

Direct Observation of Nucleation and Growth of III-Nitride Nanowires

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III-nitride semiconductor nanowires have great potential as building blocks for nanoscale electronic and optoelectronic devices. Important features of these semiconductor nanowires are their wide band gap and stability at high temperature. Also, due to their low dimensionality, nanowires often exhibit unique thermal, electrical, and optical properties. The synthesis of III-nitride nanowires has been reported using different growth methods such as chemical vapor deposition and metalorganic chemical vapor deposition. These methods usually use a metal catalyst to grow the nanowires, following the vapor-liquid-solid (VLS) mechanism as proposed by Wagner in 1970¹. Although this mechanism is widely accepted, there is a lack of understanding of the processes involved during nucleation and early stages of growth of III-nitride nanowires. Some questions, still to be answered are the phase of the catalyst, the nucleation sites, and the evolution of the catalyst-nanowire interface. This work reports direct observations of the nucleation and early stages of growth of GaN nanowires. The nanowires were grown by the formation of Au + Ga droplets on Si films, and their subsequent nitridation with ammonia (NH₃) at high temperature.

An environmental scanning/transmission electron microscope [E(S)TEM], Tecnai F20, was used for *in situ* observations and control, in real time, of the nucleation and growth process². First, Au was sputtered at room temperature onto Si or SiO_x film TEM grids. These grids were then transported in air and introduced into the E(S)TEM column and heated to 480°C, using a Gatan single-tilt heating holder, followed by the introduction of 53.3 Pa (400 mTorr) of trimethylgallium (TMG) into the column for 2 minutes. The sample area and delivery lines were evacuated and purged to remove TMG vapors. Next, the sample temperature was increased to 800°C and 0.1–5.3 Pa (0.1–40 mTorr) of NH₃ was introduced into the 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 of the GaN nanowires formed during the *in situ* observations.

A sequence of frames extracted from a digital video recorded during the formation of GaN nuclei is shown in Figure 1. It is interesting to note that nucleation started within the Au + Ga thin films left behind during coalescence of the droplets (marked with arrows Figure 1B), after 0.9 Pa (7 mTorr) of NH₃ was introduced into the sample area at 800°C. Another interesting observation is the multi-faceted nature of the droplet-nuclei interface in the initial stages of growth (Figure 1C) and later formation of a planar interface (Figure 1D). Figure 2 shows a growth sequence under 5.3 Pa (40mTorr) of NH₃ at 800°C. Additional GaN growth continues by step propagation on the interface (Figure 2 C, D), indicating that the solid-liquid-vapor boundary is a preferential site for N deposition and GaN nucleation. Structural analysis show that these nanowires were single crystals, with wurtzitic structure, characteristic of GaN (Figure 3A), and chemical analysis confirmed the presence of Ga and N in individual nanowires (Figure 3B). A detailed analysis of nucleation and growth kinetics will be presented.

References

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 [3] Financial support from National Science Foundation (NSF Grant # DMR0706631) and the use of LeRoy Eyring Center of Solid State Science at ASU is gratefully acknowledged.

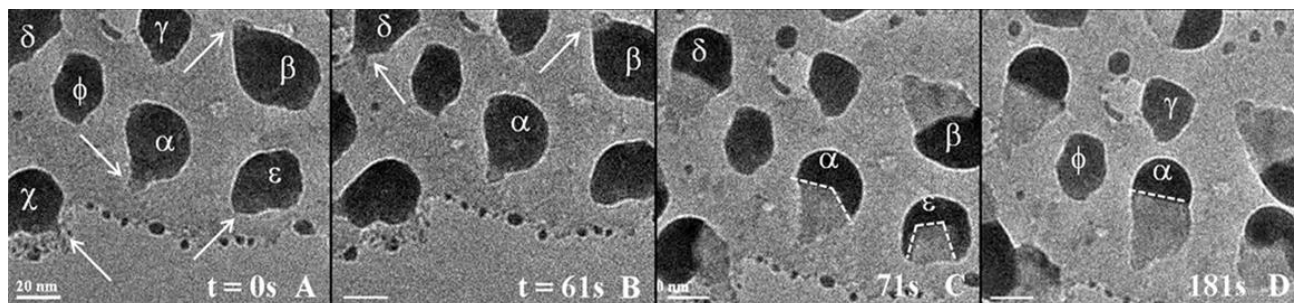


FIG. 1. Sequence of frames extracted from a digital video recorded during the nucleation of GaN nanowires. (A) Thin film regions formed during coalescence of droplets, indicated with arrows, are present at 800°C. (B) GaN nuclei form (arrows) after introducing 0.9 Pa (7mTorr) of NH_3 . (C) Multi-faceted droplet-nuclei interface in early stages of growth (α and ϵ). (D) GaN nanowire with planar interface (α), and absence GaN nuclei in solid particles (ϕ and γ).

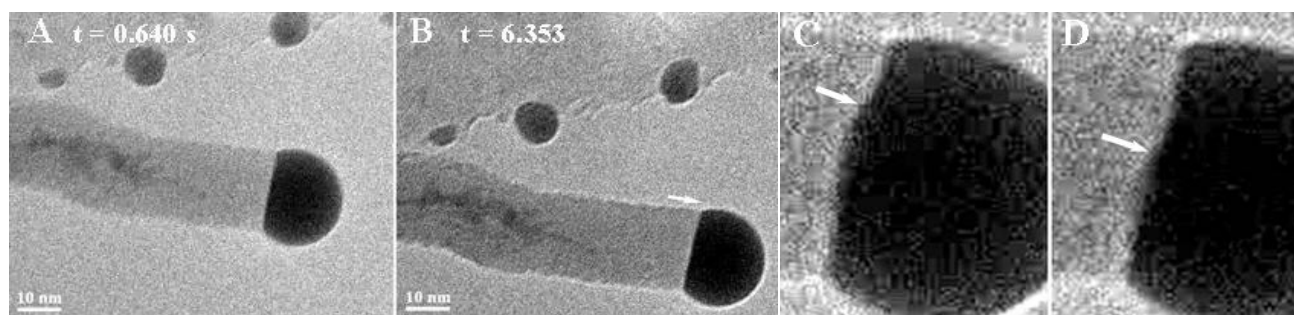


FIG. 2. Sequence of frames extracted from a digital video recorded during the growth of GaN nanowires at 800°C and 5.3 Pa (40mTorr) of NH_3 . (C) and (D) Step propagation during growth.

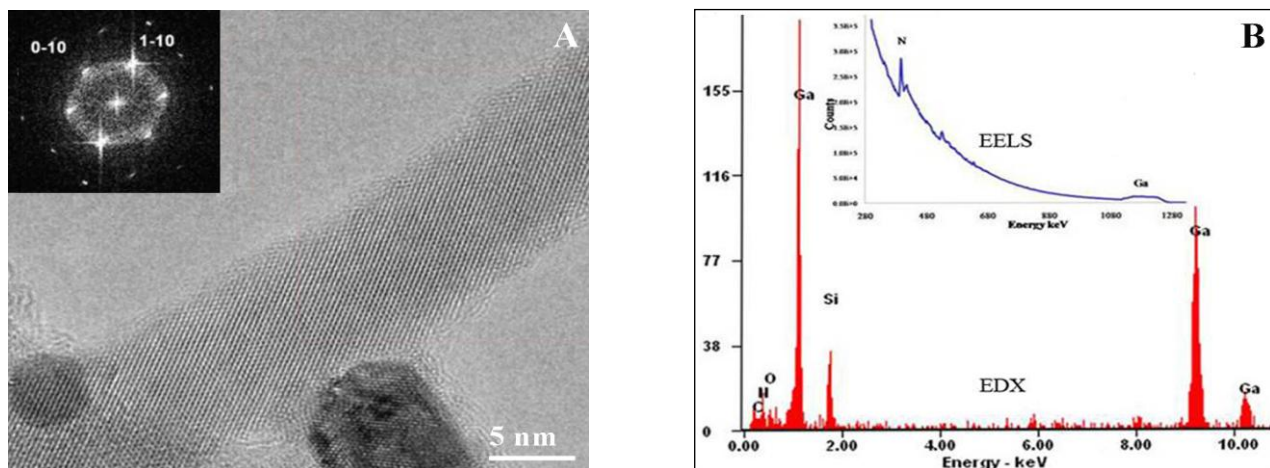


Fig. 3. (A) HREM image of a single crystal nanowire and (inset) FFT characteristic of wurzitic structure. (B) EDX and EELS spectra showing characteristic Ga and N peaks from an individual nanowire.