Understanding the kink formation in GaAs/InAs heterostructural nanowires

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Abstract— The kinks formation in heterostructural nanowires was observed to be dominant when InAs nanowires were grown on GaAs nanowires. Nanowires were grown through vapor-liquid-solid (VLS) mechanism in an MOCVD (metalorganic chemical vapor deposition) reactor. GaAs nanowires were grown in $\{\bar{1}1\bar{1}\}$ direction on a GaAs ($\{\bar{1}1\bar{1}\}$)B substrate. When InAs nanowires grown on the GaAs nanowires, most of the InAs nanowires changed their growth directions from $\{\bar{1}1\bar{1}\}$B to other $<111>$B directions. The kinks formation is ascribed to the large compressive misfit strain at the GaAs/InAs interface (7.2% lattice mismatch between GaAs and InAs) and the high mobility of indium species during MOCVD growth. The in-depth analysis of the kinks formation was done by growing InAs for short times on the GaAs nanowires and characterizing the samples. The hindrance to compressively strain InAs to form coherent layers with GaAs pushed the InAs/Au interfaces to the sides of the GaAs nanowires growth ends. New InAs/Au interfaces have generated due to lateral growth of InAs on GaAs nanowires. These new interfaces led the InAs nanowires growth in other $<111>$-B directions. The morphological and structural features of these heterostructural kinked nanowires were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques.

Keywords- nanowire; axial nanowire heterostructure; heterostructural nanowire; GaAs; InAs; kink; TEM; SEM.

I. INTRODUCTION

Semiconductor nanowires are the promising nanostructures for investigating fundamental physical properties in one-dimension and they exhibit novel optical and electronic properties. These nanostructures are expected to be the basic building blocks for future nanoscale electronic and optoelectronic devices [1]. Vapor-liquid-solid (VLS) mechanism is the most widely used mechanism for the growth of semiconductor nanowires [2]. Alteration of the reactant vapor species chemistry during the VLS growth produces the compositional variation and thereby the heterostructures formation within the single nanowires [3]. Compositional variation along the nanowires has produced the axial heterostructural nanowires [4] and the lateral compositional variation has produced the lateral heterostructural nanowires [5]. Axial heterostructural nanowires, which formed by the high lattice mismatched semiconductors, expected to have defect free and abrupt heterointerfaces, as the heteroepitaxial growth in the nanowires takes place in the nanodimensions [6, 7]. GaAs and InAs have high lattice mismatch between them, i.e. as much as 7.2%. It is also a well-known fact that, In species are highly mobile and have high diffusion lengths than that of Ga species in the MOCVD growth. The nanowire heterostructures formed by these two materials have been reported [8, 9], but no complete experimental demonstration was presented.

In this work, with the aim of exploring the fundamentals of heterostructure formation in the nanowires, GaAs nanowires were grown on GaAs ($\{\bar{1}1\bar{1}\}$)B substrate for 30min and InAs nanowires were grown for different time periods on those GaAs nanowires. In order to understand the mechanism of heterostructure formation, the morphological and structural features of resultant heterostructural nanowires have been rigorously characterized by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques and the results were discussed.

II. EXPERIMENTAL

GaAs/InAs heterostructural nanowires were grown through the VLS mechanism in a horizontal flow metal-organic chemical vapor deposition (MOCVD) reactor at a pressure of 100 mbar. The molar flow rates of trimethylgallium (TMG), trimethylindium (TMI) and AsH3 were 1.16 × 10^{-5} mol/min, 1.21 × 10^{-5} mol/min and 5.36 × 10^{-4} mol/min respectively. Poly-L-lysine (PLL) solution treated GaAs ($\{\bar{1}1\bar{1}\}$)B substrates with 30nm Au particles were annealed at 600°C for 10min and the growth was carried out at 450°C. GaAs nanowires were grown for 30 min by flowing TMG and AsH3, and then InAs nanowires were grown on them for another 30 min by switching off TMG flow and switching on TMI flow, while AsH3 flow kept constant. After the growth of InAs nanowires, TMI flow was switched off and the samples were cooled under AsH3 atmosphere. In the further experiments, InAs nanowires were grown on GaAs nanowires for different time periods (1, 3 and 5 mins) with same growth conditions as above. Structural and morphological characterizations were carried out using a JEOL 890 high-resolution scanning electron microscope (HRSEM) with a resolution of 0.6 nm, and a JEOL 2010 (at 200 kV), FEG technai-20 (at 200 kV) transmission electron microscopes.
III. RESULTS AND DISCUSSION

Figure 1 shows the HRSEM images of kinked GaAs/InAs heterostructural nanowires. GaAs nanowires were grown in \([\overline{1}1\overline{1}]B\) direction perpendicular to the GaAs(\(\overline{1}1\overline{1}\))B substrate. InAs nanowires grown on the top portion of GaAs nanowires in other growth directions and formed as kinks. This material identification is evidenced through selected area electron diffraction (SAED) studies, as GaAs nanowires have zinc-blende structure, while \(<111>B\) grown InAs nanowires have wurtzite structure [10]. This diffraction analysis is shown in Fig. 3. InAs nanowire tips are with nanoparticles of \(~30\text{nm}\) sizes, which are expected to be the Au alloy particles, as pure Au nanoparticles were deposited on the substrate to initiate the VLS growth.

![Figure 1. HRSEM images of GaAs/InAs heterostructural nanowires. First GaAs nanowires were grown on GaAs (\(\overline{1}1\overline{1}\))B substrate for 30 min and then InAs nanowires were grown on them for another 30 min. 'A' is viewed at 0° sample tilt, and 'B' is viewed at 10° sample tilt.](image)

TEM observations of these heterostructural nanowires revealed the different morphologies, and these are shown in Fig. 2. Figures 2A and 2B are the images of kinked heterostructural nanowires, whereas Fig. 2C is the image of a straight heterostructural nanowire. In both cases of Figs. 2A and 2B, InAs nanowires have grown by changing its growth direction. In the case of Fig. 2A, InAs nanowire has grown from the side of the GaAs nanowire top portion, whereas in Fig. 2B, InAs nanowire was grown just by changing its growth direction. Most of the heterostructures in the TEM observations were having similar morphologies to that showed in the images Figs. 2A and 2B.

![Figure 2. Low magnification TEM images of GaAs/InAs heterostructural nanowires. 'A' and 'B' are the images of kinked heterostructural nanowires with different morphologies at the top portion. 'C' is the image of a straight heterostructural nanowire.](image)

Out of randomly observed 60 heterostructural nanowires, 57% have the same morphology as shown in Fig. 2A, 17% are as in Fig. 2B and only 11% have grown straight as in Fig. 2C. The remaining 15% have different other morphologies, where InAs growth has terminated after growing in very small lengths. The detailed structural characterization of kinked heterostructures was carried out by using SAED in the TEM. Figure 3 shows the bright field TEM image of the top portion of a kinked heterostructural nanowire with corresponding diffraction patterns. The diffraction studies indicated that the GaAs nanowire grown in \([\overline{1}1\overline{1}]B\) direction perpendicular to the substrate and have zinc-blende structure (Fig. 3B). InAs nanowire grown at the top portion of GaAs nanowire in \([\overline{1}1\overline{1}]B\) direction and have the wurtzite structure (figs 3C and 3D). All the nanowires having morphology similar to the Figs. 2A and B showed same results as in Fig. 3, i.e. GaAs portion is grown in \([\overline{1}1\overline{1}]B\) direction and the InAs portion is growing in other \(<111>B\) directions, such as \([\overline{1}1\overline{1}]B\), \([\overline{1}\overline{1}1]B\), \([1\overline{1}\overline{1}]B\).

![Figure 3. A) Bright field TEM image of the top portion of a kinked heterostructural nanowire. SAED locations are identified with arrows. B) SAED pattern taken from the nanowire grown perpendicular to the substrate (i.e GaAs nanowire portion). C) SAED pattern taken from the InAs portion. D) SAED pattern taken from the junction portion (as indicated by a circle in A) with the same sample tilt as in C, the diffraction spots from zinc-blende structure is attached with white lines for easy identification.](image)

In order to further investigate the kinks formation in GaAs/InAs nanowire heterostructures, InAs was grown for short times (such as 1, 3 and 5 min) on GaAs nanowires. At the initial stages (1 min) of InAs growth on GaAs nanowires, it was observed that InAs nanowire/Au interface was pushed to the sides of GaAs nanowires, and the InAs nanowire growth has started in \([\overline{1}1\overline{1}]B\) direction, which is antiparallel to the initial GaAs nanowire growth direction (\([\overline{1}1\overline{1}]B\)). This phenomenon can be observed from the Figs. 4 and 5A.
Figure 4.
A) STEM (scanning transmission electron microscopy) dark field image of the growth end of a heterostructural nanowire, when InAs grown for 1 min on 30 min grown GaAs nanowire. The bright portion is InAs, as high atomic number element relatively scatter more electrons, which eventually gives much brightness in the darkfield image. B) EDX (Energy dispersive X-ray spectroscopy) line scan data on the tip of heterostructural nanowire shown in ‘A’ as a red line. The EDX line scan data is exactly matching with the contrast details of the STEM dark field image.

Figure 5.
A) TEM bright field image of the growth end of a heterostructural nanowire, when InAs grown for 1 min on 30 min grown GaAs nanowire. B) TEM bright field image of the growth end of a heterostructural nanowire, when InAs grown for 5 min on 30 min grown GaAs nanowire. Strain contrast within the nanowire can be clearly observed, which is due to the InAs lateral growth on the GaAs nanowire. Inset is the enlarged view of Au particle. Change in the Au/InAs growth interface direction can be observed by comparing the both cases (A and B). Both the images were taken when the nanowires growth ends were aligned into <110> zoneaxis.

1 min InAs growth

5 min InAs growth

IV. CONCLUSIONS
The kinks formation was dominant when InAs nanowires were grown on GaAs nanowires by VLS mechanism using ~30nm Au nanoparticles. In-depth analysis of kinks formation was done by investigating the short time grown InAs on GaAs nanowires samples. High mobile nature of indium species during MOCVD growth influenced by the compressive stresses at the growth front (Au liquid droplet/nanowire interface), causes the shift in the Au liquid droplets location from the nanowires top to the sides of the nanowires growth ends. InAs nanowires start to grow antiparallelly to the GaAs nanowires growth direction, from the side shifted Au droplets. InAs lateral growth on GaAs nanowires stops the InAs axial growth in [111]A directions and changes the InAs/Au interface perpendicular to the sides of GaAs/InAs core-shell nanowire. Eventually, InAs nanowires grow from these interfaces in [11̅1]B, [11̅1]B, [11̅1]B directions.

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REFERENCES


