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Growth and properties of III–V compound semiconductor heterostructure nanowires

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Abstract

We review various GaAs-based axial and radial nanowire heterostructures grown on (1 1 1)B GaAs substrates by metal organic chemical vapor deposition via vapor–liquid–solid mechanism. Transmission electron microscopy, time-resolved photoluminescence and micro-Raman spectroscopy have been used to understand the crystal structure, non-radiative surface and bulk defects, carrier lifetime and strain effects on the bandgap energy.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Semiconductor devices and modern solid-state physics have advanced significantly since the double heterostructure (DHS) laser was proposed independently by Alferov and Kazarinov [1], and Kroemer [2]. DHS has been a revolutionary idea to more precisely control the fundamental parameters in semiconductor crystals and devices, such as the bandgap energy, the effective mass and mobility of charge carriers and the refractive index. One cannot imagine our everyday lives without semiconductor DHS devices ranging from DHS lasers, to light-emitting diodes, bipolar transistors and low-noise, high-electron-mobility transistors.

In the last decade, nanowire heterostructures have come into focus in the field of semiconductor nanomaterials. These quasi-one dimensional structures offer unique opportunities to realize novel nanoscale semiconductor devices. III–V compound semiconductor nanowires are of particular interest for optoelectronic devices due to their high optical emission efficiency compared to indirect-bandgap group IV crystals. Various III–V compound semiconductor nanowire-based devices, including solar cells [3], single photon emitters

[4–6], photodetectors [7, 8], biosensors [9], light emitting diodes [5, 10], lasers [11–13] and single electron devices [14], have already been demonstrated. Unlike traditional epitaxy which is based on layer-by-layer deposition on a planar surface, nanowires grow as free-standing structures on a wafer offering the flexibility to construct a true three-dimensional architecture which is not possible otherwise. The typical nanowire is grown from a seed metal particle, the size of which also determines the diameter of nanowires. The growth mechanism is often described as a vapor–liquid–solid (VLS) mechanism, first proposed by Wagner and Ellis for silicon whiskers grown with a Au particle [15], although a vapor–solid–solid growth is also possible in some material systems [16, 17]. In the VLS growth, the liquid metal droplet becomes a sink for reaction species supplied from the surrounding vapor, and is readily supersaturated with reaction species. The precipitation of reaction species at the solid/liquid interface leads to highly anisotropic nanowire growth. This growth mechanism has been extremely flexible for heterostructures to form in both axial and radial directions. For example, nanowire heterostructures can be grown in either the axial direction by alternating precursors or the radial direction

(core-shell) by increasing growth temperature. This flexibility provides a rich environment for designing and fabricating novel nanostructures for illuminating new physics or enabling new technologies. On the other hand, due to the large nanowire surface area in comparison to its volume and the small contact area between a nanowire and its substrate, Zervos *et al* have shown theoretically that the strain induced at heterointerfaces in nanowires can be elastically relieved over a thickness of a few monolayers [18]. Experimentally, the formation of defect-free and sharp heterojunctions has been demonstrated in highly lattice mismatched GaAs/GaP, InAs/InP, GaAs/GaSb and InAs/InSb nanowires [19–23]. However, challenges always accompany these new opportunities. For example, in nanowire heterostructures, random kinking or branching imposes a great challenge in their growth [24, 25]. Precise control over the kinking location and direction is crucial to grow sophisticated 3D nanowire structures.

III–V semiconductor, in particular, GaAs-based heterostructure nanowires are promising for optoelectronic devices due to the superior electrical and optical properties over other material systems. The GaAs material system has already demonstrated their great importance in the current semiconductor industries for optoelectronic and electronic devices, for example, the GaAs/AlGaAs quantum well and InAs/GaAs quantum dot lasers and photodetectors. Accordingly, GaAs-based heterostructure nanowires are prime candidates for electrically and optically active nanowire devices [3, 4, 11]. Since there were two good review papers covering synthesis techniques and physical properties of heterostructure nanowires [26, 27], we hereby only focus on a few GaAs-based nanowire heterostructures synthesized by our group to understand the growth control and their implications on optical properties. First, we briefly review the experimental methods for nanowire growth, structural and optical characterization. Then, we describe the current advances and characteristic properties of several specific heterostructures including GaAs/AlGaAs, GaAs/GaP core-shell and GaAs-InAs, GaAs-GaSb axial heterostructures.

2. Growth and characterization technique

All nanowires were grown on GaAs (111)B substrates except GaAs/GaP nanowires which were grown on Si (111) (4° miscut) substrates using a horizontal flow metal organic chemical vapor deposition (MOCVD) reactor at a pressure of 100 mbar with ultrahigh purity hydrogen as the carrier gas. Trimethylgallium (TMG), trimethylaluminum (TMA) and trimethylindium (TMI) precursors were used for group III and AsH₃, PH₃ and trimethylantimony (TMSb) precursors were used for group V sources, respectively. Firstly, GaAs substrates were immersed in poly-L-lysine (PLL) solution for 60 s and rinsed with deionized water before applying a droplet of colloidal solution of 30 or 50 nm diameter Au particles. After rinsing off the excessive Au colloidal particles with DI water, the wafers were blown dry using N₂ gas and transferred into the MOCVD reactor chamber. For Si substrates, prior to this PLL treatment, a ~50 nm thick GaAs buffer layer was deposited on Si using a two-temperature

growth procedure: first grown at 400 °C with a V/III ratio of 15.4 for 60 min, followed by a rapid 10 min growth at 700 °C with a V/III ratio of 154. The buffer layer was then *in situ* annealed in an arsine atmosphere at 750 °C for 15 min, then removed from the reactor for subsequent PLL treatment (details of this buffer growth process can be found in [28]). All Au decorated wafers were annealed in the MOCVD reactor under AsH₃ at 600 °C for 10 min, to desorb contaminants on the surface. Then, the reactor was cooled down to the desired temperature (450 °C) to carry out the GaAs nanowire growth (referred to ‘one-temperature procedure’). For the ‘two-temperature procedure’, growth initiated with a 1 min ‘nucleation’ step at the nucleation temperature, T_n , of 450 °C. The temperature was then rapidly ramped down to the subsequent growth temperature, T_g , of 375 °C for further 30 min growth. For radial heterostructures, the reactor was heated up to 650 °C after the GaAs core growth for the subsequent AlGaAs or GaP shell layer growth. For axial heterostructures, InAs nanowire segment was grown at 450 °C and GaSb nanowire segment was grown at 425 °C.

The structural and crystallographic properties of nanowires were characterized by using field-emission scanning electron microscopy (FESEM) (Hitachi S4500) and transmission electron microscopy (TEM) (FEI Tecnai F30). For single nanowire micro-Raman, photoluminescence (PL) and time-resolved PL (TRPL) measurements, nanowires were transferred from the as-grown substrates to a Si substrate by rubbing the two substrate surfaces together. The PL spectra of individual nanowires were obtained at 15 K using slit confocal micro-PL spectroscopy. A 50×/0.5 NA long working distance microscope’s objective was used to collect the PL from the nanowire sample and convey it to the spectrometer. For TRPL measurements, either an avalanche photodiode (APD) or a micro-channel photomultiplier tube (MCPT) is used to detect the PL signal. For Raman measurements, the nanowire was excited using a 100×/0.7 NA long working length objective with 532 nm laser excitation focused to a 0.7 μm spot. The scattered light was dispersed using a 600 mm focal length DILOR xy triple spectrometer used in subtractive mode and detected by a liquid nitrogen-cooled CCD camera.

3. Core-shell heterostructures

Core-shell heterostructure nanowires attracted significant interest for optoelectronic, photonic or electronic devices [10, 13, 29, 30], since the shell can protect and passivate the active core nanowire surface, and provide carriers or engineer the bandgap structure if higher bandgap materials are used for the shell. However, the undesirable axial segment growth during the shell growth [31] and phase segregation [32, 33] still pose great challenges for obtaining perfect core-shell structures.

Core-shell heterostructures can be divided into two groups in terms of their lattice constant: lattice matched or mismatched. One typical example from each group will be presented as follows.

Figure 1. Morphology and structural characteristics of GaAs nanowires grown by one-temperature process: (a) SEM image showing the highly tapered shape; (b) TEM image showing high density of planar defects; (c) a high resolution TEM displaying the twinning defect.

3.1. GaAs/AlGaAs core-shell nanowires

Among various core-shell nanowires, GaAs/AlGaAs material system is probably the most popular one due to its considerable band offsets in conduction and valence bands, effective passivation, similar lattice constants, large difference of refractive index and high electron mobility [31, 32, 34–38]. In addition, GaAs/AlGaAs system has been widely used in industry for planar optoelectronic devices such as lasers and photodetectors. The mature processing techniques offer this material system a great advantage in device fabrication. In this paper, the great passivation effect from AlGaAs on GaAs nanowire surface is demonstrated.

We firstly grew GaAs nanowires at 450 °C using the one-temperature procedure. However, such nanowires show a zinc blende crystal phase with a high density of twins and stacking faults and significant tapering as shown in figure 1 [39]. These characteristics are common problems in various III–V semiconductor nanowires [40–42]. These defects can act as efficient nonradiative recombination centers in GaAs. In addition, due to the large surface recombination velocity ($5 \times 10^6 \text{ cm s}^{-1}$) [43], the free GaAs surface is particularly efficient at quenching electron-hole pairs non-radiatively, a particularly acute problem in nanowires because of their large surface-area-to-volume ratio. Therefore, the PL emission from these defective GaAs nanowires is very weak even at low temperatures (figure 2(b)). In order to increase their PL emission efficiency, an AlGaAs shell was grown to passivate the GaAs core (SEM image is shown in figure 2(a)). Our previous report from Titova *et al* has shown that this GaAs/AlGaAs core-shell structure increased the quantum efficiency of PL by two orders of magnitude over the bare GaAs nanowire [44]. However, the TRPL measurements still showed an extremely short carrier lifetime in single nanowires as shown in figure 3(d) (light-color spectrum), below the 80 ps system response time for detection by our time-correlated photon counting system [45]. This short lifetime is attributed to two possible sources: one is the high density of twin defects and stacking faults in such a nanowire grown by one-temperature process as shown in figure 1(b), and the other is the possible oxidation of the AlGaAs shell. Oxygen is well known to be an extremely effective deep level in GaAs resulting in extremely short lifetimes [46]. In order to improve the carrier lifetime in this core-shell heterostructure, we

Figure 2. (a) SEM image of GaAs/AlGaAs core-shell nanowires grown by one-temperature process; (b) PL spectra of the single bare GaAs and core-shell GaAs–AlGaAs nanowires, adapted from [22] with permission.

recently adopted a two-temperature growth procedure [47] to reduce (perhaps eliminate) the structural defects and tapering of GaAs nanowire core and, in addition, deposited a 5 nm GaAs capping layer outside the AlGaAs shell to prevent the oxidation of AlGaAs. The SEM image of such a core-shell nanowire and TEM images of the defect-free GaAs nanowire are shown in figures 3(a)–(c). The two-temperature grown GaAs core with minimal tapered shape is displayed in figure 3(b) and the high resolution TEM (figure 1(c)) shows no planar defects in such a nanowire grown by two-temperature procedure.

The carrier lifetime in such core-shell nanowires improved dramatically, exhibiting a lifetime as long as 1 ns (the dark-color spectrum as shown in figure 3(d)) which is comparable to very high quality 2D GaAs/AlGaAs wide DHSs and is consistent with an intrinsic exciton radiative recombination [48, 49]. Perera *et al* also showed that such a core-double shell nanowire heterostructure exhibits a higher quantum efficiency [50]. At high photoexcited carrier concentrations these nanowires also exhibit significant bandgap renormalization and state filling which allows us to determine the carrier density [50].

Figure 3. (a) SEM image of the GaAs/AlGaAs core-shell nanowires grown by two-temperature method; (b) TEM image of a GaAs nanowire showing minimal tapering; (c) a magnified TEM image displaying the absence of twin defects; (d) time decays of PL from two single GaAs/AlGaAs core-shell nanowires. The short time decay (80 ps) is from the one-temperature grown GaAs nanowire core while the long exponential time decay (1.1 ns) is from the two-temperature growth GaAs nanowire core with an outer 5 nm GaAs cap to prevent oxidation of the AlGaAs shell. Adapted from [23, 25] with permission.

3.2. GaAs/GaP core-shell nanowires

Strain in core-shell nanowire structure is a critical factor to be considered in bandgap engineering for device applications. Unlike their bulk counterparts, the band offsets of core-shell nanowires can be significantly affected by the strain which

has been demonstrated both experimentally and theoretically [51–54]. Recently, optimization of the strain in core-shell nanowires has been shown to enhance the device performance of GaAs/GaP and Si/Ge field emission transistors [55, 56]. However, the strain effects on band structure are difficult to be measured independently or decoupled from the quantum confinement effects [51, 54]. Here, we show a consistent picture between strain and band structure by direct measurements using Raman scattering and PL, respectively, on the same single GaAs/GaP nanowire.

The SEM and TEM images of the GaAs/GaP core-shell nanowires are shown in figures 4(a)–(c). Si surface was fully covered by the GaAs buffer layer which forms continuous islands due to the strain between GaAs and Si (as shown in figure 2(a)). GaAs/GaP core-shell nanowires nucleated on top of GaAs buffer layer and grew perpendicularly to the Si (1 1 1) substrate. The TEM image (figure 4(b)) of the bottom region of a nanowire was taken along the [1 1 2] zone axis as indicated by the arrow in figure 4(c) to maximize the strain contrast between GaAs and GaP due to the lattice mismatch of the materials ($\sim 3.6\%$). The GaAs core is identified by the moiré fringes in this side view TEM image and can be more accurately identified using cross-sectional TEM (XTEM) as shown in figure 4(c). The GaAs core is estimated to be ~ 50 nm and the GaP shell is estimated to be ~ 25 nm. The strain contrasts can also be identified at the GaAs/GaP interface in figure 4(c). Selected area electron diffraction (SAED) (not shown here) confirmed that both the GaAs nanowire core and GaP nanowire shell have the cubic zinc blende structure.

The stress in this material system can be measured by Raman scattering from phonons. We have carried out Raman scattering from three individual GaAs/GaP nanowires at room temperature in the backscattering geometry (as shown in figure 5) [52]. The Raman spectrum of an unstrained GaAs epilayer grown on a GaAs substrate is also shown as a reference. Compared to the transverse optical (TO) and longitudinal optical (LO) phonon energies of the epitaxial GaAs, the GaAs/GaP core-shell nanowires displayed a significant shift of GaAs TO phonon and LO phonon energies to higher frequencies (~ 10 cm^{-1}), indicating significant compressive stress in the GaAs core. In contrast, the GaP TO phonon and LO phonon energies show a significant downward

Figure 4. (a) SEM image of a GaAs/GaP nanowire on Si substrate with GaAs buffer. (b) TEM image taken from [1 1 2] zone axis showing the side view of the bottom section of a nanowire. (c) A typical cross-sectional TEM (XTEM) image viewing along the [1 1 1] zone axis of the bottom region of a nanowire, showing a strained core-shell structure. The arrow indicates the viewing direction of [1 1 2] for the side view image (b). Adapted from [27] with permission.

Figure 5. Raman spectra of GaAs/GaP nanowires (light-color lines) and GaAs epilayer (dark-color line) at room temperature. The dashed lines show TO and LO energies of GaP. Adapted from [29] with permission.

Figure 6. Low-temperature PL spectrum of GaAs/AlGaAs (left spectrum) and GaAs/GaP (right spectrum) core-shell nanowires. The vertical arrows show energies of HH and LH bandgap, respectively, predicted from Raman measurement. Adapted from [29] with permission.

Raman shift, indicating a tensile stress in the GaP shell. In addition, the low-energy tail of GaP TO phonon response may indicate a strain gradient in the shell. The hydrostatic and shear strain of the GaAs core have been calculated from the Raman spectra and showed good agreement with the theoretical predictions [52, 53, 57].

These large hydrostatic and shear strains in the GaAs core are expected to result in large effects in electronic states. To confirm this, micro-PL measurements were performed on single GaAs/GaP nanowires. A typical spectrum is shown in figure 6 together with a reference PL spectrum from a high quality GaAs/AlGaAs nanowire measured earlier

Figure 7. SEM images of GaAs/InAs nanowires with different InAs growth times. (a)–(c) correspond to 1, 5 and 30 min InAs growth, respectively. The images were taken when the substrate normal was tilted 20° away from the electron beam. Adapted from [32] with permission.

(figure 1(a)). The PL emission energy from GaAs core in GaAs/GaP nanowires clearly shifts to higher energies by ~260 meV from the expected 1.515 eV GaAs-free exciton peak observed in GaAs/AlGaAs nanowires. The vertical arrows show the expected emission energies for the heavy hole (HH) and light hole (LH) excitons based on the strain information calculated from the Raman spectra. The excellent agreement between the experimental data and theoretical calculation indicates that the strain obtained from the Raman measurement can be used to predict bandgap changes and the HH–LH splitting.

4. Axial heterostructures

In addition to core–shell geometry, nanowire heterostructures can also form axially along its length—so-called axial heterostructure nanowires. As mentioned earlier in the introduction, nanowires offer great advantage over their bulk counterparts in forming defect-free and sharp heterojunctions from highly lattice-mismatched materials [19–23]. In order to form DHS confinement in nanowires, the axial heterostructures must grow in a straight form and have high quality interfaces in both interface directions. However, this is not always true for axial heterostructure nanowires. In the following sections, we present two examples: InAs on GaAs and GaSb on GaAs, where one cannot form straight heterostructure nanowires (GaAs/InAs) but the other one can (GaAs/GaSb).

4.1. GaAs/InAs axial nanowires

Although GaAs/InAs two-dimensional (2D) heterostructures are one of the key material systems for optoelectronic device applications, their 1D counterparts are much less studied [24, 25, 58–64] in spite of their potential optoelectronic and electronic applications. Not being able to grow InAs nanowires straight on GaAs nanowires is probably the most difficult challenge to be overcome to form DHS [24, 25, 59]. Paladugu *et al* have used TEM to investigate the growth mechanism of GaAs/InAs axial nanowire heterostructures in detail [25, 59–63]. Figure 7 shows SEM images taken

Figure 8. A TEM image showing the mixed-sized nanowires: the thicker nanowire tends to be straight, while the thinner one tends to be bent. Adapted from [15] with permission.

from GaAs/InAs axial nanowire heterostructures grown with different growth times (1 min, 5 min and 30 min) for the InAs sections. A small branch-like structure can be found near the tip of GaAs/InAs nanowires with 5 min growth of InAs nanowire sections, as indicated by arrows in figure 7(b), but no clear branch is presented in nanowires with 1 min growth of the InAs (see figure 7(a)). In contrast, in the case of 30 min growth of InAs (figure 7(c)), each nanowire displays a well-developed branch and the overall morphology of the nanowires resembles a stem-branch nanostructure.

To determine how and why this branching phenomenon occurs, a detailed TEM investigation was firstly carried out on nanowires where InAs growth had been initiated for just 1 min. Although the nanowire growth was initiated by ~ 30 nm Au particles, the TEM analysis showed a significant number of thicker nanowires, with diameters up to 90 nm, probably due to the coalescence of Au particles during the annealing stage at 600 °C. A typical example of these mixed-size nanowires is shown in figure 8 where different morphologies can be seen: for thinner nanowires, the Au particle has moved away from the nanowire tip down to the sidewall while only sideward movement of the Au particle was observed for the thicker ones [25]. Fortunately, these thicker nanowires provide us with an opportunity to investigate the initial stage of the InAs nanowire growth. Figures 9(a)–(c) are TEM images of such nanowires showing that the Au particles are just beginning to move sideward from the tip position (GaAs/InAs interfaces are marked by arrows) in three different stages.

To understand the growth difference between InAs on GaAs nanowires (leading to a clustered InAs) and GaAs on InAs nanowires (resulting in straight nanowires as evidenced in [24, 58, 63]), we adopt the model proposed for description of heterogeneous nucleation of a solid from a metallic liquid along a solid surface of a mold [65]. This model is used because it is reasonable to assume in this study that the Au particle is in the liquid form during nanowire growth and GaAs and InAs can act as the wall of the mold and nucleated solid, respectively. Figure 9(d) shows a schematic diagram of clustered InAs formed between the Au droplet and GaAs, which is similar to the morphology shown in figure 9(a). At equilibrium, the model gives $\gamma_{Au-GaAs} = \gamma_{InAs-GaAs} + \gamma_{Au-InAs} \cdot \cos \delta$, where γ_{A-B} is the interfacial

Figure 9. (a)–(c) TEM images showing initial stages of InAs growth on GaAs nanowires. (d) A HRTEM image showing the atomic structure of the initially grown InAs in (b). (e) A schematic diagram showing the interfaces between clustered InAs, GaAs and Au at their contact point. Adapted from [15] with permission.

energy between the material A and the material B and γ is the contact angle between the clustered InAs and the GaAs surface. The interfacial energy of Au–GaAs is assumed to be less than Au–InAs; therefore, $\gamma > 0$ (clustering occurred) when InAs grows on GaAs resulting in InAs clustering at the edge and later sideward movement. While in the case of GaAs grown on InAs nanowires, straight nanowire heterostructures were obtained through layer-by-layer growth of GaAs, i.e. $\gamma = 0$. Similar morphology in heterostructure nanowires was also reported by Dick *et al* and was explained in terms of interfacial energies as well [66].

Once the Au particle has moved to the sidewalls of the GaAs nanowire (figures 8 and 9(c)), continuing sideways growth of InAs may be expected. However, as shown in figures 7(b) and (c), InAs nanowires formed branches on the GaAs nanowire stem instead. To determine the mechanism for this branched morphology, further TEM investigations were conducted on nanowires with longer growth time of InAs sections. Figures 10(a)–(d) show TEM images taken from the top portion of nanowire with 1 min, 3 min, 5 min and 30 min growth of InAs section. Note that the nanowire in figure 10(a) is the thinner one shown in figure 8. As shown in figure 10(a), after 1 min growth of InAs section, the Au particle has moved away from the GaAs nanowire tip and migrated down the GaAs nanowire sidewall. However, this downward sliding of Au particle has been retarded by radial growth of InAs around the GaAs nanowire which can be identified by the moiré fringes and the strain contrast along the nanowire in figure 10(b) with 3 min growth of InAs. Thus the Au particle

Figure 10. TEM images of GaAs/InAs nanowires with different InAs growth times. (a)–(d) correspond to 1, 3, 5 and 30 min InAs growth, respectively. The inset in (b) is the magnified image of the nanowire portion at the Au nanoparticle. The insets in (c) show the results of the EDS analyses at different locations of the nanowire and the Cu peak is from the TEM grid. Adapted from [32] with permission.

remains near the GaAs nanowire top region. Generally, in Au-assisted growth of nanowires, radial growth is related to a higher temperature process [67]. However, significant InAs radial growth has taken place even at 450 °C in this work similar to the case of GaP/GaAs [67]. With further supply of In and As vapor sources, the InAs nanowire started to ‘shoot out’ along [111] direction as a branch on GaAs, or more accurately, a GaAs/InAs core–shell nanowire stem as shown in figures 10(c) and (d). Energy dispersive spectroscopy (EDS) analysis further confirms that the branch is composed of InAs and that the stem has a core–shell structure of GaAs and InAs, as shown in the insets of figure 10(c). With further growth, this InAs nanowire branch will continue to grow as a stand-alone nanowire while the InAs shell grows thicker at the same time, resulting in a thicker GaAs/InAs core–shell nanowire stem and a well-developed InAs nanowire branch, as shown in figure 10(d).

4.2. GaAs/GaSb axial nanowires

GaSb-based III–V semiconductors are of great interest for near- and mid-infrared optoelectronic and high-speed electronic devices. Though it is very challenging to grow high quality GaSb epilayers on GaAs due to the large lattice mismatch ($\sim 7.8\%$), nanowires offer the possibility of integrating GaSb with more ‘classic’ GaAs. Understanding of the growth mechanism and growth control of GaAs/Ga(As)Sb heterostructure nanowires have advanced significantly since

Figure 11. SEM image of GaAs/GaSb nanowire heterostructures. The substrate normal was tilted 45° away from the electron beam.

GaSb nanowire lasers were first demonstrated by Chin *et al* [68] and defect-free GaSb nanowires on GaAs nanowires were first reported by Guo *et al* in 2006 [21]. More recently, GaAs/GaAsSb/GaAs DHS nanowires have been demonstrated [69, 70], indicating one more step closer to realizing operational devices based on this material system.

The general morphology of such a heterostructure grown by our group is shown in figure 11. In contrast to GaAs/InAs nanowire heterostructures, all GaAs/GaSb nanowires are straight and well aligned in a vertical direction on GaAs (111) substrate. Each individual nanowire has a tapered GaAs body with a thick column-shaped GaSb head. The length of the entire nanowire is $\sim 1 \mu\text{m}$ and the diameter of heads is in the range of several tens of nanometers.

TEM was carried out to determine detailed microstructure of these GaAs/GaSb nanowire heterostructures. Figure 12(a) is a bright-field TEM image and shows a typical top section of the nanowire containing GaAs (thin body), GaSb (thick head), as well as the Au catalyst (top hemispherical particle). It is interesting to note that the diameter of the GaSb segment is about 40% thicker than the GaAs part. This significant change in diameter was first explained as the strain relaxation via lateral expansion [21]. Though this lateral expansion still exists, it is more reasonable to believe that the composition change in Au eutectic alloy (i.e. more Ga incorporated in Au or Sb addition to form $\text{Au}(\text{GaSb})_2$ or $\text{Au}(\text{GaSb})$ types of phases) are accountable for the majority of this diameter increase [71, 72]. SAED taken from the interface between GaSb and GaAs (figure 12(b)) clearly shows two sets of $\langle 110 \rangle$ patterns with one set being GaAs and the other being GaSb. A $7.5 \pm 0.3\%$ lattice mismatch was determined by the measurement of corresponding atomic planes for GaAs and GaSb indicating a fully relaxed GaSb nanowire, since the lattice mismatch between unstrained GaAs and GaSb is 7.8%.

Although many planar defects can be clearly seen in the GaAs region (indicated by arrows in figure 12(c)), the GaSb region remains defect-free (figure 12(d)). To determine whether misfit dislocations exist at the GaAs/GaSb interface, a high resolution TEM investigation was carried out as shown in figure 12(e). Although the GaAs/GaSb interface is not

Figure 12. (a) A TEM image taken from the top section of a GaSb/GaAs nanowire heterostructure. (b) A SAED pattern showing two sets of well-distinguished (110) electron diffraction patterns. (c) A TEM image of the GaAs section showing many planar defects (marked by arrows). (d) A TEM image of the GaSb section showing no lattice defects. (e) A high-resolution image (the growth direction pointing upside) in the GaSb/GaAs interfacial region showing no misfit dislocations in the region. Adapted from [13] with permission.

clearly identified from figure 12(e), no misfit dislocations exist in this interfacial region. This suggests that the entire strain relaxation for the GaSb nanowire grown is through the lateral expansion [21] without introducing any misfit dislocations.

5. Summary and conclusions

In summary, we have reviewed the morphology, microstructure and optical properties of various GaAs nanowire-based heterostructures including GaAs/AlGaAs and GaAs/GaP core-shell structures, and GaAs/InAs and GaAs/GaSb axial structures. We found that the suppression of surface/impurity-related non-radiative combination pathways is critical for the carrier lifetime in GaAs nanowires. The strain between the core and shell can be utilized to engineer the electronic structure of the GaAs nanowire core. For axial heterostructure nanowires, the metal-semiconductor surface energy is believed to be one of the determining factors for the growth direction—whether straight or branched structures. Defect-free GaSb nanowires were achieved axially on GaAs nanowires confirming that heterostructure nanowires are strong candidates to overcome the lattice mismatch problems in conventional 2D semiconductor structures.

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