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Ultralong and Defect-Free GaN Nanowires Grown by the HVPE Process

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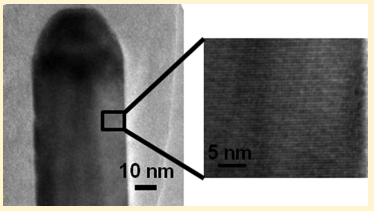
ABSTRACT: GaN nanowires with exceptional lengths are synthesized by vapor−liquid−solid coupled with near-equilibrium hydride vapor phase epitaxy technique on *c*-plane sapphire substrates. Because of the high decomposition frequency of GaCl precursors and a direct supply of Ga through the catalyst particle, the growth of GaN nanowires with constant diameters takes place at an exceptional growth rate of 130 μm/h. The chemical composition of the catalyst droplet is analyzed by energy dispersive X-ray spectroscopy. High-resolution transmission electron microscopy and selective area diffraction show that the GaN nanowires crystallize in the hexagonal wurzite structure and are defect-free. GaN nanowires exhibit bare top facets without any droplet. Microphotoluminescence displays a narrow and intense emission line (1 meV line width) associated to the neutral-donor bound exciton revealing excellent optical properties of GaN nanowires.



KEYWORDS: *Nanowires, HVPE, GaN, EDX, VLS, photoluminescence*

Nanowires are promising structures for the achievement of low defect density material systems with potential applications such as lasers,[1] light-emitting diodes (LED),[2] and transistors.[3] In particular, GaN nanowires have been subject of extensive interest from the research community during the past decade. Contrary to bulk material, the latter have intrinsically very efficient lattice relaxation. Thus, they can be grown without crystallographic defects; this constitutes the main benefit with respect to the planar structures for which photoluminescence emission and carrier lifetime are affected by these defects. Compared to other III-V nanowires, surface recombinations, which have a crucial influence on the optical and electrical properties of nanostructures, are limited because of the crystalline structure of the GaN material achieved in the nanowire growth regime.[4] Specific needs have emerged for GaN nanowires with a high aspect ratio. Ultralong GaN nanowires have a high potential for sensor devices. Sheenan et al.[5] have demonstrated that the sensitivity of the sensors increases with the length of the nanowires. More particularly, combined with the robustness and biocompatibility of the material, high aspect ratio GaN nanowires have great promises in the field of biosensing. Furthermore, the synthesis of ultralong GaN nanowires is the first step toward their large scale integration as nano-FET devices, as it has been demonstrated for Si nanowires.[6] Finally, the efficiency of LED devices based on radial heterostructures is increased due to the high active surface induced by the wire morphology.[7]

GaN nanowires are usually obtained through two paths: a catalyst-free process or a catalyst-assisted process. The catalyst-free growth of GaN nanowires is well developed by metal organic vapor phase epitaxy (MOVPE) and molecular beam epitaxy (MBE) techniques. Nanowires are generally synthesized on various substrates such as sapphire,[8,9] diamond,[10] and silicon.[11,12] In that case, the growth occurs randomly on the substrate and the nanowire diameters are uncontrolled. This can be inconvenient for applications when the uniformity of the nanowires has to be controlled and reproducible because basic properties such as emission depend on the diameter distribution.[13] GaN nanowires grown by the plasma-assisted MBE catalyst-free process exhibit high optical quality that is a characteristic of strain free nanowires. However, a strong emission is often observed around 3.45 eV that is attributed to a defect-associated band.[14,15] Moreover, the growth in this process is mainly governed by the diffusion of the gaseous precursors along the sidewalls of the nanowires leading to the growth of NWs of short lengths (<5 μm) with long process[15] time. Catalyst-free GaN nanowires grown by MOVPE have generally large diameters: hundreds of nanometers, hindering the strain relaxation induced by the wire geometry. Only recently Eymery et al.[9] have reported the growth of thin GaN nanowires by MOVPE with a rather low growth rate of 4 μm/h.

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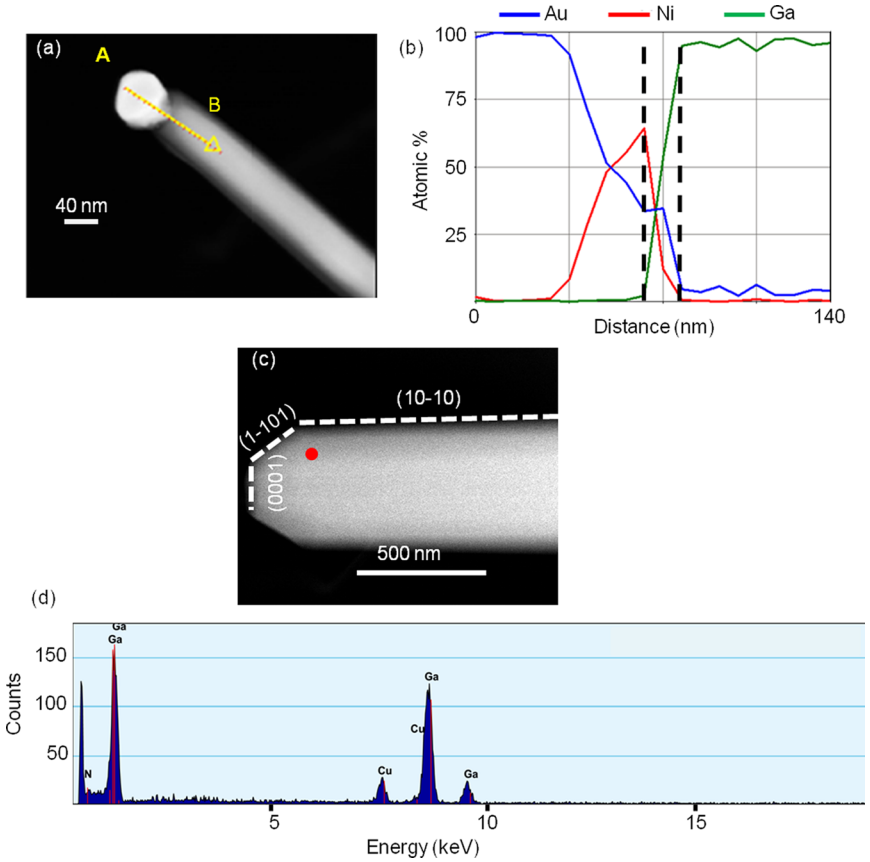

Figure 1. (a) SEM image of a GaN nanowire after 5 min of growth (dark-field STEM mode); (b) chemical composition profile collected along A–B; (c) HAADF image of a GaN nanowire after 30 min of growth with the corresponding crystallographic planes at the top of the nanowire; (d) EDX spectrum collected at the top of the nanowire (red spot in Figure 2c).

However the microphotoluminesence (μPL)-spectra did not show any luminescence because of the defects or stacking faults or any yellow luminescence usually observed in MOVPE.

In the catalyst assisted-process, metal particles are formed by annealing a metal film or simply deposited on the surface of the substrate before growth by using colloïdes. Then, GaN nanowires grow through a vapor–liquid–solid (VLS) mechanism and thereby exhibit diameters and positions correlated to the diameters and positions of the seed particles.[16] This process can be easily identified through scanning electron microscopy (SEM) investigations by the presence of a well-defined droplet located on the top of the nanowire after growth. References that relate the VLS synthesis of GaN nanowires by MBE or vapor phase epitaxy (VPE) often report stacking defects and broadening of the luminescence spectra.[17−20] Although the growth of GaN nanowires is widely developed, catalyst-assisted growth of GaN nanowires with both high aspect ratio and high structural and optical qualities are rarely reported.

In this paper, we propose to use the hydride vapor phase epitaxy (HVPE) process to grow ultralong (>50 μm) free of crystal defect GaN nanowires with high optical properties on *c*-plane sapphire. Because of its intrinsic properties, HVPE is proved to be very efficient for the synthesis of high-quality free-standing GaN quasi-substrates. In fact, HVPE is a near equilibrium growth process that involves rapid kinetics in a hot wall reactor. The vapor phase composition and the temperature can be tuned so that GaN growth can occur at a growth rate up to 100 μm/h. The fast VLS-HVPE process was previously proved to be an efficient tool for the synthesis of ultralong III–V nanowires with perfect crystal purity;[21,22] however, good enough optical properties have not been reported yet for GaN nanowires grown by VLS-HVPE.[18,19,23]

GaN nanowires were grown in a 2 in. horizontal home-designed HVPE reactor at atmospheric pressure, heated by a six-zones furnace.[24] In a first upward zone, GaCl vapor species are formed by reacting gaseous HCl with liquid gallium at 800 °C. Ammonia, used as the group V flow, is directly introduced into the central zone. This zone is heated at higher temperature for mixing the gaseous species and reducing the parasitical nucleation.[25] Samples are heated in the downstream zone of the reactor. The partial pressures of ammonia and gallium chloride are set at 4.02×10^{-2} atm and 5.67×10^{-3} atm, respectively. A mixed N_2/H_2 carrier gas with a constant additional HCl pressure of 1.52×10^{-2} atm is chosen. The growth was carried out at a temperature of 980 °C. Prior to HVPE growth, a 5 Å thick Nickel layer and a 5 Å thick Au layer were sequentially deposited on the surface of c-sapphire substrates by thermal evaporation using a calibrated effusive cell in an UHV chamber at 10^{-8} Torr at a rate of 0.08 ML per minute and 0.11 ML per minute respectively.

The crystallographic structure and growth direction of the GaN nanowires were investigated by high resolution transmission electron microscopy (HRTEM) and selective area electron diffraction (SAED) performed on a JEOL 4000EX microscope operated at 400 kV and high-angle annular dark-field imaging (HAADF) obtained on a FEI Titan Probe Corrected Microscope operated at 300 kV. The nanowires were scraped off the substrates and deposited on a holey carbon grid.

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Energy dispersive X-ray spectroscopy (EDX) was used to estimate the chemical composition of the catalyst droplets. Microphotoluminescence (μPL) measurements were carried out on a single nanowire isolated after a mechanical transfer onto a sapphire substrate.

A SEM image of nanowires grown for 5 min is reported in Figure 1a. After the first 5 min of growth, GaN nanowires present droplets on their top facets, showing that the nanowires growth is actually driven by a catalyst-assisted process. Figure 1b displays the chemical composition profile along the dotted line plotted in Figure 1a. It indicates that the droplet is made of a heterogeneous Au−Ni alloy, and it is worth to mention that Ga is not found in the droplet after growth. This result differs from (i) in situ reflection high energy electron diffraction RHEED experiments coupled to quadripole mass spectroscopy (QMS) analysis performed by Chèze et al.[26] in MBE, and (ii) ex situ XEDS performed by Redwing et al.[27] in MOVPE in which the authors found the Ga element in the catalyst droplet. A brutal change in the Ga composition is pointed out at the droplet−nanowire interface (highlighted by dashed lines in Figure 1b). Neither Au nor Ni are detected in the nanowire. This confirms the low incorporation, at least below the EDX detection limit that is about 0.5% of the metallic element, in the nanowire during growth which induces the very good crystal purity found by HRTEM. For growth time of 30 min, as shown in Figure 1c,d, neither gold nor nickel are detected in the nanowires, GaN nanowires exhibit bare top facets without any droplet (Figure 1c) and the growth stops. Only two groups reported the absence of the catalyst particle. The absence of the catalyst particle was also observed in VLS-HVPE[19] where authors suggest that the catalyst droplet has been consumed during the reaction and in VLS-MOVPE.[28]

SEM investigations show long nanowires (up to 60 μm for a growth of 30 min) grown with a record growth rate of 130 μm/h with constant diameters in the range of 70−200 nm. Nanowires exhibit an untapered shape along their entire length (Figure 2a). It should be noted that HRTEM measurements were conducted on more than 10 nanowires. We present here results concerning only one nanowire. The results are reproducible from one nanowire to another.

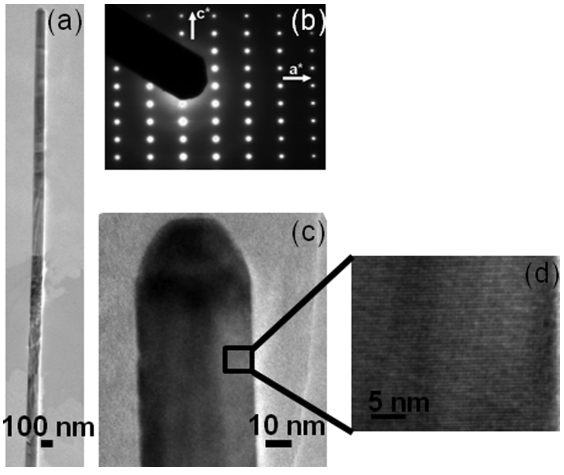

Figure 2. TEM images of GaN nanowires: (a) low-magnification image on a long GaN nanowire; (b) SAED pattern from the same nanowire; (c) HRTEM image showing the top of the nanowire; (d) zoom of (c) nanowire sidewall.

The SAED patterns (Figure 2b) from the nanowire shown in Figure 2a,c can be indexed in an hexagonal wurtzite structure and reveal that the nanowires grow along the [0001] axis. The HRTEM image of the nanowire sidewall (Figure 2d) does not show any stacking fault. The measured *c*-interplanar spacing, equal to 0.52 nm, corresponds to a fully relaxed crystal. These results are exceptional since stacking faults are commonly reported in GaN nanowires synthesized by VLS MOVPE,[17] VLS HVPE,[18,19,23] and VLS MBE.[29] The high axial growth rate, equal to 130 μm/h, and negligible radial growth suggest a direct supply of the elements from the vapor phase through the catalyst droplet. Chloride species that are adsorbed on the surface of the catalyst droplet are quickly decomposed, followed by Ga fast diffusion to the droplet−nanowire interface. This mechanism and the high temperature reached in the experiment, 980 °C against 700−800 °C in the aforementioned studies, could favor the resulting defect-free crystal structure.

The optical properties of single GaN nanowires have then been analyzed by μPL performed at 10 K by using an excitation wavelength of 266 nm. The light is focused onto the sample with a microscope objective (×20) giving a spot about 2 μm in diameter. The μPL spectrum of a single nanowire reported in Figure 3 exhibits three peaks located at 3.4705, 3.4767, and

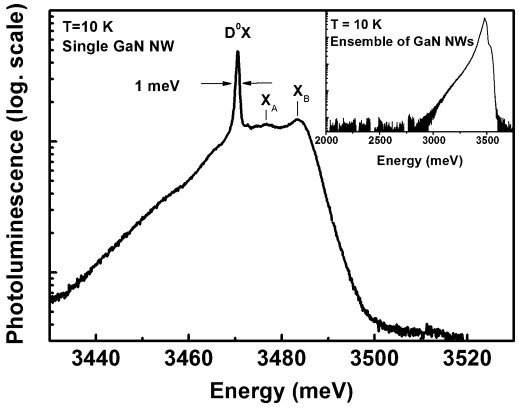

Figure 3. Microphotoluminescence spectrum of a single GaN nanowire at 10 K. In inset: microphotoluminescence spectrum of an ensemble of GaN nanowires at 10 K.

3.4834 eV. The strong emission at 3.4705 eV is attributed to the recombination of the neutral-donor bound exciton associated to A exciton (D^0X) and presents a full width at half-maximum (fwhm) of only 1 meV. This line width is remarkable for GaN nanowires obtained by VLS- HVPE and comparable to those obtained by catalyst-free MBE[15] and catalyst-free MOVPE[6] indicating the good crystalline quality. The fwhm of lines of VLS-HVPE grown GaN nanowires is generally larger, more than 100 meV; this is due to the poor crystalline quality or impurity incorporation.[18,19,23] In VLS-MOVPE, the studies presenting the optical properties of GaN nanowires report larger spectral widths and energy shifts of the spectra. Zhou et al.[17] reported a line width of about 300 meV due to impurity incorporation. The spectrum shown in Figure 3 can then be judged consistent with the hypothesis of the nonincorporation of Ni or Au from the droplet in the nanowires during the growth. At higher energies, the two peaks at 3.4767 and 3.4834 eV are identified as the recombination of free A and B excitons. In the case of bulk strain-free GaN, Torri et al.[20] reported the free exciton energies

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as follows: 3.478 eV for X_A and 3.484 eV for X_B, close to the values obtained in this work. This indicates that our VLS-HVPE grown GaN nanowires are strain-free. It is worth mentioning that the polarization of the emission has not been studied here; it is expected that X_A line (respectively X_B line) dominates for σ (respectively π) polarization.[30] Peaks at 3.42 and 3.45 eV attributed to structural defects and surface recombinations respectively[15] are not observed and confirm the good crystalline quality. In addition, it is worth noting that in the luminescence spectrum of an ensemble of GaN nanowires recorded at 10 K displayed in the inset of Figure 3, no luminescence signal is present between 2 and 3 eV. This attests the weak incorporation of impurities or defects in the GaN nanowires.

In conclusion, the growth of GaN nanowires by VLS-HVPE has been performed using the Au−Ni alloy as the catalyst. TEM analysis shows tens of micrometers long wurtzite [0001]-oriented nanowires free of stacking faults along their entire length. It appears that after 5 min of growth, an Au−Ni droplet is located at the tops of the nanowires, indicating that the growth is driven by a VLS mechanism. After 30 min of growth, the nanowires exhibit remarkable pure wurtzite structure. Furthermore, they are free of catalyst droplet. Microphotoluminescence spectroscopy analysis reveals the high optical quality of the GaN nanowires attested by a narrow line width (1 meV at 10 K) of the neutral-donor bound exciton recombination; the absence of other emission lines, usually attributed to defects, seems to indicate the nonincorporation of Au or Ni during the growth. This work proves that the VLS-HVPE process leads to the growth of ultralong nanowires with a constant diameter, a high aspect ratio, a great crystalline quality and good optical properties, which was hitherto unreported by VLS-HVPE. High crystal and optical properties GaN nanowires grown by VLS-HVPE are thus high potential candidates for optoelectronic applications.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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