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Self-branching in GaN Nanowires Induced by a Novel Vapor-Liquid-Solid Mechanism

Abstract

Nanowires have great potential as building blocks for nanoscale electrical and optoelectronic devices. The difficulty in achieving functional and hierarchical nanowire structures poses an obstacle to realization of practical applications. While post-growth techniques such as fluidic alignment might be one solution, self-assembled structures during growth such as branches are promising for functional nanowire junction formation. In this study, we report vapor-liquid-solid (VLS) self-branching of GaN nanowires during AuPd-catalyzed chemical vapor deposition (CVD). This is distinct from branches grown by sequential catalyst seeding or vapor-solid (VS) mode. We present evidence for a VLS growth mechanism of GaN nanowires different from the well-established VLS growth of elemental wires. Here, Ga solubility in AuPd catalyst is limitless as suggested by a hypothetical pseudo-binary phase diagram, and the direct reaction between NH₃ vapor and Ga in the liquid catalyst induce the nucleation and growth. The self-branching can be explained in the context of the proposed VLS scheme and migration of Ga-enriched AuPd liquid on Ga-stabilized polar surface of mother nanowires. This work is supported by DOE Grant No. DE-FG02-98ER45701.

Keywords

Gallium alloys, Dissolution, Electric wire, Gallium nitride, Liquids, Nanowires, Semiconducting gallium, Vapors, AuPd alloy, GaN nanowires, Growth modes, Growth morphology, Nucleation and growth, Polar surfaces, Spontaneous reactions, Vapor-liquid-solid mechanism, VLS growth

Comments

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Self-branching in GaN Nanowires Induced by a Novel Vapor-Liquid-Solid Mechanism

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ABSTRACT

Investigations of the growth morphology of AuPd-catalyzed GaN nanowires lead us to propose a vapor-liquid-solid (VLS) mechanism distinct from the well-established VLS growth of elemental wires. Here, nucleation and growth of GaN nanowires proceeds by direct spontaneous reaction between NH_3 vapor and Ga dissolved in liquid AuPd alloy, rather than by solubility-limited supersaturation. A frequently observed self-branching growth mode can be explained by the proposed VLS scheme and the migration of Ga-enriched AuPd liquid on Ga-stabilized polar surfaces of mother nanowires.

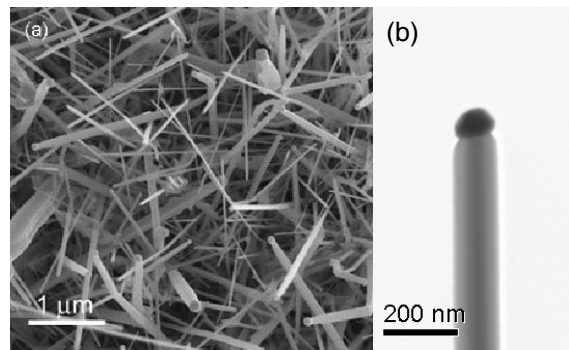


Figure 1. (a) SEM image showing as-grown VLS GaN NWs on a growth substrate. (b) Bright field TEM image of individual GaN NW showing metal catalyst at the tip.

INTRODUCTION

GaN nanowires (NWs) are of interest for nanoscale optoelectronic device applications [1-4]. Synthesis can be achieved by several methods involving vapor-liquid-solid (VLS) growth, such as thermal chemical vapor deposition (CVD) [5-7], hydride vapor phase epitaxy (HVPE) [8], molecular beam epitaxy (MBE) [9], and metalorganic CVD (MOCVD) [10]. The low N solubility in transition metals implies that nucleation of GaN from supersaturated catalyst droplets is unlikely, in contrast to elemental structures such as Si whiskers and NWs [11]. Here we study GaN NWs grown by thermal CVD using Ga_2O_3 , NH_3 and AuPd catalyst. The observed morphologies suggest a VLS mechanism distinct from the nucleation and growth of elemental nanostructures from supersaturated liquid. We consider a hypothetical pseudo-binary phase diagram and thermodynamics of GaN formation reaction to propose that NW nucleation and growth occur *via* direct reaction of dissolved Ga with NH_3 vapor. We also observe spontaneous ‘self-branching’ of large-diameter NWs into smaller diameter progeny. This is explained by the proposed VLS scheme and the high mobility of Ga-rich liquid catalyst on polar NW surfaces.

EXPERIMENTAL DETAILS

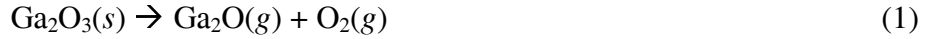
Ga₂O₃ powder (Alfa Aesar, 99.999%) in an alumina boat is placed at the center of a quartz tube in a horizontal furnace. SiO_x/Si substrates with sputter-coated AuPd (60:40 wt.%, thickness <1-2 nm) are placed downstream from the boat. Ga₂O₃ is then reacted with flowing NH₃ (20-175 sccm) at 1150 °C for 0.5-2.0 hr. NH₃ flow was maintained during furnace cooling to room temperature as details are available elsewhere [12-14].

The scanning electron microscopy (SEM) image in Fig. 1a shows NWs with 30-200 nm diameter, length up to 50 μm, and spherical metal particles at the tips. Transmission electron microscopy (TEM) confirms the wurtzite structure and identifies the tip particles as AuPd with a small amount of Ga [15,16]. The growth orientations are perpendicular to the c-axis (*e.g.* [11 $\bar{2}$ 0]), resulting in isosceles triangular cross-sections with three polar capping surfaces, *e.g.* (0001), ($\bar{2}$ 11 $\bar{2}$), and (2 $\bar{1}$ 1 $\bar{2}$) [15,17].

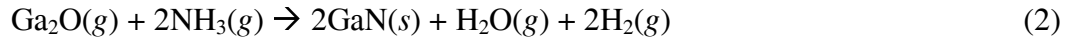
DISCUSSION

Growth reaction chemistry

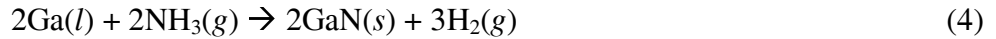
In our Ga₂O₃-sourced growth, with or without catalyst Ga₂O₃ first converts to Ga₂O(*g*) [18]:



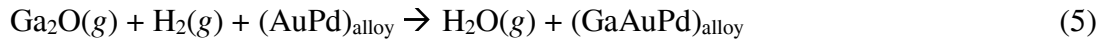
In the absence of metal catalyst, Ga₂O(*g*) then reacts with NH₃ to form GaN in the vapor or on the surface of growing GaN by [12,14]:



Direct reaction of Ga and NH₃ can also result in GaN because Ga₂O(*g*) can back-react with H₂ to form Ga [14,18]:



In our AuPd-catalyzed growth, dissolution of Ga₂O and/or NH₃ in the metal needs to be considered along with the above direct reactions to account for the appearance of spherical metal particles at the tips. Since N is virtually insoluble in Au or Pd at our growth temperature [19], we expect that only Ga₂O can dissolve *via* the following reaction:



where H₂ is provided by (2) and (4). The dissolution of Ga₂O in AuPd may be possible without being reduced by H₂, given the finite solubility of O in Pd at high temperature [20].

The solid GaAuPd alloy in (5) then melts above a critical Ga concentration and persists as a liquid as more Ga dissolves because Ga has no solubility limit at sufficiently high temperature by analogy to Ga-Au and Ga-Pd cases [19]. This suggests a novel GaN NW growth mechanism based on a hypothetical pseudobinary Ga-AuPd diagram.

Proposed growth mechanism

First notice that T_{melt} for Au and Pd are 1064 °C and 1555 °C respectively, while T_{melt} of AuPd (60:40 wt.%) is only ~100 °C below that of Pd [19]. The Ga-AuPd phase diagram is then expected to resemble that of Ga-Pd with an overall 100 °C decrease in temperature as shown in Fig. 2(a). The y-axis on the right shows pure solid AuPd up to 1460 °C. Moving to the left, increasing Ga to ~6 wt% at our 1000 °C substrate temperature signals the onset of a liquid component (X) and pure GaAuPd liquid at ~14% (Y). As more Ga dissolves by reaction (5), the liquid becomes more Ga-rich, and at some point NH₃ vapor starts reacting directly with Ga by reaction (4) to nucleate a GaN crystal (Fig. 2b).

It is important to note that the GaN formation reaction (4) is expected to be *spontaneous* at our growth temperature as it can be corroborated by calculating standard Gibbs free energy (ΔG°) and corresponding equilibrium vapor pressures of NH₃ and H₂ ($P_{\text{NH}_3,eq}$ and $P_{\text{H}_2,eq}$). From thermodynamic data [21] and $T_{\text{sub}} = 1300\text{K}$, we find $\Delta G^\circ = -100.4 \text{ kJ/mol}$ with $P_{\text{NH}_3,eq} = 0.0095 \text{ atm}$ and $P_{\text{H}_2,eq} = 0.9905$. Considering the use undiluted NH₃ with pressure ~1 atm (no evacuation of reactor) in our growth, LeChatelier principle dictates that the reaction (4) must proceed forward (*i.e.* forming GaN) always to consume ‘extra’ NH₃ and reach the equilibrium pressure.

The alloy composition at the NW tip may deviate from the nominal 60:40 ratio during growth, thus changing the critical Ga concentration for liquid formation. This however should not affect the validity of the proposed mechanism since GaN nucleation [*i.e.* reaction (4)] will occur spontaneously as long as Ga-containing liquid catalyst exists, independent of the critical concentration.

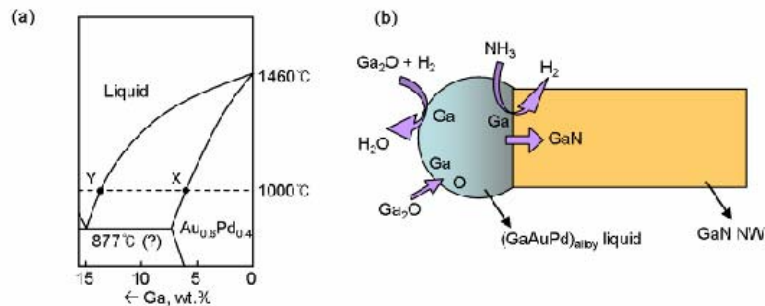


Figure 2. (a) Ga-poor end of a hypothetical pseudobinary Ga-Au_{0.6}Pd_{0.4} (wt.%) phase diagram.. During growth at 1000 °C, solid AuPd first melts at the Ga concentration X (~6 wt.%), becoming all liquid at Y (~14 wt.%). (b) Schematic VLS nucleation and growth of a GaN NW from a AuPd catalyst particle.

Once nucleated, NW growth continues at the liquid/NW interface, *i.e.* tip growth. NH₃ might be able to access the interface readily due to the short diffusion length (*i.e.* particle diameter). We note that the direct nucleation of initial GaN crystal at the surface of catalyst particle is possible and can lead a ‘root growth’ of a NW by vapor-solid type mechanism. However, as it is discussed next, we observe tip growth of NWs, so the vapor-solid type growth can be ruled out. Another possible growth scenario is the dissolution and reprecipitation of GaN crystal into/from the metal catalyst. This however is unlikely since N is insoluble in AuPd at our growth temperature as would GaN itself be. Accordingly, X-ray energy dispersive spectroscopy (XEDS)

and electron energy loss spectroscopy (EELS) show that the AuPd NW tip contains a small amount of Ga but no detectable N [15,16].

Detailed SEM examination of NWs on their growth substrates provides additional support for tip growth. Fig. 3a shows that some large diameter wires ‘crawled’ on the SiO_x surface (dark contrast indicating the absence of charging) and ended up with having tip particles larger in diameter than the radius of wires to which they are attached (*e.g.* A and B). Furthermore, the diameters of these wires taper down away from the tip, and the substrate near such wires is denuded of spherical particles (Fig. 3b). Both observations suggest tip growth to the right in Fig. 3a (along the direction labeled X). The NW diameter increases along X direction because the attached particle absorbs isolated smaller particles on the substrate. The resulting denuded zones, less than a NW diameter, are clearly seen in Fig. 3b. In contrast, the wires marked C and D grew out from the substrate plane as indicated by the bright contrast from charging, the absence of denuded zones, and the uniform NW diameters.

Spontaneous branch formation

In the SEM examination, we frequently observe small diameter NWs branched from a mother NW. Small NWs marked E and F in Fig. 3a appear to have branched from the stem of a larger diameter mother wire labeled G and grew parallel to each other. Branch growth is more clearly seen in Fig. 4a,b. The contrast difference between mother wire and progeny in Fig. 4a suggests that the branching exists as families of mutually parallel wires from the same mother. Fig. 4b shows the opposite extreme in which one mother wire spawns three apparently unrelated offspring. The parallel alignment of branches in Fig. 3a and 4a suggests homoepitaxy, which must be further confirmed or ruled out by selected area electron diffraction. The branched NWs also result from VLS growth, because spherical particles can be found at their tips (Fig. 4b inset).

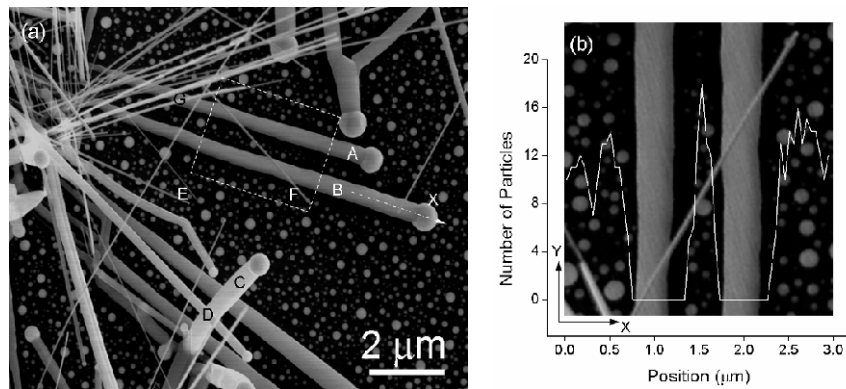


Figure 3. (a) SEM image of a sparsely covered region of a growth substrate. Isolated particles are most likely AuPd or GaAuPd. Thinner NWs E and F appear to have branched from a mother NW G. (b) Magnified view of the dashed rectangular region in (a). Plotted in white is the number of particles counted along $\sim 3 \mu\text{m}$ of wire length, sampled every 50 nm normal to the wire to show the particle-denuded zones along the NWs.

This spontaneous branch formation is distinct from some previous works on III-V and metal oxide NWs, where sequential catalyst seeding was applied to the NW ‘trunk’ to intentionally nucleate second generation branches [22,23], or rapid crystallization [24] (vapor-solid type growth) or self-catalytic growth [25,26] induced spontaneous branching. The different scenario

we envision is a direct consequence of the Ga-stabilized polar surface and the formation of liquid phase metal catalyst. As described schematically in Fig. 4c, if Ga_2O is incorporated into AuPd faster than Ga is consumed by the growing mother wire, the tip particle can become enriched with Ga and grow in diameter. This provides the opportunity for Ga-rich liquid to leave the tip particle, migrate along the surface of the growing NW, and ultimately nucleate branches. We also note that the Ga-rich AuPd liquid may have been originated from the diffusion of un-nucleated AuPd particles from the substrate as a similar phenomenon was observed in Au-catalyzed Si NW growth [27]. One may also expect the nucleation of branch NWs by the migration of AuPd particles that is not alloyed with Ga. However, in our case it should be insignificant considering its much lower mobility than the Ga-alloyed AuPd; AuPd in principle is solid at our growth temperature, and even if it is liquid phase by size-related melting point depression effect, its migration on the Ga-stabilized GaN surface is expected to be slower than that of Ga-alloyed AuPd. The fact that these NWs terminate radially at polar surfaces along the entire length, and moreover the polar surfaces are Ga-stabilized [12,14,15,17] also support the migration of Ga-rich liquid on the NW surfaces. It is worthy to note that alloy catalysts with phase equilibria matched to the NW growth conditions (*i.e.* catalysts which can form liquid phase ‘easily’ at low Ga concentration) are considered to be one of requirements for branch formation. For instance, using the identical GaN NW growth procedure, Pt catalyst yields high quality wires with no evidence for branching [13], and this is understood by the high T_{melt} of Pt (1772°C) which results in a critical Ga concentration as high as $>50\text{ wt.}\%$ for liquid Ga-Pt formation at our growth temperature 1000°C .

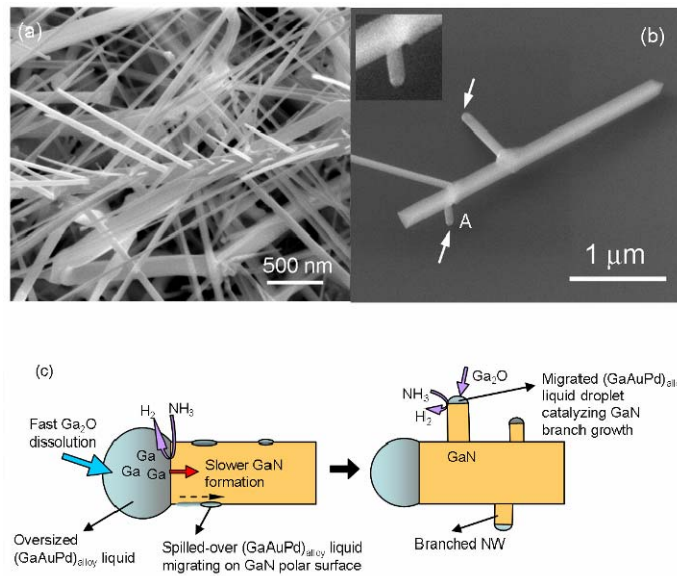


Figure 4. (a),(b) High resolution SEM images of self-branched growth from a stem of thicker NW. (a) is taken from an as-grown substrate, and (b) shows a broken piece of a NW with branches after dry-transfer to a clean Si substrate. The inset reveals spherical particles at the tip of branch A, suggesting VLS-type branch growth. (c) Schematic of the self-branching mechanism. See the text for more details.

As a final remark, we also suggest that the proposed mechanism should be applicable to the mono-composition catalyst systems such as Au or Pd. In case of Au whose melting temperature

is lower than AuPd alloy or Pd, the alloying effect will be more significant, and it may have higher catalytic activity (or growth rate) than the other systems. However, it is also reminded that the presence of Pd in fact might be important in our Ga₂O₃ sourced growth because the finite oxygen solubility of Pd can facilitate dissolution of Ga₂O vapor into the liquid catalysts.

To conclude, we proposed a VLS mechanism in which GaN NW growth was driven by spontaneous reaction between vapor NH₃ and Ga in the Ga-alloyed AuPd liquid catalyst. We observed a spontaneous branch formation, and the migration of Ga-rich catalyst liquid was expected to be responsible for it. The proposed VLS scheme would be able to explain other nitride NW growths.

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