Self-induced antimony compositional variation
GaAs/Ga(As)Sb core-shell nanowires by molecular beam epitaxy

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Abstract. Self-catalyzed GaAs/GaAsSb heterojunction nanowires (NWs) were grown on Si (111) substrate by molecular-beam epitaxy (MBE). The GaAs/GaAsSb heterojunction NWs were determined by XRD and Raman spectra. Antimony (Sb) compositional variation of GaAs/Ga(As)Sb heterojunction NWs have been clearly evidenced by XRD spectrum, energy-dispersive X-ray (EDX) spectroscopy combined with absorption spectra. Detailed electron microscopy investigations indicate that the As-Sb exchange at the GaAsSb NWs surface during growth resulting in an outward diffusion of Sb (and corresponding inward diffusion of As), the structure of GaAs/GaAsSb/GaSb and GaAsSb/GaSb core-shell NWs were formed. This study offers a possibility to grow ternary III-V NWs with complex structures that can be used for electronic and optoelectronic applications.

1. Introduction

III-V semiconductor nanowires (NWs) are prime candidates for the development of nanoscale optoelectronic and thermoelectric devices. Their unique one-dimensional geometry plays a new competition for the growth of complex radial and axial nano-heterostructures.\textsuperscript{[1]} Among the various nanowire systems, ternary III-V NWs have the advantage that their bandgap may be continuously tuned by varying their compositions. As one of the most important ternary semiconductor materials, GaAsSb is an ideal candidate for infrared wavelength optoelectronic applications due to its direct tunable range from ~0.87 \(\mu\)m (GaAs) to ~1.7 \(\mu\)m (GaSb) at room temperature.\textsuperscript{[2]} Therefore, ternary alloys GaAsSb is an attractive material for various optoelectronic applications, such as optical communication, infrared light-emitting diodes, near-infrared photodetectors, and lasers.

Nevertheless, unlike their counterparts of binary III-V materials, nonuniform composition distributions are often observed in ternary III-V materials.\textsuperscript{[3]} Recently, the spontaneous formation of core-shell heterostructures caused by element segregation in Au-assisted ternary NWs is a common phenomenon, especially in III-III-V nanowire systems, such as InGaAs and InGaP. Bauer et al.\textsuperscript{[4]} found that a large amount of In accumulated inside the Au catalyst during the growth of InGaAs NWs and remained in the Au catalyst during subsequent GaAs growth. In addition, Zou et al.\textsuperscript{[5,6]} reported that the compositional varied core-shell InGaAs or InGaP NWs grown by metal-organic chemical vapor deposition or molecular beam epitaxy, are attributed to the Au-catalyst has a stronger affinity with In than Ga, as well as Ga diffusion outward and In diffusion inward. Unlike the above, Huh et al.\textsuperscript{[7]} found
that the self-induced compositional gradients of the GaAsSb NWs were grown by MBE, the As-Sb exchange at the NW surface during growth resulting in an outward diffusion of Sb. Until now, to the best of our knowledge, the self-induced compositional variation core-shell III-V-V NWs by self-catalyzed MBE have not yet been reported. On the other hand, the compositional nonuniformity in semiconductor alloys may strongly affect their optical and electrical properties. The structural controllability plays an important role in the design of complex NWs and lays a good cornerstone for future device applications. Therefore, understanding the formation mechanism of compositional variation GaAs/Ga(As)Sb core-shell NWs is the foundation for accomplishing desired properties.

In this study, GaAs/GaAsSb heterojunction NWs were grown on Si (111) substrate by self-catalyzed in a molecular-beam epitaxy system. Through detailed electron microscopy, XRD spectrum and absorption spectra investigations, the morphological, structural, and chemical characteristics of GaAs/GaAsSb heterojunction NWs were investigated. It was found that the structure of GaAs/GaAsSb/GaSb and GaAsSb/GaSb core-shell NW was formed due to the As-Sb exchange at the GaAsSb NWs surface. The formation mechanism of these extraordinary compositional variations along the radial direction in GaAs/GaAsSb heterojunction NWs is discussed.

2. Materials and Methods

2.1. Growth

The self-catalyzed GaAs/GaAsSb heterojunction NWs were grown on n-type Si (111) substrates in a DCA P600 molecular beam epitaxy (MBE) system. The system is equipped with an infrared pyrometer specified for high temperatures to measure the growth temperature. We only treat the substrate by ultrasound. For the growth of GaAs/GaAsSb heterojunction NWs, the two-step fabrication procedures were implemented. First, Ga droplets were deposited on Si (111) substrate at 620 °C, the deposition time was 26 s, the Ga flux was 6.2 × 10^{-8} Torr, V/III=25.8. The GaAsSb shell were grown with the Ga flux, As flux, Sb flux, and substrate temperature of 6.7 × 10^{-8} Torr, 1.6 × 10^{-6} Torr, 4.5× 10^{-7} Torr and ∼620 °C, respectively. The growth time of the GaAs and GaAsSb NWs were 10 min and 20 min, respectively.

2.2. Material Characterization

The morphology and crystal structure of GaAs/GaAsSb heterojunction NWs were characterized by scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEOL 2100F, JEOL Co., Ltd., Tokyo, Japan) attached with the energy dispersive X-ray spectroscopy (EDS) detectors. The Raman experiments were conducted with a Raman Spectrometer (Raman, LabRAM HR Evolution, HORIBA Scientific, Japan) with a laser excitation wavelength of 532 nm. The solid ultraviolet-visible-infrared (UV-vis-IR) absorption spectrum within the wavelength 800-2000 nm was obtained with a Shimadzu U-4100.

3. Results & Discussion

The SEM images of the side-view of GaAs/GaAsSb heterojunction NWs is shown in Figure 1(a). TEM image of a typical GaAs/GaAsSb heterojunction NWs is shown in the inset of Fig 1(a). Energy dispersive spectroscopy (EDS) analysis was performed as shown in Figure 1(b), and it was found that the Sb element was present in the NWs. Moreover, the Raman spectra of multiple GaAs/GaAsSb heterojunction NWs on Si substrate is shown in Figure 1c. Figure 1c shows that the NWs exhibit four mode peaks, GaSb-like TO, GaSb-like LO, GaAs-like TO and GaAs-like LO, respectively. In addition to the Raman mode peaks corresponding to NWs, there is a peak of ∼303 cm^{-1}, which is labeled pentagram and comes from Si substrate.[8] In order to further determine the structure of NWs, we tested the NWs by XRD and take the GaAs NWs as a reference, as shown in Figure 1d. The full width at half maximum (FWHM) and peak position of Bragg peaks are used to characterize material mismatch. Figure 1d shows that the peak position and FWHM of GaAs (111) Bragg peak are 27.37° and 0.176°. The peak position and FWHM of GaAs (111) Bragg peak in GaAs/GaAsSb heterojunction NWs are 27.22° and 0.245°, respectively. For GaAs/GaAsSb heterojunction NWs, the GaAs (111) Bragg peak
shifts toward lower angle (0.12°) and is accompanied by significant broadening of the peak. Therefore, a large mismatch between materials in GaAs/GaAsSb heterojunction NWs. The FWHM of GaAsSb (111) Bragg peak in GaAs/GaAsSb heterojunction NWs is 0.529°. The FWHM of GaAs (111) Bragg peak is wider than GaAs (111) Bragg peak in GaAs/GaAsSb heterojunction NWs. Therefore, the GaAsSb (111) Bragg peak is derived from multiple Sb components.

Figure 1  Morphology and structural characterization of the GaAs/Ga(As)Sb heterojunction NWs. Typical SEM images of GaAs/GaAsSb heterojunction NWs grown on Si (111), side-view (a). TEM images of a typical heterojunction NW in the inset of (a). (b) Energy-dispersive X-ray (EDX) spectra collected from the whole NW in the inset of Figure1a. (c) The Raman spectra of multiple GaAs/Ga(As)Sb heterojunction NWs on Si substrate mechanically. (d) XRD diffraction curve obtained from GaAs/Ga(As)Sb heterojunction NWs, and GaAs NWs are used as a reference.

Figure 2  (a) TEM image of a typical GaAs/GaAsSb heterojunction NW. (b)–(d) Corresponding EDX spectra taken from the top (b), middle (c), and bottom (d) region of the heterojunction NW, as indicated by the yellow lines in (a). The inset show the schematic diagram of the structure corresponding to the NW.

To further confirm the complex GaAsSb heterojunction NWs and their corresponding Sb compositional distribution features, the heterojunction NW from Figure 2 was studied in detail. The EDXs from bottom and top of the heterojunction NWs are respectively marked in Figure 2 (a). To
examine the composition of this GaAs/GaAsSb heterojunction NW, EDXs were taken from the top region, middle region, and the bottom region of the NW (indicated by three yellow lines in Figure 2(a)), and the results are shown in Figure 2(b)–(d), respectively. The distribution of three atoms Ga, As, Sb in all three regions confirms the existence of GaAsSb structure. On the basis of the distribution of atoms in three regions, we can find that the bottom of the heterojunction NW is GaAs/GaAsSb/GaSb core-shell structure, and the middle and top regions are GaAsSb/GaSb core-shell structure. The schematic diagram of the structure corresponding to the GaAs/GaAsSb heterojunction NW are shown in the inset of Figure 2(b-d).

Figure 3  (a) FTIR spectrum of the GaAs/ Ga(As)Sb heterojunction NWs. (b) \((\alpha h\nu)^2\) versus \(h\nu\) curve for GaAsSb heterojunction NWs.

The Fourier transform infrared (FTIR) spectral was used to analysis the phase segregation of Ga(As)Sb heterojunction NWs. Figure 3 (a) shows the absorption spectrum of the Ga(As)Sb heterojunction NWs. The absorption spectrum consists of many absorption peaks. According to Ma et al., it is reasonable to assume that the main peak around 1.55 \(\mu\)m is the absorption for exciting electrons from the valence band (VB) to the conduction band (CB). The absorption spectrum was used to measure the optical band gap. Figure 3(b) shows the \((\alpha h\nu)^2\) versus \(h\nu\) curve of the corresponding GaAs/GaAsSb heterojunction NWs, where \(\alpha\) is the absorbance, \(h\) is the Planck constant, and \(\nu\) is the frequency. The absorption edges deduced from the linear part of the \((\alpha h\nu)^2\) versus \(h\nu\) curve allow an understanding of the energy bandgap for the GaSb, which is about 0.726 eV and is consistent with the value obtained directly from the absorption spectrum.

Figure 4  Growth mechanism schematic diagram of GaAs/GaAsSb heterojunction NWs grown on Si/SiO\(_2\) substrate. The cross-section of the NW heterostructures taken at different axial positions, showing the As-Sb exchange at the core-shell interface and Sb/As interdiffusion.

Based on our observations and discussion above, Figure 4 schematic diagram shows the compositional variation in our nanowire-shell, and their interdiffusion directions. The growth process for GaAs/Ga(As)Sb heterojunction NWs can be divided into three stages. First, Ga droplets were
deposited onto Si/SiO₂ substrate. Subsequently, the GaAs NWs were nucleated and grown by VLS growth mechanism. Finally, the GaAsSb NWs and shells were grown by VLS and VS growth mechanism. Therefore, the GaAs/GaAsSb heterojunction NWs were obtained by the growth in the above three stages. This change is reflected by the different color contrasts in the nanowire and shell in Figure 4. In addition, Figure 4 blue box shows the Ga(As)Sb/GaSb core-shell NW and dashed rectangles correspond to the various cross-sectional positions along the nanowire are shown in Figure 4 cyan and red boxes. Arrows in blue and red represent for the interdiffusions of As and Sb atoms, respectively. It is found that the As-Sb exchange at the GaAsSb NW or shell interface resulting in an outward diffusion of Sb (and corresponding inward diffusion of As), the structure of Sb compositional variation GaAs/Ga(As)Sb core-shell NWs are formed. Therefore, the structure of GaAs/GaAsSb/GaSb and GaAsSb/GaSb core-shell NWs were formed.

4. Conclusions
In conclusion, self-induced antimony compositional variation GaAs/Ga(As)Sb core-shell NWs were grown on Si (111) substrate by molecular-beam epitaxy system. In this study we demonstrated that the structure of GaAs/GaAsSb/GaSb and GaAsSb/GaSb core-shell NWs were formed by EDXs. Sb compositional variation Ga(As)Sb/GaSb core-shell NWs were evidenced by XRD spectrum, energy-dispersive X-ray (EDX) spectroscopy combined with absorption spectra. Because in the process of growth, the As-Sb exchange at the GaAsSb NW surface during growth resulting in an outward diffusion of Sb (and a corresponding inward diffusion of As), forming the structure of Ga(As)Sb core-shell NWs with Sb component gradient. This study provides insights for a more comprehensive understanding of the growth of Sb-based ternary NWs with complex structures, which is essential for future nanostructure device optoelectronic applications.

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References
[1] Yang, I., Li, Z., Wong-Leung, J., et al. (2019) Multiwavelength single nanowire InGaAs/InP quantum well light-emitting diodes. Nano Lett., 19: 3821-3829.
[2] Lukic-Zrnic, R., Gorman, B.P., Cottier, R.J., et al. (2002) Temperature dependence of the band gap of GaAsSb epilayers. J. Appl. Phys., 92: 6939-6941.
[3] Zhang, B., Qiu, W., Chen, S., et al. (2019) Effect of exciton transfer on recombination dynamics in vertically nonuniform GaAsSb epilayers. Appl. Phys. Lett., 114: 252101.
[4] Bauer, J., Gottschalch, V., Paetzelt, H., et al. (2008) VLS growth of GaAs(InGa)As/GaAs axial double-heterostructure nanowires by MOVPE. J. Cryst. Growth, 310: 5106-5110.
[5] Guo, Y.N, Xu, H.Y, Auchterlonie, G.J, et al. (2013) Phase separation induced by Au catalysts in ternary InGaAs nanowires. Nano Lett., 13: 643-650.
[6] Gao, H., Sun, W., Sun, Q., et al. (2019) Compositional Varied Core–Shell InGaP Nanowires Grown by Metal–Organic Chemical Vapor Deposition. Nano Lett., 19: 3782-3788.
[7] Huh, J., Yun, H., Kim, D.C., et al. (2015) Rectifying single GaAsSb nanowire devices based on self-induced compositional gradients. Nano Lett., 15: 3709-3715.
[8] Zhao, Y., Nakano, H., Murakami, H., et al. (2006) Controllable growth and characterization of isolated single-walled carbon nanotubes catalyzed by Co particles. Appl. Phys. A, 85: 103-107.
[9] Ma, L., Hu, W., Zhang, Q., et al. (2014) Room-temperature near-infrared photodetectors based on single heterojunction nanowires. Nano Lett., 14: 694-698.