Two Different Mechanisms for Au-free Growth of InAsSb Nanowires on Si Substrate

Wenna Du¹, Xiaoguang Yang¹, Huayong Pan², Xiaoye Wang¹, Xianghai Ji¹, Zhanguo Wang¹, Hongqi Xu², Tao Yang¹*.

¹ Key Laboratory of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences P.O. Box 912, Beijing 100083, People's Republic of China

Phone: +8010-8230-4569 E-mail: tyang@semi.ac.cn

² Key Laboratory for the Physics and Chemistry of Nanodevices, Department of Electronics, Peking University

Beijing 100871, People's Republic of China

Abstract

We report on the Au-free growth of InAsSb nanowires (NWs) on Si (111) using metal-organic vapor phase epitaxy. The effects of growth parameters have been investigated in detail. It is found the presence of two different mechanisms on the growth of the Au-free InAsSb NWs under different conditions.

1. Introduction

Semiconductor nanowires (NWs) have attracted a great deal of attention because of their unique properties and various potential applications. But, the growth mechanism of indium compound NWs without foreign metal assistance is still an open question¹⁻³ which mainly focuses on the In-droplet-catalyzed Vapor-Liquid-Solid (VLS) mode or the droplet-free Vapor-Solid (VS) growth mode. It is important to make clear the growth mechanism of the NWs because it not only significantly influences the properties of resulting NWs, but also decides the position, diameter, and crystal structure of NW's.

In this paper, the effects of growth parameters such as V/III ratio and Sb flow rate fraction (Sb-FRF, defined as TMSb/ (TMSb+AsH₃)) on the growth of InAsSb NWs have been investigated in detail. We found the presence of two different mechanisms on the growth of Au-free InAsSb NWs under different conditions.

2. Experimental Details

InAsSb NWs on Si (111) substrates were grown by metal–organic vapor phase epitaxy at a pressure of 133 mbar. Trimethylindium (TMIn), arsine and trimethylantimony were used as gas precursors and H₂ as the carrier gas. During the growth, the TMIn flow rate was kept constant at 2.0×10^{-6} mol/min. The Sb-FRF and V/III ratios were varied respectively between 0.2 - 0.8 and 5 - 50.

3. Results and Discussion

Fig.1 shows the influence of both V/III ratio and Sb-FRF on the growth of InAsSb NWs. Two remarkably different morphology characteristics can be clearly recognized from these SEM images, as demarked by the red dashed line in the figure. Under the high V/III ratio and low Sb-FRF, the NWs prefer to grow perpendicular to the (111) substrate plane. The uniformity of the NW morphol-

ogy and the absence of droplets on the top suggest a catalyst-free growth mechanism⁴. We define this kind of NWs as Type I NWs which should be grown via VS mode. In contrast, under low V/III ratio and high Sb-FRF, the NWs are quite different, where the InAsSb NWs tend to grow in multiple orientations and most of them appear to be more or less close to [1 1 1] orientation, and are nearly kink-free. The top of each NW terminates with an In-Sb alloy droplet, being totally different from the case of Type I NWs. The droplets on top of the NWs have a hemispherical shape with no defined facets. It is found that whether NWs have non-tapered or tapered cross sections depends mainly on Sb-FRF. The tapered NWs and the existence of the droplets on the top suggest a catalyst growth mechanism⁵. We define this kind of NWs as Type II NWs which should be grown via VLS mode.



Fig. 1 SEM images of InAsSb NWs as a function of Sb-FRF and V/III ratio. The inset in the top right shows the variation of growth rate with V/III ratio when Sb-FRF = 0.4.

Furthermore, it is found that the growth rate of the two types NWs is quite different. The inset in Fig.1 shows the variation of NW growth rate with the change of V/III ratio from 5 to 50 at a fixed Sb-FRF of 0.4. A remarkable decrease in growth rate can be clearly observed when the V/III ratio increases from 5 to 10, which implies a change

in growth mode from Type II to Type I. The rate of deposition via VLS process is much higher than via non-catalyzed VS deposition, as the latter is presumably a result of surface reactivity.^{6,7}

In order to further check the differences between the two types of NWs, we perform the test of scanning transmission electron microscopy (STEM) analysis with energy dispersive X-ray spectroscopy (EDS) and high-resolution transmission electron microscope (HRTEM) analysis. For type I NW (Fig. 2a), the composition of NW from the bottom to the top is homogeneous and nearly constant, while for the type II NW (Fig. 2b), the composition at the top of the NW shows a significant difference from those in the other parts. Based on the above experimental results, we can confirm that the Type I NWs grow via VS mode while the Type II ones form via VLS mode. Our HRTEM measurements ^[8] have shown NWs via VLS-mode with high crystal quality.



Fig. 2 EDS result of alloy composition distribution for (a) Type I and (b) Type II NWs showing two different characteristic shapes.

Then, we depict a scheme for the nucleation and growth of InAsSb NWs on Si (111) that can consistently accounts for two different growth modes, as illustrated in Fig.3. At low V/III ratio and high Sb-FRF, In-rich droplets forming spontaneously on Si in the beginning of the growth mediate the nucleation of InAsSb. Due to excessive supply of In flow, the In-rich droplets will be maintained up on the top of NWs during the whole NW growth process. Then the In-rich alloy droplet captures the precursor materials and catalyzes crystal growth further at the liquid-solid interface. The VLS process occurs. At high of V/III ratio and low Sb-FRF, however, since the supply of group V flow is large enough to consume all the supply of In flow, the initial droplets crystallize quickly with forming InAsSb rather than gathering to stay as In-rich droplet. In this way, InAsSb NW growth is assumed to obey the VS-mode and the crystal growth takes place along the entire surface of the NW in a layer-by-layer mode.



Fig. 3 Schematic diagram of two growth modes for InAsSb NWs.

4. Conclusions

We presented a controllable method of Au-free InAsSb NW growth chosen between the VLS and VS modes by modifying the growth conditions (Sb-FRF and V/III ratio). At low V/III ratio and high Sb-FRF the VLS process occurs. On the contrary, at high V/III ratio and low Sb-FRF the NWs grow via the VS-mode. For VS mode, all NWs have unified axial [111] direction and a uniform composition distribution, which makes them the best candidate for multiple NWs integration device, while the high crystal quality of the NWs grown via VLS mode is promising for improving the performances of single NW devices.

Acknowledgements

The authors thank the financial supports from MOST (Grant NO.2012CB932701) and NNSF (Grant NO.91433206) of China.

References

- [1] S. Hertenberger et al., Appl. Phys. Lett. 98 (2011) 123114.
- [2] A. Fontcuberta i Morral *et al.*, Appl. Phys. Lett. **92** (2008) 063112.
- [3] E. Dimakis et al., Cryst. Growth Des. 11 (2011) 4001.
- [4] W.Wei et al., Nano Lett. 9 (2009) 2926.
- [5] C. Ngo et al., J. Cryst. Growth 336 (2011) 14.
- [6] S. Kodambaka et al., Phys. Rev. Lett. 96 (2006) 096105.
- [7] S. Kodambaka et al., Science 316 (2007) 729.
- [8] W. N. Du et al., Cryst. Growth Des. 15 (2015) 2413.