Atomic Resolution *in-situ* Imaging of a Double-Bilayer Multistep Growth Mode in Gallium Nitride
Nanowires

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We study the growth of GaN nanowires from liquid Au-Ga catalysts using environmental transmission electron microscopy. GaN wires grow in either $\langle 11\bar{2}0 \rangle$ or $\langle 1\bar{1}00 \rangle$ directions, by the addition of $\{1\bar{1}00\}$ double bilayers via step flow with multiple steps. Step-train growth is not typically seen with liquid catalysts, and we suggest that it results from low step mobility related to the unusual double-height step structure. The results here illustrate the surprising dynamics of catalytic GaN wire growth at the nanoscale, and highlight striking differences between the growth of GaN and other III-V semiconductor nanowires.

Keywords: Gallium Nitride, Nanowire, Environmental Transmission Electron Microscopy, Step Flow

Nitride materials have diverse applications, including blue lasers¹, light emitting diode (LED)² lighting, and radar/communications devices³. Despite the growing ubiquity of these materials in everyday technology, questions remain regarding the microscopic nature of nitride growth. GaN is the prototypical nitride. A better grasp of the fundamental materials science behind GaN crystal growth could potentially enable growth of higher quality nitride semiconductor crystals, thereby minimizing technological roadblocks. Growth of GaN nanowire (NW) structures by the catalytic vapor-liquid-solid (VLS) method is of particular interest⁴⁻⁶, as bottom up GaN NWs have crystals of exceptional quality^{4, 7, 8} and potential applications in piezo resonators⁹, light emitting diodes⁶, lasers^{10, 11}, and energy harvesting applications¹².

Nitrides are very different from other III-Vs, and numerous growth studies have investigated some of the unique features of nitride NW growth¹³⁻¹⁸. However, the microscopic details of nitride wire growth remain poorly understood. *In-situ* transmission electron microscopy (TEM) has given new insights into the fundamental materials science of Si and Ge NW growth^{19, 20} and recently also III-V systems such as GaP²¹ and InAs²²; but until now GaN NW growth has been observed *in-situ* only in preliminary low-magnification studies²³. Here we use environmental transmission electron microscopy (ETEM) to observe GaN NW growth from a liquid Au-Ga catalyst in real time, with lattice resolution. The growth interface is $\{1\bar{1}00\}$ /liquid for both $\langle 11\bar{2}0 \rangle$ and $\langle 1\bar{1}00 \rangle$ oriented wires. Our experiments reveal several features of GaN growth that are distinct from other group IV and III-V systems studied to date.

Two features of the growth are particularly surprising: growth occurs by flow of a step train, with multiple steps present simultaneously; and each step in the train has double-bilayer height. Growth by double-bilayer steps from a liquid catalyst has not to our knowledge been previously observed in any NW system. Also, NWs generally grow with only a single step present at any time²⁴. We suggest that these two striking features are intimately connected. The formation of double-bilayer steps suggests that these steps have anomalously low formation energy. Both larger step height and lower step

formation energy can naturally lead to low step mobility, as discussed later. Low step mobility in turn can account for the presence of multiple steps²⁴.

Figure 1A shows a low magnification image from an ETEM video of GaN wires growing from Au-Ga catalyst particles in a Tecnai F20 ETEM operated at 200 kV with a base pressure of $\sim 1 \times 10^{-6}$ Torr. A Protochips Aduro Heating and Electrical Biasing holder was used for sample heating. GaN wires were nucleated and grown directly on a perforated SiN heater chip (Protochips Thermal E-chips E-AHA-01). 1 – 2 nm (nominal thickness) of Au was deposited on perforated heater chips by e-beam evaporation (Kurt J. Lesker PVD 75 e-beam evaporator). The Au deposited on the grids formed nanocrystals 5 – 12 nm in diameter. A mixture of ammonia (NH₃, Air Liquide, 99.99 % purity) and trimethylgallium (TMGa, Sigma-Aldrich, 99.999 %) was used to grow the wires. The two precursors were mixed in a gas line before the leak valve. The mixing was done consistently from one experiment to another to ensure that the III-V gas ratio was roughly the same between growth runs. The sample was heated to 800 – 900 °C and held at temperature < 30 min before flowing the gas mixture into the reaction chamber. NH₃ and TMGa were flowed into the microscope using a leak valve. During experimentation, total pressure ranged from 1×10^{-4} to 3×10^{-2} Torr of NH₃ + TMGa. The pressure in our experiment was recorded using an Edwards wide range pressure gauge located outside of the microscope column. Upon gas exposure, the Au particles incorporated Ga from the TMGa to form a liquid Au-Ga eutectic alloy²⁵. After 10 – 60 s a GaN crystal nucleates in the liquid Au-Ga alloy, similar to what has been observed in prior ETEM GaN studies²⁶. The GaN wires grow by a VLS mechanism in random directions off of the nitride substrate, see Fig. 1A. Superficially, this process appears similar to what is reported in the non-epitaxial nucleation of Si²⁷ and Ge²⁸ NWs in other ETEM experiments. Some of these wires grow away from the support (as shown in Fig. 1A), allowing high resolution transmission electron microscope (HRTEM) imaging of the growth process seen in Fig. 1B. In general, the GaN wires grew straight with occasional kinks and had diameters 5 – 30 nm. Wire growth rate generally increased with increasing pressure and increasing temperature as

expected. Wire growth was observed to occur readily at 800 – 900 °C and growth ceased at temperatures below 700 °C. As 800 – 900 °C is the temperature in the literature where high quality GaN wires are synthesized^{4, 5, 18, 29, 30}, we believe our temperature is within ± 50 °C³¹ of the stated value under the experimental conditions described here.

Here we focus on a pressure of $\sim 5 \times 10^{-3}$ Torr and temperature of ~ 800 °C, as this allows us to study the fundamental mechanism by which growth occurs: the wire growth rate at this condition allowed high-resolution imaging that could easily be tracked in our videos. Wires < 150 nm long were grown in the ETEM by flowing the TMGa + NH₃ gas mixture (3×10^{-2} Torr) at 800 – 900 °C. After 1 – 2 minutes of GaN wire growth, the TMG + NH₃ gas mixture was purged from the chamber by closing the leak valve to the gas reservoir and opening the valve between the sample area and the turbo pump. Note that short wires were grown to minimize resolution loss from wire vibrations. With wire growth halted following the removal of the gaseous precursors, the newly grown wires exhibiting HRTEM phase contrast (lattice resolved) were identified while at base pressure. Such wires were selected for imaging and wire growth was restarted by opening a leak valve, introducing 5×10^{-3} Torr of precursor gas mixture into the ETEM. High resolution videos of GaN wires growing were captured using a Gatan Orius CCD and recorded at 9 frames per second (fps) and 640 × 480 pixel resolution. A few minutes of wire growth was recorded at 800 – 900 °C and $\sim 5 \times 10^{-3}$ Torr. After recording, the gas was purged from the microscope and a new wire identified for imaging. This process was repeated as many as 10 times in each individual ETEM experiment. In total, 11 ETEM experiments were carried out collecting GaN wire growth data with Au catalysts, all under similar growth conditions. Several lattice resolved GaN wire growth videos were obtained, which displayed many of the same general growth dynamics reported here. Fast Fourier transforms (FFTs) and other measurements of the GaN wires were obtained using ImageJ. Crystallographic analysis of the FFTs in comparison to theoretical electron diffraction patterns was performed using CaRine 3.1.

Our ETEM experiment described above provides real time HRTEM data of GaN NWs growing from Au-Ga catalyst particles under CVD conditions. An HRTEM image from an ETEM video is given in Fig. 1B. HRTEM data allows us to study the dynamics of CVD GaN crystal growth from a metal catalyst seed at high resolution permitting crystallographic analysis of our NWs using the FFT. Figure 2A-B shows two lattice resolved GaN NWs with a wurtzite (wz) crystal structure.

Based on the FFT spot locations in the inset in Fig. 2A (see Methods for assignment details), we conclude that the wire shown in Fig. 2A is growing in a $\langle 1\bar{1}00 \rangle$ direction. The wire in Fig. 2B is growing in a $\langle 11\bar{2}0 \rangle$ direction. The growth of our GaN wires in the $\langle 11\bar{2}0 \rangle$ and $\langle 1\bar{1}00 \rangle$ directions is consistent with prior studies of catalytic GaN NW growth¹⁸. Of all the NWs we have analyzed in this study, none were observed growing in the $[0001]$ direction. Several prior publications on catalytic GaN wire growth have noted a triangular NW cross section^{13, 18, 32}. For $\langle 11\bar{2}0 \rangle$ oriented wires the sidewalls are composed of (0001) , $(1\bar{1}0\bar{1})$, $(\bar{1}10\bar{1})$ ^{6, 29, 32} sidewall facets. For $\langle 1\bar{1}00 \rangle$ oriented wires the sidewalls are composed of (0001) , $(\bar{1}2\bar{1}2)$, $(1\bar{2}1\bar{2})$ ^{5, 9, 13} sidewall facets. Therefore, we infer from these prior studies that the sidewalls of our $\langle 11\bar{2}0 \rangle$ wires have a polar (0001) and two semi-polar $\{1\bar{1}01\}$ sidewall facets. Moreover, our $\langle 1\bar{1}00 \rangle$ oriented wires likely have a polar (0001) and two semi-polar $\{11\bar{2}2\}$ sidewall facets.

Based on the FFTs and the observed location of the liquid-solid interface in Fig 2A-B, we conclude both $\langle 11\bar{2}0 \rangle$ and $\langle 1\bar{1}00 \rangle$ oriented wires have a liquid-solid growth interface lying in the $\{1\bar{1}00\}$ plane. We note that the $\{1\bar{1}00\}$ growth plane corresponds to a non-polar surface in GaN³³. $\langle 1\bar{1}00 \rangle$ oriented wires have a growth direction that is perpendicular to this growth plane, similar to Si and other $\langle 111 \rangle$ wires where the (111) solid-liquid growth interface is perpendicular to the $[111]$ growth direction³⁴. In contrast, the wires growing in the $\langle 11\bar{2}0 \rangle$ direction have a liquid-solid interface that is at an angle to the growth direction, as illustrated in Fig. 2B. We find in these wires that the angle between the solid-liquid interface (at one catalyst-wire-vapor tri-junction) and one of the wire sidewalls is often measured at $110^\circ - 120^\circ$. Based on the wz crystal structure, we find the $(10\bar{1}0)$ plane lies at a 30° angle

to the $[11\bar{2}0]$ direction, when viewed down the $[0001]$ axis. This results in a 120° angle between the sidewall and liquid-solid interface plane when viewed down the $[0001]$ direction. The angle at the other tri-junction in $\langle 11\bar{2}0 \rangle$ oriented wire is 60° when viewed down the $[0001]$ axis. We note that when viewing the wire down different axes, it is possible to measure angles less than the maximum sidewall-interface angle of 120° (ex: the $[2\bar{4}2\bar{3}]$ imaging axis for the wire in Fig. 2B, where the sidewall-interface angle is 110°). The non-orthogonal growth direction/plane for our $\langle 11\bar{2}0 \rangle$ oriented GaN wires is similar to $\langle 110 \rangle$ Si wires where the growth interface is observed as a $\{111\}$ /liquid interface^{35, 36}.

In addition to showing the growth plane present at the solid-liquid interface of the GaN wire, our ETEM data also allows us to observe the evolution of the wire-catalyst growth interface during wire kinking. In our data, GaN wires sometimes kink at an angle of 30° without changing their growth plane. Figure 2C-E shows a series of ETEM images of GaN wire kinking behavior. In Fig. 2C the angle between the wire sidewall and growth is measured at 111° , indicating it is likely $\langle 11\bar{2}0 \rangle$ oriented. At time 12.9 s (Fig. 2D) the wire's growth direction and sidewall facets change. At 30.2 s (Fig. 2E) the wire has assumed a new growth direction with an angle between the sidewall and growth interface of 90.3° , close to the expected right angle between the sidewall/growth plane expected for a $\langle 1\bar{1}00 \rangle$ oriented wire. During the kinking process (Fig. 2D), the wire sidewalls appear to change to an intermediate growth direction (while still retaining the $\{1\bar{1}00\}$ /liquid growth plane) before completing the transition from $\langle 11\bar{2}0 \rangle$ to $\langle 1\bar{1}00 \rangle$ oriented NW growth. Despite changing growth orientation from a $\langle 11\bar{2}0 \rangle$ to a $\langle 1\bar{1}00 \rangle$ direction, the solid/liquid growth interface remains $\{1\bar{1}00\}$ /liquid. The crystal structure of a $\langle 11\bar{2}0 \rangle$ to $\langle 1\bar{1}00 \rangle$ oriented kinked wire (without an intermediate growth orientation transition) is shown in Fig. 2F with a ball and stick crystal model viewed in the $[000\bar{1}]$ direction. The $\langle 11\bar{2}0 \rangle$ oriented part of the wire is given in blue/black atom model, and the $\langle 1\bar{1}00 \rangle$ oriented segment of the wire is given in the red/grey atom model. The $\{1\bar{1}00\}$ bilayer at the solid-liquid growth interface is traced by a broken black line in Fig. 2F.

In common with prior NW studies^{20, 21, 24}, we see growth by step flow. However, the step flow dynamics appear strikingly different in GaN than in other NW systems. VLS wire growth nearly always occurs by the flow of single bilayer steps²⁴. Figure 3A is an image from an ETEM video showing a GaN wire, likely $\langle 11\bar{2}0 \rangle$ oriented based on the angle of the liquid-solid interface, growing with multiple steps at the catalyst-wire interface. Figure 3A is taken from an ETEM video capturing wire growth (Video S1, 9 fps). In Fig. 3A the GaN wire is growing into (or out of) the imaging plane allowing an off axis view of the catalyst-wire interface. Three steps are visible, each indicated by a white arrow in Fig. 3A. The steps are observed to propagate across the wire-catalyst interface during growth. During the entire course of the video two steps or more are generally observed at the growth interface.

A different GaN wire in Fig. 3B-E shows the multi-step flow wire growth process at higher magnification in a $\langle 1\bar{1}00 \rangle$ oriented wire. The uncropped ETEM video of the wire in Fig. 3B-E is Video S2. The NW in Fig. 3B-E is viewed down the $[\bar{1}\bar{1}23]$ imaging axis. Based on the FFT and full micrograph of the GaN wire (not shown), the wire is growing into (or out of) the plane at 26.4° with respect to the imaging axis. Details of the crystallographic analysis for the wire in Fig. 3B-E are found in Crystallography S3. In Fig. 3B a crystal step is initially formed, indicated by the red arrow. The measured projected step height is roughly 0.6 nm (shown in Fig. 3B). We correct for measured step height enlargement in projection of the wire step height (associated with growth at 26.4° into/out of the imaging plane) by multiplying the measurement by $\cos(26.4^\circ) = 0.896$. This gives us the value of 0.5 nm for the true step height. This corresponds to twice the $\{1\bar{1}00\}$ bilayer spacing (0.276 nm), within our uncertainty.

To our knowledge, no previous *in-situ* studies report wire growth by step of height greater than a single bilayer in VLS growth, though there have been reports during the vapor-solid-solid (VSS) growth of Si NWs²⁰. In VLS, only single-bilayer steps have been seen. Yet strikingly, for GaN we uniformly see growth by steps of double-bilayer height, for both $\langle 1\bar{1}00 \rangle$ and $\langle 11\bar{2}0 \rangle$ wires. Out of 13 observations of single-crystal defect-free NWs, we saw only one instance of single-bilayer steps – the GaN wire shown in

Fig. 1B. Growth by double bilayers has been reported in *in-situ* molecular beam epitaxy scanning tunneling microscopy experiments on GaN (0001)³⁷. For (0001), successive bilayer steps alternate in structure, giving them different step-flow velocities leading to kinetic pairing of single-bilayer steps into double-bilayer steps³⁷. In contrast, for the $\{1\bar{1}00\}$ growth plane of our GaN NWs, successive bilayer steps are equivalent. Thus the formation of double-bilayer steps must have a different origin here.

As wire growth continues beyond 0.0 s in Fig. 3B the double $\{1\bar{1}00\}$ bilayer step flows across the GaN liquid-solid interface, Fig. 3C. Before the step reaches the other edge of the wire, a second step appears on the right side of the wire near the tri-junction, indicated by the blue arrow Fig. 3D. This new step continues to flow across the wire-catalyst interface Fig. 3E. Based on measurements from the ETEM data in Fig. 3B-E, we estimate the GaN steps growth speed at 3 nm/s. In contrast, prior observations of VLS growth show step flow so fast that it cannot be resolved at video rates of 9 fps for Ge³⁸ or 30 fps for GaP²¹. We also observe that GaN, unlike Ge and GaP NWs, lacks a significant “incubation time” between the appearance of one step and nucleation of the next step. In the videos associated with Fig. 3A and Fig. 3B-E (Supporting Video S1 and Video S2 respectively), steps nucleate readily forming every 1 – 3 seconds while other steps are still present at the liquid-solid growth interface. No *in-situ* studies we are aware of have reported NWs in any other system growing from a liquid catalyst by simultaneous flow of multiple steps as shown in Fig. 3. Intriguingly, multiple simultaneous steps have been noted in VSS Si NW growth²⁰.

Previous *in-situ* studies of Si, Ge, and GaP NWs have almost invariably observed that VLS growth involves the flow of a single step at the liquid-solid interface, with a new step nucleating only after the previous step has disappeared by completing a layer. The reason that only a single step is present in most systems is that a step can flow rapidly enough to absorb all the incoming material. Thus, the supersaturation doesn't rise high enough to nucleate another step until the first step disappears. However, if the step mobility is too low, the step won't move rapidly enough and the supersaturation

will increase until one or more additional steps nucleate to absorb the incoming material. As discussed in Ref.[24], this will occur if

$$k\Delta\mu_c \ll \frac{\alpha PR}{b} \quad \text{Eqn. 1}$$

In Eqn. 1 P is the precursor partial pressure, R is the wire radius, and b is the step height. The step mobility k governs the velocity of step propagation $v = k\Delta\mu$. $\Delta\mu$ is the supersaturation, the difference between the chemical potentials of the semiconductor constituents in the liquid catalyst and solid NW. α , as defined in Ref.[24], is the geometrically weighted kinetic coefficient reflecting the capture of material from the gaseous precursor, as the term αPR^2 describes the arrival rate of material at the catalyst. The term $\Delta\mu_c$ is the supersaturation required for step nucleation. Step nucleation is essentially a statistical process³⁹. However, the nucleation rate increases exponentially with rising supersaturation⁴⁰. There is a narrow range of $\Delta\mu$ where nucleation goes from being negligibly slow to a very fast process. Eqn. 1 represents a simplification, approximating this range of supersaturation values by a single value $\Delta\mu_c$, ie. the “critical” supersaturation.

We can't be certain which factor in Eqn. 1 makes GaN wire growth different from other NW systems, but we have a strong clue in the observation of double-bilayer steps. Growth by double bilayers is unexpected and striking. A possible explanation for such double bilayers is that they could have lower energy than two separate bilayer steps, presumably reflecting some associated reconstruction or relaxation. In the framework of a continuum step nucleation model, nucleation of double-bilayer steps is kinetically favored over single-bilayer steps only if $\lambda_2 < \sqrt{2}\lambda_1$, where λ_1 and λ_2 are the effective line energies for single-bilayer and double-bilayer steps, respectively; see Derivation S4 for details. This is more stringent than the condition $\lambda_2 < 2\lambda_1$ for single-bilayer steps to bind into double-bilayer steps; see Derivation S4 for details. The increased step height could naturally lead to lower step mobility k , by raising the activation barrier for step motion, simply because the unit for kink formation and migration is larger than for a single-bilayer step.

In conclusion, we have used lattice-resolved ETEM observations of GaN wire growth from liquid Au-Ga catalyst particles to elucidate the wire structure and growth mechanism. The wires have a wz crystal structure and grow in either $\langle 11\bar{2}0 \rangle$ or $\langle 1\bar{1}00 \rangle$ directions. We capture wire kinking and note that the interface between the liquid catalyst and the wire remains $\{1\bar{1}00\}$ during the kinking process. We observe that wire growth in either of these two directions nearly always occurs via a multi-step flow mechanism, with double-bilayer steps, and we resolve the transit of the steps across the catalyst-wire interface. We suggest that NW growth by multiple steps is due to the low mobility of double bilayer steps. These results illustrate how *in-situ* TEM can capture the atomistic details of NW nitride crystal growth, observing processes typically inaccessible to *ex-situ* studies, and highlighting the key differences between GaN and other group IV and III-V NW growth mechanisms.

Methods:

The FFT of the wire body is shown in the upper right inset of both Fig. 2A and B. The FFT inset in Fig. 2A matches a GaN wz crystal structure with lattice parameters $a = b = 3.186 \text{ \AA}$, $c = 5.186 \text{ \AA}$, and symmetry group $P6_3mc$ viewed down the $[\bar{2}11\bar{3}]$ imaging axis. The percent deviation between the ratios of reciprocal distances (d-spacing) R was computed using the following formula $(R_M/|R_T - R_M|) \times 100 \%$, where R_T and R_M correspond to the theoretical and measured d-spacing ratios respectively. A similar formula was used to compute the percent deviation in the between predicted and measured angle ratios. The assignment of the FFT spots is within $< 4 \%$ deviation in angles and $< 3.5 \%$ deviation in d -spacings respectively. The FFT inset in Fig. 2B of the GaN wire matches the spot pattern associated with wz GaN viewed down the $[2\bar{4}2\bar{3}]$ imaging axis. The percent deviation between the theoretical and measured angles and d -spacing is $< 1 \%$ and $< 3.1 \%$ respectively. Our ETEM setup limits us to FFTs of a single crystallographic projection, rather than a more rigorous multiple-axis approach. All of the defect free wires we analyzed from our ETEM study showed a GaN wz crystal structure.

Supporting Information:

Video S1: An ETEM video of the GaN wire growing in Fig. 3A.

Video S2: The full uncropped video showing the GaN NW growing by a step-flow mechanism in Fig. 3B-E.

Crystallography S3: Crystal structure analysis and orientation of the wire shown in Fig. 3B-E.

Derivation S4: Derivation of the inequality $\lambda_2 < \sqrt{2}\lambda_1$.

Author Information:

The authors declare no competing financial interest.

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Figure 1: A) A low magnification micrograph of a GaN NW growing in an ETEM at 800 °C and 5.5×10^{-2} Torr of $\text{NH}_3 + \text{TMGa}$. B) An HRTEM micrograph of a GaN wire growing from an Au-Ga catalyst particle in a different ETEM experiment, but under comparable conditions, at 2×10^{-3} Torr and 800 °C.

Figure 2: An HRTEM micrograph from an ETEM video of an A) $\langle 1\bar{1}00 \rangle$ oriented GaN growing in 2×10^{-3} Torr of $\text{NH}_3 + \text{TMGa}$ at 800°C and B) $\langle 11\bar{2}0 \rangle$ oriented GaN wire growing in 8×10^{-3} Torr of $\text{NH}_3 + \text{TMGa}$ at 800°C . Note that the scale bar for (A) and (B) are identical. The FFT associated with the wires is given as an inset in (A) and (B) for the $\langle 1\bar{1}00 \rangle$ and the $\langle 11\bar{2}0 \rangle$ wires respectively. The assignments in the FFT based on the angles between the spots and the relative measured distances of the spots viewed down the $[\bar{2}11\bar{3}]$ and $[2\bar{4}2\bar{3}]$ for the wires in (A) and (B) respectively. C) 0.0 s wire growth in 3.8×10^{-2} Torr and 850°C . Based on the measured angle between the wire sidewall and the catalyst-wire interface (111°) this NW is likely growing in a $\langle 11\bar{2}0 \rangle$ direction. D) At 12.9 s into the video we find the orientation of the wire has changed until later at E) 30.2 s wire growth continues in a new direction, presumably the $[1\bar{1}00]$

growth direction based on the measured sidewall catalyst-wire interface (90.3°). F) A ball and stick crystal growth model illustrating the crystal structure of a kinked wire. Here the wire segment corresponding to the initial $[2\bar{1}\bar{1}0]$ growth direction is illustrated by the model with the blue and black atoms. The subsequent section of the wire grown in the $[1\bar{1}00]$ direction is indicated by the segment of the crystal with the red-grey atoms. The location of the $\{1\bar{1}00\}$ plane at the solid-liquid growth interface is traced by the broken black line.

Figure 3: A) Images from an ETEM video of a GaN wire growing in 3×10^{-2} Torr of $\text{NH}_3 + \text{TMGa}$ at 800°C . In this figure multiple steps are observed at the catalyst-wire interface. These steps are indicated by the white arrows. B) 0.0 s another GaN wire ($\langle 1\bar{1}00 \rangle$ oriented) growing in 5×10^{-4} Torr of $\text{NH}_3 + \text{TMGa}$ at 800°C . This wire is growing at 26.4° into (or out of) the imaging plane based on the spots in the FFT and sidewall plane location (see Crystallography S3 for more details). The projected step height is measured (indicated by the two red arrows) at roughly 0.6 nm. C) 1.1 s the newly nucleated step continues to grow across the catalyst-wire interface, its position indicated by the red arrow. D) 2.0 s as the initial step (indicated by the red arrow) approaches the other end of the wire a second step nucleates on top of the newly formed GaN layer, indicated by the blue arrow. E) The step originally formed at 0.0 s grows to the edge of the wire as the step nucleated earlier at 2.0 s continues to expand across the catalyst-wire growth interface. The arrows shown in B-E illustrate the approximate locations of the GaN double

bilayer growth plane. The exact trajectory of these planes cannot be determined unambiguously as this process is not viewed perpendicular to the growth direction.

ToC Figure

References

1. Nakamura, S.; Senoh, M.; Nagahama, S.-i.; Iwasa, N.; Yamada, T.; Matsushita, T.; Kiyoku, H.; Sugimoto, Y.; Kozaki, T.; Umemoto, H.; Sano, M.; Chocho, K. *Appl. Phys. Lett.* **1998**, *72*, 2014-2016.
2. Nakamura, S.; Mukai, T.; Senoh, M. *Appl. Phys. Lett.* **1994**, *64*, 1687-1689.
3. Mishra, U. K.; Shen, L.; Kazior, T. E.; Yi-Feng, W. *Proc. IEEE* **2008**, *96*, 287-305.
4. Huang, Y.; Duan, X.; Cui, Y.; Lieber, C. M. *Nano Lett.* **2002**, *2*, 101-104.
5. Kuykendall, T.; Pauzauskie, P. J.; Zhang, Y.; Goldberger, J.; Sirbuly, D.; Denlinger, J.; Yang, P. *Nat. Mater.* **2004**, *3*, 524-528.
6. Qian, F.; Gradečak, S.; Li, Y.; Wen, C.-Y.; Lieber, C. M. *Nano Lett.* **2005**, *5*, 2287-2291.
7. Ertekin, E.; Greaney, P. A.; Chrzan, D. C.; Sands, T. D. *J. Appl. Phys.* **2005**, *97*, 114325.
8. Colby, R.; Liang, Z.; Wildeson, I. H.; Ewoldt, D. A.; Sands, T. D.; García, R. E.; Stach, E. A. *Nano Lett.* **2010**, *10*, 1568-1573.
9. Nam, C.-Y.; Jaroenapibal, P.; Tham, D.; Luzzi, D. E.; Evoy, S.; Fischer, J. E. *Nano Lett.* **2006**, *6*, 153-158.
10. Gradečak, S.; Qian, F.; Li, Y.; Park, H.-G.; Lieber, C. M. *Appl. Phys. Lett.* **2005**, *87*, 173111.
11. Johnson, J. C.; Choi, H.-J.; Knutsen, K. P.; Schaller, R. D.; Yang, P.; Saykally, R. J. *Nat. Mater.* **2002**, *1*, 106-110.
12. Huang, C.-T.; Song, J.; Lee, W.-F.; Ding, Y.; Gao, Z.; Hao, Y.; Chen, L.-J.; Wang, Z. L. *J. Am. Chem. Soc.* **2010**, *132*, 4766-4771.
13. Kuykendall, T.; Pauzauskie, P.; Lee, S.; Zhang, Y.; Goldberger, J.; Yang, P. *Nano Lett.* **2003**, *3*, 1063-1066.
14. Geelhaar, L.; Chèze, C.; Weber, W. M.; Averbek, R.; Riechert, H.; Kehagias, T.; Komninou, P.; Dimitrakopoulos, G. P.; Karakostas, T. *Appl. Phys. Lett.* **2007**, *91*, 093113.
15. Chèze, C.; Geelhaar, L.; Jenichen, B.; Riechert, H. *Appl. Phys. Lett.* **2010**, *97*, 153105.
16. Chèze, C.; Geelhaar, L.; Trampert, A.; Brandt, O.; Riechert, H. *Nano Lett.* **2010**, *10*, 3426-3431.
17. Lim, S. K.; Crawford, S.; Haberer, G.; Gradečak, S. *Nano Lett.* **2013**, *13*, 331-336.
18. Kuykendall, T. R.; Altoe, M. V. P.; Ogletree, D. F.; Aloni, S. *Nano Lett.* **2014**, *14*, 6767-6773.
19. Ross, F. M. *Rep. Prog. Phys.* **2010**, *73*, 114501.
20. Hofmann, S.; Sharma, R.; Wirth, C. T.; Cervantes-Sodi, F.; Ducati, C.; Kasama, T.; Dunin-Borkowski, R. E.; Drucker, J.; Bennett, P.; Robertson, J. *Nat. Mater.* **2008**, *7*, 372-375.
21. Chou, Y.-C.; Hillerich, K.; Tersoff, J.; Reuter, M. C.; Dick, K. A.; Ross, F. M. *Science* **2014**, *343*, 281-284.
22. Lenrick, F.; Ek, M.; Deppert, K.; Samuelson, L.; Reine Wallenberg, L. *Nano Res.* **2014**, *7*, 1188-1194.
23. Stach, E. A.; Pauzauskie, P. J.; Kuykendall, T.; Goldberger, J.; He, R.; Yang, P. *Nano Lett.* **2003**, *3*, 867-869.
24. Wen, C. Y.; Tersoff, J.; Reuter, M. C.; Stach, E. A.; Ross, F. M. *Phys. Rev. Lett.* **2010**, *105*, 195502.
25. Elliott, R.; Shunk, F. *Bull. of Alloy Phase Diagrams* **1981**, *2*, 356-358.
26. Diaz, R. E.; Sharma, R.; Jarvis, K.; Zhang, Q.; Mahajan, S. *J. Cryst. Growth* **2012**, *341*, 1-6.
27. Kim, B. J.; Tersoff, J.; Kodambaka, S.; Reuter, M. C.; Stach, E. A.; Ross, F. M. *Science* **2008**, *322*, 1070-1073.
28. Gamalski, A. D.; Tersoff, J.; Sharma, R.; Ducati, C.; Hofmann, S. *Nano Lett.* **2010**, *10*, 2972-2976.
29. Li, Q.; Wang, G. T. *Nano Lett.* **2010**, *10*, 1554-1558.
30. Espinosa, H. D.; Bernal, R. A.; Filleter, T. *Small* **2012**, *8*, 3233-3252.
31. Picher, M.; Mazzucco, S.; Blankenship, S.; Sharma, R. *Ultramicroscopy* **2015**, *150*, 10-15.
32. Huang, J. Y.; Zheng, H.; Mao, S. X.; Li, Q.; Wang, G. T. *Nano Lett.* **2011**, *11*, 1618-1622.

33. Northrup, J. E.; Neugebauer, J. *Phys. Rev. B* **1996**, 53, R10477-R10480.
34. Ross, F. M.; Tersoff, J.; Reuter, M. C. *Phys. Rev. Lett.* **2005**, 95, 146104.
35. Schwarz, K. W.; Tersoff, J.; Kodambaka, S.; Chou, Y. C.; Ross, F. M. *Phys. Rev. Lett.* **2011**, 107, 265502.
36. Kodambaka, S.; Hannon, J. B.; Tromp, R. M.; Ross, F. M. *Nano Lett.* **2006**, 6, 1292-1296.
37. Xie, M. H.; Seutter, S. M.; Zhu, W. K.; Zheng, L. X.; Wu, H.; Tong, S. Y. *Phys. Rev. Lett.* **1999**, 82, 2749-2752.
38. Gamalski, A. D.; Ducati, C.; Hofmann, S. J. *Phys. Chem. C* **2011**, 115, 4413-4417.
39. Glas, F.; Harmand, J.-C.; Patriarche, G. *Phys. Rev. Lett.* **2010**, 104, 135501.
40. Porter, D. A.; Easterling, K. E.; Sherif, M. Y., *Phase Transformations in Metals and Alloys*. CRC Press: Boca Raton, FL, 2009.

Supplementary Information

Atomic Resolution *in-situ* Imaging of a Double-Bilayer Multistep Growth Mode in Gallium Nitride

Nanowires

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Crystallography of the Wire in Fig. 3B-E:

An environmental transmission electron microscope (ETEM) image of the wire shown in Fig. 3B-E is given in Fig. S1A. The fast Fourier transform (FFT) of this wire is provided in the inset of Fig. S1A. A model of a $\langle 1\bar{1}00 \rangle$ wire was constructed in CaRine 3.1 for a wurtzite GaN nanowire (NW) with sidewall facets corresponding to (0001) , $(\bar{1}2\bar{1}\bar{2})$, $(1\bar{2}1\bar{2})$ ¹⁻³ planes. An orientation that both matches the angles and d-spacings in the observed wire in Fig. S1A is the $[\bar{1}\bar{1}23]$ axis. The $[\bar{1}\bar{1}23]$ axis provides a < 4% discrepancy between the measured and predicted d-spacing values and a < 1.25% discrepancy between the measured and predicted angles (see methods section in the manuscript for details on how discrepancies are calculated).

The NW orientation shown in Fig. S1B that matches the FFT and projected angles in Fig. S1A, is actually growing into the page slightly at an angle of 26.4°. The orientation of the NW relative to the e-beam and image plane is shown in Fig S1C. Wire growth slightly into or out of the image plane viewed down the $[\bar{1}\bar{1}23]$ axis best explains the angle between the catalyst-growth interface and the sidewall

(measured at 97.6° and predicted at 98.1°) and provides a reasonable match with the FFT spot pattern d-spacing associated with the lattice resolved NW. Based on Fig. S1 and the analysis of the FFT, we can conclude the wire in Fig. 2B-E is $\langle 1\bar{1}00 \rangle$ oriented.

Figure S1: A) An ETEM image of the GaN NW shown in Fig. 2B-E. The FFT of the GaN NW is provided in the image inset. The angle between the liquid-solid growth interface plane and wire sidewall is also shown. B) A $\langle 1\bar{1}00 \rangle$ NW model constructed in CaRine 3.1 with (0001), $(\bar{1}2\bar{1}\bar{2})$, $(1\bar{2}1\bar{2})$ sidewalls. This wire orientation produces an electron diffraction spot pattern than matches (A) viewed down the $[\bar{1}\bar{1}23]$ direction and also reproduced the liquid-solid growth interface sidewall angle (also indicated). C) The wire in the orientation shown in Fig. S1B is growing into the page 26.4°. The orientation of the wire, image plane, and electron beam are indicated.

Edge Energy and Nucleation for Single vs Double Bilayers:

In nucleating a new layer on the growth facet, the free energy for forming an “island” (partial layer) of area A bounded by a step (denoted ΔG) is⁴

$$\Delta G = \sqrt{A}\lambda_{\text{eff}} - \frac{Ab\Delta\mu}{\Omega} \quad \text{Eqn. S1}$$

Here b is the step height, Ω is the bi-atomic volume, and $\Delta\mu$ is the supersaturation for the Ga + N bi-atomic pair (which in NW growth is the difference between chemical potentials for a Ga + N pair in the liquid and in the solid, $\Delta\mu = \mu_L - \mu_S$). We are concerned with nucleation, which involves very small islands, so we can assume that the island shape is approximately independent of area A . λ_{eff} is the effective step

energy, i.e. energy per unit length of the island edge times a shape-dependent geometrical factor. λ_{eff} includes the line energy of the step on the growth facet, surface energy associated with extending the wire sidewall (if nucleation occurs at the edge as expected), and the geometrical relationship between the perimeter and area. The barrier for step formation, which we denote ΔG^* , corresponds to the maximum value of ΔG , which from Eqn. S1 is

$$\Delta G^* = \frac{\Omega \lambda_{\text{eff}}^2}{4b\Delta\mu} \quad \text{Eqn. S2}$$

Only double-bilayer steps are observed in our ETEM experiment. This suggests that the barrier for step formation associated with a double bilayer (denoted ΔG_2^*) is lower than the barrier for a single bilayer (denoted ΔG_1^*), i.e. $\Delta G_2^* < \Delta G_1^*$. Letting b_0 denote the height of a single bilayer and using Eqn. S2, we can calculate the energy barriers to nucleate single and double bilayer steps,

$$\Delta G_1^* = \frac{\Omega \lambda_1^2}{4b_0\Delta\mu} ; \quad \Delta G_2^* = \frac{\Omega \lambda_2^2}{8b_0\Delta\mu} \quad \text{Eqn. S3}$$

Here λ_1 and λ_2 are the effective edge energies for the single and double bilayer respectively. Thus the inequality $\Delta G_2^* < \Delta G_1^*$ implies that

$$\lambda_2 < \sqrt{2}\lambda_1 \quad \text{Eqn. S4}$$

In other words, in the framework of our continuum model described above, the effective edge energy of the double bilayer step λ_2 must be less than $\sqrt{2}$ times the effective edge energy of a single bilayer λ_1 for double bilayer formation to preferentially occur. Double bilayer steps are energetically favorable whenever $\lambda_2 < 2\lambda_1$, relative to two single bilayers, so we cannot rule out the possibility that single steps nucleate and then coalesce into double steps. However, since double bilayer formation is consistently observed in our ETEM data, this suggests that double-bilayer steps nucleate directly, requiring that the more stringent condition of Eqn. S4 is met.

References:

1. Nam, C.-Y.; Jaroenapibal, P.; Tham, D.; Luzzi, D. E.; Evoy, S.; Fischer, J. E. *Nano Lett.* **2006**, 6, (2), 153-158.

2. Kuykendall, T.; Pauzauskie, P. J.; Zhang, Y.; Goldberger, J.; Sirbuly, D.; Denlinger, J.; Yang, P. *Nat. Mater.* **2004**, 3, (8), 524-528.
3. Kuykendall, T.; Pauzauskie, P.; Lee, S.; Zhang, Y.; Goldberger, J.; Yang, P. *Nano Lett.* **2003**, 3, (8), 1063-1066.
4. Howe, J. M., *Interfaces in Materials*. John Wiley & Sons, Inc.: New York, 1997.