Growth and Characterization of Vertically Aligned High-Density Gallium Nitride Nanowires

Edgar A. Peralta, Applied & Engineering Physics, Cornell University
NNIN REU Site: Howard Nanoscale Science & Engineering Facility, Howard University

NNIN REU Principal Investigator: Dr. Gary Harris, Howard Nanoscale Science & Engr Facility, Howard University
NNIN REU Mentor: Dr. Maoqi He, Howard Nanoscale Science & Engineering Facility, Howard University
Contact: eap39@cornell.edu, gharris@msrce.howard.edu

Abstract:

Synthesis of vertically aligned, single crystal Gallium Nitride nanowires (GaN NWs) was achieved through a catalyst-assisted vapor-liquid-solid (VLS) process by the reaction of Ga with NH_3 in the presence of a nickel (Ni) catalyst. Such products are important in the fabrication of optoelectronic nanodevices. The experiments were carried out inside a tube furnace at 1000°C, a pressure of 5 Torr, and an anhydrous ammonia flow rate of 20 sccm. Metal Ga and Ni-patterned substrates were placed on separated boron nitride (BN) boats in a quartz liner inside the furnace.

The optimal growth parameters were determined on silicon substrates, which generated a high density of nanowires with diameters between 30-70 nm, several micrometers in length, growing in random directions. MgO <111> substrates were then used for controlled growth orientation, which produced vertically aligned GaN nanowires.

Introduction:

Single-crystalline one-dimensional semiconducting nanostructures are considered to be one of the critical building blocks of nanoscale optoelectronic devices [1]. GaN's large band gap (~3.4 eV at room temperature), its short wavelength (UV to blue) light-emission, its large dielectric breakdown field, and its high melting point, make this material ideal for high-power/high-temperature optoelectronic applications.

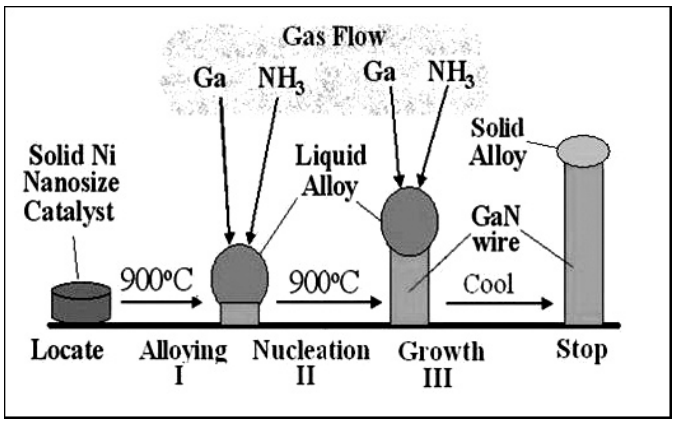

Figure 1: The vapor-liquid-solid (VLS) growth mechanism.

The most common growth techniques used in the synthesis of GaN NWs include: laser-ablation [2], carbon-nanotube confined reaction [3] and catalytic reaction [4]. We achieved synthesis through a catalytic reaction; $Ga + NH_3 \rightarrow GaN + H_2\uparrow$, based on a vapor-liquid-solid (VLS) growth mechanism [5], illustrated in Figure 1.

Unfortunately, not many studies have been done on controlling the orientation of catalytic NW growth without the use of MOCVD [6] or templates [7]. Control of the crystallographic growth direction of the nanowires is desired since anisotropic parameters such as thermal/electrical conductivity, index of refraction, piezoelectric polarization, and band structure among other optical/electrical properties often depend on this orientation. Our approach to achieve this growth orientation control was based on the results obtained by T. Kuykendall et al. [6], where they determined that matching the symmetry and lattice constant between the substrate—which must be single crystal—and GaN strongly influences the NW growth direction.

Essentially, any desired growth orientation could be obtained as long as that match was made. Our particular interest, GaN NWs perpendicular to the surface, required substrates which match the threefold symmetry of the <001> plane of GaN and lattice constant a = 3.19 Å. We used <111> MgO, having threefold symmetry and an interatomic separation of 2.98 Å for atoms in the <111> plane.

Experimental Procedure:

We first experimented with silicon substrates to determine the optimal conditions to use for the <111> MgO. The silicon substrates were prepared for metal deposition by a photolithography process using a thinned down Shipley S1818 photo resist spun at 4000 RPM for 9 seconds, and then developed to leave 3 μm diameter holes with 2 μm separation between holes. Nickel films were then evaporated at 7, 10, 15 and 30 Å thicknesses and liftoff was performed. Thicknesses were confirmed by ellipsometry and AFM.

The substrates were then cut into 10 x 5 mm^2 rectangular samples and evenly distributed on top of a boron nitride (BN) boat (1 x 4 cm^2 x 5 mm) inside a quartz liner about 1 cm from the gallium boat. The quartz liner was then placed inside a tube furnace (see Figure 2), and evacuated to pressures of 4-5 Torr. The furnace was ramped to 1000°C in 25 min, and remained at this temperature for 5-15 min and then cooled down. Anhydrous NH_3 flowed in the furnace at 20-30 sccm during the heating process; once cooled below

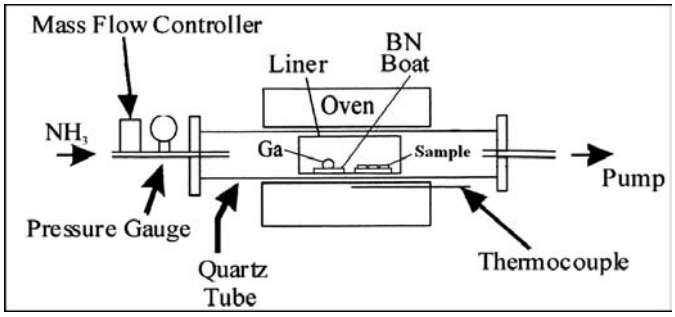

Figure 2: Illustration of tube furnace setup.

700°C, we switched to N_2 at 50 sccm. The resulting samples were then observed under the optical microscope and SEM to determine the characteristics of the grown NWs, and thus determine the optimal conditions for growth on <111> MgO.

Results and Conclusions:

First, we determined the appropriate reaction time: 5 min at 1000°C produced NWs with the smallest tips, while 10 min yielded slightly thicker, longer NWs. The 15 min reaction produced a "mesh" of nanowires, which was completely undesirable. We wanted small tips and dimensions that would be suitable for vertical growth so we chose a time of 8 minutes.

Second, we determined the appropriate Ni deposition thickness to use. Although all resulting samples had NWs ranging from 30 to 70 nm in diameter, those corresponding to the 10 Å depositions had the least amount of big crystalline structures and not so curved and entangled NWs. This suggests that the VLS process favors thin layers of Ni which are nearer the substrate surface than thick ones. This is a very important result because when using the <111> MgO, the substrate plays a key role on the growth direction, so the thinnest Ni deposition would yield better results. However, when we attempted to grow on the 7 Å Ni samples, there were no resulting NWs, mainly because such thin layers would evaporate before the GaN deposition. For this reason, we chose the 10 Å Ni deposition.

Third, we determined the best location along the BN boats that would yield vertical growth NWs once the <111> MgO was used. When we had three samples on a BN boat, only at the right of the second, and left of the third, we obtained a large number of NWs without the presence of large crystalline structures. For our sample holder BN boat having 4 cm along which to place samples, the best location was the region between the 2 and 3 cm mark.

After a few tries using the <111> MgO and getting the same results as with Si, with no vertical growth yet present, we experimented with a smaller amount of Ga (0.33g rather than 0.5g) because during one run such an amount produced straighter NWs on the Si (see Figure 3). Finally, at a pressure of 5 Torr, a NH_3 flow rate of 25 sccm, at 1000°C for 8 min, and with 0.33g of Ga, samples with 10 Å thick Ni films produced good results—namely, vertically aligned GaN nanowires with diameters ranging from 80 to 140 nm (see Figure 4). It is evident from comparing Figure 3 and Figure 4 that the <111> MgO substrate served its key function of favoring perpendicular growth of the nanowires. This can be seen not only by looking at a big area of the sample but also by looking at the insert on the top right corner of Figure 4 which shows the hexagonal cross section of one of these NWs. Since only the top of the NWs is visible, they therefore must be oriented perpendicular to the substrate.

Acknowledgements:

I'd like to thank the following people for their support and guidance: Dr. Harris, Dr. He, Mr. Griffin, Dr. Zhou, Mr. Taylor, and the rest staff at HNF. I'd also like to thank Ms. Melanie-Claire Mallison for giving me the opportunity to participate in the program, and NSF for providing the funding for it.

References:

[1] Xia, Y. et al. Adv.Mater. 2003, 15, 353.
[2] Duan, X. F.; Lieber, C. M. J. Am. Chem. Soc. 2000, 122, 188.
[3] Han, W.; Fan, S.; Li, Q.; Hu, Y. Science 1997, 277, 1287.
[4] Chen, C.C.; Yeh, C.C. Adv. Mater. 2000, 12, 738.
[5] Wu, Y.; Yang, P.; J. Am. Chem. Soc. 2001, 123, 3165.
[6] Kuykendall, T et al., Nature Materials, 2004, 3, 524.
[7] Cheng G. et al. Mat. Sci. & Eng. 2000, 165-168.

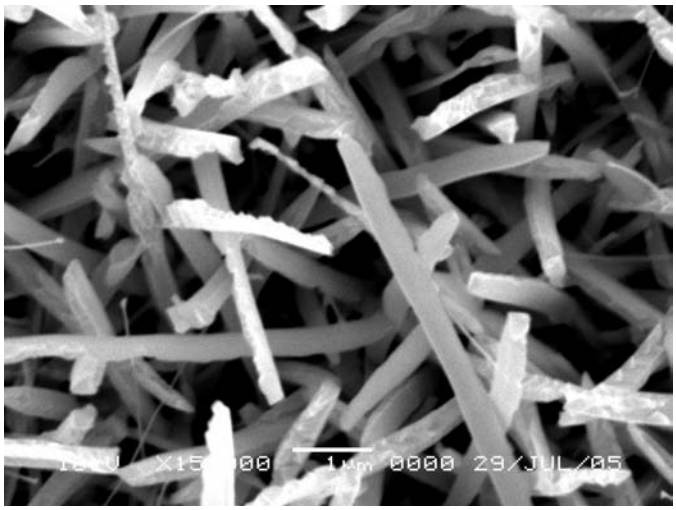

Figure 3: SEM of GAN NWs grown on silicon.

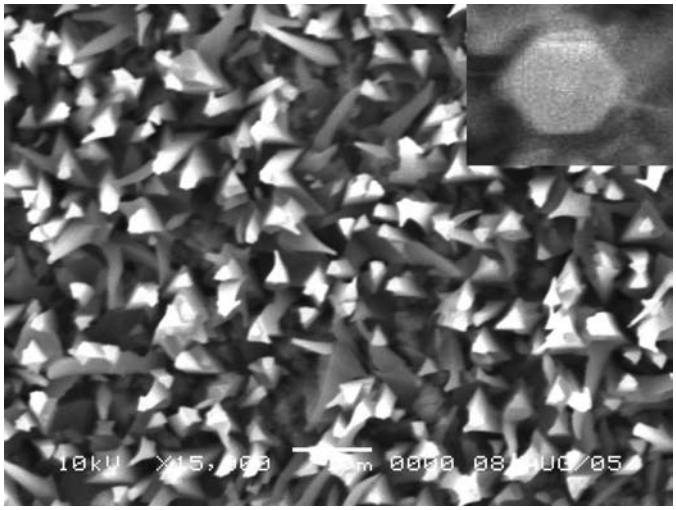

Figure 4: SEM of GaN NWs grown on <111> MgO.