Phase Separation Induced by Au Catalysts in Ternary InGaAs Nanowires

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Supporting Information

ABSTRACT: We report a novel phase separation phenomenon observed in the growth of ternary InGaAs nanowires by metalorganic chemical vapor deposition. A spontaneous formation of core–shell nanowires is investigated by cross-sectional transmission electron microscopy, revealing the compositional complexity within the ternary nanowires. It has been found that for InGaAs nanowires high precursor flow rates generate ternary InGaAs cores with In-rich shells, while low precursor flow rates produce binary GaAs cores with ternary InGaAs shells. First-principle calculations combined with thermodynamic considerations suggest that this phenomenon is due to competitive alloying of different group-III elements with Au catalysts, and variations in elemental concentrations of group-III materials in the catalyst under different precursor flow rates. This study shows that precursor flow rates are critical factors for manipulating Au catalysts to produce nanowires of desired composition.

KEYWORDS: III–V semiconductor nanowires, phase separation, core–shell nanowires, ternary semiconductors, InGaAs nanowires

Semiconductor nanowires have attracted global research interest due to their distinct physical and chemical properties that can potentially lead to a wide range of new applications. These advanced functional materials have emerged as versatile building blocks for nanophotonics, nanoelectronics, and biosensing devices.1–4 Among various nanowire systems, ternary III–V nanowires show great potential for optoelectronic devices since their band gap energy can be tuned, simply by varying the composition of the nanowires.5–7 As one of the most important ternary semiconductor systems, InGaAs may be tuned to span the optical range from the near-infrared to the mid-infrared region, which makes this suite of materials superior for many optoelectronic applications.8,9 As for InGaAs nanowires, many studies have demonstrated their tunable photoluminescence,10,11 as well as their fascinating electrical characteristics.12–14 Therefore, it is of great significance to understand the growth mechanisms of InGaAs nanowires.

Currently, the most common approach for nanowire synthesis is the vapor–liquid–solid (VLS) mechanism15,16 in which metallic nanoparticles are used to catalyze anisotropic crystal growth. Since in situ TEM studies suggest that vapor–solid–solid mechanism may also be possible,17,18 the commonly accepted nanowire growth model may be considered as follows. At the beginning of nanowire growth, at elevated temperature and optimal supply of precursors the catalysts on the substrate absorb the decomposition products of the precursors from ambient vapor to become alloyed nanoparticles or liquid droplets. With the continuous supply of precursors through the vapor and subsequent absorption into the nanoparticles, nanowires are grown by precipitation at the interface between the catalyst and the substrate. The nanowires continue to grow with the catalysts remaining at the growth front of the nanowires. It is important to note that, during VLS growth, unwanted 2D epitaxial growth can be thermally activated, resulting in lateral growth of the nanowires on their sidewalls via the vapor–solid (VS) growth mechanism.19 This phenomenon leads to nanowire tapering.

It is anticipated that the synthesis of InGaAs nanowires by VLS growth in a metal–organic chemical vapor deposition...
(MOCVD) system may allow for production of homogeneous epitaxial InGaAs nanowires with different values of $x$, by simply altering the ratio between precursors in the vapor. However, many studies have shown compositional variations along the axial direction, and/or along the radial direction of VLS-grown III–V ternary nanowires, including InGaAs, InGaP, AlGaAs, and AlGaAs nanowires. As previous studies have suggested, one way to produce homogeneous ternary III–V nanowires is to eliminate nanowire tapering in VLS growths. Alternatively, one can use catalyst-free epitaxial growth techniques to achieve uniform depositions of ternary nanowires. Obvi-ously, compositional inhomogeneity has been a long-standing issue in catalyst-assisted VLS-grown ternary III–V nanowire systems, so that detailed structural and compositional characterizations, as well as a better understanding of the growth mechanism, are required for progress. It is of interest to note that a previous study examining the interfaces between InAs/GaAs and GaAs/InAs heterostructured nanowires revealed that In may have a higher affinity for the Au catalyst than Ga, resulting in the growth of an InGaAs ternary segment when GaAs was grown on InAs nanowires using a Au catalyst. A similar result was also observed in InGaAs/InAs heterostructured nanowires. Additionally, Bauer et al. found that a considerable amount of In accumulated inside the Au catalyst during InGaAs nanowire growth and remained in the catalyst during subsequent InGaAs growth. These independent studies suggest that the Au catalyst may preferentially alloy with In rather than Ga, when both In and Ga are present, as occurs during the growth of InGaAs nanowires. This alters the composition of the ternary nanowires during growth, which may account for the inhomogeneity observed in ternary nanowires.

In this study, advanced electron microscopy on both entire and sectioned nanowires was employed to investigate the growth of InGaAs nanowires. A variation in elemental composition across the diameter of the nanowire was found to exist in a distinct core–shell structure with a higher concentration of In observed in the shell. The precursor flow rates were found to effect the elemental composition of ternary nanowires such that at low flow rates, nanowire cores were determined to be binary GaAs. First-principle calculations along
with thermodynamic considerations were used to explore the fundamental reasons behind this phenomenon and provide fresh insight into the mechanism of nanowire growth.

Epitaxial In$_{0.05}$Ga$_{0.95}$As nanowires (the nominal composition being a function of respective precursor flow rates, which is not necessarily the actual molar composition of nanowires) were grown on GaAs(111)B substrates at 450 °C using a horizontal flow MOCVD reactor at a constant pressure of 100 mbar and 15 l/min total flow. Au nanoparticles of 50 nm diameter (Ted Pella Inc.) were used as catalysts for nanowire growth. Trimethylindium (TMI), trimethylgallium (TMG), and AsH$_3$ were used as the precursors for supplying In, Ga, and As, respectively. Two samples, denoted A and B, were grown under low and high flow rates respectively. A V/III (As/(In+Ga)) ratio of 44 and TMI/(TMI+TMG) ratio of 0.05 were kept constant for both samples. The TMI flow rate for sample A was $7.13 \times 10^{-7}$ mol/min and sample B $8.20 \times 10^{-6}$ mol/min. In order to achieve similar lengths of nanowires in both samples, growth times were set to 45 min for sample A and 5 min for sample B. The morphological, structural, and chemical characteristics of as-grown nanowires in both samples, growth times were set to 45 min for sample A and 5 min for sample B. The morphological, structural, and chemical characteristics of as-grown nanowires were investigated by field-emission scanning electron microscopy (SEM, JEOL-7800) and transmission electron microscopy (TEM, Philips Tecnai-F20) equipped with X-ray energy dispersive spectroscopy (EDS). Individual nanowires for TEM observations were prepared by mechanical dispersion onto holey carbon films supported by Cu mesh grids. The preparation of individual nanowire cross sections for TEM observations was carried out by embedding nanowires in resin (EPON), and then sectioning with an ultramicrotome (Leica EM UC6). The epitaxial relationship of the nanowires to the original substrates was well preserved during this process. The initial section was from the bottom of the nanowires with the location and thickness of each subsequent cross-sectional slice carefully controlled and measured. The thin sections were then transferred onto carbon-coated Formvar films, supported by Cu mesh grids for TEM analyses.

Figure 1 is SEM images taken from both samples, where most of the nanowires show vertical growth with respect to the substrate, that is, along the [111] direction. Both samples of tapered nanowires have similar densities of 0.4–0.5 μm$^{-2}$. To understand their structural and chemical characteristics, TEM investigations were performed on over a dozen nanowires from each sample. The crystal structure of the nanowires was determined to be zinc blende for both samples. Figure 2a,d shows bright-field (BF) TEM images of a typical nanowire from each of the samples A and B, respectively, and Figure 2b,e shows EDS spectra obtained at different locations along the nanowires. Of great significance, In is not detected in the tip of the nanowire directly below the catalyst (point 2 in Figure 2b) for sample A (low flow rate), while for sample B (higher flow rate) In is found at the same region (point 2 in Figure 2e). It should be noted that the detection limit for EDS on the ternary nanowire is well under 1 atom %. From the EDS results on both samples, In was present in the catalysts, while no Ga was detected. The catalyst in sample B appeared to contain more In than in sample A (refer to spectra 1 in Figure 2b,e).

Interestingly, Moiré contrasts can be clearly observed in the nanowire bases (refer to Figure 2c,f), indicating that both nanowires have a core–shell structure with the core and shell having different lattice parameters and thus different elemental compositions. The morphological difference of nanowire segments shown in Figure 2c,f is caused by lateral growth near twinned areas of the
nanowires, that is, the area in Figure 2c contains twins, while the area shown in Figure 2f is twin-free.

To determine the compositions of the cores and shells of nanowires, cross sections of individual nanowires from different axial locations were investigated by TEM. Figure 3 and 4 represent these results, in which Figure 3a and 4a and Figure 3b and 4b are cross-section TEM images obtained from the middle (marked as A1 and B1 in Figure 2a,d) and base (marked as A2 and B2 in Figure 2a,d) sections of typical nanowires in sample A and B, respectively. The axial locations of different cross sections obtained along the nanowires can be estimated because the nanowires sections commenced from the nanowire base. Additionally, comparison of the morphology of the nanowire cross sections (Figure 3a,b and Figures 4a,b) and the top-view SEM images (insets in Figure 1a,c) indicate that such an estimation of axial locations of nanowire cross sections can be considered reliable.

From Figures 3a,b and 4a,b, all nanowire cross sections shown contain a hexagonal core and a truncated-triangular shell with an abrupt boundary, confirming that the nanowires have a...
core−shell nature. Our TEM investigations of nanowire cross sections, obtained from different axial locations for both samples, indicated that the lateral thickness of the shell changed significantly along the axial direction while the diameter of the core remained unchanged. This confirms that the diameter of the nanowire core is uniform throughout the length of the nanowires and that the tapering of the nanowires is caused only by lateral growth of the shells. To clarify the compositional variation between the cores and shells, EDS line scans were performed and examples are shown in Figures 3a and 4a. The background noise signal was extracted by applying an energy window with the same width as the In−L peak in the neighborhood of In−L peak in the EDS spectrum. In Figure 3a, the background signal level is comparable to the In−L signal from the nanowire core, which indicates that there is no detectable In within the core. As further confirmed in Figure 3c,d, no In signals were detected from the nanowire core in sample A, implying that the core is indeed the binary GaAs. In contrast, a small amount of In was observed in the nanowire core in sample B (refer to the EDS line scan and spectra in Figure 4a,c,d). Nevertheless, shells in both samples contain enriched In than their corresponding cores, which is further confirmed by EDS analysis on nanowire cross sections taken from different axial locations, as shown in Figure 3c,d and Figure 4c,d. Additionally, EDS analysis of shells along axial locations suggests that the shells are compositionally uniform along their axial direction. On the basis of these comprehensive TEM investigations outlined above, the structural models of the typical nanowires in both samples can be schematically illustrated in Figure 3e and 4e in which the nanowire core in sample A is binary GaAs and that in sample B is ternary InGaAs.

The fact that In was absent in the nanowire cores when the ternary nanowires were grown under low precursor flow rates indicates that (1) a barrier exists for In incorporation into the nanowire core during nanowire axial growth, and (2) such a barrier was overcome by an increase in the precursor flow rate, as shown in the case of sample B. Since nanowire core growth is directly induced by the catalyst via VLS, it is anticipated that this barrier is closely related to the nanowire growth front, that is, the interface between the catalyst and the nanowire. To fundamentally understand this phenomenon, two issues need to be addressed. The first issue is why is In preferentially alloyed with Au, while Ga is expelled by the catalyst. The second issue is why In does not precipitate out of the catalysts during nanowire growth at low flow rates (sample A), but does so at high flow rates (sample B), even though In is continuously provided in the vapor and found in the catalyst in both cases.

To address the first issue, the thermodynamic affinities of Au−In and Au−Ga were calculated under Au-rich conditions from first-principle calculations based on density-functional theory within the generalized-gradient approximation as implemented in the Vienna ab initio simulation package. The details of the calculations can be found in ref 34. In these calculations, the surface adsorption and incorporation of two group-III species (Ga and In atoms) on a Au(111) surface were considered to obtain their affinities with Au, respectively. Three different adsorption sites, including top, face-centered cubic (fcc), and hexagonal close-packed (hcp) sites, were considered as the adsorption sites of the adatoms, as illustrated in Figure 5a. One substitutional (IIIa) and three interstitial sites (Figure 5b) were considered as the incorporation sites. For on-surface adsorption, the calculated formation energies show that the fcc site was the preferred site for both In and Ga adsorption on the Au(111) surface, as shown in Figure 5c. It was found that the formation energy for In at the fcc site is smaller than that of Ga, which indicates a higher stability of In on the Au(111) surface. Similar behavior is found at other adsorption sites. For
surface incorporation, as seen in Figure 5c, In and Ga atoms have a preference for the substitutional site (III$_{Au}$ in Figure 5c), while the interstitial sites are unfavorable due to higher formation energies. The formation energy of In at the substitutional site was estimated to be $-0.91$ eV, which is $0.33$ eV smaller than that of Ga (Figure 5c). This indicates that the In atoms were more easily incorporated into Au than the Ga atoms. The calculated results for both surface adsorption and incorporation therefore suggest that Au–In affinity is stronger than that of Au–Ga, which results in the fact that during the nanowire growth the Au catalysts preferentially transport Ga to the growth front while In was retained within the catalysts.

To understand the second issue, the effect of precursor flow rate on the nanowire growth requires clarification. In general, flow rates affect the axial growth rate of nanowires with higher flow rates resulting in faster nanowire growth.\(^{36}\) However, it has been suggested that precursor flow rate in MOCVD can affect the chemical potentials of nanowire materials in the catalysts.\(^{37,38}\) In this study, the possible effect of precursor flow rates on the catalyst composition was taken into account by investigating the compositional variation of the catalysts generated under different flow rates. EDS investigations show that the catalysts in sample B contains significantly more In than in sample A. Figure 6a shows the distribution of the In concentrations in individual catalysts, where $\sim10 \pm 2$ and $\sim21 \pm 5$ atom % In (the errors are standard deviations) are found in the catalyst of samples A and B, respectively. Ten catalysts were studied for each sample, and the standardless $k$-factor method was used for the quantification of the EDS spectra, where the $k$ factors for the elements analyzed (Au, In) remained constant during the analytical process. This result suggests that the composition of the catalyst alloy was affected by the precursor flow rates, where the high flow rate resulted in higher In concentration in the catalyst. To consider the fundamental reason behind this, we note that the In concentration in the catalyst scales with the In thermodynamic activity in the catalyst (Au–In alloy), which is affected by the In partial pressure in the vapor.\(^{39}\) The TMI flow rate (with the vast amount of H$_2$ carrier gas kept constant, and all the other precursors in small amount) determined the In partial pressure in the vapor, that is, the In activity and in turn the In concentration in the catalyst. Therefore, during the nanowire growth, the In concentration in the catalysts should be lower in sample A than in sample B. On the other hand, we consider the In chemical potential in the catalyst and the chemical potential of underlying nanowire cores in both samples. It is of interest to note that Au–In alloy has been consistently found to be retained within the catalyst, which induced the growth of Ga-containing binary nanowires.\(^{40,41}\) Even more interestingly, when the growth of GaAs followed the growth of InGaAs and InAs segments, In was found in the Au catalyst, and its concentration in the catalyst did not depend upon the length of GaAs segment.\(^{28,42}\) These independent studies strongly indicate that In-containing Au alloys may have even lower chemical potential (In chemical potential) than GaAs, which is the reason that In was retained within the Au catalyst in this study (sample A), and Au–In alloyed catalysts induce only binary GaAs nanowires with themselves being stable at the interface with GaAs. Moreover, in a recent study of the heterojunction between the GaAs and InAs in nanowires, Dick et al.\(^{42}\) demonstrated that the composition of Au–In alloyed catalysts remained unchanged as long as the nanowire material is fixed, regardless of the growth conditions. For GaAs nanowire growth, catalysts contain $15\pm 20$ atom % In; for InAs nanowire growth, catalysts contain $30 \pm 2$ atom % In. This observation strongly suggests a threshold of In concentration in the catalysts, and its value depends upon the nanowire material. Precipitation of In into the nanowire does not take place if the In concentration in the catalyst is below a threshold. In this study, the GaAs may set a chemical potential threshold for In to be saturated. Beyond this point, In will precipitate out of the catalysts, and ternary InGaAs nanowires will be grown. In this case, a higher In chemical potential threshold set by the ternary nanowires will vary with their composition. As a consequence, a new equilibrium between the catalyst and the ternary nanowire (in terms of the In chemical potential) may be reached under such conditions, where In continuously precipitates from the catalysts to participate in the growth of InGaAs nanowire cores. Given the fact that (1) In concentration in the catalysts of sample A is much lower than that of sample B, and (2) a binary GaAs core is found for sample A and ternary InGaAs.
core for sample B, the relationship between In chemical potential in the catalyst $\mu_C$ and that in the GaAs $\mu_{GaAs}$ can be deduced for both samples, as illustrated in Figure 6c. For sample A, the fact of $\mu_C \leq \mu_{GaAs}$ prevents formation of ternary InGaAs nanowires; while for sample B, the fact of $\mu_C > \mu_{GaAs}$ leads to In precipitation and ternary InGaAs nanowire formation.

To verify the proposed mechanism, we carried out additional experiments on In$_{0.1}$Ga$_{0.9}$As nanowires. Two samples (C and D) were grown under the flow rates of TMI $= 3.23 \times 10^{-6}$ and $1.28 \times 10^{-5}$ mol/min, respectively. The V/III ratio and growth temperature remained the same as samples A and B. TEM results of typical nanowires from samples C and D are given in Supporting Information. The results show that Ga-rich cores exist in both samples. Moreover, In concentrations in the catalysts of samples C and D are higher than that of sample A, which agrees with the trend observed in the catalysts of samples A and B. This trend shows precursor flow rate does have an effect on the composition of catalysts, that is, increased TMI flow rate results in more In incorporation in the catalysts. As a consequence, In can only precipitate out from Au catalysts once In concentration reaches a threshold.

By now, the growth mechanism of the two distinct types of In$_{x}$Ga$_{1-x}$As nanowire cores is clear. It is of interest to note that in all cases nanowire shells are InGaAs with the In concentrations being always higher than their corresponding nanowire cores. To understand this, we note that nanowire shells are grown via nanowire lateral growth by the direct impingement of nanowire materials available from the vapor (VS growth) onto sidewalls of the nanowire cores. For this reason, ternary InGaAs shells are expected in all cases. In the case of comparatively high flow rates (samples B, C, and D), since Au catalysts preferentially transport Ga to the growth front while keeping In alloyed within the catalysts, the In concentration in the nanowire cores is less than that in the vapor. As a consequence, In enriched InGaAs shells are formed. On the basis of these observations, it is anticipated that the key to homogeneous growth of InGaAs nanowires is to eliminate tapering, so that ternary nanowires only consist of the VLS-induced cores.

In conclusion, we demonstrated the structural and compositional complexities of ternary InGaAs nanowires grown under typical conditions using MOVCVD. Our direct evidence proved that the formation of core–shell nanowires with cores and shells grown via different mechanisms is the reason for the observed complexities in ternary nanowires, when two group-III elements competitively alloy with the Au catalyst. These detailed investigations indicate that precursor flow rates play a key role in the determination of the concentration of nanowire species in the catalysts, which in turn alters the composition of the nanowires. This finding provides a new insight into the role of the catalyst, as well as the effect of precursor flow rates in catalyst-assisted VLS nanowire growth.

**ASSOCIATED CONTENT**

1. Supporting Information
   Additional figures and information. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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(34) The Au(111) surface was modeled using seven Au layers and a 15 Å vacuum region. The surface Brillouin-zone sampling has been performed with Gamma-centered grid of \( 8 \times 8 \) for the \( (2 \times 2) \) surface. All atoms in the supercell except for the bottom two Au layers have been relaxed until the remaining forces acting on the atoms are less than \( 1.0 \times 10^{-3} \) eV/Å.

(35) The formation energy per Ga (or In) atom on Au(111) surface is defined as

\[
e_{\text{form}} = E_{\text{tot}} - E_{\text{ref}} - \Delta n_{\text{Au}} \mu_{\text{Au}} - \Delta n_{\text{i}} \mu_{\text{i}}
\]

where \( E_{\text{tot}} \) and \( E_{\text{ref}} \) are the total energy of Au(111) surface with and without the adatom, respectively, \( \mu_{\text{Au}} \) and \( \mu_{\text{i}} \) are the chemical potentials of Au and group-III species (Ga and In atoms), \( \Delta n_{\text{Au}} \) and \( \Delta n_{\text{i}} \) represent the difference in the number of atoms of each species with respect to the reference surface.


