InAs/GaSb core-shell nanowires grown on Si substrates by metal-organic chemical vapor deposition

Xianghai Ji [‡], Xiaoguang Yang [‡], Wenna Du [‡], Huayong Pan [§], Shuai Luo [‡], Haiming Ji [‡], Hongqi Xu [§] and Tao Yang [‡]

[‡]Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China
[§]Key Laboratory for the Physics and Chemistry of Nanodevices and Department of Electronics, Peking University, Beijing 100871, China

E-mail: tyang@semi.ac.cn

Abstract. We report the growth of InAs/GaSb core-shell heterostructure nanowires with smooth sidewalls on Si substrates using metal-organic chemical vapor deposition (MOCVD) with no assistance from foreign catalysts. Sb adatoms were observed to strongly influence the morphology of the GaSb shell. In particular, Ga droplets form on the nanowire tips when a relatively low TMSb flow rate is used, whereas the droplets are missing and the radial growth of the GaSb is enhanced due to a reduction in the diffusion length of the Ga adatoms when the TMSb flow rate is increased. Moreover, transmission electron microscopy measurements revealed that the GaSb shell coherently grew on the InAs core without any misfit dislocations.

1. Introduction

Among the III-V semiconductor materials, InAs and GaSb are direct band gap compounds with extremely high electron and hole mobility, respectively. In addition, a low lattice mismatch of 0.6% and a unique type-II-broken band alignment between InAs and GaSb make this heterostructure system attractive. Based on one-dimensional nanowire geometry, InAs/GaSb core-shell nanowires have been used in many applications such as tunneling-based devices [1], ambipolar field-effect transistors [2,3], research on electron-hole hybridization [4].

Thus far, InAs/GaSb or GaSb/InAs core-shell nanowires have been mainly grown with the assistance of Au catalysts [2-6]. However, the introduction of Au may degrade the electronic properties of nanowires [7]. Therefore, it is highly desirable to develop the growth of nanowires without the use of any foreign catalysts. In this paper, we present the growth of InAs/GaSb core-shell nanowires on Si(111) substrates using metal-organic chemical vapor deposition (MOCVD) with no assistance from foreign catalysts. In particular, the influence of Sb on the growth of the GaSb shell is investigated in detail. Finally, a homogeneous GaSb shell around the InAs core is achieved through careful control of the growth conditions.

2. Results and discussions

Figure 1a shows a representative SEM image of bare InAs nanowires. The nanowires were observed to be vertically grown on the substrate without tapering. To investigate the influence of Sb adatoms on the GaSb shell growth, a series of InAs/GaSb core-shell nanowires were grown using different TMSb flow rates of 1.3×10^{-6} mol/min, 2.6×10^{-6} mol/min and 3.9×10^{-6} mol/min, respectively. However, the TMGa flow rate was fixed at 0.25×10^{-6} mol/min. The growth time of the GaSb shell was 15 min. The majority of the nanowires in Figure 1b have Ga droplets on their tips. However, the situation changed when the TMSb flow rate was increased to 2.6×10^{-6} mol/min. The droplets were missing, and a uniform GaSb shell around the InAs core was achieved, as shown in Figure 1c. Moreover, the radial growth of GaSb was clearly observed to be enhanced when the TMSb flow rate was increased from 1.3×10^{-6} mol/min to 2.6×10^{-6} mol/min. When the TMSb flow rate was further increased to 3.9×10^{-6} mol/min, the sidewalls of the nanowires became rough.

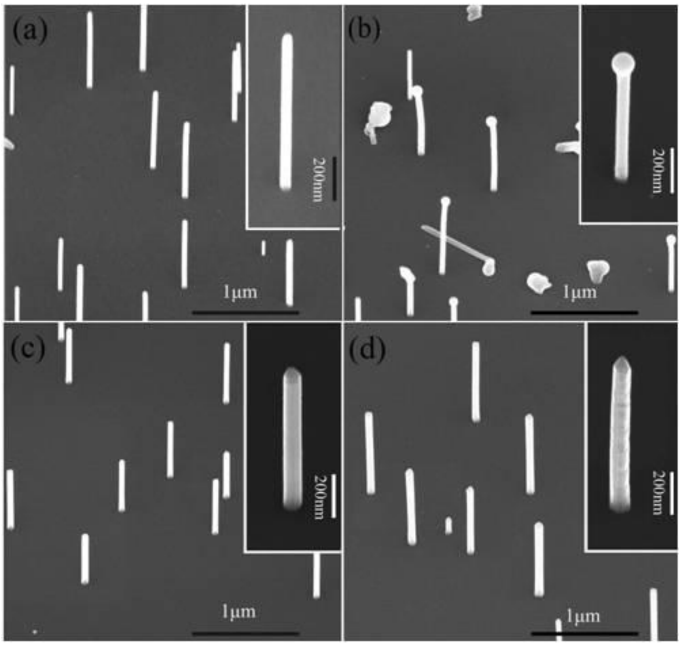

Figure 1. 30°-tilted SEM images of the bare InAs and InAs/GaSb core-shell nanowires: (a) InAs core nanowires, (b-d) InAs/GaSb core-shell nanowires with the TMSb flow rate of (b)1.3×10^{-6}mol/min, (c)2.6×10^{-6}mol/min, (d)3.9×10^{-6}mol/min. The TMGa flow rate was kept constant at 0.25×10^{-6}mol/min. Insets in (a-d) show higher-magnification SEM images.

Generally, Ga atoms are collected by the droplet via three pathways [8]: (i) direct impingement of Ga atoms on the droplet; (ii) adsorption of Ga atoms onto the nanowire side facets and subsequent diffusion to the nanowire tip; (iii) adsorption of Ga atoms onto the substrate surface and subsequent diffusion to the nanowire tip along the nanowire sidewalls. Because the growth temperature and the TMGa flow rate were unchanged for the growth of the GaSb shell in Figures 1b-d, the Ga atoms from pathway(i) should be the same for all cases. Additionally, we assume that the contribution in this manner is weak because of the small surface area of the droplet. In terms of the contribution from pathway(iii), Ga adatoms can hardly diffuse from the substrate surface to the tip of nanowires because of the relatively low growth temperature of the GaSb shell (440 ℃) [9]. Moreover, the GaSb shell without tapering in Figure 1c also indicates that the Ga adatoms that diffused from the substrate surface to the sidewalls of nanowires can be ignored. Therefore, the main contribution to the droplet should be from pathway(ii). Furthermore, we speculate that the missing of Ga droplets is a consequence of the reduction in the surface diffusion length of the Ga adatoms. Specifically, Sb, which has a heavier atomic mass and lower volatility than As and P, is easier to adsorb onto the nanowire side facets. To move, Ga adatoms must break their temporary bonds with the adsorbed Sb. Eventually, the surface mobility of the Ga adatoms on the nanowire side facets is suppressed kinetically, and the diffusion length of the Ga adatoms is gradually reduced under increasing TMSb flow rate. Therefore, the Ga droplets cannot be formed when the diffusion length of the Ga adatoms is reduced to a certain degree, resulting in enhancement of the radial growth of the GaSb via vapor-solid (VS) mechanism, as schematically illustrated in Figure 2. Additionally, when the TMSb flow rate was further increased to 3.9×10^{-6}mol/min, the diffusion length of the Ga adatoms was so short that the nucleation of GaSb was not homogeneous on the whole InAs sidewalls. Therefore, to obtain good morphology of the GaSb shell, the TMSb flow rate should be carefully controlled.

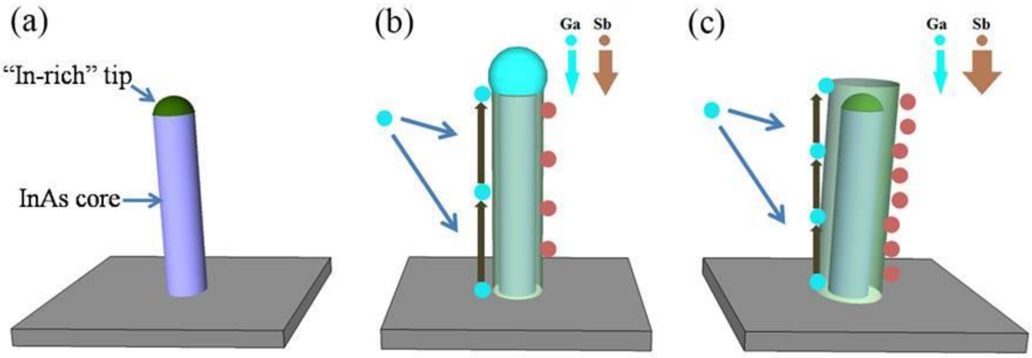

Figure 2. Schematic of the effect of Sb on the morphology of the InAs/GaSb core-shell nanowire:(a) bare InAs nanowire, (b) with a small amount of Sb, and (c) with relatively more Sb.

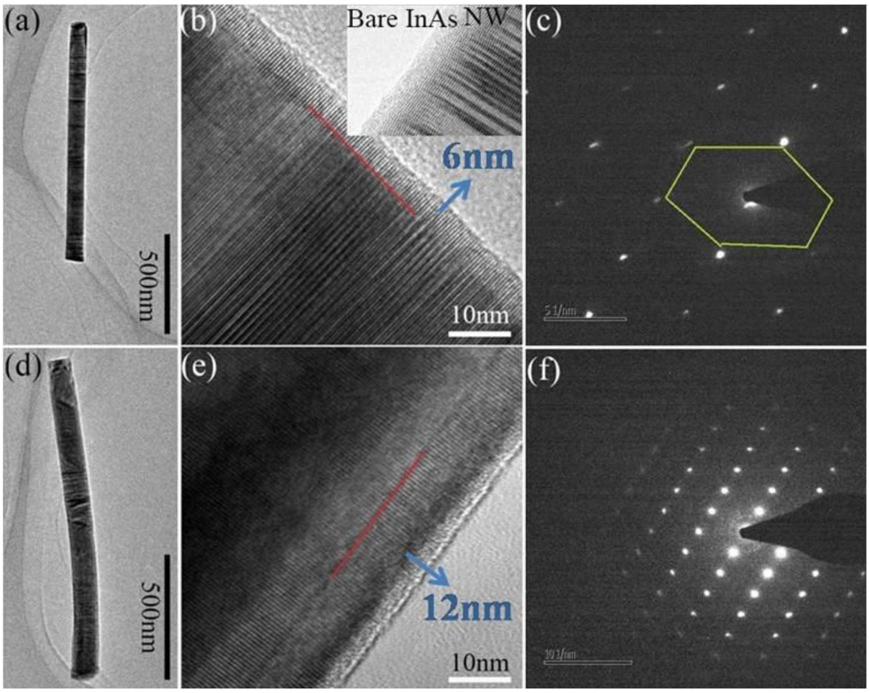

Figure 3. TEM images and SAED patterns of the InAs/GaSb core-shell heterostructure nanowires with the shell growth times of (a-c) 15 min, (d-f) 30 min, respectively. (a, d) Low-magnification TEM image of the corresponding nanowire. (b, c) High-resolution TEM image and corresponding SAED pattern of the nanowire shown in (a) viewed along the <110> zone axis. (e, f) High-resolution TEM image and corresponding SAED pattern of the nanowire shown in (d) viewed along the <211> zone axis. The inset in (b) shows a typical high-resolution TEM image of a bare InAs nanowire.

Detailed TEM investigations are shown in Figure 3. The TMSb and TMGa flow rates were of 2.6×10^{-6}mol/min and 0.25×10^{-6}mol/min, respectively; while the growth times of the GaSb shells investigated in Figures 3a-c and d-f were varied. Figure 3a shows a low-resolution TEM image of the nanowire with the shell growth time of 15 min. A corresponding high-resolution (HR) TEM image viewed from the <110> zone axis was shown in Figure 3b. A GaSb shell, approximately 6 nm in thickness, was observed to be radially grown around the InAs core. The nanowire is wurtzite (WZ)-

dominated and contains a large number of planar defects along its growth direction, which is very common in self-catalyzed InAs nanowires, as shown in the inset of Figure 3b. We speculate that these planar defects were recorded from the InAs core to the GaSb shell. In fact, such a phenomenon has been observed in core-shell nanowires of other material systems [10,11]. This behavior highlights the need to improve the crystal quality of the self-catalyzed InAs core nanowires.We note that, in Figures 3d and e, the TEM images were acquired from the <211> zone axis and the growth time of the GaSb shell was extended to 30 min. Planar defects cannot be observed from the <211> zone axis [12]. However, because the sidewalls of the InAs core are six {110}-family facets, this direction can always provide a clear contrast between the InAs core and the GaSb shell. Moreover, no Moiré fringes are visible in Figure 3e, which means that no plastic relaxation occurred. This lack of plastic relaxation is attributed to the relatively thin GaSb shell and the small lattice difference between the InAs and GaSb.

3. Conclusion

In summary, we have demonstrated the growth of InAs/GaSb core-shell heterostructure nanowires on Si substrates using MOCVD. The impact of Sb adatoms on the growth behavior of the GaSb shell is investigated in detail. Ga droplets form on the tips of nanowires but without visible axial GaSb growth under a relatively low TMSb flow rate. However, the droplets were missing and the radial growth of GaSb was enhanced with increasing the TMSb flow rate because of the reduction in the diffusion length of the Ga adatoms. Detailed TEM analyses revealed that the overgrowth of the GaSb shell was highly uniform and coherent with the InAs core without misfit dislocations. The results presented here may provide a new understanding of the growth of other antimonide nanowires. Furthermore, the as-grown InAs/GaSb core-shell nanowires on Si substrates may introduce new possibilities for applications in future nanowire-based devices

References

[1] Dey A W, Svensson J, Ek M, Lind E, Thelander C and Wernersson L E 2013 *Nano Lett.* **13** 5919
[2] Ganjipour B, Ek M, Mattias B B, Dick K A, Pistol M E, Wernersson L E and Thelander C 2012 *Appl. Phys. Lett.* **101** 103501
[3] Ganjipour B, Sepehri S, Dey A W, Tizno O, Borg B M, Dick K A, Samuelson L, Wernersson L E and Thelander C 2014 *Nanotechnology* **25** 425201
[4] Ganjipour B, Leijnse M, Samuelson L, Xu H Q and Thelander C 2015 *Phys. Rev. B* **91** 161301
[5] Jan G G, Martin L, Bahram G and Kimberly A D 2015 *Acs Nano* **9** 7033
[6] Namazi L, Nilsson M, Lehmann S, Thelander C and Dick K A 2015 *Nanoscale* **7** 10472
[7] Wang X Y, Du W N, Yang X G, Zhang X W and Yang T 2015 *J. Cryst. Growth* **426** 287
[8] Ye H, Yu Z Y, Kodambaka S and Shenoy V B 2012 *Appl. Phys. Lett.* **10** 263103
[9] Wu J, Borg B M, Jacobsson D, Dick K A and Wernersson L E 2013 *J. Cryst. Growth* **383** 158
[10] Ghalamestani S G, Munshi A M, Dheeraj D L, Fimland B O, Weman H and Dick K A 2013 *Nanotechnology* **24** 405601
[11] Kawaguchi K, Heurlin M, Lindgren D, Borgstrom M T, Ek M and Samuelson L 2011 *Appl. Phys. Lett.* **99** 131915
[12] Johansson J, Karlsson L S, Svensson C P T, Martensson T, Wacaser B A, Deppert K, Samuelson L and Seifert W 2006 *Nat. Mater.* **5** 574

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