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Polarity driven formation of InAs/GaAs hierarchical nanowire heterostructures

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The structural and morphological characteristics of InAs/GaAs radial nanowire heterostructures were investigated using transmission electron microscopy. It has been found that the radial growth of InAs was preferentially initiated on the $\{112\}_A$ sidewalls of GaAs nanowires. This preferential deposition leads to extraordinarily asymmetric InAs/GaAs radial nanowire heterostructures. Such formation of radial nanowire heterostructures provides an opportunity to engineer hierarchical nanostructures, which further widens the potential applications of semiconductor nanostructures.

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Semiconductor nanowires can be used in a wide range of applications including nanoscale electronic and optoelectronic devices,¹ biosensors,² and chemical sensors.³ These semiconductor nanowires are generally grown via the vapor-liquid-solid mechanism using metal nanoparticles to catalyze nanowire growth.^{4,5} This mechanism has been exploited to produce well controlled single-crystalline nanowires (in terms of their diameter, shape, and location),^{6,7} branched nanowire heterostructures,^{8,9} and nanowire networks.¹⁰ Nanowire heterostructures can be produced by modulating the composition of a nanowire axially¹¹ and radially.¹² Radial nanowire heterostructures consist of core and shell (or multishell) morphologies, which offer flexibility to engineer the band gaps of a radial nanowire heterostructure and thereby, desired properties can be obtained.^{13,14} Many potential applications have been demonstrated using these radial nanowire heterostructures including multicolor light-emitting diodes,¹⁴ address decoders,¹⁵ high electron mobility transistors,¹⁶ and nonvolatile crossbar switches.¹⁷

Exploration of the fundamental mechanism(s) of radial growth is essential to produce the practically useful radial nanowire heterostructures with desired composition, structure, and morphology. During the growth of radial nanowire heterostructures, material of different compositions is deposited on the nanowire sidewalls. Therefore, the crystallography, topography, and morphology of the nanowires' sidewalls can play a critical role in the nucleation and growth of radial nanowire heterostructures. Due to the difference in the polarity of III-V nanowires' sidewalls, different faceting behaviors can be observed, depending on the growth conditions.^{18,19} For example, GaAs nanowires grown in arsenic rich conditions show rapid radial growth on $\{112\}_A$ facets than $\{112\}_B$ facets of the nanowire sidewalls,¹⁹ although this radial growth can be restricted by reducing the growth temperature.²⁰ However, if this radial growth phenomenon can be intentionally adopted in the growth of radial

nanowire heterostructures, it is possible to design nanowire heterostructures with extraordinary structural characteristics.

In this letter, we demonstrate our architecture of InAs/GaAs radial nanowire heterostructures with a structural characteristic shown in Fig. 1(a) with a cross-sectional feature given in Fig. 1(b) by preferential radial deposition of InAs on the $\{112\}_A$ sidewalls of GaAs nanowires. This unusual structural characteristic paves a way of constructing extraordinary hierarchical nanostructures and is anticipated to widen potential applications.

GaAs nanowires with $\{112\}$ sidewalls were first grown on a GaAs ($\bar{1}\bar{1}\bar{1}$) substrate using Au catalysts with an average diameter of 30 nm. InAs was then deposited on these nanowires for 30 s and 3 min, respectively. The entire growth was carried out in a horizontal flow low pressure (100 mbar) metal-organic chemical vapor deposition reactor at a growth temperature of 450 °C using trimethylgallium (TMG) and AsH₃ precursors for GaAs nanowires. Subsequently, InAs was deposited by switching off the TMG flow and switching on the trimethylindium (TMI) flow while maintaining constant AsH₃ flow. The flow rates of TMG, TMI, and AsH₃

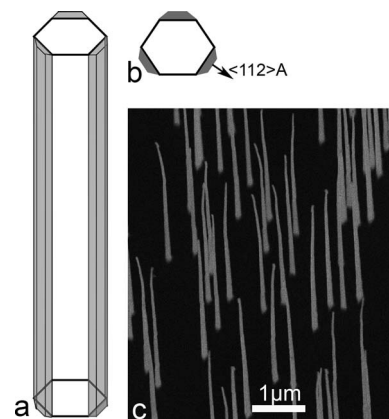


FIG. 1. [(a) and (b)] Schematics of asymmetrically formed InAs/GaAs radial nanowire heterostructure and its cross section, respectively. (c) SEM image showing InAs/GaAs nanowire heterostructures.

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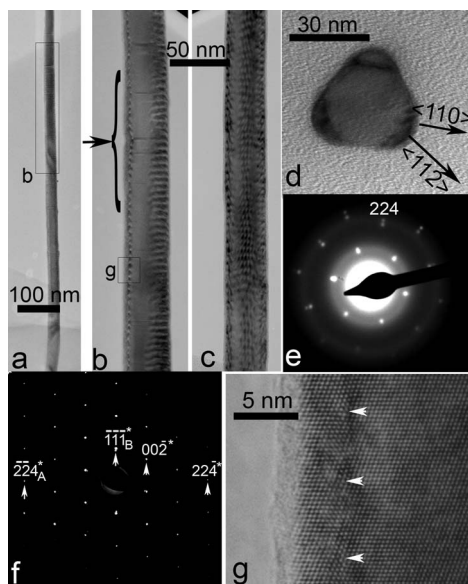


FIG. 2. (a) Low magnification TEM image showing a section of a typical InAs/GaAs nanowire heterostructure. [(b) and (c)] TEM images of InAs/GaAs nanowire taken along the $\langle 110 \rangle$ and $\langle 112 \rangle$ zone axes, respectively. (d) TEM image of cross section of an InAs/GaAs nanowire heterostructure and (e) the corresponding diffraction pattern. (f) $\langle 110 \rangle$ zone axis electron diffraction pattern taken from a section in (b). (g) High resolution TEM image of InAs/GaAs interface region with misfit dislocations arrowed.

were 1.2×10^{-5} , 1.2×10^{-5} , and 5.4×10^{-4} mol/min, respectively. Scanning electron microscopy (SEM) (JEOL 890) and transmission electron microscopy (TEM) (Philip Tecnai F20) investigations were carried out to understand the structural and morphological characteristics of the nanowires. TEM specimens were prepared through ultrasonication of the nanowires in ethanol for 10 min and dispersing them on holey carbon films. Cross sections of the InAs/GaAs radial nanowire heterostructures for TEM investigations were prepared by embedding the nanowires in resin and then by cutting the nanowires in cross section using ultramicrotome.

Figure 1(c) is a SEM image of InAs/GaAs nanowire heterostructures with InAs grown for 30 s and shows that all the nanowires have grown vertically to the substrate surface, i.e., in the $[\bar{1}\bar{1}\bar{1}]$ direction. As can be seen from Fig. 1(c), the nanowires are tapered due to the radial growth.^{18,19} However, based on our previous study,¹⁹ the initially grown GaAs nanowires can have equilateral hexagonal cross sections at the top region of the nanowires, i.e., before radial growth took place.¹⁸ It is anticipated that when the InAs growth starts, InAs can contribute to the radial growth on sidewalls of nanowires with hexagonal cross sections. To understand the radial growth of InAs on these sidewalls of GaAs nanowires, TEM investigations were carried out to determine the detailed structural and morphological characteristics of the InAs radial growth. Figure 2(a) shows a low magnification TEM image of a typical section of InAs/GaAs nanowire with 30 s InAs deposition. Figures 2(b) and 2(c) are high magnification TEM images of a section of the nanowire in Fig. 2(a) along its $\langle 110 \rangle$ and $\langle 112 \rangle$ zone axes, respectively. As can be seen from Fig. 2(b), asymmetric contrasts appear on both sides of the nanowire: on the left side of the nanowire, a thin band of strain contrast can be observed, while on the right side, Moiré fringes occupying nearly half the nanowire width can be seen. It is of interest to note that the asymmetric contrasts disappear in the TEM image taken along the $\langle 112 \rangle$

direction [refer to Fig. 2(c)], where Moiré fringes appear all over the nanowire. To determine the structural characteristic of the grown nanowire heterostructures, TEM investigations were carried out on cross-sectioned nanowire heterostructures and a typical example is shown in Fig. 2(d). The cross section shows triangular morphology with strain contrast appearing at the triangular corners. Figure 2(e) is the corresponding selected area electron diffraction (SAED) pattern and shows two sets of $\langle 111 \rangle$ electron diffraction patterns. The lattice mismatch between the two sets of SAED patterns can be determined as $6.5 \pm 0.5\%$, which nearly agrees with the 7.2% difference between the equilibrium lattice parameters of GaAs and InAs. This suggests that in Fig. 2(d), the hexagonal core is GaAs and the strain contrast is due to the presence of InAs at the corners. Furthermore, by examining the orientational geometry of the nanowire's cross section and the corresponding SAED pattern, the nanowire sidewalls can be determined to be parallel to $\{112\}$. According to crystallography, the zinc-blende structure possesses polarity [i.e., $(h, k, l) \neq (\bar{h}, \bar{k}, \bar{l})$], leading to the six $\{112\}$ possible sidewalls dividing into two sets of equivalent $\{112\}$ atomic planes [i.e., $\{112\}_A$ and $\{112\}_B$] and they appear alternately in the six $\{112\}$ sidewalls.¹⁹

The triangular morphology of InAs on the alternating $\{112\}$ sidewalls, as shown in Fig. 2(d), suggests that InAs preferentially grew on either the $\{112\}_A$ or the $\{112\}_B$ facets. To determine the nature of $\{112\}$ planes on which InAs preferentially grew, the SAED pattern was taken on the nanowire shown in Fig. 2(b) [the $\langle 110 \rangle$ direction] and is shown in Fig. 2(f). Since nanowires grew along the $[\bar{1}\bar{1}\bar{1}]$ direction and since stacking faults [several were shown in Fig. 2(a)] cannot change this polarity,¹⁹ we can then uniquely determine the $(\bar{1}\bar{1}\bar{1})^*$ diffraction spot in Fig. 2(f). For convenience, the nearby $\{200\}^*$ type of diffraction spot can be arbitrarily indexed as $(002)^*$ (note that this arbitrary choice would not cause any change in the nature of the $\{112\}$ planes). In turn, other diffraction spots can be indexed; some are shown in Fig. 2(f). According to crystallography, $[\bar{2}\bar{2}\bar{4}]$ and $[22\bar{4}]$ are along the $\langle 112 \rangle_A$ and $\langle 112 \rangle_B$, respectively. The comparison of Figs. 2(b) and 2(d) shows that the thin band of the strain contrast shown in Fig. 2(b) must be due to the interface between InAs and GaAs. To further confirm this, high-resolution TEM was performed in the thin band and an example is shown in Fig. 2(g), where the InAs/GaAs interface with regular misfit dislocations can be seen.²¹ Taking all these detailed TEM investigations into account, we determine that preferential InAs growth took place on the $\{112\}_A$ sidewalls of the GaAs nanowires. Crystallographically speaking, each unit cell on the $\{112\}_A$ surface contains two group III atoms with each having a single dangling bond and one group V atom with double dangling bonds. While, in the case of $\{112\}_B$ surface, each surface unit cell consists of two group V atoms with each having a single dangling bond and one group III atom with double dangling bonds.²² We anticipate that, when In atoms are deposited on the sidewalls ($\{112\}_A$ or $\{112\}_B$) of a GaAs nanowire under the As rich condition, In atoms would preferentially bond with As atoms on the $\{112\}_A$ surface because this In atom may recover three broken bonds with three neighboring As surface atoms. For the case of $\{112\}_B$, the In atom may only recover one or two

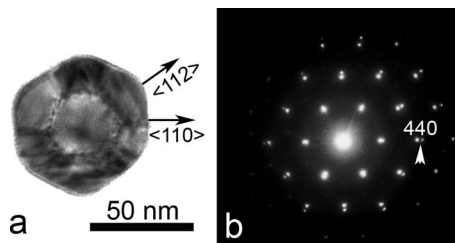


FIG. 3. (a) TEM image of the cross section of InAs/GaAs nanowire with 3 min InAs deposition. (b) The corresponding electron diffraction pattern.

broken bonds with neighboring As surface atoms.¹⁹ As a consequence, it is energetically favorable for InAs to be rapidly grown on the $\{112\}_A$ surfaces.

In the case of radial growth of GaAs nanowire homostructures, truncated triangular shaped cross sections were ultimately obtained as a result of the faster deposition of GaAs on the $\{112\}_A$ sidewalls.¹⁹ Since the initial radial InAs growth also preferentially takes place on the $\{112\}_A$ sidewalls, it is necessary to examine the ultimate structural characteristic as such a structural characteristic is critical to the ultimate properties. For this reason, TEM investigations were performed on the cross sections of InAs/GaAs nanowire heterostructures with a longer InAs deposition, in this case, 3 min. Figure 3(a) shows a TEM image of a cross-sectioned nanowire heterostructure along with the corresponding diffraction pattern in Fig. 3(b). The GaAs core and InAs shell morphology can be identified by the strain contrast. One notable structural characteristic of the InAs/GaAs nanowire heterostructures is their equalized hexagonal cross section when compared with the truncated triangular cross section for radially grown GaAs homostructures.¹⁹ To understand this, we note that the InAs shell has the $\{110\}$ sidewalls, whereas the GaAs core shows $\{112\}$ sidewalls. Such a facet variation in the shell sidewalls might be related to the variation in the chemical potentials of the sidewalls during the radial growth.²³ It should be noted that the atoms on the $\{112\}_A$ and $\{112\}_B$ surfaces have different configurations (leading to the different polar surfaces), while atoms in all the $\{110\}$ surfaces are identical. As a consequence, all six InAs $\{110\}$ sidewalls are identical. We anticipate that the equilateral InAs shells are driven by the alteration of nanowire sidewalls from $\{112\}$ for GaAs to $\{110\}$ for InAs, upon the radial growth of InAs on the GaAs sidewalls, possibly due to the lowered chemical potential.²³ Therefore, such an alteration of sidewalls might not be influenced by the polarity of GaAs. Clearly, although the radial growth of InAs was initiated from $\{112\}_A$, as evident in Fig. 2(d), InAs radial growth eventually forms stable $\{110\}$ facets. These nonpolar $\{110\}$ sidewalls are approximately equal in dimensions. We believe that when the triangular cross section is approached by the initial growth of InAs on the $\{112\}_A$ sidewalls, InAs will also start to grow on $\{112\}_B$ with further growth of InAs.¹⁹ As evidenced by Fig. 3(a), the InAs shells tend to form nonpolar $\{110\}$ sidewalls. We anticipate that, as growth of InAs proceeds, $\{110\}$ facets start to form and tend to adopt equilateral hexagonal cross section due to minimized surface areas, as equilateral hexagonal cross section can have the smallest perimeter than the other shapes.

It is of interest to note that, from Fig. 1(c), nanowires are tapered due to the radial growth of GaAs. To eliminate the

tapering and to develop InAs/GaAs radial nanowire heterostructures with uniform diameter, we grew InAs on the $\{112\}$ sidewalls of two-temperature grown GaAs (Ref. 20) and found similar InAs radial growth behavior.

Based on the evolution of radial growth of InAs on GaAs nanowires with $\{112\}$ sidewalls, it can be seen that asymmetric InAs/GaAs radial heterostructures can be formed during the early stages of InAs growth [Fig. 2(d)]. This preferentially grown InAs thin layer can be a perfect dimension for quantum confinement. As a consequence, it is anticipated that such extraordinary structures can exhibit unique physical properties and can be adopted as building blocks to extend the applications of semiconductor nanostructures to a wider range.

In conclusion, by using TEM, we found that during initial stages of InAs radial growth on the GaAs nanowires, InAs tends to grow preferentially on $\{112\}_A$ facets. This preferential growth results in asymmetrically formed InAs/GaAs radial nanowire heterostructures. These novel nanostructures could have potential applications with suitable band gap engineering.

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