In-situ catalytic growth of Gallium Nitride Nanowires

R.E. Diaz[1], R. Sharma[2], K. Jarvis[1] and S. Mahajan[1]

1. School of Materials, Arizona State University, Tempe, AZ85287
2. Center for Solid State Science, Arizona State University, Tempe, AZ85287

rosa.diazrivas@asu.edu

Group III nitride large band gap semiconductors have attracted special interest for applications in number of optoelectronics devices [1, 2]. Multi-layer epitaxial structures required for various devices are generally grown on (0001) sapphire and silicon carbide substrates. Lattice mismatches between the III nitrides and these substrates result in a high density of dislocations, which in turn reduces the efficiency of the device. One possible solution for this problem is to substitute semiconductor nanowires for epitaxial films. Nanowires often have stress-free surfaces and similar or even better electrical and optical properties [3]. Vapor-liquid-solid (VLS) catalytic growth is one of the most common methods used to synthesize 1-D nanostructures [4]. Although ex-situ catalytic growth of gallium nitride (GaN) nanowires has been achieved [5, 6], there is not a complete understanding of the role of the catalyst, the growth mechanisms and the interface dynamics involved in this process. This work presents a dynamic observation of the nucleation and growth mechanisms of GaN nanowires which were formed by direct reaction of ammonia (NH3) with gold (Au) – gallium (Ga) alloy liquid particle.

An environmental scanning/transmission electron microscope (E(S)TEM), Tecnai F20, was used for in situ observations. Au was deposited on silicon-perforated membrane TEM ready grids by sputtering. These grids were introduced into the E(S)TEM column and heated up to 400C using a heating holder. Next, 60 mTorr of Trimethylgallium (TMG) was introduced in to the column for 3 minutes to deposit Ga particles. Subsequently, the sample temperature was increased to 800C and 40-70 mTorr of NH3 was introduced into the E(S)TEM column. Low and high magnification images and digital videos (15fps) were recorded using Gatan Orius 600SC camera. JEOL 2010F TEM/STEM was used for ex-situ imaging and chemical analysis (EDS) of the samples.

GaN nanowires grew at 800 C after 40 mTorr of NH3 was introduced. Several nanowires with different length, diameter and growth direction were observed over the whole substrate, thus growth due to electron beam effect is discarded. Figure 1 shows a sequence of frames extracted from digital video during nucleation and growth of GaN nanowires with the conditions mentioned above. Figure 2 shows a growth sequence under 70 mTorr of NH3. Diameters and lengths of the nanowires are found to be dependent on the size of the Au-Ga alloy droplet. Growth lengths also appear to depend on the Au/Ga ratio in the liquid particle. On the other hand, nanowires with diameters ranging from 10 to 35 nm have calculated growth rates from 3 to 10nm/s. Direct observations also revealed that after initial nucleation, nanowires growth continued at a decreased rate even after temperature and NH3 pressure were lowered. Figure 3 shows an energy dispersive X-ray spectrum (EDS) of a nanowire, and the inset shows the respective STEM image. This spectrum shows the presence of Ga and N which confirms the results from the electron loss energy spectroscopy (not shown) performed after growth in the E(S)TEM. Figure 4 shows the high resolution TEM (HRTEM) images of two different GaN nanowires with the respective fast Fourier transform (FFT) images in the insets confirming the wurzite structure for GaN.

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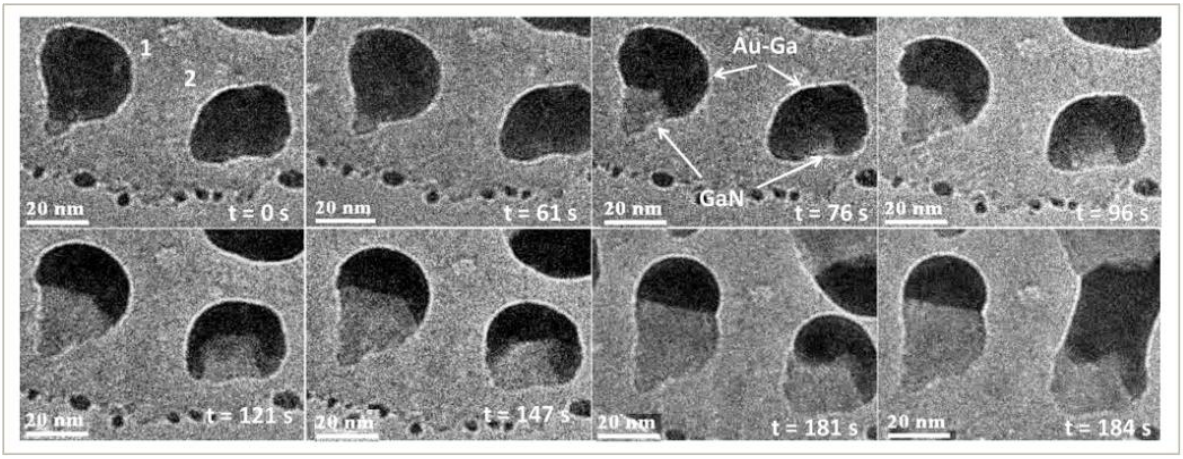

Figure 1. Sequence of frames extracted from digital video during nucleation and growth of GaN nanowires at 800C and 40mtorr of NH3.

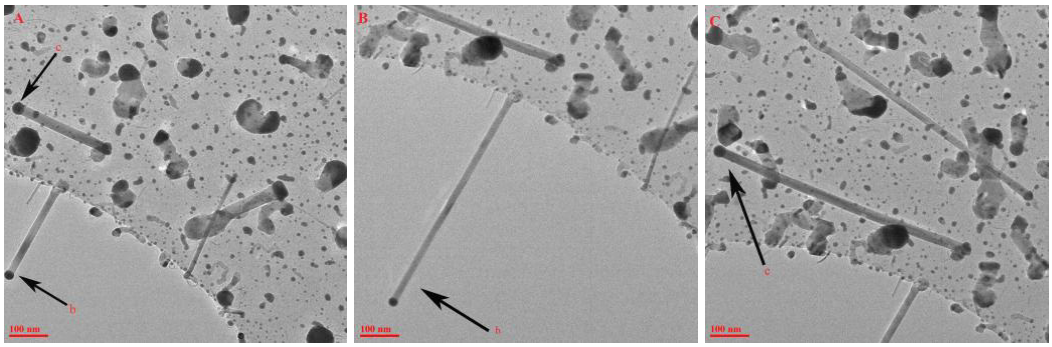

Figure 2. Low magnification TEM images of the same area, A taken 51 minutes after NH_3 was introduce, B and C taken 46 minutes after A. Note the change in length of the wire marked 'b' in (B) and the one marked c in (C).

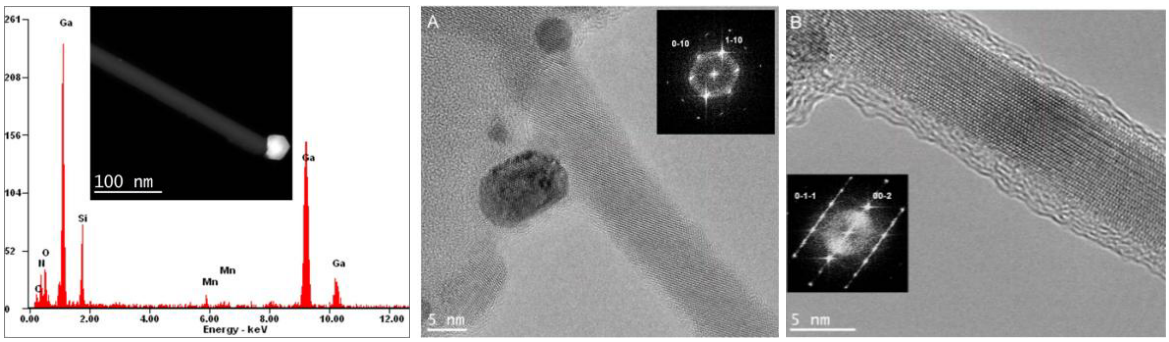

Figure 3. STEM image of a wire with its energy-dispersive x ray spectra of the wire body. FIG. 4. A and B are HRTEM images with respective FFT inset showing the wurzite structure for GaN.

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