations with a Burgers vector along the c-axis of the NWs has been examined in reference 5 and should lead to an AlN critical shell thickness of the order of some tens of nm. This is consistent with the experimental observation that the critical shell thickness, if any, would be beyond 12 nm.





Figures (a) and (b): *SEM in transmission mode images of a core-shell nanowire with (a) an asymmetrical shell and (b) a symmetrical shell. The step on one side of the GaN core is clearly visible in the case of the asymmetrical shell.*

Figure (c): *strain within the GaN core, computed from resonant XRD data (open and full triangles) and theoretically calculated from an atomistic valence force field model (dashed line).*

References:

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