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## **Abstract**

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 axes 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 morphology variations in terms of the Ga/N ratio and the different characteristic lengths of  $\{0001\}$  polar surfaces in the different nanostructures.

## **Comments**

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Effect of the polar surface on GaN nanostructure growth and morphology

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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 axes 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 morphology variations in terms of the Ga/N ratio and the different characteristic lengths of  $\{0001\}$  polar surfaces in the different nanostructures.

Despite numerous reports on gallium nitride (GaN) nanostructures, such as nanowires<sup>1</sup> and nanobelts (or nanoribbons)<sup>2</sup>, only a few studies have concentrated on controlling these morphologies within a given synthesis method. Synthesis schemes mostly involve 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 we expect the dominant morphology to be nanowires because nucleation and growth are defined by a liquid catalyst particle.<sup>1</sup> Without this constraint, i.e. for VS, one might expect the nanostructure morphology to be more easily influenced by growth conditions and thus more varied.

ElAhl et. al. recently reported a morphology variation of GaN structures under different growth conditions during direct reaction of Ga and ammonia ( $\text{NH}_3$ ).<sup>3</sup> They observed nanowires and microrods but did not observe a transition to the nanobelt morphology. In this letter, we report the morphological evolution of GaN nanostructures from nanowires to polyhedral crystals to nanobelts by varying the  $\text{NH}_3$  flow rate in the thermal reaction of gallium oxide ( $\text{Ga}_2\text{O}_3$ ) and  $\text{NH}_3$  at  $1100^\circ\text{C}$ . We propose that the Ga/N ratio in the vapor phase plays an important role in determining the resulting morphology, based on the observed relationship between the morphology and the *characteristic length* of  $\{0001\}$  polar surfaces.

No catalyst was used in the synthesis. Micro Raman spectroscopy (Renishaw 1000) and X-ray diffraction (XRD) confirmed that all morphologies 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.

0.3 g of  $\text{Ga}_2\text{O}_3$  powder (Alfa Aesar 99.999%, mesh size 350,  $\sim 40 \mu\text{m}$ ) in an alumina boat was placed at the center of a 36" long quartz tube with 3/4" diameter in a horizontal three-zone tube furnace (figure 1). Cleaned Si substrates with only a native  $\text{SiO}_x$  layer were placed downstream 7-10" from the source. The furnace was ramped to  $300^\circ\text{C}$  and held for 1 hr while purging with 60 sccm  $\text{N}_2$ . Next, the gas was switched to  $\text{NH}_3$ , and the temperature of the center zone was ramped to  $1100^\circ\text{C}$  and held for 2 hr while the flow rate was maintained at either 75 or 175 sccm. Substrate temperatures at different positions were determined from a previously measured temperature profile, and the pressure in the reactor was  $\sim 1$  atm at all conditions.

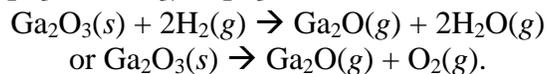
Figure 2 shows SEM images of three typical morphologies obtained at different growth conditions; table 1 provides a summary. At 75 sccm, nanowires were observed for all substrate positions, the temperature being in the range  $921\text{-}1034^\circ\text{C}$ . Lengths up to  $50 \mu\text{m}$ , and diameters from 50 nm to 300 nm,

were observed (figure 2a). In contrast, at 175 sccm different products were obtained on different substrate positions. For 7-8" downstream (1034-1000 °C), a mixture of nanowires, nanobelts (figure 2b) and polyhedral crystals (figure 2c) was obtained, while for 9-10" (970-921 °C) only nanobelts were obtained. Nanobelts could be more than 500 nm wide, with similar lengths to the nanowires and smooth broad surfaces. Polyhedral crystals were up to 10 μm long with diameters from ~500 nm to ~5 μm, and well-defined six side facets suggesting growth orientation parallel to the c-axis (<0001>).

TEM revealed two distinct nanowire morphologies: relatively coarse with corrugated surfaces (figure 3a), or thin and smooth-surfaced (figure 3b). 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 (SADP) 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 <0001>, e.g. <2-1-10> and <10-10>, while the corrugated ones had growth orientations parallel to <0001>, or occasionally containing a c-axis component, e.g. <-1101>. 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 (figure 3b,c), orientations perpendicular to <0001> with the broad face corresponding to {0001}.

Wurtzite GaN contains polar and non-polar surfaces. In the following we suggest that the difference in the growth rates of these chemically and structurally distinct surfaces have a major influence on the resulting nanostructure morphologies. 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 non-polar surfaces generally maintain their Ga-N stoichiometry.<sup>4,5</sup> 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 ( $T_{\text{melt}}=30\text{ °C}$ ).<sup>4</sup> An important consequence is that, similar to GaN thin film growth<sup>6</sup>, 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 non-polar 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.<sup>4</sup> We apply this reasoning to understand the observed morphology variations. First, we estimate the Ga/N reactant ratios vs. substrate position from the reaction chemistry and the reactant's dispersion in the reactor.

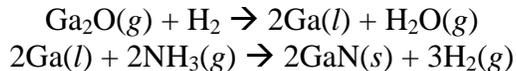
In the thermal reaction of Ga<sub>2</sub>O<sub>3</sub> and NH<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub> will first be converted to Ga<sub>2</sub>O(g):<sup>7</sup>



The Ga<sub>2</sub>O(g) then reacts with NH<sub>3</sub> to form GaN either on the surface of growing GaN or in vapor by the following reaction:



We expect direct reaction of Ga and NH<sub>3</sub> to be also possible because Ga<sub>2</sub>O(g) can back react with H<sub>2</sub> to form Ga on the GaN surface, i.e.:<sup>7</sup>



For simplicity, we use the former GaN formation reaction in the discussion. To estimate Ga/N reactant ratio vs. substrate position, we need to understand the distribution of Ga<sub>2</sub>O(g) in the stream of NH<sub>3</sub>. Since the equilibrium vapor pressure of Ga<sub>2</sub>O(g) at the reaction temperature (T=1100 °C) is very small (~10<sup>-6</sup> atm)<sup>7</sup> while the total pressure in the reactor is 1 atm, the dispersion of Ga<sub>2</sub>O(g) in our experiment can be treated as a continuous Ga<sub>2</sub>O(g) point source diffusion under NH<sub>3</sub> advection, which implies that the forced diffusion of Ga<sub>2</sub>O(g) by NH<sub>3</sub> "carrier gas" is more important than the molecular diffusion driven by a concentration gradient. The Reynolds number for our reactor at 175 sccm NH<sub>3</sub> and at 1100 °C is less than 30, so we expect the NH<sub>3</sub> 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.<sup>8</sup> 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 of 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 somehow 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 reaction conditions evolve from relatively Ga-rich to N-rich (i.e. Ga/N ratio higher to lower), the dominant growth morphology changes from broad and smooth-surfaced nanobelts to faceted polyhedral crystals. We introduce the notion of a variable “characteristic length” of polar surface to explain the connection between reaction conditions and nanostructure morphologies.

Note that the Ga diffusion is, as introduced, more significant on the polar surfaces than on the non-polar surfaces, and the diffusion length on the polar surfaces varies depending on the reaction condition (Ga- or N-rich) while that on the non-polar surfaces is expected to be relatively constant regardless of the reaction conditions due to Ga-N stoichiometry on these surfaces. Then, we expect the morphology variation 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 non-polar surface. That is, polar surfaces might be expected to display larger lengths, or surface areas, under high Ga flux. In contrast, under more N-rich reaction conditions, a less anisotropic morphology with smaller lengths of polar surfaces 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 observed a unique variation in the characteristic length in our nanostructure morphologies. In the TEM data, the nanobelt’s broad face was always {0001} polar surface with the growth orientation perpendicular to <0001> direction. As illustrated in figure 4, the {0001} surface thus extends lengthwise along the growth direction of the nanobelt. For the thin smooth-surfaced nanowire grown perpendicular to <0001>, several polar surfaces, including {0001}, exist on the nanowire surface and extend lengthwise along the growth direction. 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 <0001>, the characteristic lengths of the {0001} polar surfaces are no more than  $\sim 5 \mu\text{m}$  and  $\sim 1 \mu\text{m}$  respectively, i.e. the diameters of two morphologies.

This variation in the characteristic length reveals the relationship between reaction conditions and favored nanostructure morphologies. The characteristic length of the {0001} surfaces decreases as the reaction condition varies from Ga-rich to N-rich, and concurrently, the favored morphology evolves in the sequence: nanobelt, thin smooth-surfaced nanowire, polyhedral crystal and coarse corrugated nanowire (figure 4). We can safely exclude the temperature effect on the morphology variation 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 of wurtzite GaN nanostructures can be controlled by changing the  $\text{NH}_3$  flow rate during thermal reaction of  $\text{Ga}_2\text{O}_3$  and  $\text{NH}_3$ . When the lower  $\text{NH}_3$  flow rate (75 sccm) was used, only nanowires were observed, while polyhedral crystals and nanobelts were obtained when the higher  $\text{NH}_3$  flow rate (175 sccm) was applied. 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 the variation

of Ga/N reactant ratio with substrate positions determines the resultant GaN nanostructure morphology. Specifically, as the reaction condition varies from relatively Ga-rich to N-rich condition, the favored growth morphology changes from nanobelts, thin smooth-surfaced nanowires, and polyhedral crystals to coarse corrugated nanowires

## ACKNOWLEDGMENT

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## REFERENCES

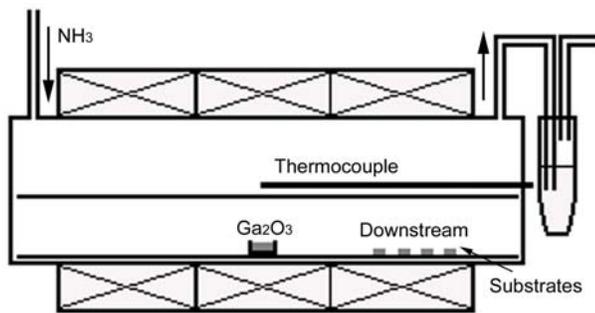
- Duan, X.; Lieber, C. M. *J. Am. Chem. Soc.* 2000, *122*, 188.
- Li, J. Y.; Qiao, Z. Y.; Chen, X. L.; Cao, Y. G.; Lan, Y. C.; Wang, C. Y. *J. Appl. Phys. A* 2000, *71*, 587.
- ElAhl, A. M. S.; He, M.; Zhou, P.; Harris, G. L.; Salamanca-Riba, L.; Felt, F.; Shaw, H. C.; Sharma, A.; Jah, M.; Lakins, D.; Steiner, T.; Mohammad, S. N. *J. Appl. Phys.* 2003, *94*, 7749.
- Zywietz, T.; Neugebauer, J.; Scheffler, M. *Appl. Phys. Lett.* 1998, *73*, 487.
- Smith, A. R.; Feenstra, R. M.; Greve, D. W.; Shin, M. S.; Skowronski, M.; Neugebauer, J.; Northrup, J. E. *J. Vac. Sci. Technol. B* 1998, *16*, 2242
- Botchkarev, A.; Salvador, A.; Sverdlov, B.; Myoung, J.; Morkoç, H. *J. Appl. Phys.* 1995, *77*, 4455.
- Butt, D. P.; Park, Y.; Taylor, T. N. *J. Nucl. Mater.* 1999, *264*, 71.
- Fischer, H. B.; List, E. J.; Koh, R. C. Y.; Imberger, J.; Brooks, N. H. *Mixing in Inland and Coastal Waters*, Academic Press: San Diego, CA, 1979; pp 50-54.

Table 1. Summary of growth conditions and corresponding GaN morphologies.

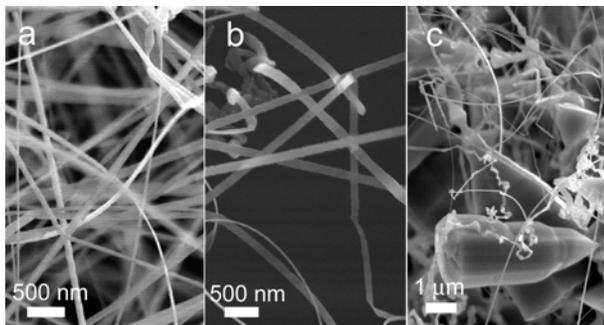
NH <sub>3</sub> flow rate	Substrate position (inch away from the source)	
	7, 8	9, 10
75 sccm	NW	NW
175 sccm	NW+XL+NB	NB

NW: Nanowire, NB: Nanobelt, XL: Polyhedral crystal

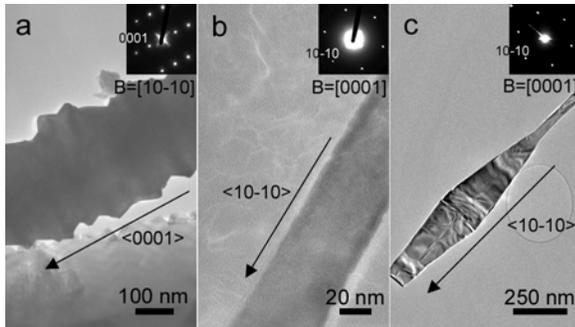
**Figure 1.** Schematic illustration of a GaN reactor. The substrate temperature is varying from 1034 °C to 921 °C as the substrate position goes downstream.



**Figure 2.** SEM micrographs of (a) nanowires, (b) nanobelts and (c) polyhedral crystals grown on a Si substrate. No metal coating was applied for SEM imaging.



**Figure 3.** 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.



**Figure 4.** Model for the relationship between the GaN nanostructure morphology 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  $\langle 0001 \rangle$  is always non-polar.

