

Direct observation of nucleation and early stages of growth of GaN nanowires

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Abstract

We report for the first time direct observations of the nucleation and early stages of growth of GaN nanowires. The nanowires were formed by exposing Au + Ga droplets to ammonia. The formation process was observed *in situ*, and controlled in real time using an environmental transmission electron microscope. Observations show that the nucleation starts at thin regions of the droplets as they supersaturate with nitrogen. The droplet-nanowire interfaces in the initial stages are multi-faceted, and become planar during the growth. Chemical and structural analysis shows that the resulting nuclei are GaN with the wurtzitic structure.

Keywords

A1. Nucleation

B1. GaN nanowires

A1. In situ TEM

A3. Chemical vapor deposition process

A3. Vapor-Liquid-Solid mechanism

B1. Au catalyst

1. Introduction

Due to their special characteristics, the group III nitride semiconductors have attracted considerable interest for applications in a number of optoelectronics devices, such as light emitting diodes, solid state lasers, and ultraviolet detectors. The binary nitrides have direct band gaps and can emit at wavelengths from the ultraviolet to the infrared. Another important feature is their stronger bond length relative to the other compound semiconductors, which make them thermally more stable [1,2].

Multi-layer epitaxial structures required for various devices are generally grown on (0001) sapphire and silicon carbide substrates. As-grown films have high dislocation densities, which in turn reduce the efficiency and life time of the device [1]. One possible solution is to substitute single crystal semiconductor nanowires for epitaxial films. Due to their low dimensionality, nanowires often exhibit

unique thermal, electrical, and optical properties [3,4]. In particular, GaN nanowires have shown great potential for nanoscale devices and interconnects [5,6,7].

The synthesis of GaN nanowires has been reported using different growth methods such as laser ablation [8], chemical vapor deposition [9,10], and metalorganic chemical vapor deposition (MOCVD) [11]. Most of these methods use a metal catalyst to grow the nanowires, following the vapor-liquid-solid (VLS) mechanism first proposed by Wagner in 1964 [12]. Although this mechanism is widely accepted, there is a lack of understanding of the processes involved during nucleation and early stages of growth of GaN nanowires. Some questions, still to be resolved, concern the phase of the catalyst, the nature of nucleation sites, and the evolution of the catalyst-nanowire interface.

In situ observations on self-catalytic growth of GaN nanowires have been reported by Stach et al [13]. GaN nanowires were formed by decomposing a GaN film at high temperature inside a transmission electron microscope (TEM) column. The decomposition of the GaN film produced Ga droplets and Ga/N vapor species. Then, Ga droplets dissolved N from the vapor, resulting in GaN nanowires. Although this is an interesting observation and a novel technique to synthesize GaN nanowires, they were not able to observe the nucleation events or early stages of growth of the nanowires.

Recently, Hoffman et al. [14] and Kim et al. [15] have shown that *in situ* observations of nucleation events using a TEM can provide unambiguous insight into the nucleation of nanowires; in these cases Si. In both studies the growth process followed several steps: 1) disilane (Si_2H_6) introduction into the TEM column, 2) Si_2H_6 adsorption and dissociation at metal catalyst interface, and 3) Si supersaturation of the metal catalyst and later nucleation of solid Si on the edge of the metal-Si catalyst particle. Even though these early studies showed that *in situ* electron microscopy is a powerful tool to study the nucleation of semiconductor nanowires, they only focused on the formation of solid Si from Au-Si and Pd-Si catalyst particle. In both cases, the only reaction involved was the dissociation of Si_2H_6 at the surface of the catalyst. In the present study, we prove that a more complicated system, i.e., a system with more than one reaction involved during the growth of compound semiconductor nanowires, can be

investigated, but requires both a careful design of the experiments and precise control of the introduction of gas precursors.

2. Experimental Setup

An environmental scanning/transmission electron microscope [E(S)TEM], FEI Tecnai F-20^{*}, was employed for the simultaneous acquisition of atomic level chemical and structural information at elevated temperatures [16], and to introduce different gases into the sample area. First, Au was sputtered at room temperature onto porous polycrystalline Si film (200 μm thickness) TEM grids. The Si grids were not pretreated to remove oxide layers prior Au deposition. These grids were then transported in air and introduced into the E(S)TEM column and heated to 480 $^{\circ}\text{C}$, using a Gatan single-tilt heating holder^{*} ($T_{\text{max}} = 900$ $^{\circ}\text{C}$). This was followed by the introduction of 53.33 Pa (400 mTorr) of trimethylgallium (TMG) into the column for 2 minutes. The sample area and delivery lines were evacuated and purged to remove any residual TMG vapor. Next, the sample temperature was increased to 800 $^{\circ}\text{C}$ and 0.13 Pa to 5.33 Pa (0.1 mTorr to 40 mTorr) of ammonia (NH_3) was introduced into the E(S)TEM column. Low and high magnification images and digital videos with 15 frames per second time resolution were recorded using a digital video camera. A TEM/STEM JEOL F2010^{*} was used for *ex situ* imaging and chemical analysis of the GaN nanowires formed during the *in situ* observations.

3. Results and Discussion

Figure 1 shows a TEM image of Au particles deposited on a polycrystalline Si film after heating the sample to 480 $^{\circ}\text{C}$. The speckle contrast in the high resolution electron microscopy (HREM) image (inset lower right hand corner in Figure 1) is characteristic of amorphous layers. There is no pre-treatment of the polycrystalline Si film before Au deposition or before introduction in the E(S)TEM column: exposing the sample to air produces a thin oxide layer on the polycrystalline Si film. The Au

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particles exhibit sizes ranging from 2 nm to 16 nm, and show a combination of faceting and banding contrast (indicated by arrows in Figure 1) that is consistent with particles being solid. The solid nature, as well as the polycrystallinity of the Au particles, is corroborated by a diffraction pattern obtained at 480 °C (inset upper right hand corner in Figure 1).

The decomposition temperature of TMG is above 400 °C [17]. Thus, after the introduction of TMG into the sample area at 480°C, the resulting Ga atoms dissolved into the Au solid particles and Au + Ga liquid droplets were observed to form (Figure 2). Initially, the newly formed droplets (marked i in Figure 2 a) showed a rounded configuration, but as the TMG pressure increased, neighboring droplets experienced surface migration and coalescence, creating a new set of larger droplets with a tear drop configuration (marked i + ii in Figure 2b). It appears that most of the small droplets were partially consumed by the large ones leaving a thin wetting layer along their migration path (indicated by arrows in figure 2b). X-Ray energy-dispersive spectroscopy (EDS) analysis of these tapered droplets Ga content, derived based on thin film approximation, varied from 22% g/g to 52 % g/g in liquid particle with an average value of 36 ± 10 % g/g. Note that all liquid droplets had Ga content greater than 10 % g/g, i.e. within the liquid region in the Au-Ga phase diagram at 480°C [18]. EDS point measurements at different locations within several tapered droplets (line-scans) were also performed in STEM mode. These measurements indicated that the relative concentrations of Ga and Au varied along the tapered droplets, with the concentration of Ga increasing from the droplet centers to the tapered edges. (Supporting information, Figure F1).

Direct observations indicated that the Au + Ga tapered droplets experience some preferential Ga evaporation while heating the sample to 800 °C, nonetheless these droplets were liquid at all times. To further verify this, a series of diffraction patterns were taken during the formation of these tapered droplets. These diffraction patterns showed both Au and Si reflections before introducing TMG (Figure 3a), and only Si reflections after both introducing TMG (Figure 3b) and increasing the temperature to 800 °C (Figure 3c). Also, HREM images of the Au + Ga tapered droplets were recorded at 800 °C. Fast Fourier Transforms (FFT) of crystalline areas indicated that the lattice fringes observed at the tapered

edge of the Au + Ga droplets correspond to the polycrystalline Si film underneath these droplets (supporting information, Figure F2).

Our observations indicated that GaN nanowires began to nucleate after 0.93 Pa (7 mTorr) of NH₃ was introduced into the sample area at 800 °C. This growth temperature was preferred for two reasons. First, even though growth of GaN by MOCVD starts at 450 °C [19], the crystallinity of GaN has been reported to improve by increasing the growth temperature up to 925 °C [20]. The second reason was the upper temperature limit that is restricted by the TEM heating holder used for these experiments.

The sequences of frames extracted from one of the digital videos (Supporting information, video V2) recorded during the formation of GaN nanowires are shown in Figure 4. It is clear from these images that the tapered edge of the Au + Ga droplets are still present after increasing the temperature to 800 °C (indicated by arrows in Figure 4a). The first GaN nuclei were observed to form within the tapered edges in droplets β and δ (Figure 4b) after 60 s of introducing NH₃. As the growth continues, more GaN nuclei were observed to form in other droplets (α and χ in Figure 4c).

An interesting feature observed was the faceting of the GaN nuclei at the droplet-nanowire interface. If we focus our attention on the nanowires formed from particles α and ε in figure 4d, we can see that particle α contains two facets, while particle ε contain three facets at the droplet - nanowire interface. As the nanowire grows these facets disappear for particle α and the interface becomes planar (Figure 4e), whereas for the particle ε there is only a reduction in the number of facets (Figure 4e) from three to two within the time were the video was recorded. The angle between the facets in Figure 4d is °130 which correspond to the angle between M plane (01-11) and A plane (-2-130).

Another interesting observation is that particles φ and γ remain inactive for GaN nucleation (Figure 4e). Their inactivity could be attributed to their crystalline nature, which might cause N to diffuse at a very slow rate or not diffuse at all into the solid. In either case, N does not dissolve appreciably in the Au rich particles that will be solid at our reaction condition. Chemical analysis of these particles, EDS measurements in STEM mode, confirmed that these particles contain a high concentration of Au, greater than 95% g/g, which falls in the solid region of the Au – Ga phase diagram at 800°C [18]. To further

corroborate the crystallinity of the faceted particles, FFT of high-resolution images were taken at 800 °C. These patterns indicate that all the particles that remain inactive for GaN formation are crystalline. The GaN nuclei contained both Ga and N as shown by *in situ* electron energy loss spectroscopy (EELS) (Figure 5). The EELS spectrum was taken at 800 °C in high vacuum mode after evacuating the gases from the sample area and the measurements were performed on individual nuclei. Additionally, Selected Area Diffraction (SAD) patterns (Figure 6) show that these nuclei have the wurtzite structure characteristic of GaN.

Based on the *in situ* observation described above, the nucleation of GaN nanowire may be rationalized by referring to a schematic shown in Figure 7. Thermal decomposition of NH_3 starts at 400 °C [17]. Therefore, when NH_3 is introduced into the system at 800 °C, it decomposes and the resulting N atoms dissolve into the Ga + Au tapered droplet, forming an intermediate liquid solution (Au + Ga + N). Additional incorporation of N atoms creates a situation depicted in Figure 7b, where the tapered edge of the droplet has a higher concentration of N than that in the rest of droplet. As a result, the solubility limit of N in the tapered edge is exceeded first, and the Ga and N atoms inside this region come together to form a GaN nucleus. The Au atoms that exceed the solubility limit of Au in GaN are expelled into the attached liquid droplet, creating a situation as illustrated in Figure 7c. Using a similar argument, additional growth of GaN results in the migration of the droplet-nanowire interface.

In addition, faceting might result from external perturbations, such as the evaporation of Ga or absorption of N at the tapered edge, or as the result of the surface being thermodynamically unstable. According to a theory developed by Herring [21], surfaces other than those found on the equilibrium crystal shape will decompose into a hill-and-valley structure in order to reduce the overall surface free energy. Thus, the first GaN nuclei to form might not have the same orientations and when they coalesce, faceted solid-liquid interface could be created. As the nanowires grow, some of the vicinal facets win out leading to reduction in the number for facets at the solid-liquid interface. These facets are not atomically flat, and some of them must have higher interfacial energy than others. Then steps on

facets with higher interfacial energy move laterally, faster than the steps on facets with lower energy, leading to the formation of a planar interface as shown in Figure 4e.

In summary, GaN nanowire growth was successfully achieved by first forming Au + Ga droplets and subsequently exposing them to NH_3 . High magnification images of the formation of GaN nuclei were obtained using an environmental transmission electron microscope. Chemical and structural analysis confirmed that these nuclei were GaN having the wurtzite structure.

Several interesting observations emerge from this study. First, the coalescence of the Au + Ga droplets leads to the formation of tapered droplets appear to wet the underlying oxide layer on the Si substrate. Second, the nucleation and growth of GaN nanowires occur only within liquid droplets following the well know VLS mechanism. GaN nuclei were not observed to form within Au + Ga solid particles, which could be attributed to the reduced solubility of N within these solid particles. Third, under these particular growth conditions, the origin of the GaN nuclei is at the tapered edge of the Au + Ga droplets. Finally, at early stages of growth, there is more than one facet of the droplet - nanowire interface, which might be related to the thermal instability within the tapered droplet. Additional GaN growth continues by step propagation on the interface, resulting in a planar interface.

In order to use compound semiconductor nanowires as building blocks for nanoscale devices, a precise control of the nanowire structure, crystallinity, morphology, and chemistry is necessary. This could be achieved by understanding the nucleation and growth of compound nanowires. These findings suggest that our approach can be used for this purpose and can be extended to other binary semiconductor compounds such as GaP, GaAs, and InP, or even ternary compounds such as InGaN. However, further experimental work is required to fully elucidate the kinetic effects on the growth process and effects of temperature and pressure on the crystallinity and morphology of nanowires.

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Supporting Information Available. *In situ* observations in AVI format (Video V1, V2) and images of complementary chemical and structural analysis (Figure F1, F2) are available online <http://www.sciencedirect.com/>.

References

- [1] S. Nakamura, *Science* 281 (1998) 956
- [2] S. N. Mohammad, A.A. Salvador, H. Morkoç, *Proc. IEEE* 83 (1995) 1363
- [3] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.* 15 (2003) 353
- [4] J. Hu, T.W. Odom, C.M. Lieber, *Acc. Chem. Res.* 32 (1999) 433
- [5] J.C. Johnson, H.J. Choi, K.P. Knutsen, R.D. Schaller, P. Yang, R.J. Saykally, *Nature* 416 (2002) 106
- [6] Y. Huang, X. Duan, Y. Cui, C.M. Lieber, *Nano Lett.* 2 (2002) 101
- [7] F. Qian, Y. Li, S. Gradecak, D. Wang, C.J. Barrelet, C.M. Lieber, *Nano Lett.* 4 (2004) 1975
- [8] X. Duan, C.M. Lieber, *J. A. Chem. Soc.* 12 (2000) 188
- [9] X. Chen, J. Li, Y. Cao, Y. Lan, H. Li, M. He, C. Wang, Z. Zhang, Z. Qiao, *Ad. Mater.* 12 (2000) 1432
- [10] C.C. Tang, S.S. Fan, H.Y. Dang, P. Li, Y.M. Liu, *Appl. Phys. Lett.* 77 (2000) 1961
- [11] T. Kuykendal, P. Pauzauskie, S. Lee, Y. Zhang, J. Goldberger, P. Yang, *Nano Lett.* 3 (2003) 1063
- [12] R.S. Wagner, W.C. Ellis, *Appl. Phys. Lett.* 4 (1964) 89
- [13] E.A. Stach, J. Pauzauskie, T. Kuykendall, J. Goldberger, R. He, P. Yang, *Nano Lett.* 3 (2003) 867
- [14] S. Hoffman, R. Sharma, C.T. Wirth, F. Cervantes-Sodi, C. Ducati, T. Kasama, R. Dunin-Borkowski, J. Drucker, P. Bennet, J. Robertson, *Nature Materials* 7 (2008) 372
- [15] B.J. Kim, J. Tersoff, S. Kodambaka, M.C. Reuter, E.A. Stach, F.M. Ross, *Science* 322 (2008) 1070
- [16] R. Sharma, *Journal of Materials Research* 20 (2005) 1695
- [17] G. Stringfellow, *Organometallic Vapor-Phase Epitaxy*, Second ed., Academic Press, California, 1999

- [18] B. Predel, O. Madelung, Landolt-Bornstein, Group IV Physical Chemistry – Phase Equilibria, Crystallographic and Thermodynamic Data of Binary Alloys, Volume 6 – Electronic Materials and Semiconductors New Series IV/5, Springer-Verlag, 1991-1998
- [19] S. Nakamura, Jpn. J. Appl. Phys. 30 (1991) 1705
- [20] J.D. MacKenzie, C.R. Abernathy, J.D. Stewart, G.T. Muhr, J. Cryst. Growth 164 (1996) 143
- [21] C. Herring, Phys. Rev. 82 (1951) 87

Figure Captions

Figure 1. TEM image of Au particles on a polycrystalline Si film at 480 °C, the randomly distributed Au particles are faceted and exhibit banding contrast which is consistent with solid particles. The rings in the selected area diffraction pattern (inset in upper right hand corner) indicate the polycrystallinity nature of Au particles and the Si. The oxide amorphous layer is shown by the speckle contrast in the HREM image (inset in lower right hand corner).

Figure 2. TEM images extracted from a digital video recorder during the introduction of TMG into the sample area at 480 °C. These images show the coalescence of neighboring Au + Ga droplets and formation of droplets with a tear drop configuration. Figure a shows droplets (i - ii) before they coalesced and figure b shows the resulting larger droplet (i + ii) with tapered edges (indicated by arrows). The time difference between frames is less than a second for each case. (Supporting information, video V1).

Figure 3. Series of diffraction patterns extracted from a digital video recorded during the formation of Au + Ga liquid droplets. (a) Au and Si reflections at 480 °C. There is an absence of Au reflections after (b) introduction of TMG at 480 °C and (c) heating the sample up to 800 °C.

Figure 4. Sequences of frames extracted from a digital video recorded during the formation of GaN nuclei and their evolution into nanowires. (a) The tapered edges of the Au + Ga droplets, indicated with arrows, are still present at 800 °C. (b) First appearance of GaN nuclei (arrows) within particles β and δ

after 61 s of introducing 0.933 Pa (7 mTorr) of NH_3 . (c) Appearance of GaN nuclei within particles α and χ after 67 s. (d) GaN nanowires (α and ε) in early stages of growth presenting a multi-faceted droplet-nanowire interface. (e) GaN nanowires with no faceting (α) and with smaller number of facets (ε). Also particles φ and γ , with faceted shapes, do not catalyze GaN nuclei. (Supporting information, video V2).

Figure 5. *In situ* EELS spectrum of individual nuclei recorded without any gas in the sample area at 800 °C. This spectrum shows the characteristic peaks for Ga and N.

Figure 6. SAD pattern obtain from a single GaN nucleus on the polycrystalline Si film.

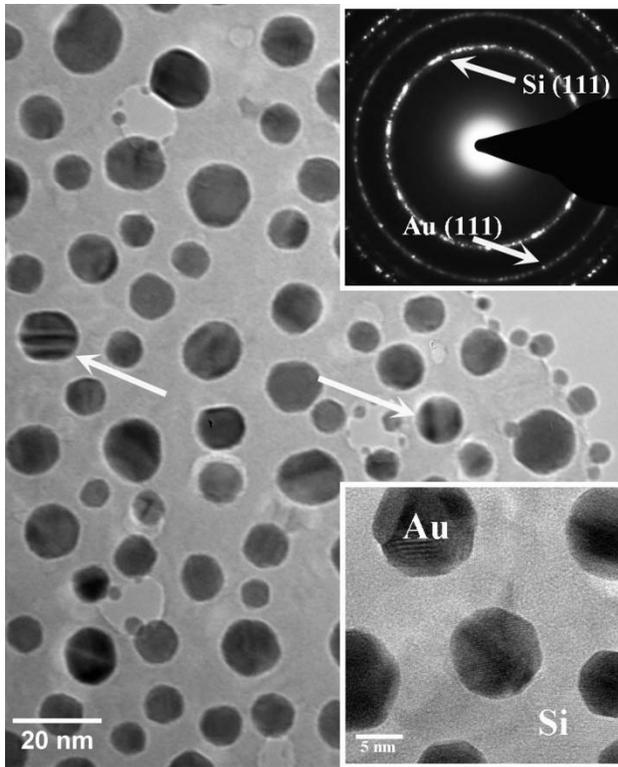


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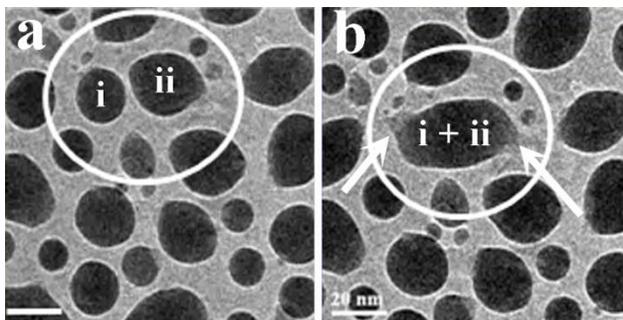


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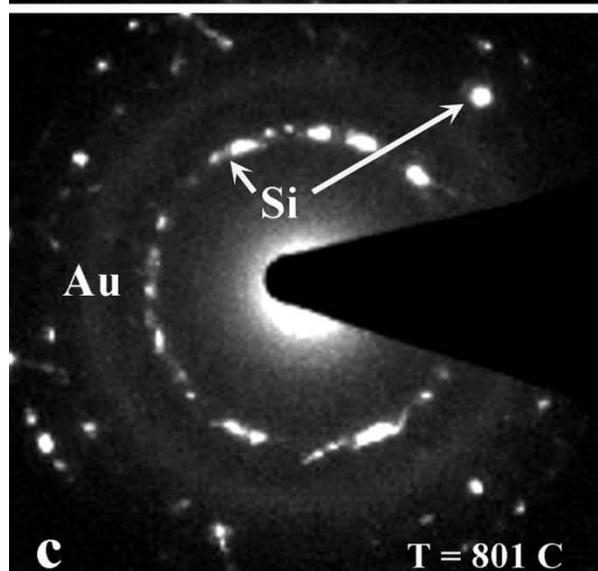
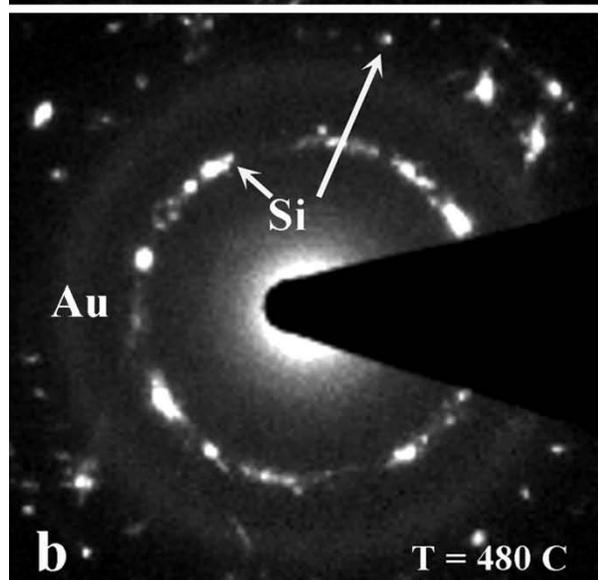
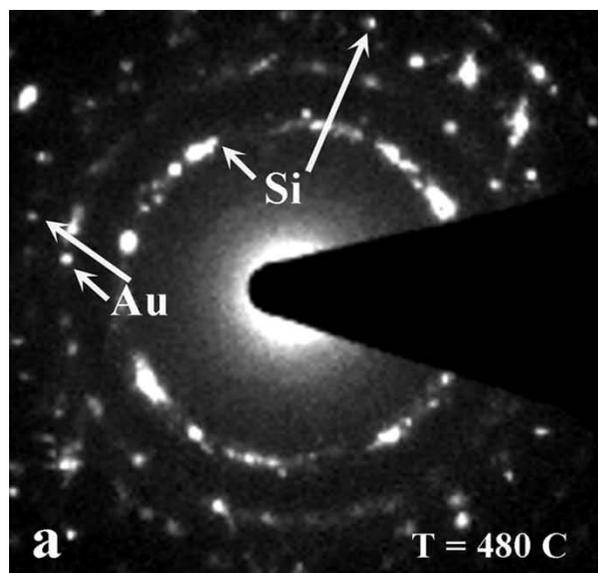


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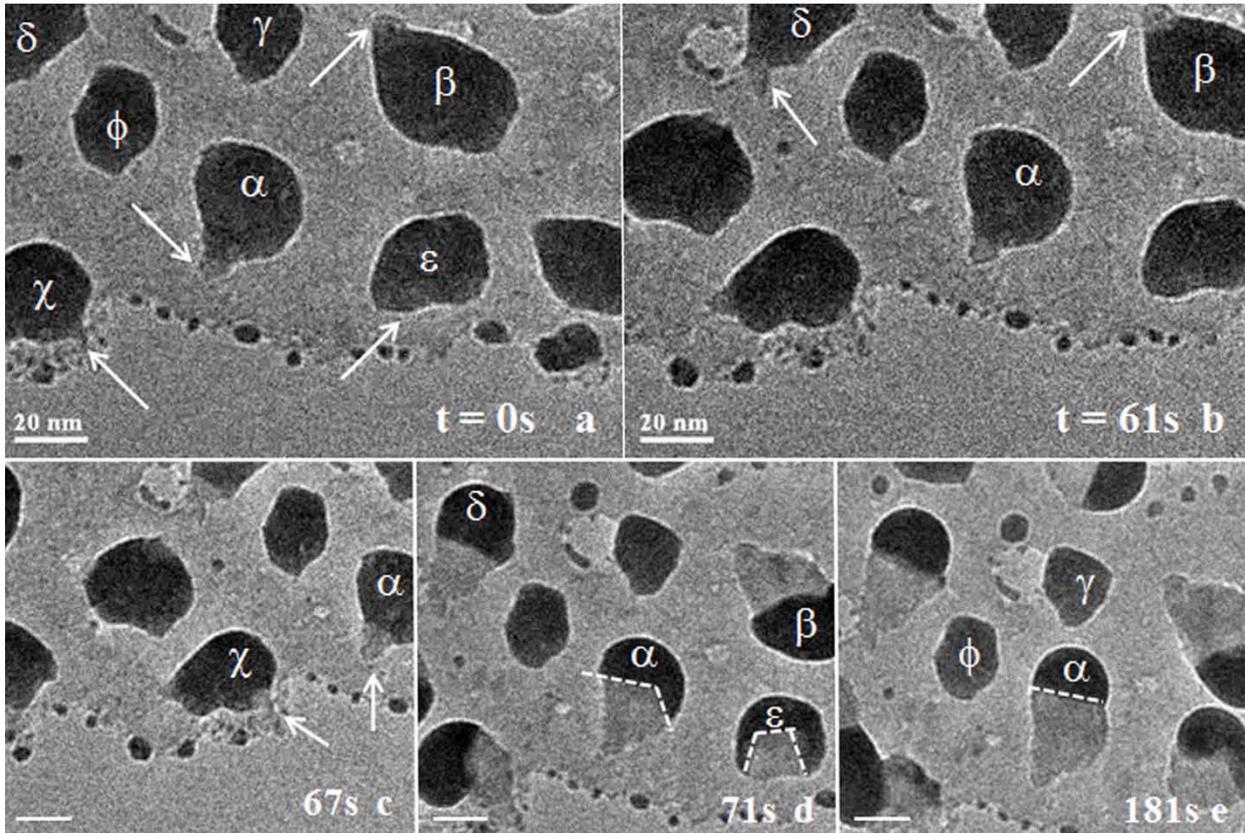


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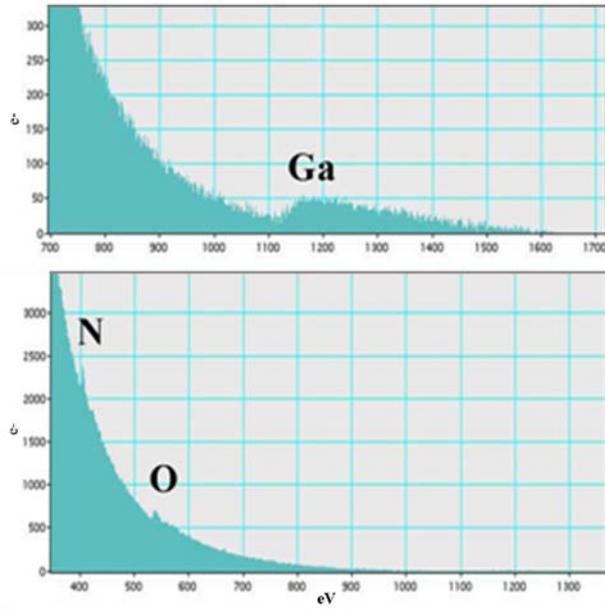


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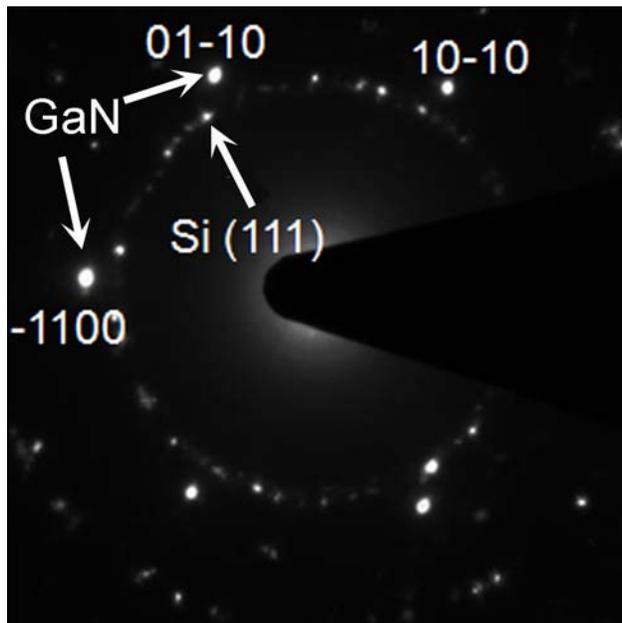


Figure 6. SAD pattern of an individual nucleus with the polycrystalline Si film underneath.

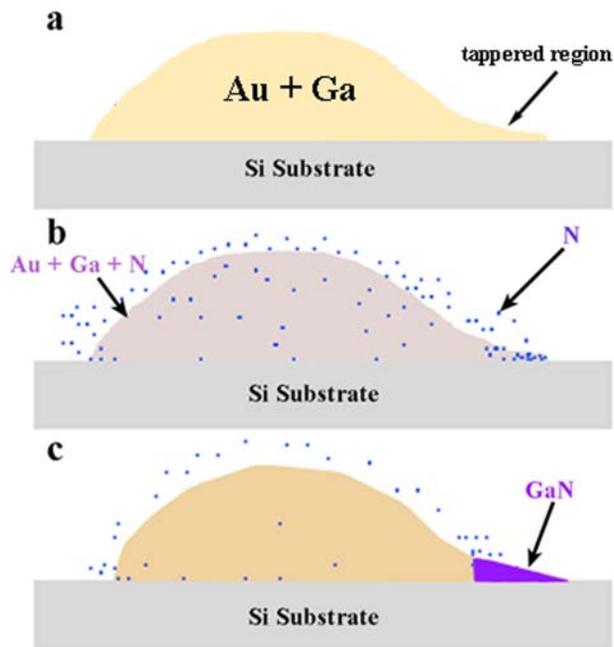


Figure 7. Schematic showing (a) the Au + Ga droplet before NH_3 was introduced into the sample area, (b) the arrival of N atoms onto the surface of the Au + Ga droplets and substrate, and the accumulation of N inside the thin film region, and (c) the formation of GaN nuclei when the solubility limit of N is exceeded in thin film region.