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GaN-based radial heterostructure nanowires grown by MBE and ALD

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Abstract. A combination of molecular beam epitaxy (MBE) and atomic layer deposition (ALD) was adopted to fabricate GaN-based core/shell NW structures. ALD was used to deposit a HfO_2 shell of onto the MBE grown GaN NWs. Electron transparent samples were prepared by focussed ion beam methods and characterized using state-of-the-art analytical transmission and scanning transmission electron microscopy. The polycrystalline coating was found to be uniform along the whole length of the NWs. Photoluminescence and Raman spectroscopy analysis confirms that the HfO_2 ALD coating does not add any structural defect when deposited on the NWs.

1. Introduction

Vertically aligned radial nanowire (NW) heterostructures, consisting of a gallium nitride (GaN) core and an outer shell made of a material with a larger band gap, are good candidates as building blocks for UV optoelectronic and electronic devices [1]. A full control and understanding of their growth mechanism is required to tailor the geometry and the properties of these structures.

MBE growth of dislocation-free plain GaN NWs has already successfully been proven on Si and sapphire substrates [2, 3]. Although AlGaN would be the natural material of choice for the deposition of GaN-based heterostructures, the growth of high quality, free standing, axial and core/shell GaN/AlGaN NWs heterostructures using MBE, can be challenging [4, 5]. In the core/shell case, this difficulty is associated to the NWs growth mechanism, which requires Ga-rich growth conditions to obtain radial growth [2, 3]. This leads to an enlargement of the NW core/shell structures at the growth tips, resulting in irregular shell thickness and eventual coalescence of the NW as reported in [5].

Here we adopted an alternative route to manufacture GaN-based core/shell NW structures, using atomic layer deposition (ALD) of HfO_2 as large band gap material for the shell deposition on to MBE-grown GaN NWs. The microstructure and uniformity of the HfO_2 coatings on were studied using state-of-the-art analytical (scanning) transmission electron microscopy (S)TEM techniques in addition to photoluminescence (PL) and Raman analysis.

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2. Methods

GN NWs were grown by plasma-assisted MBE on a Si (100) substrate under N-rich conditions. The growth followed the recipe described in [6] with a N/Ga flux ratio of 5:1 for 75 minutes and a substrate temperature of 730°C. The as-grown sample was transferred to an Aixtron AIX 200FE AVD reactor, fitted with a modified liquid injection system [7]. 250 cycles of ALD were undertaken using $[(MeCp)_2HfMe(OMe)]$ dissolved in toluene (0.05M) as the Hf precursor and H_2O as oxidizing agent. Inter-cycle purges were obtained by introducing research grade purity (6N) argon as the carrier gas at the inlet of the reactor, the flux being regulated by a mass flow controller.

A sample for TEM investigations was then prepared using a dual beam microscope FEI Quanta 3D 200 equipped with a C gas injector and an Omniprobe lift-out system. A $2 \times 1 \times 2$ μm^3 carbon mask was deposited on the sample before rough milling of a TEM lamella by focused Ga^+ ion beam. The lamella was then in-situ lifted-out and transferred to a Cu Omniprobe grid, followed by low current milling, until electron transparent (down to a thickness of 100nm).

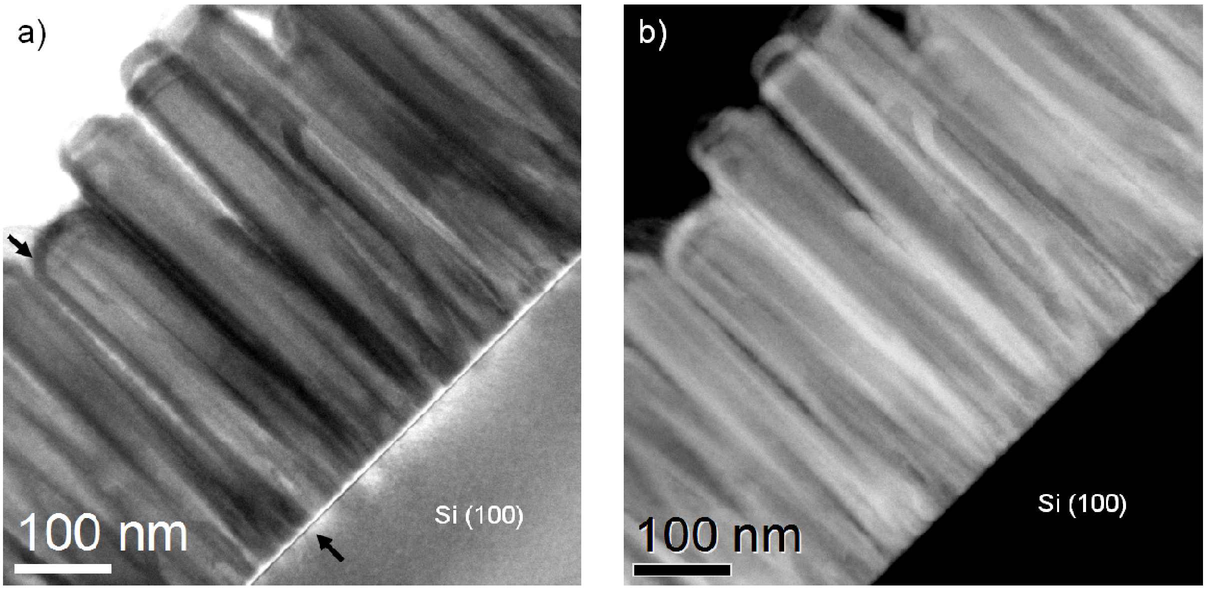

Figure 1. BF-STEM (a) and ADF-STEM (b) image showing the free standing NWs coated by a layer of Hf. Differences in contrast between core and coating are due to the larger density of HfO_2 with respect to GaN. The uniformity of coating is visible where the NWs are separated (see black arrows)

TEM analysis was performed using an aberration corrected JEOL 2200FS FEG-(S)TEM operating at 200kV and a JEOL 2010F FEG-TEM microscope operating at 197kV equipped with a scanning unit and an Oxford Instruments Si:Li Pentafet EDX detector with ultrathin window and Link ISIS 300 acquisition software. Raman spectra were acquired using a Jobin-Yvon LabRam HR consisting of a confocal microscope, coupled to a single grating spectrometer equipped with a notch filter and a CCD camera detector. All of the spectra were recorded in backscattering geometry. PL spectra of the NWs were recorded employing the same LabRam HR instrument. PL data was acquired at room temperature using the 325nm line of a He–Cd laser as the excitation source.

3. Results and discussion

Figure 1(a) and 1(b) show NWs after the ALD coating process and are imaged in their full length. Due to the difference in average atomic number between GaN and HfO_2, the HfO_2 coating appears darker than the GaN core in the Bright-Field (BF)-STEM image of Figure 1(a), whereas the contrast is switched in the Annular Dark Field (ADF)-STEM image of Figure 1(b). The NWs are uniformly coated from top to bottom by a layer of HfO_2. This is best visualized where NWs are not superimposing each other in the field of view, as indicated by the black arrows in Figure 1(a).

Although the GaN core diameters range from 20nm to ~80 nm, the HfO_2 coating thicknesses are independent of the size of the NW cores and the orientation of the NW surfaces (including the top one) which is ~15nm.

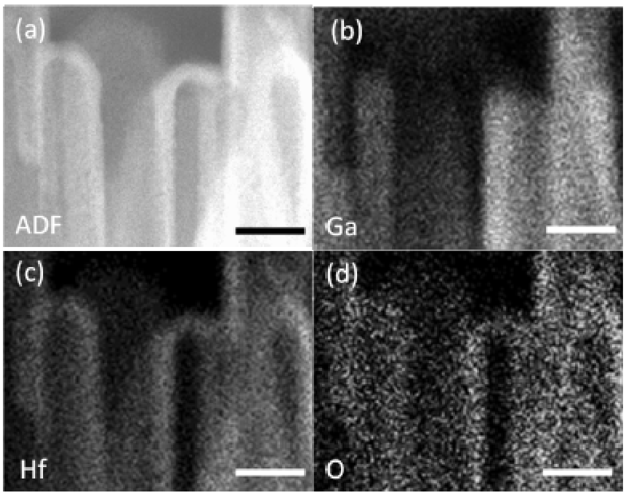

Figure 2. (a) ADF image of GaN/ HfO_2 Core/Shell nanowires structures. (b) gallium map showing the GaN cores. (c) and (d) hafnium and oxygen map highlighting the shell surrounding the core. Scale bars correspond to 100nm

EDX maps as shown in Figure 2 were acquired to confirm the elemental distribution in the sample. Maps were acquired from the area shown by the ADF image in Figure 2(a). EDX energy windows (200 eV wide) were centered on Ga-Kα (9.251 keV), Hf-Lα (7.898 keV) and O-Kα (0.525 keV). The GaN cores are clearly identified in Figure 2b) while Hf and O distributions follow exactly the coating around the cores [Figure 2(c) and 2(d)].

High-Resolution TEM images, as shown in Figure 3(a), acquired at the interface of the NWs with the Si substrate show, as expected, the presence of an amorphous Si_xN interlayer, typical of this mode of NW growth [3]. The polycrystalline coating reaches the NW base. The cubic silicon substrate is imaged along the [110] zone axis which is parallel to the [11-20] zone axis of the GaN wurtzite structure, as shown in the fast Fourier transform (FFT) image inset in Figure 3 (a).

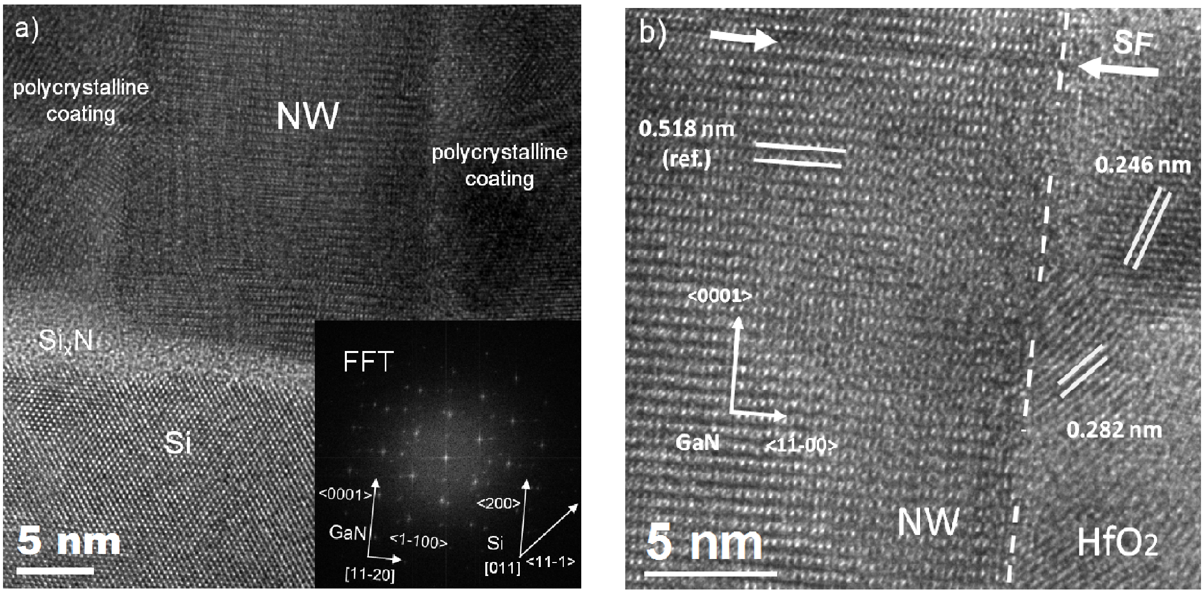

Figure 3. Aberration-corrected HR-TEM images of (a) NW to substrate interface and (b) NW side wall, where dashed lines indicate the interface with the coating. Inset in (a) is the FFT from the image showing the epitaxial relation between the NW and the substrate. A white arrow in (b) indicates a basal stacking fault (SF) present in the NW.

The as-grown GaN NWs are free-standing structures with the growth direction <0001> perpendicular within 5 degrees to the substrate [3]. The HfO_2 polycrystalline coating can be seen at the NW sides right down to the NW/substrate interface. The sharpness of the NW/coating interface is highlighted by dashed lines in Figure 3(b) where the value of 0.518nm [1] for the GaN (0001) lattice plane interdistance was taken as a reference for the internal calibration of the image. This allowed identification of the main lattice fringes within the polycrystalline HfO_2. The set of lattice fringes, shown in Figure 3(b), with distances measured as (0.246±0.003)nm and (0.282±0.003)nm can be attributed respectively to (1,0,-2) planes (0.2489 nm [8]) and (1,1,1) planes (0.2825 nm [8]) of the monoclinic (P 1 21/c 1; zirconia-like) HfO_2 structure. As highlighted by the white arrow in Figure 3(b) an intrinsic stacking fault is present along the NWs. This is a NW growth defect visible only along <11-20> directions [9].

In Figure 4(a), PL spectra show pronounced band edge emission peaks at 3.4eV both before and after the coating treatment. Similarly, UV Raman spectra shows enhanced longitudinal optical (LO) and 2LO modes in both cases (Figure 4(b)). Optical spectroscopy results indicate that the coating treatment did not induce any pronounced changes in the spectra, suggesting that the optical properties were not deteriorated.

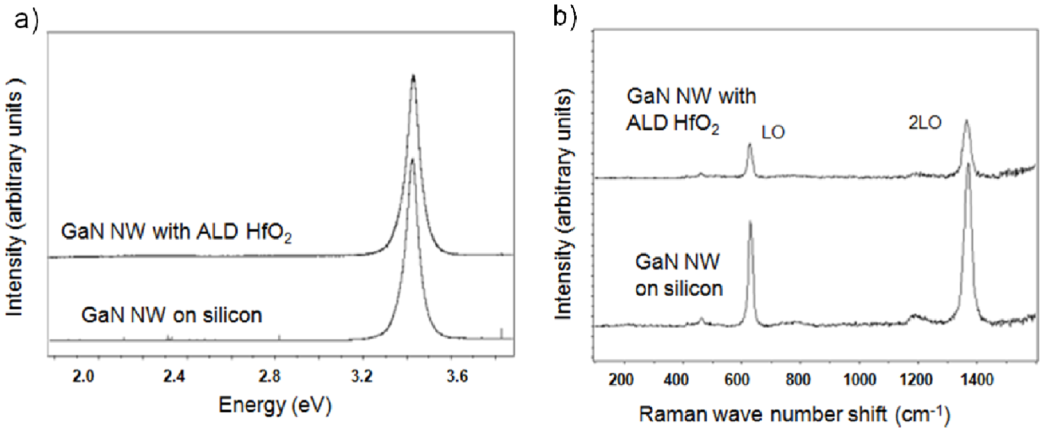

Figure 4. PL (a) and Raman Spectroscopy spectra (b) acquired at room temperature before and after the HfO_2 deposition by ALD.

4. Conclusions

In this work we have reported the successful growth of GaN/HfO_2 core/shell NW heterostructures by combining catalyst-free MBE growth of GaN NWs on Si (100) substrates with ALD of HfO_2. The uniformity of the HfO_2 coating along the whole length of the NWs was demonstrated as well as the sharpness of the NW/coating interface. Optical properties were found to remain unchanged by the subsequent coating. These results highlight the reliability and the potential versatility of this combination of deposition techniques for the growth of future optoelectronic devices components

Acknowledgements

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