

Effect of the polar surface on GaN nanostructure morphology and growth orientation

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(Received 25 June 2004; accepted 30 August 2004)

Wurtzite gallium nitride nanostructures were grown by thermal reaction of gallium oxide and ammonia. The resulting morphology varied depending on ammonia flow rate. At 75 sccm only nanowires were obtained, while polyhedral crystals and nanobelts were observed at 175 sccm. Scanning electron microscopy and transmission electron microscopy revealed both thin smooth and thick corrugated nanowires. The growth orientations of most of the smooth ones, as well as the nanobelts, were perpendicular to the *c* axis ($\langle 0001 \rangle$), while the corrugated nanowires and the large polyhedra grew parallel to $\langle 0001 \rangle$. We propose a model to explain these variations of morphology and growth orientation in terms of the Ga/N ratio and the different characteristic length of $\{0001\}$ polar surface in the different nanostructures. © 2004 American Institute of Physics.
[DOI: 10.1063/1.1829780]

Gallium nitride (GaN) has been a significant wide-band gap semiconductor due to its applications in blue light emission and high power electronic devices.¹ Along with recent explosive research interest in nanotechnology, there have been extensive efforts to synthesize GaN one-dimensional nanostructures, such as nanowires² and nanobelts (or nanoribbons),³ for nanodevice applications.⁴

GaN nanostructure synthesis mostly involves one of two typical growth mechanisms. The vapor–liquid–solid (VLS) mechanism utilizes a transition metal catalyst while the vapor–solid (VS) mechanism relies on direct crystallization from the vapor. For VLS the dominant morphology is generally nanowire because nucleation and growth are defined by a liquid catalyst particle.² However, undesired contamination can occur from the catalyst. In contrast, for VS more varied morphologies, e.g., nanobelts, are possible due to the absence of constraints by the catalyst. Furthermore, the growth scheme is simple, and contamination can be avoided.

From this perspective, numerous groups reported the synthesis of GaN nanowires or nanobelts using VS-type growth methods,^{3,5,6} e.g., oxide-assisted chemical vapor deposition, but so far no report is available with regard to understanding the variation of the morphology and the crystallographic growth orientation among these structures. Such information would be critically important for building up devices out of these nanostructures, and for tuning the device characteristics given the highly anisotropic physical properties of GaN.⁷

In this letter, we report the morphological evolution of GaN nanostructures, from nanowires to polyhedral crystals to nanobelts, by varying the NH₃ flow rate in the thermal reaction of gallium oxide (Ga₂O₃) and NH₃ at 1100 °C. We propose that the Ga/N ratio in the vapor phase plays an important role in determining the resulting morphology and growth orientation, based on the observed relationship between the morphology and the *characteristic length* of $\{0001\}$ polar surfaces.

For GaN nanowire synthesis, Ga₂O₃ powder (0.3 g) (Alfa Aesar 99.999%, mesh size 350, ~40 μm) in an alumina boat was thermally reacted with flowing NH₃ at 1100 °C for 2h in a 36-in.-long horizontal tube furnace with cleaned Si substrates, with only a native SiO_x layer, placed downstream 7–10 in. from the source. The NH₃ flow rate was maintained at either 75 or 175 sccm, and the pressure in the reactor was ~1 atm at all conditions. Substrate temperatures at different positions were determined from a previously measured temperature profile. Micro Raman spectroscopy (Renishaw 1000) and powder x-ray diffraction (INEL) confirmed that all products retrieved from the substrates were wurtzite GaN. Scanning electron microscopy (SEM, JEOL 6300FV) and high-resolution transmission electron microscopy (TEM, JEOL 2010F) were used to investigate the detailed morphology and crystallography of grown structures.

Figure 1 shows SEM images of three typical morphologies obtained at different growth conditions; Table I provides a summary. At 75 sccm, nanowires were observed for all substrate positions, the temperature being in the range 921–1034 °C. Lengths up to 50 μm, and diameters from 50 to 300 nm, were observed [Fig. 1(a)]. In contrast, at 175 sccm different products were obtained on different substrate positions. For 7–8 in. downstream (1034–1000 °C), a mixture of nanowires, nanobelts [Fig 1(b)] and polyhedral crystals [Fig. 1(c)] was obtained, while for 9–10 in. (970–921 °C) only nanobelts were obtained. Nanobelts

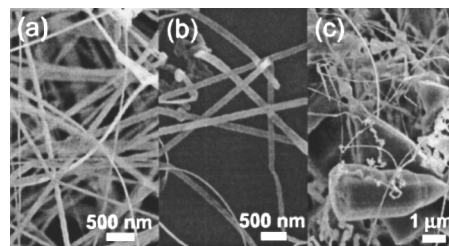


FIG. 1. SEM micrographs of (a) nanowires, (b) nanobelts, and (c) polyhedral crystals grown on a Si substrate. No metal coating was applied for SEM imaging.

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could be more than 500 nm wide, with smooth broad surfaces and lengths similar to the nanowires. Polyhedral crystals were up to 10 μm long with diameters from ~ 500 nm to ~ 5 μm , and well-defined six-sided facets suggesting growth orientation parallel to the c axis ($\langle 0001 \rangle$).

TEM revealed two distinct nanowire morphologies: relatively coarse with corrugated surface [Fig. 2(a)], or a thin and smooth-surfaced one [Fig. 2(b)]. Diameters of smooth-surfaced nanowires were uniform along their lengths, while for the corrugated ones the diameters oscillated along the length. Selected area diffraction patterns showed unambiguously that both types of nanowires were single crystals, the corrugated surfaces being in fact crystal facets. More interestingly, the two surface morphologies correlated well with two different growth orientations. Most of the smooth-surfaced nanowires had growth orientations perpendicular to $\langle 0001 \rangle$, e.g., $\langle 2-1-10 \rangle$ and $\langle 10-10 \rangle$, while the corrugated ones had growth orientations parallel to $\langle 0001 \rangle$, or occasionally containing a c -axis component, e.g., $\langle -1101 \rangle$. It is significant that smooth wires were much more prevalent than corrugated ones for all growth conditions. Nanobelts had the same growth orientations as smooth wires (Fig. 3(b) and 3(c)), orientations perpendicular to $\langle 0001 \rangle$ with the broad face corresponding to $\{0001\}$.

Wurtzite GaN contains polar and nonpolar low-index surfaces. In the following we suggest that the difference in growth rates of these chemically and structurally distinct surfaces has a major influence on the resulting nanostructure morphologies and growth orientations. It should be noted that, unlike other III-V semiconductors such as GaAs, polar surfaces in GaN, e.g., $\{0001\}$, always tend to be Ga stabilized independent of the chemical environment (Ga or N rich), whereas nonpolar surfaces generally maintain their Ga-N stoichiometry.^{8,9} Ga atoms thus have a significantly lower diffusion barrier on the polar surface because the adsorbate-surface interaction is predominantly realized by very weak delocalized metallic Ga-Ga bonds ($T_{\text{melt}} = \sim 30$ °C).⁸ An important consequence is that, similar to GaN thin film growth,¹⁰ the nanostructure morphology will mainly display broad and smooth two-dimensionally grown polar surfaces under Ga-rich growth conditions, while under N-rich conditions it will mainly exhibit rough surfaces or facets composed of polar and nonpolar surfaces. It is known that excess N (or N reactant) reduces the Ga effective diffusion length on the polar surface, and this in turn induces rough or faceted surfaces.⁸ We apply this reasoning to understand the observed morphology variations. First, we estimate the Ga/N reactant ratio versus substrate position, from the

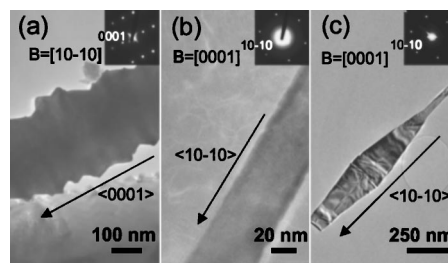
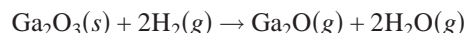


FIG. 2. TEM micrographs of typical (a) coarse corrugated nanowire, (b) thin smooth-surfaced nanowire and (c) nanobelt. In the image, B denotes zone axis, and the indices next to arrows indicate growth orientations. Note that while corrugated nanowire's growth orientation is parallel to the c axis ($\langle 0001 \rangle$) of a wurtzite structure, both smooth-surfaced nanowire and nanobelt's growth orientations are perpendicular to $\langle 0001 \rangle$ direction. In the nanobelt's image, the fringes on the surface are due to strain.

reaction chemistry and the reactant distribution in the quartz tube.

In the thermal reaction of Ga_2O_3 and NH_3 , Ga_2O_3 will first be converted to $\text{Ga}_2\text{O}(g)$,¹¹ and it will react with NH_3 to form GaN either on the surface of growing GaN or in vapor phase, i.e.



We expect direct reaction of Ga and NH_3 to also be possible because $\text{Ga}_2\text{O}(g)$ can back react with H_2 to form Ga on the GaN surface.¹¹ However, for simplicity we invoke the former reaction in what follows. To estimate Ga/N reactant ratio versus substrate position, we need to understand the distribution of $\text{Ga}_2\text{O}(g)$ in the stream of NH_3 . Since the equilibrium vapor pressure of $\text{Ga}_2\text{O}(g)$ at the reaction temperature ($T = 1100$ °C) is very small ($\sim 10^{-6}$ atm)¹¹ while the total pressure in the reactor is 1 atm, the dispersion of $\text{Ga}_2\text{O}(g)$ in our experiment can be treated as a continuous $\text{Ga}_2\text{O}(g)$ point source diffusion under NH_3 advection.

This implies that the forced diffusion of $\text{Ga}_2\text{O}(g)$ by NH_3 "carrier gas" is more important than the molecular diffusion driven by a concentration gradient. The Reynolds number for our reactor at 175 sccm NH_3 and at 1100 °C is less than 30, so we expect the NH_3 flow to be laminar at all conditions. Then, we can apply the mass-balance equation to estimate the steady state $\text{Ga}_2\text{O}(g)$ concentration profile. A general solution for uniform flow field in Cartesian coordinates is available in the literature.¹² Although more rigorous treatment is required to account for the cylindrical geometry of the reactor and the shear dispersion of flow field, the solution still predicts that in this type of diffusion there generally exists a maximum in the $\text{Ga}_2\text{O}(g)$ concentration downstream from the source, and as the flow rate increases the maximum moves farther downstream.

From the above, we expect the maximum $\text{Ga}_2\text{O}(g)$ concentration to be slightly downstream from the source at 75 sccm; increasing to 175 sccm shifts the whole profile farther downstream, leaving the region adjacent to the source relatively N rich [i.e., depleted of $\text{Ga}_2\text{O}(g)$] while Ga-rich conditions apply farther downstream. We assume that this variation in the $\text{Ga}_2\text{O}(g)$ concentration profile is connected to the sequential appearance of *faceted* polyhedral crystals and *broad* and *smooth-surfaced* nanobelts at the higher flow rate. Conversely, analogous to GaN thin film growth, as re-

TABLE I. Summary of growth conditions and corresponding GaN morphologies.

NH ₃ flow rate	Substrate position (inch away from the source)	
	7, 8	9, 10
75 sccm	NW ^a	NW ^a
175 sccm	NW ^a +XL ^c +NB ^b	NB ^b

^aNW: Nanowire.

^bNB: Nanobelt.

^cXL: Polyhedral crystal.

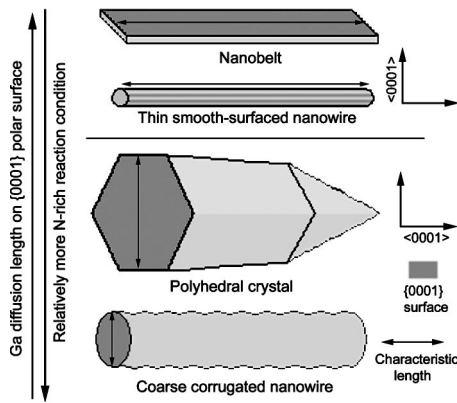


FIG. 3. Model for the relationship among the GaN nanostructure morphology, the growth orientation, and the reaction condition. The shaded area indicates $\{0001\}$ polar surface. As the reaction condition becomes relatively more N rich the characteristic length of $\{0001\}$ surface decreases in the morphologies. In the smooth-surfaced nanowire, there should be only two tangential $\{0001\}$ polar surfaces running parallel to the growth orientation, but extra shaded lines were inserted to indicate other possible tangential polar surfaces on the nanowire surface, e.g., $\{1-101\}$. Note in a wurtzite structure there is no polar plane running parallel to $\langle 0001 \rangle$ direction, the growth orientation of polyhedral crystal or corrugated nanowire, i.e., any surfaces running parallel to $\langle 0001 \rangle$ are always nonpolar.

action conditions evolve from relatively N rich to Ga rich (i.e., Ga/N ratio lower to higher) along the downstream, the dominant growth morphology changes from faceted polyhedral crystals to broad and smooth-surfaced nanobelts. We introduce the notion of a variable “characteristic length” of polar surface to explain the connection between reaction conditions and nanostructure morphologies and thus growth orientations.

Note that the Ga diffusion is, as introduced, more significant on the polar surfaces than on the nonpolar surfaces, and the diffusion length on the polar surfaces varies depending on the reaction condition (Ga or N rich) while that on the nonpolar surfaces is expected to be relatively constant regardless of the reaction conditions due to Ga–N stoichiometry on these surfaces. Then, we expect the variation of morphology and growth orientation at different reaction conditions to be dominated by the change of the “relative length scale” of polar surface, which increases under Ga-rich conditions (longer Ga diffusion length and more Ga flux), and vice versa. For instance, if the reaction condition is relatively more Ga rich, we expect significant anisotropy in the morphology due to the larger difference of Ga diffusion length between the polar surface and the nonpolar surface. That is, polar surfaces might be expected to display larger lengths, or surface areas, under high Ga flux, and the growth orientation must be compatible with this constraint. In contrast, under more N-rich reaction conditions, a less anisotropic morphology with smaller lengths of polar surfaces and with different growth orientations is expected owing to the decreased diffusion length difference and Ga flux. This length scale of polar surface in the morphologies defines a *characteristic length*.

Interestingly, we can notice a unique relationship among the characteristic lengths, the growth orientations and the nanostructure morphologies. As in the TEM data, the nanobelt’s broad face was always a $\{0001\}$ polar surface with the growth orientation perpendicular to $\langle 0001 \rangle$. As illustrated in Fig. 3, the $\{0001\}$ surface thus extends lengthwise along the

growth direction of the nanobelt. For the thin smooth-surfaced nanowire grown perpendicular to $\langle 0001 \rangle$, several polar surfaces, including $\{0001\}$, exist on the nanowire surface and extend lengthwise along the growth direction analogously to the nanobelt. Then, the characteristic length for these two morphologies is $\sim 50 \mu\text{m}$, i.e., the length of nanobelt or smooth-surfaced nanowire. However, for the polyhedral crystals and most of the corrugated nanowires, grown parallel to $\langle 0001 \rangle$, the characteristic lengths of the $\{0001\}$ surfaces are no more than ~ 5 and $\sim 1 \mu\text{m}$, respectively, i.e., the diameters of two morphologies.

This variation in the characteristic length reveals the relationship among reaction conditions and favored nanostructure morphologies and growth orientations. The characteristic length of the $\{0001\}$ polar surfaces decreases as the reaction condition varies from Ga rich to N rich, and concurrently, the favored morphology, which is interconnected with the favored growth orientation, evolves in sequence as in Fig. 3: nanobelt ($\perp \langle 0001 \rangle$), thin smooth-surfaced nanowire ($\perp \langle 0001 \rangle$), polyhedral crystal ($\parallel \langle 0001 \rangle$) and to coarse corrugated nanowire ($\parallel \langle 0001 \rangle$). We can safely exclude the temperature effect on the variation of morphology and growth orientation since the difference between the highest and the lowest substrate temperatures was only $\sim 100^\circ\text{C}$, which leads to virtually no difference in the surface diffusivity for any given surface.

In summary, the morphology and growth orientation of wurtzite GaN nanostructures can be controlled by changing the NH_3 flow rate during thermal reaction of Ga_2O_3 and NH_3 . Based on SEM and TEM observations, and considering $\text{Ga}_2\text{O}(g)$ profile and the variation of the characteristic length of $\{0001\}$ polar surfaces, we propose that the variation of Ga/N reactant ratio with substrate positions determines the morphology and the growth orientation. Specifically, as the reaction condition varies from relatively Ga rich to N rich, the favored morphology and orientation evolve from nanobelts ($\perp \langle 0001 \rangle$), thin smooth-surfaced nanowires ($\perp \langle 0001 \rangle$), and polyhedral crystals ($\parallel \langle 0001 \rangle$) to coarse corrugated nanowires ($\parallel \langle 0001 \rangle$).

This research was supported by the NSF/NIRT Program, Grant No. DMR03-04178. The authors also acknowledge the use of shared facilities supported by NSF/MRSEC: DMR02-03378.

¹S. Nakamura, *Science* **281**, 956 (1998).

²X. Duan and C. M. Lieber, *J. Am. Chem. Soc.* **122**, 188 (2000).

³J. Y. Li, Z. Y. Qiao, X. L. Chen, Y. G. Cao, Y. C. Lan, and C. Y. Wang, *Appl. Phys. A: Mater. Sci. Process.* **71**, 587 (2000).

⁴Y. Huang, X. Duan, Y. Cui, and C. M. Lieber, *Nano Lett.* **2**, 101 (2003).

⁵J. Jian, X. L. Chen, M. He, W. J. Wang, X. N. Zhang, and F. Shen, *Chem. Phys. Lett.* **368**, 416 (2003).

⁶H. Y. Peng, X. T. Zhou, N. Wang, Y. F. Zheng, L. S. Liao, W. S. Shi, C. S. Lee, and S. T. Lee, *Chem. Phys. Lett.* **327**, 263 (2000).

⁷J. W. Orton and C. T. Foxon, *Rep. Prog. Phys.* **61**, 1 (1998), and references therein.

⁸T. Zywiets, J. Neugebauer, and M. Scheffler, *Appl. Phys. Lett.* **73**, 487 (1998).

⁹A. R. Smith, R. M. Feenstra, D. W. Greve, M. S. Shin, M. Skowronski, J. Neugebauer, and J. E. J. Northrup, *J. Vac. Sci. Technol. B* **16**, 2242 (1998).

¹⁰A. Botchkarev, A. Salvador, B. Sverdlov, J. Myoung, and H. J. Morkoç, *J. Appl. Phys.* **77**, 4455 (1995).

¹¹D. P. Butt, Y. Park, and T. N. Taylor, *J. Nucl. Mater.* **264**, 71 (1999).

¹²H. B. Fischer, E. J. List, R. C. Y. Koh, J. Imberger, and N. H. Brooks, *Mixing in Inland and Coastal Waters* (Academic, San Diego, 1979).