Understanding the Effect of Catalyst Size on the Epitaxial Growth of Hierarchical Structured InGaP Nanowires

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ABSTRACT

Understanding the effect of catalyst on the growth of nanowires is crucial for their controllable synthesis. In this study, we report the growth of InGaP nanowires induced by different-sized Au catalysts by metal-organic chemical vapor deposition. Through electron microscopy characterization, two types of InGaP nanowires are identified and the difference in catalyst size is shown to cause their different morphological, structural and compositional characteristics. Furthermore, the influencing mechanism of catalyst size on the formation of hierarchical structures in nanowires are discussed. This study provides an insight for a better understanding of the growth of ternary nanowires, especially the effect of catalyst size, which can be a promising approach to control the ternary nanowire growth, and is therefore beneficial for the design of corresponding nanowire-based device.

INTRODUCTION

Due to their unique physical natures, III-V nanowires have been recognized as promising building blocks for electronic and optoelectronic applications, including light emission devices,¹ logic,² sensors,³ and solar cells.⁴ So far, there have been extensive studies in binary III-V nanowires, such as GaAs nanowires,^{5, 6} InAs nanowires,⁷ InP nanowires,^{8, 9} and their heterostructures^{10, 11}. Compared to binary III-V nanowires, ternary III-V nanowires possess tunable bandgap depending on the group III or V alloy composition, which is their unique advantage for the device applications.¹² For example, the InGaP material system is an ideal candidate for efficient LEDs in the red to yellow wavelength region and photovoltaic applications due to its direct bandgap in the range of 1.35 to 2.26 eV.^{13, 14} In another case, the whole compositional range of In has been realized in $\text{In}_x\text{Ga}_{1-x}\text{As}$, where its band gap can be tuned from 1.42 to 0.34 eV by varying x from 0 to 1, whilst the electron mobility can be enhanced from 1000 to 6000 $\text{cm}^2 \text{V}^{-1}\text{s}^{-1}$.¹⁵

Different from elemental or binary nanowires, the segregations of group III or V elements in ternary nanowires could result in the inhomogeneous composition, which has been an long-standing issue.¹⁶ Particularly, the spontaneous core-shell or even core-multi shell formation have been frequently reported in ternary nanowires grown by Au-catalyzed vapor-liquid-solid (VLS) method and their formation mechanisms have been intensively studied in recent years.¹⁷⁻²³ The formation of the core-shell structure largely depends on factors such as different affinity of elements with Au catalysts,^{14, 16, 24} and diffusivity of atoms²⁰⁻²². For instance, Ga-enriched nanowire cores can be formed in InGaAs and InGaP nanowires because In has better affinity with Au and hence, Ga is preferably expelled from the catalyst above oversaturation point. On the other hand, it has been well documented that catalyst size can strongly affect the VLS growths of binary III-V nanowires, resulting in morphological and/or structural changes.²⁵⁻²⁸ However, the effect of

catalyst size on the VLS growth of ternary III-V nanowires is less studied. The understanding of this issue is crucial as ternary nanowires are often used in devices due to their large bandgap tunability to match the required applications, as mentioned earlier.

In this study, we investigate epitaxial growth of InGaP nanowires on GaAs (001) substrates by the VLS technique in a metal-organic chemical vapor deposition (MOCVD) system. Through detailed electron microscopy investigation, it is found that Au catalysts with two different sizes can induce the growths of two types of $\langle 111 \rangle_B$ nanowires with different morphological, structural and compositional characteristics. The larger catalyst induced the growth of shorter nanowires in a zinc-blende (ZB) phase with the Ga-enriched core and the In-enriched shell. The smaller catalyst, on the other hand, resulted in the formation of longer nanowires with more complex hierarchical structures, in which a Ga-enriched core and an In-enriched shell are formed in upper, ZB dominated segment only, while the radial composition is homogeneous in the lower, wurtzite (WZ) dominated segment. The effect of catalyst size on the growths of two types of nanowires are clarified with a discussion of the associated mechanisms.

EXPERIMENTAL

In this study, the nanowires were grown in an AIXTRON 200/4 horizontal flow MOCVD system. Trimethylindium (TMIn), trimethylgallium (TMGa) and PH_3 were used as the precursors of group III and V species with flow rates of 6.248×10^{-6} , 5.288×10^{-6} and 4.464×10^{-3} mol/min, respectively. This resulted in a V/III ratio of 387 and the ratio between Ga and In in the gas phase (TMGa / TMIn) to be 55:45. 50 nm diameter colloidal Au nanoparticles (British Biocell International—Ted Pella, Inc.) were used as catalysts to induce the nanowire VLS growth on a GaAs (001) substrates. First, the epi-ready GaAs substrate was firstly pre-treated by immersion into poly-L-lysine and then in 100 μL of Au colloidal solution for 20 seconds. After rinsing with deionized water and dried by N_2 gas, the substrate decorated with the Au nanoparticles was then loaded onto the susceptor inside the reaction chamber of MOCVD system. Before starting the nanowire growth, the substrate was first heated up to 600 $^\circ\text{C}$ and annealed for 10 minutes in AsH_3 ambient to desorb surface contaminants and to form Au-Ga eutectic. Then the chamber was cooling down to 460 $^\circ\text{C}$ before growth was initiated by switching in TMIn, TMGa and PH_3 , whilst simultaneously removing AsH_3 . After 30 minutes, TMIn and TMGa sources were shut off to cease nanowire growth and the substrate was naturally cooling down under PH_3 ambient until 350 $^\circ\text{C}$.

The nanowires were characterized via electron microscopy. Scanning electron microscopy (SEM; JEOL 7800F operated at 5 kV) was employed to investigate the morphology of the nanowires while transmission electron microscopy (TEM; PHILIPS TECNAI F20, 200 kV) was used to study their structural properties. The compositions of the nanowires were determined by energy dispersive X-ray spectroscopy (EDS), equipped in the TEM. Convergent beam electron diffraction (CBED) technique was performed in the TEM to determine the orientations of the nanowires. SEM specimen was prepared by cleaving the substrate, with nanowires on it, along the

{110} planes. Individual nanowires for TEM characterization were obtained by ultrasonically removing the nanowires from the substrate in ethanol and then dispersing the ethanol droplets onto carbon film supported by copper grid. The lamella specimen for CBED characterization was prepared from the substrate (after the attached nanowires were removed by ultrasonication) by focus ion beam (FIB; SCIOS) and parallel to the substrate cleavage edge.

RESULTS AND DISCUSSION

Figure 1a is the top-view SEM image of as-grown nanowires on the GaAs (001) substrate, clearly showing that they are inclined with respect to the substrate. Interestingly, most of them with their projections are parallel to the $\{110\}$ cleavage edge (as marked by right angle), indicating that they grow along the $\langle 11n \rangle$ directions where n is an integer.²⁹ In addition, by careful analysis of their projected morphology, they can be distinguished into two types of nanowires with different morphologies, i.e. the shorter and thicker nanowires as majority (marked as type A), and the longer and thinner nanowires as minority (marked as type B). To determine their growth direction, cross-section SEM specimen was prepared with the view direction towards to the side $\{110\}$ cleavage edge, so that the inclined angles can be directly measured. Figure 1b is such a side-view SEM image and shows mainly two sets of oriented nanowires with the same but opposite angles of 35° with respect to the substrate surface, indicating that these nanowires grew along the $\langle 111 \rangle$ directions. Since there are 4 possible $\langle 111 \rangle$ directions associated with the (001) surface, i.e. $[\bar{1}11]$, $[1\bar{1}1]$, $[11\bar{1}]$ and $[\bar{1}\bar{1}\bar{1}]$, it is necessary to determine the growth directions of our inclined nanowires. By applying the CBED in the TEM (see details in Figure S1), the view direction of Figure 1b can be determined as $\pm[110]$.^{29, 30} Consequently, based on SEM observation and CBED result, the two growth directions of the nanowires can be determined as $[1\bar{1}1]$ and $[\bar{1}11]$, both belonging to the $\langle 111 \rangle_B$ direction.³¹ By tilting the substrate to 55° , the electron beam would be parallel to the growth direction of some of the nanowires and their cross-sections can be observed, as illustrated in Figure 1c. Figure 1d is the magnified SEM image showing details of the two types of nanowires that have different morphology and different catalyst size (highlighted by yellow circles, note that the catalysts deviate from the center due to nanowire bending under electron beam). Additionally, hexagonal (type B) and truncated triangular (type A) shapes of the nanowire

cross sections can be seen as indicated by the red dashed lines in Figure 1d. By referring to the $\{110\}$ cleavage planes of the substrate (as marked in Figure 1c), the nanowire side-facets can be determined as $\{112\}/\{1100\}$.^{1, 32}

Figure 1. (a) SEM top-view of nanowires on GaAs (001) substrate; (b) SEM side-view of nanowires; (c–d) 55° tilted-view SEM images of nanowires on the substrate, showing the cross-sectional shapes and catalysts on the tips, as marked in dash lines in (d).

To understand the structural characteristics of as-grown nanowires, TEM investigations were performed. Figure 2a is a typical bright-field (BF) TEM image showing a type A nanowire viewed along a $\langle 110 \rangle$ zone-axis, where a tapered morphology and zigzag side-facets can be seen. The inset in Figure 2a shows the magnified image of the nanowire tip with a hemispheric catalyst with a

diameter of ~ 50 nm, which is corresponding to the standard colloidal Au nanoparticle size and suggesting the VLS growth process.⁶ The nanowire tapering morphology suggests significant vapor-solid (VS) lateral growth on the nanowire sidewalls.³³⁻³⁵ Figures 2b–c are the high resolution TEM (HRTEM) images of the marked areas in Figure 2a with the corresponding selective area electron diffraction (SAED) patterns in the insets. From the results, we can infer the nanowire has a ZB crystal structure and grew along the $[1\bar{1}1]$ direction. Therefore, the truncated triangular shape of the nanowire cross-section can be understood because of polarity dependence in ZB $\{112\}$ side-facets, commonly observed in ZB nanowires.^{1, 36} Moreover, twins and lateral stacking faults can be found in Figure 2b, of which rotational twins have been reported in Au-catalyzed InP, GaP and GaAs nanowires in previous studies.³⁶⁻³⁹ In Figure 2c, stacking faults in ZB structure can be observed along the nanowire growth direction.

Figure 2. (a) BF-TEM image of individual type A nanowire along a $\langle 110 \rangle$ zone axis; (b–c) HRTEM images of marked areas in the upper part (b) and lower part (c) of nanowire in (a).

TEM characterization was then performed on type B nanowires. Figure 3a is a typical BF-TEM image viewed along a $\langle 110 \rangle / \langle 11\bar{2}0 \rangle$ zone-axis and Figure 3b shows the magnified tip region. The type B nanowire is thick and nearly untapered in the lower part while it becomes tapered in the upper part. Our statistical investigation indicates that the length of type B nanowires is much greater than that of type A nanowires, suggesting higher axial growth rate of the former. The catalyst of the type B nanowire has a diameter of ~ 15 nm, which is much smaller than that of the

type A nanowire (~50 nm). These smaller catalysts are due to the minority of Au nanoparticles deviated from the standardized size in the colloid. Indeed, compared with type A nanowires, the density of type B nanowires is very low (refer to Figure 1). Figure 3c–h is HRTEM images and their corresponding Fast Fourier Transform (FFT) / SAED patterns taken from the three different regions on the nanowire as indicated in Figure 3a, indicating the nanowire grew along the $\langle 111 \rangle_B$ (or $\langle 0001 \rangle$) direction and different structural features from the top to bottom of the nanowire. In Figure 3c–d, the upper part of the nanowire has a ZB structure with twins; however, the lower part of the nanowire is WZ dominant (Figure 3g–h), which explains the nanowire hexagonal cross-sectional shape because unlike $\{112\}$ in ZB structure, $\{1100\}$ in WZ structure are non-polarized planes.¹ In between these two distinct parts, there exists a “transition area”, which has a ZB-WZ polytype structure (Figure 3e–f).

Figure 3. (a) BF-TEM image of individual type B nanowire; (b) magnified tip of the nanowire; (c-h) HRTEM images and corresponding FFT/SAED patterns of marked position on the top (c-d), middle (e-f) and lower (g-h) parts of nanowire in (a).

Since spontaneous formation of core-shell structures have been reported in ternary III-V nanowires,^{19, 40-42} it is necessary to check the radial elemental distribution in our nanowires. Figure 4 shows representative TEM images (viewed along the $\langle 110 \rangle / \langle 11\bar{2}0 \rangle$ zone-axes) and EDS linescan profiles respectively taken from the two types of nanowires. Figure 4a shows a type A nanowire and Figure 4b–c shows the magnified view of the marked areas in Figure 4a. A core-shell structure can be seen in Figure 4b–c (indicated by arrows) with the core diameter approximately 50 nm, which is close to the diameter of catalyst, indicating that the nanowire core is induced by the catalyst via VLS mechanism.¹⁶ The EDS linescan profiles in Figure 4d confirm the formation of a core-shell structure with a Ga-enriched core and an In-enriched shell in the upper part and a Ga-enriched core in the lower part. Additionally, quantitative EDS analyses were performed on different axial positions of type A nanowires, and Figure S4 shows the representative EDS results, indicating that the In concentration increases from the nanowire top to bottom, which further confirms Ga-enriched cores and In-enriched shells configuration in type A nanowires.^{43 16}

¹⁸ Figure 4e shows a type B nanowire and Figure 4f–g is BF-TEM images of the marked areas in Figure 4e. In Figure 4f, core-shell interface can be clearly identified in the upper tapered segment (indicated by arrows) and the core diameter is ~17 nm, which is close to the catalyst size, suggesting its VLS growth mechanism. However, a core-shell interface cannot be observed in the lower part of nanowires in Figure 4g. In Figure 4h, EDS linescan profiles verify the core-shell configuration in the upper part of the nanowire while there is a lack of radial elemental segregation

in the lower part of the nanowire. EDS quantitative analyses performed on the lower part of type B nanowires (refer to Figure S5) also indicate a homogeneous composition radially.

Figure 4. TEM characterization on core-shell structures in type A and type B nanowires. (a) BF-TEM image of a representative type A nanowire; (b-c) TEM images showing the magnified areas in (a); (d) EDS linescan profiles at Position 1 and 2 in (a); (e) BF-TEM image of a representative type B nanowire; (f-g) TEM images showing the magnified areas in (e); (h) EDS linescan profiles at Position 3 and 4 in (e).

Through our detailed electron microscopy characterization, two types of $\text{InGaP } \langle 111 \rangle_B$ nanowires were grown on GaAs (001) substrate depending on the catalyst size: type A, the shorter

core-shell ZB nanowires and type B, the longer nanowire formed by a core-shell ZB structure in the upper part and a compositionally homogeneous WZ structure in the lower part. To understand the different natures in these two types of nanowires that co-exist on the same substrate, three questions need to be answered: compared with type A nanowires, (1) what is the reason causing remarkably lengthy type B nanowires; (2) how do type B nanowires switch from the WZ structure to the ZB structure from lower part to upper part and become tapered in the upper part; and (3) why only the upper segments of type B nanowires have the core-shell structure while the lower segments are in radial homogeneous composition?

To answer the first question, we note that the catalysts of type B nanowires are much smaller than those of type A nanowires. It has been well documented that smaller catalysts can generate relatively higher III concentration because of their larger surface-volume ratio, compared with larger catalysts.^{44, 45} Hence, the supersaturation level would be higher for smaller catalysts and therefore longer nanowires.^{25, 45-47} However, in our case, the post-growth catalysts of both type A and type B nanowires are Au-In alloys with similar compositions, which cannot provide direct evidence for the higher supersaturation levels of type B catalysts. This is understandable because In has better affinity with Au and therefore Ga should be preferably expelled from the catalyst during growth and cooling process.^{48, 49} Therefore, the group III concentration in the post-growth catalysts cannot indicate their supersaturation levels during growths. Although we cannot verify the difference in supersaturation between type A and type B catalysts by their compositions after growth, we believe that during growth the smaller catalysts of type B nanowires has a higher supersaturation level resulting in longer nanowires.⁵⁰

As for the second question, the variation in the structural characteristics from the bottom to the top of type B nanowires should be closely related with the change of the catalyst supersaturation

level during growth. The crystal phase of the III-V nanowire can be influenced by the catalyst supersaturation level in the VLS growth.^{51, 52} It has been demonstrated that ZB structure is preferably adopted if the catalyst supersaturation level is low, which is the case for our type A nanowires based on their larger catalysts and shorter lengths; while WZ structure should be promoted if the catalyst supersaturation level is relatively high in the catalysts.^{48, 53} In this regard, the higher supersaturation level in the smaller catalyst will contribute to WZ formation at the early stages of growth in type B nanowires, i.e. the lower part of the nanowire. Then, we need to understand why the nanowire switched from WZ to ZB structure at later stage of the nanowire growth, i.e. why upper parts of type B nanowires have the ZB structure. It is well known that Au catalysts can collect group III atoms from three sources in the Au-catalyzed VLS growth of nanowires: direct impingement of III species from ambient, substrate diffusion, and sidewall diffusion of III adatoms.^{7, 31, 54} With increasing the nanowire length, less III atoms are expected to diffuse upwards to the catalyst-nanowire interface, and thus the contribution from substrate diffusion is largely reduced at the later stages of growth, which has been found in other Au-catalyzed III-V nanowires growths^{7, 54, 55}. Consequently, the III concentration in the catalyst should decrease, and in turn the supersaturation level is lowered, resulting in a ZB structure in the upper part. As shown in Figure 3e, in the middle part of type B nanowires, the polytypism of the ZB and WZ structures suggests the gradual decrease of the catalyst supersaturation with increasing nanowire length. In fact, adatom diffusion and different crystal structures can also contribute to the different morphologies in the upper and lower parts of the type B nanowire. It has been documented that the lateral growth on $\{112\}/\{1100\}$ nanowire sidewalls may result in a tapered morphology for twin-defected ZB nanowires,³⁶ while WZ nanowires are more likely to remain untapered.^{48, 56, 57} Furthermore, since lower parts of type B nanowires are closer to the substrate,

the influence of adatom diffusion from the substrate is more significant, resulting in substantial radial growth without tapering on the WZ crystal phase.^{7, 31, 58} However, the upper part of type B nanowires has a ZB structure with twins, and tapering becomes more dominant. In addition, since this section is further away from the substrate, adatom diffusion from the substrate has less influence, resulting in less radial growth (smaller diameter).

To address the third question, the core-shell structures in type A nanowires and the upper parts of type B nanowire are formed by similar mechanism that has been well documented in previous studies on InGaAs and InGaP nanowires.^{16, 22, 42, 43} Interestingly, the core-shell structures were not observed in lower parts of type B nanowires. To understand this, we note that the misfit between different materials could promote the mass transport through their hetero-interface, by which way strain would be released.^{22, 59} We also note that the elemental diffusion may play a crucial role in the growth of other nanowire systems, such as boron carbide nanowires, where the boron migration assisted by phase-transformation proceeded in the polytypic nanowires to achieve the relatively stable boron carbide crystal phase.⁶⁰ Moreover, it has been reported that radial strain can be released faster in the hetero-structured nanowire with greater shell thickness.⁶¹ In our previous study, we also found that the compositional difference between the core and the shell decreased via radial In/Ga inter-diffusion in InGaP $\langle 111 \rangle_B$ nanowires.⁴³ In this regard, we believe that the radially homogeneous composition in the lower WZ segment is attributed to In and Ga inter-diffusion through an initially formed core-shell interface. The lower segment was formed earlier, therefore it had been subjected to growth temperature for a longer time and the significant lateral growth resulted in a thick shell, both of which facilitated the inter-diffusion of group III atoms through the core-shell interface. On the other hand, the core-shell upper part of the type B nanowire was formed at a later stage. Therefore, the inter-diffusion process was inadequate to form a uniform

radial composition. Additionally, EDS linescan was performed at bottoms of tapered segments in type B nanowires (refer to Figure S6), showing slight compositional difference between the nanowire core and shell, suggesting a gradual change in the radial composition uniformity from the top to the bottom in type B nanowires.

Based on the characterizations and discussions above, Figure 5 illustrates the configurations of a type A (Figure 5a–b) and a type B nanowire (Figure 5d–e). Figure 5c is a schematic showing different Au catalyst size on the GaAs (001) substrate, in which the larger catalyst induces the type A nanowire and the smaller catalyst induces the type B nanowire. Since Au atoms have a stronger affinity to In atoms, Ga atoms are preferably expelled from the catalyst. Therefore, a Ga-enriched core is formed in the type A nanowire (refer to Figure 5a) and the upper part of the type B nanowire (refer to Figure 5e). The smaller catalyst has a relatively higher supersaturation level, particularly at the earlier stages of type B nanowire growth, resulting in longer nanowire than type A (compare Figure 5b and Figure 5d). However, as the nanowire grows longer, there is a decrease in the number of adatoms that are able to diffuse to the growth front and hence the catalyst supersaturation level becomes lower in the type B nanowire, leading to its structural phase change from WZ to ZB (refer to the cross-sections in Figure 5e). Additionally, In/Ga radial inter-diffusion results in the homogenous composition profile of the lower segment while core-shell structure still remains in the later formed, upper part of the type B nanowire.

Figure 5. Illustration shows the formation of hierarchical structures in the type A and the type B nanowires.

CONCLUSION

In conclusion, we demonstrate the effect of Au catalyst size on the VLS growth of InGaP nanowires in MOCVD. Our systematic electron microscopy characterizations suggest two types of $\langle 111 \rangle_B$ InGaP nanowires with different morphological, structural and compositional features. The smaller catalyst-size of type B nanowire is the major reason that causes its greater length than the type A nanowire. And the decrease of supersaturation level in the catalyst results in the structural change in type B nanowire. We demonstrate that the core-shell structures in type A nanowires and upper parts of type B nanowires are mainly attributed to the better affinity of In, than Ga, with Au catalysts; and the homogeneity in the lower regions of type B nanowires is attributed to the core-shell inter-diffusion. This study provides insights for understanding the effect

of catalyst on the ternary nanowire growth, which can be a new contribution to their controllable growth for applications.

ASSOCIATED CONTENT

Supporting Information. SEM/TEM images showing the the substrate after FIB milling and the lamella sample for CBED experiment; SEM images showing the process of sample tilting; TEM image suggesting the co-existence of the type A and type B nanowires; EDS quantitative analyses on the type A nanowire and type B nanowire; EDS linescan profile at the bottom of tapered segment in the type B nanowire.

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Notes

The authors declare no competing financial interest.

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