Structural properties of GaN nanowires and correlation to their functional properties

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1. INTRODUCTION

Catalyst-free GaN nanowires (NWs) are known for the high quality of their crystal structure whatever the growth substrate is. They are intensively investigated worldwide to fabricate improved optoelectronic devices. Plasma-assisted molecular beam epitaxy (MBE) is a well-established technique to elaborate these NWs, but some aspects of their growth are not perfectly understood. In particular, the control of their crystal polarity is an important issue. Indeed, in such wurtzite crystals, a large number of properties such as growth kinetics, impurity or dopant incorporation and direction of piezoelectric field are driven by the crystal polarity.

The control of the nanowire morphology is far from being optimized and the kinetics of their formation needs to be clarified.

Core-shell nanowires (NWs) represent an important class of semiconductor nanostructures giving rise to numerous optoelectronic applications, such as NW light-emitting diodes and lasers, solar cells, high-current battery electrodes, etc. The shell can significantly impact the structural, electrical, and optical properties of the nanowire core.

In this study, we will show how the high resolution STEM and associated techniques give striking methods to understand and determine the structural properties and to correlate these properties to the functional properties of the NWs.

2. RESULTS

2.1 Experimental techniques

The NWs were synthesized by plasma assisted MBE on Si(111) substrates. Growth was initiated by the deposition at 600°C of a small amount of Al, equivalent to 5.6 monolayers of Al. Then, the sample was exposed to a N flux for 1 min. Finally, the substrate temperature was increased to 800°C and the Ga and N fluxes were supplied simultaneously to form NWs.

The STEM observations have been performed using a Cs-probe aberration corrected JEOL 2200 FS microscope. We investigated the NW polarity by CBED analyses performed in TEM mode in the same microscope. The strain in the core-shell structure has been investigated by Geometrical phase analysis (GPA) on STEM images. Complementary analyses have been performed by grazing incidence X-ray Diffraction (GIXRD) using a Rigaku Smartlab diffractometer equipped with a rotating anode.

2.2 Growth mechanism and control of single polarity

The polarity of GaN nanowires grown on Si (111) by molecular beam epitaxy is determined by convergent beam electron diffraction. Thick specimens lead to unambiguous results showing their N polarity. Complementary sample etching indicates that all the nanowires have the same N-polarity and are surrounded by a Ga-polar two-dimensional layer. A correlation with the initial growth stage which uses consecutive exposures of the Si substrate to Al and N is established. Al-Si liquid droplets are formed and produce AlN columnar pedestals playing the role of seeds for the GaN nanowires. On the surrounding Si surface, the GaN layer nucleates with the opposite Ga polarity [1].

2.3 Growth kinetics

We have used thin AlN layers as time markers inside the NWs to investigate the chronology of their formation. These markers should be compatible in structure and thin enough to do not affect the nominal growth of the nanowires. We have used AlN layers as time markers. The Cs-probe aberration corrected STEM allows to identify very thin layers. The figure 2 shows in (a) a STEM HAADF image of a GaN NW with 3 monolayers-thick AlN markers and in (b) the elongation rate as a function of growth time deduced from the length of GaN segments separated by the AlN markers measured on several NWs. The fit of this curve allows us to determine the Ga adatom diffusion length on the side-wall and its contribution to the NW axial growth. We estimated this value as 40 nm, which explains very well the relatively low growth rate of these catalyst-free NWs [2].

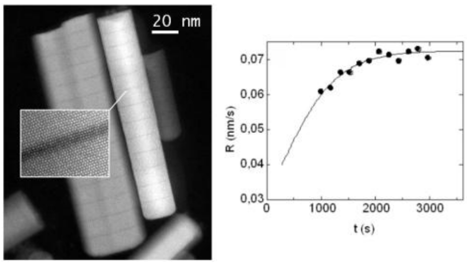

Figure 1. STEM-HAADF<11-20> zone axis image of a GaN nanowire with AlN markers and elongation rate R as a function of growth time. Experiments (dots) and calculation (full line)

2.4 Core-shell strain engineering and correlation to the optical properties

We have analyzed the correlation between the structural and optical properties of GaN/AlN coherent core-shell nanowire heterostructures, with different AlN shell thicknesses.

We have measured the local strain of individual NWs using GPA on HRSTEM-HAADF and BF images. We compared the results obtained on individual NWs to results obtained on assembly of NWs by GIXRD. These results are in agreement with a pure elastic relaxation as confirmed by simulations. The presence of an AlN shell induces a nearly uniaxial compressive strain in the core $\varepsilon c\ zz$ oriented along the nanowire axis, which translates into a blueshift of the photoluminescence. The dependence of the photoluminescence shift on the uniaxial strain is experimentally established on the basis of correlated microphotoluminescence and high-resolution STEM on a large number of single nanowires [3].

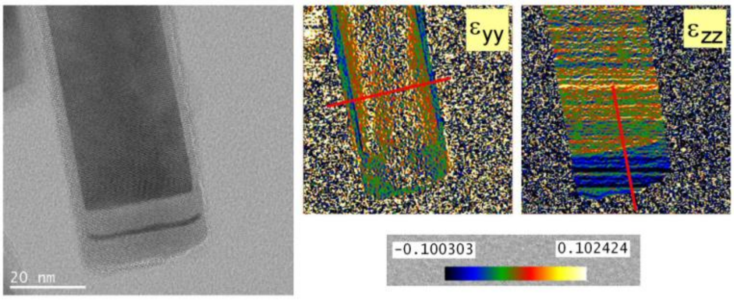

Figure 1. STEM BF <11-20> zone axis image and GPA treatment

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