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Catalyst-free growth of high-optical quality GaN nanowires by metal-organic vapor phase epitaxy

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Catalyst-free GaN wires with 100–200 nm diameters are grown on bare c-sapphire substrates by a *metal-organic vapor phase epitaxy* approach using both low V/III ratio and V-III precursor flows that favor a reaction-limited growth regime. The polarity control of the initial seeds allows obtaining pencil-shape wires with very sharp pyramids at their top (~5 nm diameter). These defect-free nanowires evidence excellent structural and optical properties as shown by a sharp photoluminescence linewidth (1–3 meV at 5 K). © *2011 American Institute of Physics*. [doi:10.1063/1.3671365]

Nitride nanowires (NWs) have witnessed fruitful researches for the development of nanoscale optoelectronic devices as light emitting diodes, lasers, photodetectors, and solar cells.[1] Semiconductor NWs are usually fabricated by the metal catalyst-assisted vapor-liquid-solid approach despite the possibility to harm transport and optical properties with metallic contaminations.[2] To overcome this drawback, catalyst-free methods have been widely applied to GaN NWs by using molecular beam epitaxy (MBE)[3] under N-rich condition.[4] In contrast, the catalyst-free growth of GaN NWs by metal organic vapor phase epitaxy (MOVPE) appeared more challenging despite the strong impact of this technique for mass production of compound semiconductors. Few works have reported how to promote the formation of GaN wires using pulsed precursor,[5] silane flow addition,[6] or N_2/H_2 carrier gas mixture.[7] These methods require some process optimizations related to reactor geometries, so that they cannot really be considered as generic approaches. Another limitation comes from the typical diameter of the catalyst-free GaN wires grown by MOVPE, which is generally around several hundreds of nanometers. This value is much larger than those synthesized by catalyst-assisted MOVPE (Ref. 8) or catalyst-free MBE (Refs. 3 and 4) (in the 30–100 nm range). It obviously hinders some appealing advantages of the NWs such as the elastic strain relaxation for large lattice-mismatch heterostructures and the use of quantum dot confinement in light emitters. Furthermore, the reported linewidth of the photoluminescence (PL) near band edge (NBE) emission for GaN MOVPE wires is about several hundred meV at 5 K,[9] i.e., about two orders of magnitude larger than high-quality GaN NWs grown by MBE.[10,11]

In this letter, we present a general *catalyst-free* route to obtain by MOVPE *nanoscale epitaxial* GaN wires exhibiting *high optical quality*. This approach, whose physics ingredients will be discussed is simply based on the use of bare c-sapphire substrates—without nitridation process and buffer layer deposition—and on the decrease of precursor flow but with similar low V/III ratio compared to the standard GaN wire growth.

The growth is carried out on c-sapphire substrate in a 3×2 in. MOVPE close-coupled showerhead reactor using trimethylgallium (TMG) and ammonia (NH_3) precursors. In a first step, the substrate is baked *in situ* under H_2 in a standard way at 1100 °C for 20 min. Then, the reactor temperature and pressure are directly set to the wire growth condition at 1000 °C and 100 mbar without any surface nitridation. The wire growth is performed by injecting simultaneously 3.4 μmol min^{-1} of TMG and 89 μmol min^{-1} of NH_3 under N_2 carrier gas flow (2000 sccm, 100 mbar) for 30 min. The nominal V/III ratio is set to 26 corresponding to a usual value for the wire growth, but note that the injected precursor quantity is at least two orders of magnitude lower than in standard planar[12] and wire[5–7] GaN MOVPE growths.

Fig. 1(a) shows a 45°-tilted scanning electron microscopy (SEM) image of the as-grown GaN wire assembly. They grow perpendicularly to the substrate and their average density is about 1.3×10^3 cm^{-2}. As shown in the inset of Fig. 1(a), GaN NWs have 100–200 nm diameters and a pencil shape composed of a stem with vertical sidewall facets and a pyramidal top terminated by inclined facets. The growth rate is very low (~4 μm/h) and much lower than continuous growth under silane that may reach 150 μm/h.[6] We have recently reported that the geometry of wurtzite GaN nanostructures in MOVPE growth can be governed by the crystal polarity: the pyramidal (resp. hexagonal prismatic) shape corresponding to the Ga-polar (resp. N-polar) c-growth direction.[13] We can, therefore, suppose that the pyramidal shape of the NW top results from the Ga-polar growth induced by the nucleation on non-nitridated c-sapphire surface, in agreement with Ref. 14. To check this point, a similar growth has been performed by adding a surface nitridation step using NH_3 treatment (2000 sccm, 1050 °C, 100 mbar) for 90 s before the NW growth to force the N-polar crystal c-orientation.[14] As shown in Fig. 1(b), hexagonal prismatic nanostructures with large diameter (1–2 μm) are observed, confirming that the Ga-polar crystal growth orientation is required within our conditions to form nanoscale pencil-shaped GaN wires. In order to further investigate the growth mechanism and in

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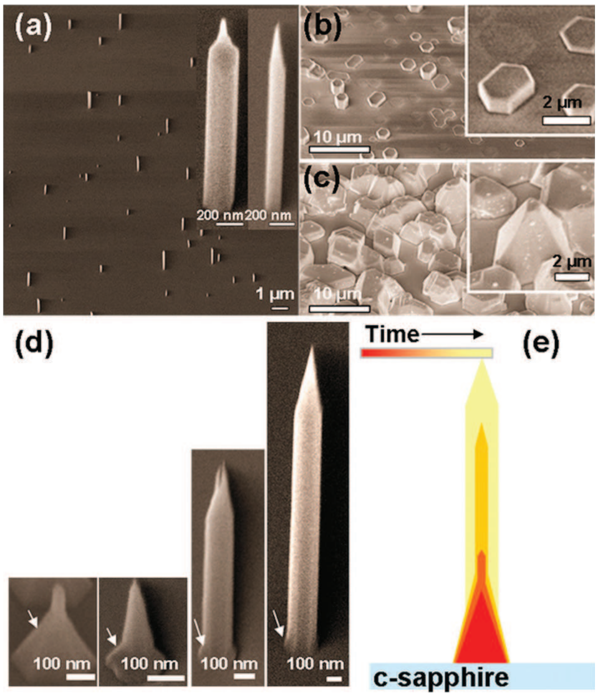

FIG. 1. (Color online) (a) 45°-tilted scanning electron microscopy image of GaN wires grown on a non-nitridated c-sapphire surface at low precursor flows. Comparison with similar growths on (b) nitridated sapphire surface (same flows) and (c) non-nitridated surface, but with larger precursor flows. (d) Shape evolution of the GaN wire as a function of time and (e) schematics.

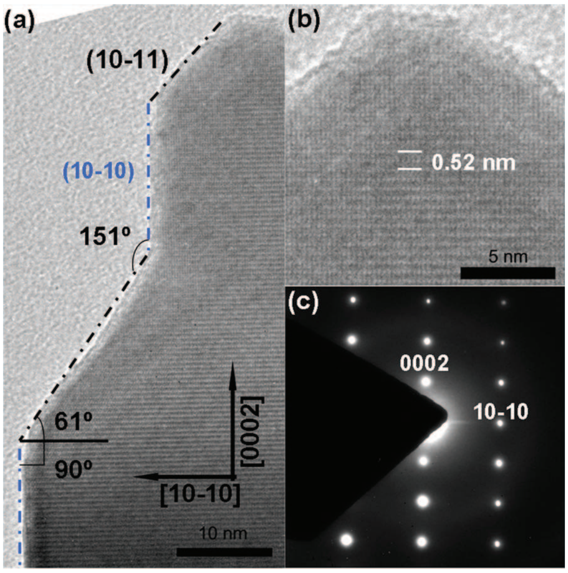

FIG. 2. (Color online) High resolution transmission electron microscopy of GaN wires along the $[11\bar{2}0]_{\mathrm{GaN}}$ zone-axis at (a) sidewall and (b) tip positions with corresponding selective area electron diffraction pattern (c).

particular the morphology evolution, SEM observations were performed at different stages of the NWs synthesis (see Figs. 1(d) and 1(e)). Interestingly, at the early stage of the growth, a pyramid is formed, followed by a NW nucleation on its top. Afterwards, NWs undergo a relatively fast vertical extension for longer growth durations with a limited lateral growth maintaining the wire geometry with a pyramidal top. In addition, inclined facets are always observed at the base of the NWs (see Fig. 1(d)) as a signature of the initial Ga-polar pyramid seed.

The NWs have been scraped off from the as-grown sample and dispersed onto Cu/C grids for high resolution transmission microscopy (HRTEM) measurements. Observations along the $[11\bar{2}0]_{\mathrm{GaN}}$ zone-axis are shown in Figs. 2(a) and 2(b). The corresponding selective area electron diffraction (SAED) patterns (see Fig. 2(c)) confirm the NW wurtzite crystal structure and the c-axis growth direction. No defects like threading dislocations and stacking faults have been observed and the measured c-interplanar distance (0.52 nm) corresponds to a fully strain relaxed crystal (see Fig. 2(b)). The tapering results from the change of facet orientations on the NW sidewalls with alternating vertical $\{10\bar{1}0\}$ and inclined $\{10\bar{1}1\}$ planes. This facet evolution supposes a small difference between surface energies consistent with the transition between pyramidal seeds with six $\{10\bar{1}1\}$ planes[15] and NWs as discussed in Fig. 1(d). This small energy difference and the resulting shape transition are directly related to the low precursor flow growth and kinetics (as suggested in Ref. 16). Indeed, by employing a higher precursor flow (TMG: 135.2 μmol min^{-1} and NH_3: 2232 μmol min^{-1}) keeping constant the other growth parameters, we observe in Fig. 1(c) truncated pyramidal nanostructures without the appearance of vertical $\{10\bar{1}0\}$facets. The low flow of the precursors decreases the Damköhler number[17] $Da = k\delta/D$, where k is the average rate constant of the heterogeneous surface reaction, δ is the boundary layer (fixed mainly by the carrier gas), and D is the diffusion constant. This dimensionless number corresponds to the ratio between the chemical reaction and the mass transfer rates. At low-flow conditions (decreasing mainly k and keeping D almost constant), the system may become more reaction-rate limited rather than kinetically limited. The system should, therefore, reach more easily the theoretical equilibrium shapes predicted for GaN nanostructure grown along the Ga-polar c-direction in favor of m-planes exhibiting low surface energy.[18] Another way to decrease Da is to increase the growth temperature T to benefit from a faster increase of D than k. This proposal has been checked with high temperature growth (∼1150 °C) where pyramid-like structures transform to wires with m-plane facets.[19]

The epitaxial relationships of the wires on the sapphire substrate and the crystallographic analysis have been studied by XRD at the European Synchrotron Research Facility (ESRF, Grenoble, France). X-ray reflectivity (XRR) and Grazing incidence x-ray diffraction (GIXRD) have been performed to analyse the wire assembly and the overgrowths.[19,20] XRR indicated the deposition of a 2.9 ± 0.1 nm thick layer on sapphire consistent with a flat overgrowth between 3D objects and GIXRD evidenced that the GaN NW phase corresponds to the usual 30° rotation of the GaN around the sapphire c-axis with a fully relaxed lattice parameter (i.e., bulk value) and with a c-axis tilt of about 2°.

The optical properties of single GaN NWs have been studied by μPL at 5 K using a 244 nm frequency-doubled continuous wave Ar^+ laser excitation source focused to $\sim 2\,\mu$m diameter spot. Benefiting from the low density of the GaN NWs assembly, PL spectra were obtained on as-grown single NWs without any dispersion step that could modify

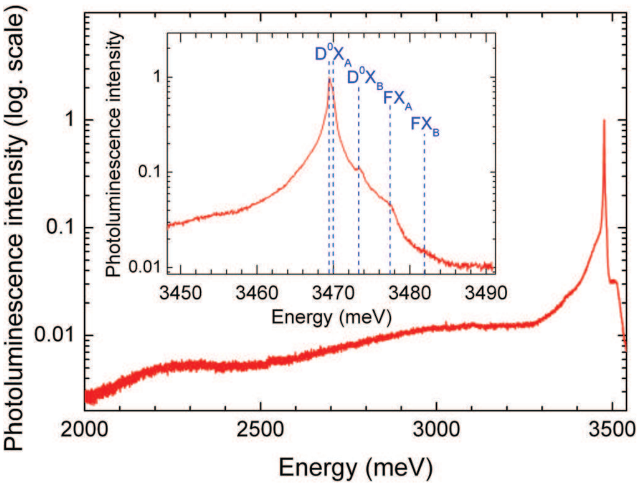

FIG. 3. (Color online) Typical low temperature (5 K) micro-photoluminescence measurement of single GaN wires. The peak full width at half maximum of this near band edge emission is 0.95 meV. Donor bound exciton recombinations (D^0X_A and D^0X_B) and free A and B excitons (FX_A and FX_B) are indicated. Intensities are in arbitrary units and in log scale; the inset shows a magnification of the main peak.

the optical properties.[11] Fig. 3 shows a typical PL spectrum of single standing wire that exhibits only one intense sharp peak centered at ∼3.47 eV assigned to the NBE emission from GaN while no important contribution from deep defect bands is observed. The dominant contribution, related to donor bound excitons recombination (D^0X_A), is located at 3.470 eV and has a full width at half maximum of only 0.95 meV. This peak is actually composed of two contributions with linewidths 320 and 720 μeV, tentatively ascribed to excitons bound to various donor species. While the displayed spectrum corresponds to the narrowest linewidth that was probed, the typical linewidths for the D^0X_A peak on this sample range is 1–3 meV. These peak widths are remarkable for NWs grown by MOVPE and are comparable to what can be obtained by MBE.[11] At higher energies, three shoulders, respectively, at 3.473, 3.477, and 3.482 eV can be ascribed to the donor bound exciton with a B-type hole (D^0X_B), the free A and B excitons ($FX_{A,B}$). Note also that the emission around 3.41–3.42 eV associated to excitons bound to stacking faults in MBE GaN NWs (Ref. 2) is not observed in this sample. The fact that donor bound exciton recombination dominates the 5 K PL with a narrow 0.95 meV linewidth at the fully relaxed position value (3.470 eV) confirms the excellent NW crystalline quality and homogeneity.

In conclusion, we have demonstrated the *MOVPE* growth of *catalyst-free* GaN wires with 100–200 nm diameters on bare c-sapphire substrates. Pencil-shape wires with pyramids at their top are obtained after a standard H_2 sapphire annealing by using both low V/III ratio and V-III precursor flows, which favor reaction-limited mechanisms rather than diffusive-limited (kinetic) transport. The sharpness of the NW tip (∼5 nm diameter) can be used as a template for naturally confined nanostructures and opens the way for the realization of quantum dot *by MOVPE*. The GaN wires are free of extended defects as verified by HRTEM and XRD. Their excellent optical emission properties with a 1–3 meV photoluminescence NBE linewidth at 5 K and negligible deep defect band emission show that they are made of relaxed homogeneous material with few point defects.

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