Radial Growth Evolution of InGaAs/InP Multi-Quantum-Well Nanowires Grown by Selective-Area Metal Organic Vapor-Phase Epitaxy

Inseok Yang,† Xu Zhang,†,‡ Changlin Zheng,∥ Qian Gao,‡ Ziyuan Li,‡ Li Li,‡ Mark N. Lockrey,‡ Hieu Nguyen,§ Philippe Caroff,†,# Joanne Etheridge,⊥ Hark Hoe Tan,‡,† Chennupati Jagadish,† Jennifer Wong-Leung,*† and Lan Fu*†

†Department of Electronic Materials Engineering, Research School of Physics and Engineering, ‡Australian National Fabrication Facility, Research School of Physics and Engineering, and ∥Research School of Engineering, The Australian National University, Canberra, Australian Capital Territory 2601, Australia
§National Center for International Joint Research of Electronic Materials and Systems, Henan Key Laboratory of Laser and Opto-electric Information Technology, School of Information Engineering, Zhengzhou University, Zhengzhou 450052, People’s Republic of China
⊥Monash Centre for Electron Microscopy, Monash University, 10 Innovation Walk, Clayton, Victoria 3800, Australia

Supporting Information

ABSTRACT: III–V semiconductor multi-quantum-well nanowires (MQW NWs) via selective-area epitaxy (SAE) is of great importance for the development of nanoscale light-emitting devices for applications such as optical communication, silicon photonics, and quantum computing. To achieve highly efficient light-emitting devices, not only the high-quality materials but also a deep understanding of their growth mechanisms and material properties (structural, optical, and electrical) are extremely critical. In particular, the three-dimensional growth mechanism of MQWs embedded in a NW structure by SAE is expected to be different from that of those grown in a planar structure or with a catalyst and has not yet been thoroughly investigated. In this work, we reveal a distinctive radial growth evolution of InGaAs/InP MQW NWs grown by the SAE metal organic vapor-phase epitaxy (MOVPE) technique. We observe the formation of zinc blende (ZB) QW discs induced by the axial InGaAs QW growth on the wurtzite (WZ) base-InP NW and propose it as the key factor driving the overall structure of radial growth. The role of the ZB-to-WZ change in the driving of the overall growth evolution is supported by a growth formalism, taking into account the formation-energy difference between different facets. Despite a polytypic crystal structure with mixed ZB and WZ phases across the MQW region, the NWs exhibit high uniformity and desirable QW spatial layout with bright room-temperature photoluminescence at an optical communication wavelength of ∼1.3 μm, which is promising for the future development of high-efficiency light-emitting devices.

KEYWORDS: III–V compound semiconductors, selective-area epitaxy, MOVPE, nanowires, InGaAs/InP quantum wells, growth mechanism

III–V compound semiconductor nanowires (NWs) has drawn much attention because they are promising candidate nanoscale light sources for integrated photonics due to their small size, superior optical and electrical properties, and strain-relaxation feature enabling the monolithic growth on lattice mismatched substrates.1,2 In particular, NWs grown by the catalyst-free selective-area epitaxy (SAE) technique have many advantages, such as the controllability of their size and position and high uniformity in diameter and length as well as compatibility with the complementary metal-oxide-semiconductor (CMOS) process to facilitate the integration with other electronic devices. In addition, a single standing NW itself can act as a vertical optical cavity3 and an array composed of several tens to thousands of NWs may also act as a photonic crystal,4,5 both of which could be beneficial for design and implementation of high-power light-emitting diodes (LEDs) and lasers. Among many SAE-grown III–V NWs, InP-based NWs have been intensively investigated as a potential light source due to its direct band gap and low surface...
Figure 1. (a–c) SEM images at top view (above) and 30° tilted view (below) of 1QW-, 3QW-, and 5QW-NW samples grown by the SAE-MOVPE technique, respectively. The yellow dashed line in panel c indicates the planes for the FIB cross-sectioning. (d) Statistical result of top-InP shape of 1QW-, 3QW-, and 5QW-NW samples, respectively. T, H, RH, and N represent a triangle with {112} facets, a hexagon with {110} facets, a rotated hexagon with {110} facets, and a nonagon, respectively. (e) SEM image of a 5QW-NW transferred onto a substrate for morphology assessment. (f) Schematic diagram of the overall QW-NW growth process.

In this paper, we demonstrate the successful growth of InGaAs/InP multiquantum-well nanowires (MQW-NWs), simultaneously forming an axial and radial QW, on (111)A InP substrate by the SAE technique using metal organic chemical vapor deposition (MOCVD) and reveal a distinctive facet evolution process driven by the insertion of InGaAs QWs, which form zinc blende (ZB) layers in a WZ InP NW architecture. Although the facet evolution induced by the QW insertion in this work appears similar to those observed previously in different III–V heterostructure growths,6,7,10 the mechanism of facet formation is shown to be completely different. We observe that with the addition of an increasing number of InGaAs QWs, the lateral facets of WZ InP NW known to have m-plane orientation evolve into a-plane facets. Aberration-corrected scanning transmission electron microscopy (AC-STEM) shows that the axial InGaAs QW is ZB, and the subsequent radial growth of InP barrier surrounding the ZB QW maintains the ZB structure and becomes the driving force for the facet change during the subsequent QW growth. We also calculate the formation energies in each QW growth step and confirm that the facet evolution is initiated by the reduction of the formation energy. Furthermore, the NWs in this work exhibit good uniformity and desirable QW spatial distribution for the further realization of p–n junction-based devices such as electrically injected light-emitting devices. Because the QWs by our SAE MOVPE growth consist of both the axial and the radial components with different composition and thickness, bright photoluminescence at two different wavelengths have been observed that may be further applicable to the development of multiple-wavelength light sources or an integrated self-switchable wavelength selector.

RESULTS AND DISCUSSION

The SEM images of the NW arrays containing 1-, 3-, and 5 QWs are shown in panels a–c in Figure 1, respectively. For all samples, the growth conditions were the same for the InP base, QW, InP barrier, and top InP, and the only difference is the number of QWs grown. In all cases, the InP base has {112} or {1100} facets, as previously reported for SAE InP growth. The diameter of the top InP segment increased with the number of QWs with the diameter ranging from 280 to 440 nm for 1-, 3-, and 5-QW samples, respectively.
contrast, the diameters of InP base for all samples were nearly the same ranging from 280–380 nm regardless of the number of QWs. The increased diameter with the number of QWs implies significant radial growth during the QW/barrier formation.

As shown in the tilted images in Figure 1a–c, NWs have inclined facets in all cases, and this suggests that the radial growth is more significant at the top of the InP base. Furthermore, we note that the top of the NW evolves into a more uniform hexagon shape with additional QW growth. To understand the relationship between side-facet morphology and the number of QWs, we perform statistical analyses of morphology from about 450 NWs in each of the 200 μm × 200 μm array sample. SEM images were taken and analyzed from nine equidistant locations on a diagonal line in a square array to obtain the average location-dependent effect, and the result of which is presented in Figure 1d. We note that in 98.8% of the 5 QW NWs, there is 30° rotation in the hexagonal shape observed at the top of QW with respect to the InP base. In contrast, the NWs with a single QW consist of various shapes such as triangles with {112} facets, non-rotated hexagons (identical to base InP), 30° rotated hexagons, and nonagons. In fact, the triangles with {112} facets are observed to be nonagons with predominantly {112} facets. The nonagon is a signature of the 3-fold symmetry typically observed for ZB structure.24 Indeed, ZB GaAs NWs have a truncated triangular shape with wide polar (112)B facets and small (112)A facets. Thus, the nonagon is a combination of the truncated triangular shape in which each (112)A facet is replaced by two (110) facets. It is interesting that with an increasing number of QWs, the cross-section of the NW evolves toward a 30° rotated hexagon with {110} side facets, thus clearly suggesting that the most-stable facets for the QWs and barriers are {110}, which correspond to the {1120} planes in WZ. The radial growth evolution will be discussed with Figure 5 in more detail later.

Figure 1e presents the final SEM image of a 5QW-NW, clearly showing the side facet rotation from {112} to {110} with additional inclined facets connecting these two rotated facets. Figure 1f is the schematic diagram describing the entire growth process of InGaAs/InP MQW-NW. First, the InP base is grown, filling the SiO2 trench hole of 220 nm (Figure 1f-1) as initially defined on the InP (111)A substrate until the lateral surfaces finally form perfect {112} planes that are the most-stable facets in WZ InP 7 (Figure 1 f-2). Further growth prevailed mainly in the axial direction, retaining the diameter of the hexagon until the growth of the InP base is stopped (Figure 1f-3). During the subsequent growth of QWs and barriers, the side facets are modified (Figure 1f-4). We note that the change in side facet is restricted to the top of InP base, clearly indicating that QW layers and barriers grow predominantly near the top of the InP base. Finally, the subsequent top InP segment growth closely follows its modified shape until the end of growth (Figure 1f-5).

For an understanding of the complete growth evolution, microstructural analyses by AC-STEM of the 5QW sample were carried out on NWs prepared by FIB cross-sectioning in both the vertical and the horizontal directions. In particular, the vertical cross-sectional sample was cut along the (110) or (1120) plane marked with the yellow dashed line (1) in Figure 1c. The vertical cross-sectional AC-STEM image in Figure 2a was imaged along the [110] or [1120] zone axis. The five InGaAs QWs (thin bright regions) are clearly visible due to ZB structure.
Figure 3. (a) AC-STEM image taken along the [110] or [1120] zone axis from the region marked with A in Figure 2a. ZB and WZ regions along the axial direction are marked with dashed lines separating the WZ (purple) and ZB (yellow) regions. The brightness profile is superimposed, and the estimated thickness of each axial QW from the profile is also presented. (b) AC-STEM image enlarged from the rectangular area in panel a. (c–f) Left panels: enlarged images from the rectangular region labeled in panel b. Right panels: illustrations of the corresponding atomic structures of regions c–f. The colors for each atom are shown on the left side of this whole figure. The truncated plane of base-InP has ∼43° over the horizontal plane in panel b, consistent with that of (1102) in panel e.

contrast, indicating that these layers are either indium- or arsenic-rich. These layers also exhibit both axial growth along the InP base and radial growth on the sidewalls of the area near the top of the InP base. The AC-STEM image also clearly showed the preferred facets to be {1101} from their inclination (see Figure S1) and the InP barriers were observed to induce the formation of outward facing facets well below the position of the QWs. These facets are distinctly different from inclined facets reported in SAE grown InAs-InSb NWs with ZB-inclined facets.20 In our case, the positions of these inclined {1101} facets show some variations and are asymmetric in all NWs. For example, the NW in Figure 2 has two major inclined facets on the left side and one on the right side. This is closely related to the non-uniform coverage by the InP barriers. Even if a barrier is being grown simultaneously, the area being covered on each side of the NW may be different due to the 3-fold symmetry. The dimensions of Lx and Ly labeled in Figure 2a highlight the difference, where L indicates the length covered by the barrier from the top of the InP base. The InP base of hexagonal column exposes six faces and each face can be named from a to f (see Figure 4c). The fact that Lx and Ly are different suggests that the coverage of each barrier varies from face to face, causing the asymmetric facet formation. The different number of inclined facets on each side can be attributed to the radial growth rate difference on each side and this will be discussed further with Figure 4c. The three angled facets in Figure 2 have similar angles of ∼28° with respect to the growth direction, which corresponds to the {1101} plane. For chemical composition analysis, the energy-dispersive X-ray spectroscopy (EDX) line scan along the NW axis was also conducted and superimposed. The EDX line scan was measured only along the axial direction because the measurement along the radial direction is inaccurate, especially if the facets are not viewed edge-on and the QWs are too close to each other to be resolved. As shown in Figure 2a, the first axial QW showed a brighter contrast compared with successive QWs. This is consistent with the EDX line scan, which shows a higher concentration of arsenic in the first QW compared with successive QWs. We note that all QWs show a reduction in the indium and phosphorus concentration commensurate with the increase in gallium and arsenic concentrations, respectively, indicating that the bright Z contrast is due to the presence of arsenic in the QWs. Here, we note that some residual P is observed in the QW layers, implying that the QW has a quaternary InGaAsP composition instead of the intended InGaAs growth; this is attributed to the interdiffusion due to the high growth temperature. Selected-area electron diffraction (SAED) patterns obtained from the middle of the top InP segment and the InP base are presented in panels b and c of Figure 2, respectively, confirming that both segments are WZ structures. Here, it is noticeable that a satellite peak representing (002) of the ZB phase was found only from the top InP, while the base InP was observed in a nearly pure WZ phase. This is indicative of the presence of the ZB phase in the top segment in addition to the predominant WZ phase. The diffraction spots shown in Figure 2c are elliptical and elongated in the axial direction. This indicates a larger variation in the lattice parameter in the axial direction, consistent with the fact that the lattice parameter in the radial direction is constrained, allowing strain relaxation along the growth direction.

For the horizontal cross-sectioned SQW-NW, FIB cross-sectioning was performed in the region where the inclined facets were found to capture the radial QWs. A high-angle annular dark field (HAADF) image of this cross-section viewed along the [0001] direction is shown in Figure 2d. Considering the thickness of the FIB lamella of 50–100 nm and the number of visible QWs and their dimensions, this sample could be deduced to come from a section of the NW that includes QW1, QW2, and QW3–5. We note that the lack of QW contrast along the 3 alternate <112> directions is associated with a faster radial growth and known to show {110} facets. This suggests very little arsenic incorporation within the
InGaAs QWs in these directions. The blue-dashed-lined hexagon represents the expected position of InP base. We can track the growth of InP barriers by looking at the spaces between neighboring radial QW and confirmed that the radial growth of the QWs evolved from triangular nonagons toward a hexagonal shape with {110} or {1120} facets. Interestingly, the modification in the form of nonagonal barriers shown above is in good agreement with the statistical results obtained from Figure 1d implying that the nonagon would be the intermediate shape prior to the formation of 30° rotated hexagon. Thus, it is clear that the driving force behind the facet change from {1100} to {1120} planes is the growth of QW and barrier. For this reason, subsequent growth of additional QWs enables more NWs to achieve successful radial growth evolution to {1120} facets.

AC-STEM was carried out to determine the local structure of the QWs. Figure 3a was taken along the [1120] zone axis from the region “A” marked with blue dashed rectangle in Figure 2a showing all 5 axial QWs. Figure 3b is the magnified image of the area marked with yellow rectangular box in Figure 3a, showing the presence of a 43° inclined facet corresponding to (1102) plane at the corner of top of InP base. These facets were observed at both corners of InP base, signifying that the InP base has a bevelled edge with {1120} facets prior to QW growth. The TEM analysis confirms that the InGaAs layer filling this corner also has a WZ phase and implying that it grows laterally with InP as the growth template (Figure 3e). We note that all axial components of QWs are stacked in the ZB phase, whereas the radial QWs in the WZ phase. Figure 3c,d shows the interfaces of InGaAs QWs grown axially in the ZB phase on WZ (0001) templates of InGaAs QW corner and InP base, respectively. Using the convention in the report by Zou et al., it is clear that the left-hand sidewall of the ZB section is (112)B, while the right-hand sidewall is (112)A. The phases of all QWs grown axially were confirmed and presented in Figure 3a. The NW has, alternately, ZB and WZ phases along the NW axis in the QW-barrier region. The starting positions of each ZB layer match the start of the InGaAs QW layers and the WZ segment growth corresponds to the subsequent barrier growth. Basically the (0001) plane of WZ InP used as a growth template for axial QWs is nearly identical to the ZB (111) plane, and each InGaAs QW growth initiates the ZB phase.25 This is consistent with the SAE growth of InP/AlInP core−shell and GaP/AlGaP core−shell NWs, where top segments had a ZB structure, while the shells had a WZ structure consistent with the core.12,13 Similarly, the axial InP barriers adopted the WZ phase, in agreement with the base InP grown in identical conditions.

However, the radial growth is a completely different story because growth is initiated on the side facets, which now determine the crystal structure. As mentioned earlier, the lateral facets for WZ and ZB have different polarity considerations as well as surface energy, making the phase transition between the two complicated. Hence, the radial QW follows the structure of the core NW in contrast to the axial QW case. For the same reason, the subsequent radial barrier has two crystal structures as growth templates in terms of radial growth, the WZ sections, and the ZB QW sections. Thus, the radial barrier has mixed phases with the template of two different phases, and consequently, the n-th grown radial InP barrier has alternately grown mixed-phase layers of 2n + 1. For example, the third grown radial InP-barrier has seven alternately grown mixed-phase layers.

To determine the thickness of the QWs, the interfaces between the QWs and barriers have to be well-defined first. As can be observed in Figure 3b, the sharpness of InP−InGaAs interface and InGaAs−InP interface are quite different. The interface abruptness issues due to the atomic interdiffusion
between arsenic and phosphorus have been reported previously in thin-film QW growth.\textsuperscript{26,27} Besides, arsenic adatoms have a low desorption rate,\textsuperscript{28} thus explaining its incorporation during the subsequent InP barrier growth.\textsuperscript{26,27} These factors change both the composition and the thickness of the QW layers and, thus, the broadening of the luminescence spectrum. The thicknesses of the axial QWs were estimated from the brightness profile of AC-STEM images and highlighted in Figure 3a. The first and second QWs are around 5 nm thick, while the rest are thinner than 3 nm. It is worth noting that the estimated QW thicknesses are close to the thicknesses of the ZB layers, indicating that the introduction of arsenic and gallium trigger the transition to the ZB phase.\textsuperscript{21}

Likewise, the staggered two and three inclined facets on the left-hand sidewall is consistent with a similar growth rate for the cross-section of the NW evolves in a 3-fold symmetry, as mentioned earlier. In particular, when one looks at the cross-section of the NW adopts a ZB phase, while the radial QW adopts the WZ structure of the InP base. Now the following InP barrier could have 3 different structures: the axial (111)/{110} planes as found in Figure 3b, and these chamfered edges disappear with the growth of the first QW. Subsequently, the first axial QW adopts a ZB phase, while the radial QW adopts the WZ structure of the InP base. The lattice mismatch strain energy term $E_{\text{strain}}=\frac{1}{2}E_{\text{bulk}}(1-\nu)^2\Delta \mu V$ and lattice mismatch strain energy term $E_{\text{strain}}=\frac{1}{2}E_{\text{bulk}}(1-\nu)^2\Delta \mu V$ is the difference of chemical potentials between the vapor and the solid phases and $V$ is the volume, $e_{\text{in}}, e_{\text{m}}$ is the lattice misfit, $E$ is the Young’s modulus, and $\nu$ is Poisson’s ratio of the material) is identical for different shapes; hence, these terms are canceled in the following equations. It is therefore sufficient to consider only the surface energy contributions. The hexagon surface energy generated upon the formation of ZB disc can be put into the following form:

$$G_{\text{Hex}} = 6R_s W(\gamma_{\text{ZB}}^{(211)} + \gamma_\ell - \gamma_s)$$

with $\gamma_{\text{ZB}}^{(211)}$ as the side-wall surface energy of (211) facet, $\gamma_s$ as the interfacial energy, $\gamma_\ell$ as the surface energy of InGaAs QW layer, and $W$ as disc height on the sidewalls. Here, $L = \sqrt{6} R_s$, and $l = 1.02 R_s$ (see Figure 4d and the Supporting Information). In the same way, the surface energy of the triangle and the nonagon are written as:

$$G_{\text{Tri}} = 3LW(\gamma_{\text{ZB}}^{(211)} + \gamma_\ell - \gamma_s)$$

$$G_{\text{Nona}} = 6Wl \sin(\beta)(\gamma_{\text{ZB}}^{(211)} + \gamma_\ell - \gamma_s) + 6Wl \sin\left(\frac{\pi}{3} - \beta\right) \tan\left(\frac{\pi}{6}\right)(\gamma_{\text{ZB}}^{(110)} + \gamma_\ell - \gamma_s)$$

with $\gamma_{\text{ZB}}^{(110)} = 1.3$ as the sidewall surface energy of (110) facet.\textsuperscript{35} Finally, the calculated formation energy of hexagon, triangle, and nonagon ZB discs during the first QW barrier growth follows $G_{\text{Nona}} < G_{\text{Hex}} < G_{\text{Tri}}$. This indicates that the nucleation probability of the nonagon is the most preferable. Using a similar approach, we compare the formation energy of the rotated hexagon, nonagon, and triangle of the final growth state and readily obtained $G_{\text{Hex}} < G_{\text{Nona}} < G_{\text{Tri}}$ (see Figure S2b). This result indicates that the formation energy of nonagon becomes smaller as the length of the stable (110) facets grows longer. Finally, the (211) facets of the nonagon disappear and its cross-section transforms into a rotated hexagon. We conclude that the formation of the rotated hexagon is driven by the lowest surface energy of the ZB disc during its nucleation process. This is consistent with the statistical analysis of Figure 1d, clearly suggesting that the additional QW acts as a driving force in the radial growth evolution, facilitating the completion of radial growth evolution into the most-stable 30° rotated hexagon. As mentioned earlier, a small number of triangles with (110) facets mostly observed from the single QW NW array are triangular-like nonagons with very short (110) facets. The MQW structure introduces more ZB discs and evolves toward a rotated hexagonal shape in which (110) facets are the most-stable facets (see in Figure 4c). The additional ZB discs promote radial growth, which results in a rotated hexagon with well-defined (110) facets with the lowest formation energy as detailed in the theoretical calculations presented above. The detailed calculation of formation energies of various shaped facets is provided in Figure S2.
It is noted that the radial InP barrier does not cover the whole NW but forms an inclined \{1\overline{1}01\} facet. This is consistent with the slow radial growth associated with the WZ sidewalls. In addition, the inclined semi-polar plane \{1\overline{1}00\} has the same polarity termination (see Figure S1). We also note that \{1\overline{1}00\} facets are gradually exposed as the top InP segment grows axially, signifying the reverse evolution back to \{1\overline{1}00\} facets preferred in WZ InP as observed in the InP base (see Figure S3).

The optical properties of the QW-NWs were also characterized by microphotoluminescence (micro-PL) and cathodoluminescence (CL) techniques. The left panel of Figure 5a shows the micro-PL intensity mapping measured at 80 K from a single QW-NW. It can be clearly seen that the strong luminescence is centered in the QW region. The spectrum was mapped (middle panel) along the most-intense luminescence area marked on the left panel of Figure 5a to observe the position distribution of the PL wavelength. It is found that the single QW-NW displays two separate peaks at the wavelength around 1110 and 1180 nm, with the longer wavelength arising from positions 1 to 3, while the shorter wavelength was from positions 2 to 5. Considering the scanning direction, the 1110 and 1180 nm peak can be determined to originate from the radial QW, and the axial QW with the ring QW formed at the thickest corner, respectively.

The corresponding PL spectra at 300 and 80 K acquired from positions 1, 2, and 3 are presented in Figure S4. Figure 5b shows the micro-PL intensity and wavelength mapping measured at 80 K from a SQW-NW. From the measurement with multiple NWs, we observed unexpected peaks at random wavelength positions over 1200 nm from position 3 to 5 together with the main peak at around 1190 nm. This may be ascribed to the coalescence of radial QWs from the bending position of inclined facets as labeled in the NW schematic diagram in Figure 5b (right). Figure 5c shows the cross-sectional CL panchromatic image from a 5QW-NW array measured with an InGaAs detector (coverage of 1–1.6 μm) at room temperature overlaid on its corresponding SEM image. In agreement with the PL result, an intense and localized luminescence in the wavelength of 1–1.6 μm can be observed around the inclined facets of the NWs, where the QWs are located. As is clearly shown in this image, the luminescent regions are long and well-aligned vertically, which are promising for future device applications including high-power LEDs, photonic crystal lasers, QWIPs, etc.

CONCLUSIONS

In conclusion, we have demonstrated the growth of InGaAs/InP QW-NWs by MOCVD using the SAE technique.
microstructures and faceting of the MQW were thoroughly investigated by AC-STEM and EDX, respectively. We observed that the lateral facets of WZ InP were rotated by 30° with the addition of InGaAs QWs and revealed that the ZB disc induced by the axial QW growth is the main driving force for the radial growth evolution, resulting in distinctive QW formation with different crystal phases in the axial and radial components. We also compared the formation energies in each growth evolving step confirming the growth evolution with the facet formation-energy change. The optical properties of the QW-NWs were also characterized by micro-PL and CL measurements. It is found that QWs formed in both the radial and the vertical directions of the NW produce strong PL at different wavelengths. The NW arrays also display good uniformity in dimension and desirable QW spatial distribution for future implementation of electrical structures (such as the p–n junction) for device applications. Our detailed morphological structural and optical study of the InGaAs/InP QW-NW structures provides important insights and guidance for the further improvement of material quality and design and the demonstration of QW-NW-based nanoscale devices for a wide range of optoelectronic applications. The methodology demonstrated in this work could also serve as a guide to mapping relevant information about fully 3D heterostructured, mixed-crystal-phase semiconductor nanocrystals in a large number of materials systems.

EXPERIMENTAL METHODS

Preparation of Nanowire Growth Template. To form a mask pattern for SAE growth, a SiO2 layer of 30 nm was first deposited on a (111) A InP wafer at 300 °C by atomic layer deposition (ALD). Subsequently, the mask patterns with a nominal hole diameter of 100 nm and pitch of 800 nm in a 200 μm × 200 μm hexagonal array were defined by electron-beam lithography (EBL) in a Raith 150 EBL system. The final hole diameter obtained after wet chemical etching in a solution of 48% hydrofluoric acid diluted in ammonium fluoride with a ratio of 1:4 was ~220 nm.

Nanowire Growth Process. The SAE growth was conducted in an AIXTRON 200/4 MOCVD system, a horizontal flow reactor with a base pressure of 100 mbar using H2 as the carrier gas. Trimethylindium (TMIn) and trimethylgallium (TMGa) were used as precursors for group III elements, while phosphine (PH3) and arsine (AsH3) were used as precursors for group V elements, maintaining a total flow rate of 14.5 l/min in all growths. The patterned substrate was annealed in situ at 750 °C for 10 min under a PH3 protective flow of 50 sccm prior to growth. After annealing, the base InP NW segment was grown at 700 °C for 8 min at a V-to-III ratio of 80.9 using molar fractions of 6.07 × 10⁻⁶ and 4.91 × 10⁻⁴ for TMIn and PH3, respectively. The InGaAs quantum-well layers were grown with a V-to-III ratio of 80.7 by setting molar fractions for TMIn, TMGa, and AsH3 to 3.37 × 10⁻⁵, 8.80 × 10⁻⁵, and 9.82 × 10⁻³, respectively. For the QW growth, the InGaAs QW layer was grown for 5 s, while the InP barrier was grown for 40 s using the same conditions as those used for the base by alternatively switching precursors for the different layers depending on the number of QWs (1, 3, and 5 in this work). The structures were terminated with a final InP NW segment growth of 7 min using the same conditions as those used for the InP base and barrier segments.

Characterization Method. The morphology and dimensions of NWs were characterized by SEM using a FEI Helios 600 Nanolab focused-ion beam system, and the images were taken at the location, which was 50 μm × 30 μm away from a corner of the 200 μm × 200 μm array under an accelerating voltage of 5.0 V and current of 43 pA. The microstructure and chemical composition were analyzed by TEM equipped with energy dispersive X-ray spectroscopy detector using a JEOL 2100F system. The high-resolution STEM and high-angle annular dark field images were acquired from a double-aberration-corrected FEI Titan instrument. The optical property of NWs was characterized by CL and PL techniques. CL was acquired under an electron excitation voltage of 5 kV and current of 0.4 nA. PL was measured by using a 532 nm laser of 1.6 × 10⁻⁴ W/μm² at room temperature and 1.6 × 10⁻⁸ W/μm² at 80 K, respectively.

ASSOCIATED CONTENT

§ Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.8b05771.
Additional details on the inclined facet and radial QW thickness analysis, calculation of formation energies of various shaped facets, reverse radial facet evolution of the top InP segment, and position-dependent photo-luminescence spectra (PDF)

AUTHOR INFORMATION

Corresponding Authors
*E-mail: jenny.wongleung@anu.edu.au.
*E-mail: lan.fu@anu.edu.au.

ORCID
Inseok Yang: 0000-0001-9805-9817
Ziyuan Li: 0000-0001-9400-6902
Hieu Nguyen: 0000-0003-1667-1135
Joanne Etheridge: 0000-0002-3199-3936
Jennifer Wong-Leung: 0000-0002-5050-4202
Lan Fu: 0000-0002-9070-8373

Present Address
*Microsoft Station Q, Delft University of Technology, Building 22, Faculty of Applied Sciences, Lorentzweg 1, 2628 CJ Delft, Netherlands

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the Australian Research Council for financial support. The authors also acknowledge the Australian National Fabrication Facility (ACT node), the Australian Microscopy and Microanalysis Research Facility (ACT node) for facility support, and the Monash Centre for Electron Microscopy for access to FEI Titan3 80-300 S/TEM funded by the ARC grant no. LE0454166. The authors thank Prof. D. Macdonald for access to the micro-PL facility at the College of Engineering and Computer Science at the Australian National University. I.Y. acknowledges the support of AGRTP scholarship from the Australian Government. H.N. acknowledges the support of a fellowship from the Australian Centre for Advanced Photovoltaics.

REFERENCES


(33) Ghalamestani, S. G.; Munshi, A. M.; Dheraj, D. L.; Finland, B.-O.; Weman, H.; Dick, K. A. Self-Catalyzed MBE grown GaAs/ GaAsSb1−x Core−Shell Nanowires in ZB and WZ Crystal Structures. *Nano technology* 2013, 24, 405601.
