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Watching GaN Nanowires Grow

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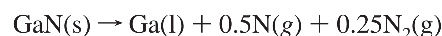
ABSTRACT

We report real-time high temperature transmission electron microscopy observations of the growth of GaN nanowires via a self-catalytic vapor–liquid–solid (VLS) mechanism. High temperature thermal decomposition of GaN in a vacuum yields nanoscale Ga liquid droplets and gallium/nitrogen vapor species for the subsequent GaN nanowire nucleation and growth. This is the first direct observation of self-catalytic growth of nanowires via the VLS mechanism and suggests new strategies for synthesizing electronically pure single-crystalline semiconductor nanowires.

Crucial to nanotechnology is the creation of nanoscale building blocks of various sizes and shapes.[1] Nanostructures of wide band-gap gallium nitride are of particular interest because of their applications in short-wavelength optoelectronic devices and high-power/high-temperature electronics. GaN nanowires represent unique building blocks that can be used as high mobility field effect transistors as well as miniaturized UV-blue nanolasers.[2,3] The synthesis of GaN nanowires via the vapor−liquid−solid (VLS) process[1,4] commonly relies on transition metal clusters such as Ni, Fe, and Co, which inevitably results in undesired contamination within the otherwise single-crystalline nanowires. Here we report real-time transmission electron microscopy (TEM) observations of the growth of GaN nanowires via a self-catalytic VLS mechanism. These nanowires nucleate and grow from Ga droplets formed during thermal decomposition of GaN at elevated temperatures in a vacuum. This is the first direct observation of self-catalytic growth of nanowires via the VLS mechanism and suggests new strategies for growth of semiconductor nanowires without unintentional doping.

The TEM samples studied in this work were pure GaN thin films grown to a thickness of 12 μm via hydride vapor phase epitaxy (HVPE) on the c-plane of sapphire. The GaN film was subsequently removed from the sapphire substrate using the laser lift-off technique (LLO) to create a free-standing pure GaN layer.[5] This free-standing layer was argon ion milled to electron transparency ($\leq$300 nm thickness). The samples were then heated in-situ in a 200 kV transmission electron microscope to a temperature of $\sim$1050 °C at a vacuum level of $\sim 1 \times 10^{-7}$ Torr. It is known that at temperatures above 850 °C in high vacuum GaN decomposes via the following possible reactions:[6]



$$GaN(s) \rightarrow Ga(l) + 0.5N(g) + 0.25N_2(g)$$

It has also been proposed and experimentally demonstrated that congruent sublimation of GaN is possible, which yields diatomic or polymeric vapor species.[7,8]

$$GaN(s) \rightarrow GaN(g) \text{ or } [GaN]_x(g)$$

By heating the GaN sample in-situ, it is possible to observe this decomposition and the resulting nanostructure evolution in real time and at high spatial resolution.

During this in-situ study, we serendipitously discovered the self-catalytic growth of GaN nanowires. In Figure 1, a series of video frames grabbed from observations of the GaN decomposition process at elevated temperatures is presented.[9] The nucleation and growth of a single GaN nanowire from a Ga liquid droplet is outlined in these images. The initial decomposition of the GaN thin film results in isolated nanoscale Ga droplets,[7] seen as dark spots in the TEM images (A). The decomposition of GaN also generates atomic nitrogen species as well as a small percentage of congruent evaporated diatomic or polymeric GaN species.[6−8] It is interesting to note here that liquid Ga droplets have been shown to further catalyze the decomposition of GaN.[10,11] The vapor species then redissolve into the Ga liquid droplets and initiate the VLS nanowire growth by supersaturating the liquid Ga and establishing a liquid-Ga/solid-GaN interface (B−F). The process resembles previous in-situ observations of Ge nanowire growth on Au clusters,[12] where three stages, including alloying (Figure 1A), nucleation (B), and axial

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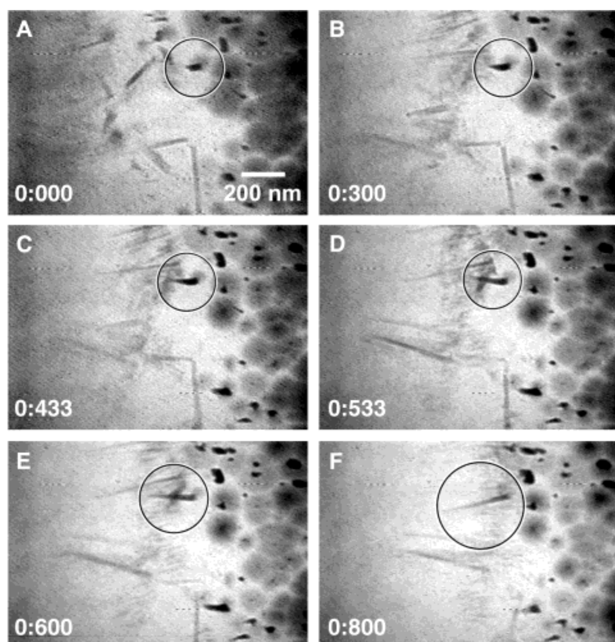

Figure 1. A series of video frames grabbed from observations of GaN decomposition at ≈1050 °C, showing the real-time GaN nanowire growth process. The number on the bottom left corner of each frame is the time (second: millisecond).

growth (C−F), are readily resolved. The growth rate of these GaN nanowires, however, was estimated to be 300 nm/s, orders of magnitude faster than those of nanowires grown at high pressure (∼300 nm/min) in a chemical vapor deposition process.[13]

After the in-situ growth, the sample was cooled and examined using conventional TEM methods at room temperature. In Figure 2(A), the sample is oriented close to the [0001] zone axis of the GaN substrate, where individual nanostructures of GaN can be observed in an end-on geometry. The selected area electron diffraction pattern (Figure 2A inset) indicates that these nanostructures are indeed pure, single crystalline GaN. When the sample is tilted to approximately 30° away from the [0001] zone axis, we see that these individual islands are indeed well-oriented GaN nanowire arrays with average diameters of around 50 nm.

Although vapor−liquid−solid nanowire growth has been previously observed in the Ge−Au systems by this group,[12] the current observation of VLS GaN nanowire growth without any foreign transition metal catalysts opens up an interesting and important possibility of producing semiconductor nanowires through a self-catalytic process. As a result, we should be able to effectively avoid undesired contamination from foreign metal atoms. This type of growth indeed has been reported previously in the literature where direct reaction of Ga with NH_3 or direct evaporation of GaN was used to produce GaN nanowires.[14,15] To confirm this unique GaN nanowire growth behavior, separate experiments were carried out in a vapor deposition reactor. Direct evaporation of GaN powder pellets were examined from 900 to 1100 °C under ammonia flow (20 sccm). We have been able to observe the growth of GaN nanowires on the surface of pure GaN powder pellet. Figure 3 shows TEM images of the

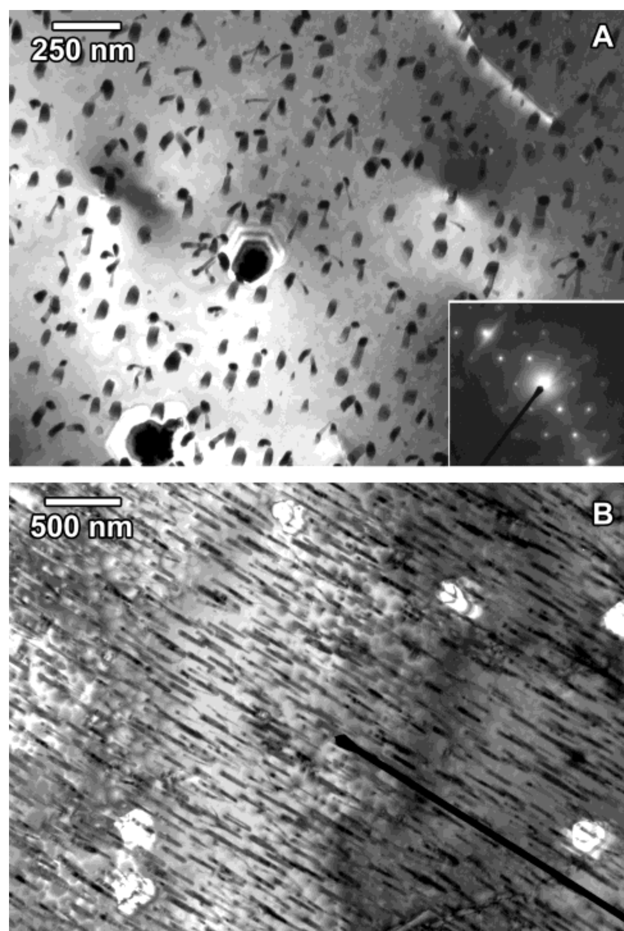

Figure 2. Room-temperature TEM images of GaN nanowire arrays observed nearly along the [0001] zone axis (A) and 30 degrees away from the [0001] zone axis (B). The inset in (A) is a selected area electron diffraction pattern recorded from the array, indicating that the islands are single-crystalline GaN.

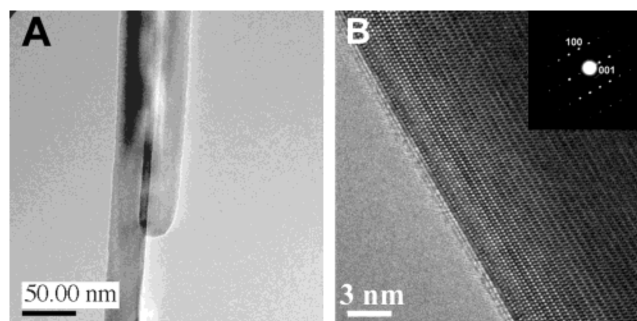

Figure 3. TEM images of GaN nanowires synthesized via direct evaporation of GaN in ammonia at 1100 °C. Inset in (B) is an electron diffraction pattern recorded on this nanowire along the [010] zone axis.

obtained GaN nanowires. The atomic resolved lattice in Figure 3B and the electron diffraction pattern (Figure 3B inset) indicate these single-crystalline wires grow perpendicular to the (100) lattice planes. Unlike those GaN nanowires grown using foreign metal catalysts, the ends of these nanowires are rather smooth (Figure 3a) without obvious liquid droplet tips. No efforts have been placed on the optimization of GaN nanowire yield using this method. Because of the possible nitridation of the Ga liquid droplets

during and after the nanowire growth, we have not detected Ga-rich nanoparticles at any of the GaN nanowire tips. On the other hand, we do not exclude the possibility of GaN nanowire growth via a direct vapor−solid process in our vapor-deposition reactor.

In summary, both the in-situ high temperature nanowire growth observation and room temperature examination of the products unambiguously demonstrate the feasibility of self-catalytic VLS nanowire growth, thus opening up the possibility of synthesizing electronically pure single-crystalline semiconductor nanowires.

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Supporting Information Available: Real-time observations in mpeg movie format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Wu, Y.; Fan, R.; Yang, P. *Int. J. Nanosci.* **2002**, *1*, 1−39.
(2) Huang, Y.; Duan, X.; Cui, Y.; Lieber, C. M. *Nano Lett*. **2002**, *2*, 101.
(3) Johnson, J.; Choi, H.; Yang, P.; Saykally, R. *Nature Mater*. **2002**, *1*, 101
(4) Duan, X.; Lieber, C. M. *J. Am. Chem. Soc*. **2000**, *122*, 188.
(5) Wong, W. S.; Sands, T.; Cheung, N. W. *Appl. Phys. Lett*. **1998**, *72*, 599.
(6) L'vov, B. V. *Thermochim. Acta* **2000**, *360*, 85.
(7) Koleske, D. D.; Wickenden, A. E.; Henry, R. L.; Culbertson, J. C.; Twigg, M. E. *J. Cryst. Growth* **2001**, *223*, 446−483.
(8) Munir, Z. A.; Searcy, A. W. *J. Chem. Phys*. **1965**, *42*, 4223.
(9) The real-time observations are presented as supplemental information in mpeg movie format.
(10) Schoonmaker, R. C.; Buhl, A.; Lemley, J. *J. Phys. Chem.* **1965**, *69*, 3455.
(11) Pisch, A.; Schmid-Fetzer, R.; *J. Cryst. Growth* **1998**, *187*, 329.
(12) Wu, Y.; Yang, P. *J. Am. Chem. Soc*. **2001**, *123*, 3165.
(13) Wu, Y.; Fan, R.; Yang, P. *Nano. Lett*. **2002**, *2*, 83.
(14) He, M.; Zhou, P.; Mohammad, S. N.; Harris, G. L.; Halpen, J. B.; Jacobs, R.; Sarney, W. L.; Salamanca-Riba, L. *J. Cryst. Growth,* **2001**, *231*, 357−365.
(15) Zhou, S. M.; Feng, Y. S.; Zhang, L. D. *Chem. Phys. Lett.* **2003**, *369*, 610−614.

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