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Xiaojun Chen, Guillaume Perillat-Merceroz, Diane Sam-Giao, Christophe Durand ...+1 more authors

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Homoepitaxial growth of catalyst-free GaN wires on N-polar substrates

X.J. Chen,[1] G. Perillat-Merceroz,[2,3] D. Sam-Giao,[1] C. Durand,[1,4] and J. Eymery[1,a)]

[1] *Equipe mixte CEA-CNRS "Nanophysique et semiconducteurs", CEA, INAC, SP2M, NPSC, 17 rue des Martyrs, 38054 Grenoble cedex 9, France*

[2] *CEA, LETI, Minatec Campus, 38054 Grenoble Cedex 9, France*

[3] *CEA, INAC, SP2M, LEMMA, 17 rue des Martyrs, 38054 Grenoble cedex 9, France*

[4] *Université Joseph Fourier, Grenoble, France*

The shape of c-oriented GaN nanostructures is found to be directly related to the crystal polarity. As evidenced by convergent beam electron diffraction applied to GaN nanostructures grown by metal-organic vapor phase epitaxy on c-sapphire substrates: wires grown on nitridated sapphire have the N-polarity ($[000\bar{1}]$) whereas pyramidal crystals have Ga-polarity ($[0001]$). In the case of homoepitaxy, the GaN wires can be directly selected using N-polar GaN freestanding substrates and exhibit good optical properties. A schematic representation of the kinetic Wulff's plot points out the effect of surface polarity.

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a) Electronic mail : joel.eymery@cea.fr

Group-III nitride semiconductors have gained great importance in optoelectronic devices, although the complete optimization of their potential properties suffers from high dislocation density in bidimensional growth. In this context, nitride nanowires (NWs) have motivated a strong interest for device fabrication due to their defect-free features.[1] Contrary to molecular beam epitaxy (MBE), metallic catalysts are generally required to grow NWs in metal-organic vapor phase epitaxy (MOVPE).[2] Recently, the possibility to grow catalyst-free GaN NWs using MOVPE on c-sapphire has been demonstrated. [3] However, conducting substrates are usually preferred for direct integration of NW array into photonic devices.[4] The catalyst-free MOVPE homoepitaxial growth of GaN NWs is an interesting way to address this issue. Nevertheless, in the last decade most of MOVPE GaN nanostructures grown on GaN templates exhibit pyramidal shapes[5,6] rather than wire geometry, which has been only reported by a pulsed precursor growth mode.[7] Otherwise, the crystal polarity is known to impact the growth kinetics and shapes of the epitaxial growth of polar wurtzite crystals.[8,9] For instance Zn-polar surface is required to grow MOVPE homoepitaxial ZnO wires[10] and preferential growth along [0001] is reported for MBE GaN wires.[9]

In this letter, a direct relationship will be first established between the shape and the polarity of GaN nanostructures grown by catalyst-free MOVPE on c-sapphire. Then, it will be shown in the case of homoepitaxy that the GaN nanostructure shapes can be directly tuned by the GaN substrate polarity, *i.e.* the N- and Ga-polarities[11] result in wires and pyramids, respectively. Finally, the optical properties of N-polar wires will be demonstrated by photoluminescence spectroscopy validating our approach to get high quality catalyst-free GaN wires.

C-oriented GaN nanostructures were firstly grown on c-sapphire substrates using self-assembled growth (SG) and selective area growth (SAG) approaches. In the SG approach, a surface nitridation was performed after hydrogen annealing which gives usually N-polar two dimensional GaN layers.[12] A thin SiN_x mask layer was then *in-situ* deposited using silane and ammonia precursors. In the SAG approach, a thicker Si_3N_4 layer (~5nm), which was *ex-situ* deposited and patterned by nanoimprint, acts as a mask for selective growth. Identical growth conditions were used for both methods (see experimental details in Ref. 3). The morphology was characterized using field emission scanning electron microscopy (SEM). Cross sectional samples for transmission electron microscopy (TEM) were prepared either by the cleaved edge method or by mechanical polishing followed by ion milling. They were examined on a microscope operating at 300 kV and scanning TEM (STEM) images were acquired with a high angle annular dark field detector. Convergent beam electron diffraction patterns (CBED) were carried out along a $<10\bar{1}0>$ zone axis.[13] Simulations were performed with the JEMS software[14] to index the $[0002]$ and the $[000\bar{2}]$ directions on the experimental patterns and consequently to deduce the nanostructure polarities.

Figure 1 presents the SG and SAG of GaN nanostructures grown on c-sapphire substrates. Fig. 1(a) shows a 45°-tilted SEM image of as-grown self-assembled GaN wires. These wires grow vertically along the c-axis in epitaxy with the substrate.[3] Fig. 1(b) shows a STEM image of a representative wire where two different regions separated by an inversion domain boundary (IDB, indicated by the white arrow) are observed: one with a flat top facet and the other with an inclined top facet at the wire edge. CBED patterns collected for these two domains are shown in Fig. 1(c) and (d) respectively. By comparing the contrast inside the experimental disks with the simulation [Fig. 1(j)], it is deduced that the small domain on the left side of the IDB with an inclined facet has a [0 0 0 1] growth direction (Ga-polarity), whereas the main domain on the right side with a flat top surface exhibits a $[000\bar{1}]$ growth direction (N-polarity) in agreement with the nitridated surface preparation.[12] This behavior tends to show that N-polar crystals favor the wire geometry formation with vertical sidewalls, while Ga-polar crystals present inclined facets that may limit the vertical extension and in some extent may lead to the formation of pyramidal geometry. The longitudinal change of polarity can not occur spontaneously during the crystal growth (except using heavily Mg-incorporation[15]). Thus, the polarity of GaN crystal is probably imposed by the nucleation seeds, which are related to the surface state, *i.e.* to the thin *in situ* deposited SiN_x layer or to the thin AlN layer formed during the sapphire surface nitridation.[3Erreur ! Signet non défini.] To verify this assumption, we performed SAG on patterned c-sapphire substrates using a thicker Si_3N_4 layer to position precisely the mask and to identify its influence on the crystal polarity. Short growth duration (~200 s) was chosen for SAG to obtain only the GaN-wire nucleation seed array [see Fig. 1(e)]. Three areas are observed by STEM on the typical as-grown seed shown in Fig. 1(f): a central part with a flat top surface surrounded by two crystals with inclined facets. The size of the central part is around 400 nm (*i.e.* the diameter of the patterned holes). Two vertical IDBs are located close to the mask edge opening (indicated by white arrows in Fig. 1(f)). An ion-milled seed [Fig. 1(g)] was analyzed by CBED showing that the flat top crystal is N-polar [Fig. 1(h)] while the inclined one is Ga-polar [Fig. 1(i)]. It confirms the co-existence of opposite polarities in

GaN crystals correlated to the nature of the surfaces: Ga-polar crystal is preferentially formed on SiN_x mask and N-polar crystal on AlN/c-sapphire surface.

Based on these results concerning the shape dependence on the polarity, we then performed a standard SG growth of GaN nanostructures directly on N-polar c-GaN freestanding substrates to get the wires geometry. The same growth on Ga-polar substrate was carried out for comparison. The 45°-tilted SEM images of as-grown samples on N-polar and Ga-polar surfaces are shown in Fig. 2(a) and (f) showing the impact of the substrate polarity on the crystal growth shapes. The nanostructure polarities were checked by CBED taking into account the simulation references given in Fig. 2(k) and (l) corresponding to the observed area thicknesses [Fig. 2(b) and (g)]: the growth on N-polar GaN [Fig. 2(e)] exhibits N-polar wires [Fig. 2(d)],[16] whereas the growth on Ga-polar GaN [Fig. 2(j)] exhibits Ga-polar pyramidal shape nanostructures [Fig. 2(h) and (j)]. As expected, the polarity is maintained between the substrate and the nanostructures as it is schematized in Fig. 3 (a) and (c).

The kinetic Wulff's plots (v-plot) giving the growth velocities along different orientations are usually used to describe the MOVPE growth features to take into account non equilibrium phenomena.[17,18] Recently, the GaN non-equilibrium shapes obtained by MOVPE have been measured or calculated for different growth conditions on polar,[19] semipolar and nonpolar[20,21] surfaces. The anisotropy of the growth rate along <0 0 0 1> coming from the crystal polarity has been pointed out without mentioning the influence of the substrate polarity. Our present results allow obtaining the schematic representation of the v-plot considering the substrate polarity effect (see Fig. 3 (b) and (d) where the measured growth velocity values are noted by dots). For N-polar GaN, cusps along

$[000\bar{1}]$ and $\langle 10\bar{1}0 \rangle$ are in agreement with literature, and the relative observed velocities lead to c-oriented wires with $\{10\bar{1}0\}$-sidewalls. For Ga-polar GaN, the $[0001]$ and $\langle 10\bar{1}0 \rangle$ cusps are not observed, but rather the $\langle 10\bar{1}n \rangle$ giving the pyramidal shape (n=1,3… depending on local growth conditions).

Optical properties of as-grown pyramidal and wire-shaped nanostructures were measured at room temperature by photoluminescence (PL) excited with a 244 nm laser beam using the same experimental conditions (see Fig. 4 (a)). The optical property of the as-grown GaN wires is better than the pyramidal shaped nanostructures without a defect-related yellow band (YB) luminescence. In order to rule out the signal coming from the substrate, μ-PL was also made on single GaN wires at room temperature (see Fig. 4 (b)). The spectrum shows a good near band edge emission peak at 351 nm without YB indicating the high crystal quality of the wires.

In summary, we have shown that the N-polar wire growth is determined by the substrate polarity in the case of homoepitaxy. Growths on c-sapphire and freestanding GaN substrates evidenced that an N-polar surface leads to wire shape, whereas a Ga-polar one leads to pyramidal shapes. This shape selection method gives a novel approach to grow by MOVPE catalyst-free high crystal quality GaN wires showing good optical properties. It may be generalized to many other systems to get nanowires using other growth techniques combined with polarity-controlled substrates.

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Figures

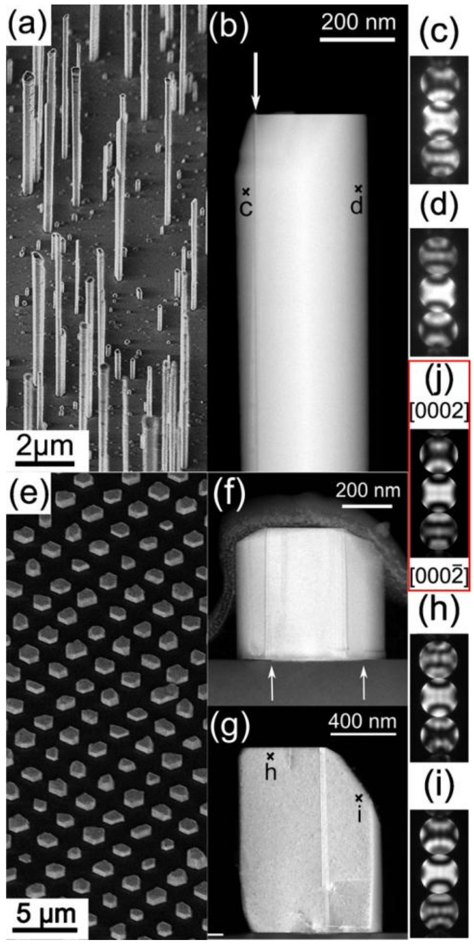

FIG. 1. (Color online) *Self-assembled growth* (SG) of GaN wires on c-sapphire. (a) 45°-tilt SEM view and (b) STEM image of a single wire. *Selective area growth* (SAG) of a wire seed array: (e) 45°-tilt SEM view and (f, g) STEM images of single seeds. Experimental CBED patterns of the points marked c, d and h, i in (b) and (g) are given in (c), (d) and (h), (i) respectively. As a reference, the simulated CBED pattern[14] for 110 nm thickness is given in (j). CBED patterns show Ga-polarity of the domains with inclined facets (c and i), and N-polarity of the ones with horizontal facets (d and h).

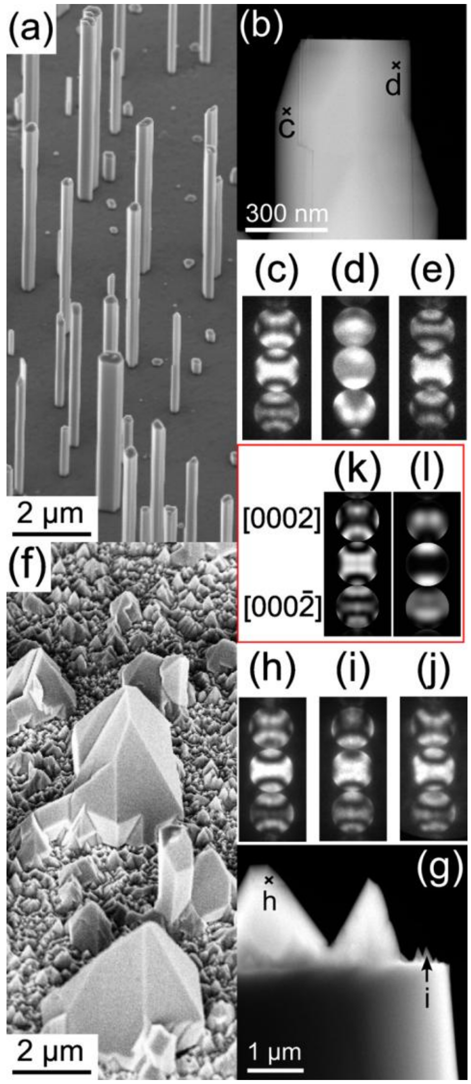

FIG. 2. (Color online) *Self-assembled growth* of GaN wires on N-polar GaN: (a) 45°-tilt SEM view, (b) STEM image of a single wire. Experimental CBED patterns showing (c) Ga polarity of the domain with an inclined facet (marked c), (d) N polarity of the one with a horizontal facet (marked d), and (e) N polarity of the GaN substrate. *Self-assembled growth* of GaN pyramids on Ga-polar GaN: (f) 45°-tilt SEM view, (g) STEM image. Experimental CBED patterns showing Ga polarity of (h) big pyramids, (i) small pyramids, and (j) the GaN substrate. As references, the simulated CBED patterns[14] for 110 and 60 nm thicknesses are given in (k) and (l) respectively.

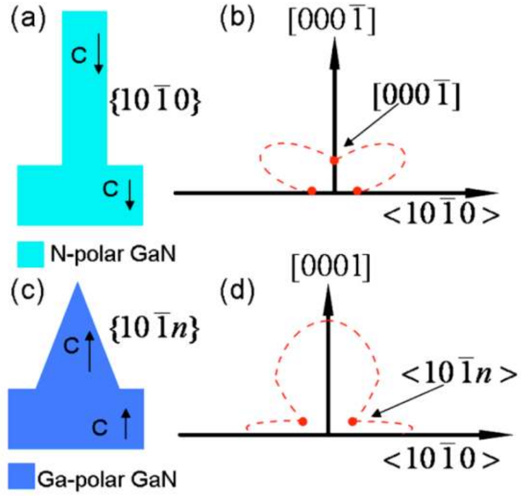

FIG. 3. (Color online) Schematics of the GaN nanostructure shape selection for growths on (a) N-polar and (c) Ga-polar GaN. The corresponding kinetic Wulff's plots map on the $(11\bar{2}0)$ plane are given in (b) and (d): dots correspond to observed planes and dotted lines are extrapolated velocity values.

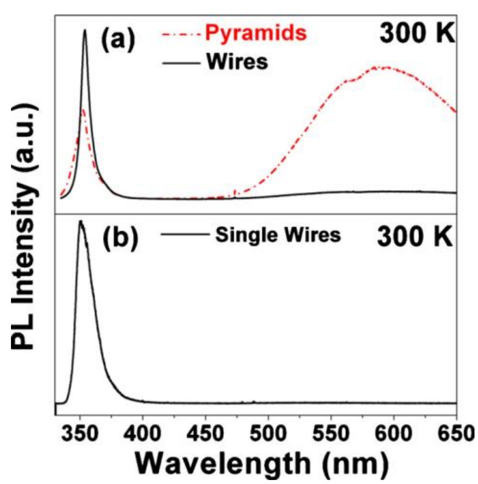

FIG. 4. (Color online) Room temperature (300 K) photoluminescence (PL) spectra of (a) as-grown pyramids and wires on GaN freestanding substrates having respectively the Ga- and N-polarities and (b) Micro-PL of a single wire dispersed on a Si substrate.