Growth of large-scale GaN nanowires and tubes by direct reaction of Ga with NH₃

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Large-scale wurtzite GaN nanowires and nanotubes were grown by direct reaction of metal gallium vapor with flowing ammonia in an 850–900 °C horizontal oven. The cylindrical structures were as long as 500 μm with diameters between 26 and ~100 nm. Transmission electron microscopy, scanning electron microscopy, and x-ray diffraction were used to measure the size and structures of the samples. Preliminary results show that the size of the nanowires depends on the temperature and the NH₃ flow rate. The growth mechanism is discussed briefly. The simple method presented here demonstrates that GaN nanowires can be grown without the use of a template or catalyst, as reported elsewhere. © 2000 American Institute of Physics. [S0003-6951(00)01949-5]

GaN thin-film growth is an important focus of current research because of the promise for use as UV or blue emitters, detectors, high-speed field-effect transistors, and high-temperature electronic devices. Low-dimensional quantum-confinement structures are crucial for understanding fundamental concepts underlying the observed electronic, optical, and mechanical properties of materials. They might also be used as interconnects in microelectronic devices. Using density-functional calculations, Lee et al. suggested that the GaN band gap should decrease with decreasing GaN nanotube diameter. Unfortunately, there has been little published work on fabrication of low-dimensional GaN structures. Lee’s suggestion has not yet been tested. Han et al. synthesized GaN nanorods through a carbon-nanotube-confined reaction. Subsequently, Han et al. produced GaN–carbon composite nanotubes and nanorods by arc discharge in nitrogen atmosphere. Duan and Lieber formed single-crystal GaN nanowires by laser-assisted catalytic growth. Chen and Yen produced wirelike structures using polycrystalline indium powder as a catalyst. Li et al. fabricated GaN nanorods by a sublimation of GaN powder under an ammonia flow. In a parallel effort, Cheng et al. formed GaN nanowires in anodic alumina membranes through gas-phase reaction of Ga₂O vapor with flowing NH₃. In addition, Yoshizawa et al. grew self-organized GaN nanocolumns on Al₂O₃ substrates by rf-radical-source molecular-beam epitaxy. Three-dimensional GaN structures were prepared by direct reaction of Ga vapor with flowing NH₃ above 900 °C.

In this letter, we report growth of GaN nanowires and nanotubes through direct reaction of metal gallium vapor with flowing ammonia in a horizontal oven. The diameters ranged between 26 and ~100 nm and some were as long as 500 μm. Preliminary results indicate that the nanostructure size depends on the temperature and the NH₃ flow rate. This is an extremely simple and direct approach for synthesizing very long and pure GaN nanowires and nanotubes without any contamination by template or catalyst materials. The growth stages and mechanism are discussed briefly.

Figure 1 schematically shows the experimental setup for nanowire synthesis. About 3 g of pure metal Ga (99.999%, metals basis, Alfa AESAR Inc.) was put in a small boron-nitride (BN) boat and placed at the bottom of a liner. The liner is made of boron nitride or quartz for collecting samples and protects the quartz tube of the oven from contamination during growth. A water-cooled Cu block was also put at the downstream end of the oven for sample collection. Ammonia (99.999%, MG Industries) was introduced into the quartz tube through a mass-flow controller (MKS Instruments, Inc., model 1259B) at rates of 50–100 sccm. During growth, the total pressure (mostly ammonia) upstream was kept at 15 Torr as measured by a capacitance manometer (MKS Instruments, Inc., model 220CA). The temperature of the oven (Sigma Inc., temperature program controlled) was set between 850 and 900 °C for 3–4 h to allow the GaN nanowires to crystallize. The overall reaction is

\[ \text{Ga} + \text{NH}_3 \rightarrow \text{GaN} + \text{H}_2 \]

Figure 1. Schematic diagram of the setup for direct reaction of GaN with NH₃.

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and one expects it to be influenced by availability of ammonia and Ga at the growth surface. Nanosized GaN crystals formed spontaneously without intentional nucleation in this experiment. At the end of the reaction, samples were collected from the wall of the BN boat, the linear, and the surface of the cooled Cu block for measurements. The size and structure of the samples were measured by scanning electron microscopy (SEM) with 50 nm resolution (JEOL, model JSM-35CF), transmission electron microscopy (TEM) with 0.25 nm resolution (JEOL 4000FX TEM), and x-ray diffraction (XRD) (SIEMANS DIFRAKTOMETER D5000).

SEM scans in Fig. 2 show an amorphous-GaN matrix with occasional hillocks consisting of many small crystal plates, each about as thick as the nanowire diameters. A sparse network of GaN nanowires lies atop both matrix and hillocks like a highway interchange. Observed through an optical microscope, the longest nanowires reach approximately 500 μm.

A sample grown at 900 °C in a NH₃ flow of 100 sccm was taken from the quartz liner and characterized by XRD. The result shown in Fig. 3 indicates that the sample is single-crystal hexagonal wurtzite GaN. Miller indices are indicated on each diffracted peak.

Diameters of wires in this sample were measured by TEM. The thinnest had a 26 nm diam, the fattest were about 100 nm across. Figure 4 is a TEM image of one of the thinnest wires. The inset in the upper-right-hand corner of Fig. 4 is an electron diffraction pattern of the wire sample, which can be indexed to the diffraction of wurtzite GaN [001]. Some of the cylindrical nanostructures are tubes. Figure 5 shows one with an outside diameter of 122 nm and an inside diameter of 58 nm. The nanotubes appear to be cylindrical, not two layered. The tube ends that have been observed are round. Imaging by SEM and TEM reveals no obvious seams, although flaws in the crystal structure are occasionally observed. The samples containing nanowires and nanotubes were collected from the BN boat walls or the quartz liner. Samples taken off the water-cooled Cu block contain only amorphous aggregates.

Generally, the higher the temperature in the range 850–900 °C and the faster the flow rate between 50 and 100 sccm, the larger the nanowire diameter. The nanowire length depends mostly on the length of the growth cycle above 3 h. A detailed investigation of the growth mechanism is currently in progress. However, we might briefly describe the stages as follows. It is well known that at 850 °C NH₃ decomposes stepwise to NH₂, NH, and N on many surfaces and that liquid Ga will vaporize and deposit on the surface of the boat and liner. N and Ga atoms can either desorb as N₂ or Ga, or react on surfaces yielding GaN molecules. At first, they build the dark-gray amorphous GaN matrix. During the
second stage, very thin hexagonal-like GaN crystal plates grow in layers on the matrix forming polycrystalline hillocks on the boat and liner. Finally, as observed by SEM, the wires appear to grow from the side of the crystal plates, but not from their surface. The diameters of the nanowires are roughly the same as the thickness of the plates at the point where they are joined. This implies that the edges of the thin hexagonal GaN crystal plates, which should be especially rich in defects, function as nanowire seeds. Tubes grow from the flat side of the platelets. This point is under active investigation. Gallium atoms and ammonia molecules in the vapor deposit continually on the tip of wires or tubes providing material for growth along the axis. Slow to no growth on the sides of the wires may be attributed to the absence of sites for NH₃ decomposition. Addition of H₂ to the gas flow over a sample including the nanowires, transforms them into a polycrystalline mass as the H₂-induced faults on all surfaces.

In summary, large-scale hexagonal wurtzite GaN nanowires and nanotubes with diameters between 26 and ~100 nm and lengths up to 500 μm were formed by direct reaction of metal gallium vapor with ammonia flowing at rates of 50–100 sccm in a horizontal oven at 850–900 °C. The best temperature and flow rate for growth of nanowires are about 870 °C and 80 sccm, respectively. We are currently studying other factors which influence the growth of these cylindrical nanostructures, including pressure, carrying gas, and sample location, as well as trying to gain an understanding of the detailed growth mechanism.

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