



# HOKKAIDO UNIVERSITY

|                     |                                                                                                 |
|---------------------|-------------------------------------------------------------------------------------------------|
| Title               | Growth and Characterization of Phosphide-based III-V Semiconductor Nanowires                    |
| Author(s)           | 石坂, 文哉                                                                                          |
| Degree Grantor      | 北海道大学                                                                                           |
| Degree Name         | 博士(工学)                                                                                          |
| Dissertation Number | 甲第12625号                                                                                        |
| Issue Date          | 2017-03-23                                                                                      |
| DOI                 | <a href="https://doi.org/10.14943/doctoral.k12625">https://doi.org/10.14943/doctoral.k12625</a> |
| Doc URL             | <a href="https://hdl.handle.net/2115/65457">https://hdl.handle.net/2115/65457</a>               |
| Type                | doctoral thesis                                                                                 |
| File Information    | Fumiya_Ishizaka.pdf                                                                             |



Doctoral Dissertation

博士論文

# **Growth and Characterization of Phosphide-based III-V Semiconductor Nanowires**

(リン系 III-V 族化合物半導体ナノワイヤの成長と評価に関する研究)

Graduate School of Information Science and Technology,  
Hokkaido University

北海道大学大学院情報科学研究科

Fumiya Ishizaka

石坂 文哉



© 2017 Fumiya Ishizaka

A dissertation submitted in partial fulfillment  
of the requirements for the degree of Doctor of  
Philosophy (Engineering)  
in Hokkaido University, February, 2017.

Dissertation Supervisor  
Professor Junichi Motohisa

# Acknowledgements

This dissertation describes a part of research work carried out at Research Center for Integrated Quantum Electronics (RCIQE) and Graduate School of Information Science and Technology, Hokkaido University, under the direction of Professor Takashi Fukui from 2011 to 2016 and Professor Junichi Motohisa from 2016 to 2017, while I was a graduate student at the Graduate School of Information Science Technology.

I would like to express my deepest gratitude to Professor Takashi Fukui. This work would never be accomplished without his invaluable support, guidance, and encouragement. I am greatly happy to study and research for six years under his supervision.

I would like to express my sincere thanks to Professor Junichi Motohisa, Associate Professor Katsuhiko Tomioka, and Associate Professor Shinjiro Hara for their continual support and encouragement.

I would like to express my appreciation to Professor Tamotsu Hashizume, Professor Eiichi Sano, Professor Kanji Yoh, Professor Seiya Kasai, Associate Professor Masamichi Akazawa, Associate Professor Taketomo Sato, and Associate Professor Masayuki Ikebe for their encouragement and fruitful discussions.

I would like to express my appreciation to Professor Masafumi Yamamoto, Professor Ikuo Suemune, Professor Masato Motomura, Professor Yasuo Takahashi, Professor Akihiro Murayama, Professor Kazuhisa Sueoka, Professor Akihisa Tomita, Professor Hiromichi Ohta, Professor Tetsuya Asai, Professor Tetsuya Uemura, and Professor Hajime Igarashi for their invaluable lectures and encouragement.

I would like to say thanks to the member of our research group, Dr. Keitaro Ikejiri, Dr. Masatoshi Yoshimura, Dr. Yoshinori Kohashi, Dr. Eiji Nakai, Mr. Masatoshi Yatago, Mr. Yuta Kobayashi, Mr. Takahito Endo, Dr. Shinya Sakita, Ms. Ayana Yamamoto, Mr. Hiromu Fujimagari, Ms. Aya Onodera, Mr. Shogo Yanase, Mr. Hiroaki Kato, Mr. Toshihiro Wada, Mr. Yungoo Ro, Mr. Mui Chen, Mr. Yoshihiro Hiraya, Mr. Ryutaro Kodaira, Mr. Akihito Sonoda, Mr. Hiroki Kameda, Mr. Naoto Tamaki, Mr. Kyohei Kabamoto, Mr. Akinobu Yoshida, Mr.

Kohei Chiba, Mr. Ryoma Horiguchi, Mr. Masahiro Sasaki, Mr. Yusuke Minami, Mr. Shinya Yamamoto, Dr. Matthias T. Elm, Dr. Yong Joon Hong, Dr. Martin Fischer for their technical supports, valuable discussions and encouragement. I would also like to express my sincere thanks and appreciation to Dr. Hajime Goto, Dr. Natsuo Nakamura, and Dr. Takanori Maebashi for their invaluable discussions, support and encouragement.

I wish to say thanks for RCIQE researchers and students, Dr. Zenji Yatabe, Dr. Joel T. Asubar, Dr. Keita Konishi, Dr. Kota Ohi, Dr. Yujin Hori, Dr. Tomo Tanaka, Mr. Kazuhiro Takahagi, Mr. Yuki Nakano, Mr. Toru Muramatsu, Mr. Yudai Imai, Mr. Tomohito Kudo, Mr. Kenichiro Mori, Mr. Yuya Takatsuka, Mr. Satoshi Takeya, Dr. Taketsugu Ishikura, Dr. Zhixin Cui, Mr. Liumin Zou, Mr. Masaki Sato, Mr. Takayuki Tanaka, Mr. Naoki Azumaishi, Mr. Ryohei Jinbo, Dr. Xiang Yin, Mr. Yusuke Kumazaki, Mr. Takuma Nakano, Mr. Ryota Kuroda, Mr. Yuri Imai, Mr. Takahiro Hiraki, Mr. Lennart-Kund Liefeth, Mr. Yushi Abe, Mr. Shinya Inoue, Mr. Yutaka Senzaki, Mr. Takao Miyamoto, Mr. Akio Watanabe, Mr. Masahito Chiba, Mr. Kenya Nishiguchi, Mr. Yuki Inden, Mr. Masaaki Edamoto, Ms. Sayaka Ohmi, Mr. Shoma Okamoto, Mr. Hirofumi Kida, Mr. Kentaro Sasaki, Mr. Atsushi Seino, Mr. Shun Takayashiki, Mr. Takuya Miyajima, Mr. Yukinori Wakita, Mr. Keisuke Ito, Mr. Kenta Saito, Mr. Satoru Matsumoto, Mr. Shota Kaneki, Mr. Shota Toiya, Mr. Taito Hasezaki, Mr. Dai Hasegawa, Mr. Shota Hiramatsu, Mr. Naoshige Yokota, and I also express thank for the other RCIQE students for their friendship.

I would like to extend my deepest gratitude to Mr. Kenji Takada, Mr. Kiyotake Nagakura, Ms. Satoko Takeuchi, Ms. Mizuho Tanaka, Ms. Yuki Watanabe, Ms. Yuka Kamoto, and Ms. Chieko Akiyama for their businesslike supports and encouragements.

Finally, I am particularly grateful to my wife, Minami Ishizaka, who deeply understands what I am and always kindly supported when I was mentally and physically exhausted. I would also like to appreciate my parents and brother, Akihiro Ishizaka, Michiko Ishizaka, and Yuhei Ishizaka, who have always provided heartfelt support and encouragement. Thank you with all my heart.

February 2017  
Fumiya Ishizaka

# Table of Contents

|                        |      |
|------------------------|------|
| Acknowledgements ..... | i    |
| Contents .....         | iii  |
| List of Figures.....   | vii  |
| List of Tables .....   | xiii |

## Chapter 1

|                                                        |          |
|--------------------------------------------------------|----------|
| <b>Introduction .....</b>                              | <b>1</b> |
| 1.1 Background .....                                   | 1        |
| 1.2 Phosphide-based III-V semiconductor nanowires..... | 2        |
| 1.3 Objective .....                                    | 4        |
| 1.4 Outline of this thesis.....                        | 5        |
| Bibliography .....                                     | 7        |

## Chapter 2

|                                                              |          |
|--------------------------------------------------------------|----------|
| <b>Semiconductor Nanowires.....</b>                          | <b>9</b> |
| 2.1 Introduction .....                                       | 9        |
| 2.1.1 History of nanowire growth.....                        | 9        |
| 2.1.2 Advantages of nanowires .....                          | 10       |
| 2.2 Nanowire growth method.....                              | 11       |
| 2.2.1 Catalyst-assisted vapor-liquid-solid growth .....      | 11       |
| 2.2.2 Selective-area metal organic vapor phase epitaxy ..... | 13       |
| 2.3 Phosphide-based nanowires.....                           | 15       |
| 2.3.1 Wurtzite and zinc blende .....                         | 15       |
| 2.3.2 Energy band structure .....                            | 17       |
| 2.3.3 Crystal structure transfer method.....                 | 19       |
| Bibliography .....                                           | 21       |

## Chapter 3

|                                                       |    |
|-------------------------------------------------------|----|
| <b>Experimental Techniques</b> .....                  | 25 |
| 3.1 Introduction .....                                | 25 |
| 3.2 Principles of MOVPE .....                         | 25 |
| 3.2.1 Overview .....                                  | 25 |
| 3.2.2 MOVPE growth process.....                       | 26 |
| 3.2.3 MOVPE system.....                               | 27 |
| 3.3 Nanowire fabrication by selective-area MOVPE..... | 29 |
| 3.4 Characterizations.....                            | 30 |
| 3.4.1 Scanning electron microscopy.....               | 30 |
| 3.4.2 Transmission electron microscopy .....          | 30 |
| 3.4.3 Photoluminescence .....                         | 30 |
| 3.4.4 Chathodoluminescence.....                       | 31 |
| 3.4.5 X-ray diffraction.....                          | 32 |
| Bibliography .....                                    | 33 |

## Chapter 4

|                                                      |    |
|------------------------------------------------------|----|
| <b>Growth of InGaP Nanowires on InP (111)A</b> ..... | 35 |
| 4.1 Introduction .....                               | 35 |
| 4.2 Experimental procedure .....                     | 36 |
| 4.3 Group III supply ratio dependence.....           | 37 |
| 4.4 V/III ratio dependence.....                      | 40 |
| 4.5 Compositional characterization.....              | 41 |
| 4.6 Conclusions .....                                | 43 |
| Bibliography .....                                   | 44 |

## Chapter 5

|                                                                        |    |
|------------------------------------------------------------------------|----|
| <b>Crystal Structure Transfer in InP/GaP Core-Shell Nanowire</b> ..... | 47 |
|------------------------------------------------------------------------|----|

---

|                                                              |    |
|--------------------------------------------------------------|----|
| 5.1 Introduction .....                                       | 47 |
| 5.2 Experimental procedure .....                             | 48 |
| 5.3 Growth of InP/GaP core-shell nanowires .....             | 49 |
| 5.4 Crystal structure transfer in core-shell nanowires ..... | 53 |
| 5.5 Conclusions .....                                        | 54 |
| Bibliography .....                                           | 55 |

## Chapter 6

### **Growth of Wurtzite InP/AlGaP Core-Multishell Nanowires ..... 57**

|                                                      |    |
|------------------------------------------------------|----|
| 6.1 Introduction .....                               | 57 |
| 6.2 Experimental procedure .....                     | 58 |
| 6.3 Nanowire growth and quantum well structure ..... | 60 |
| 6.4 Structural characterization.....                 | 62 |
| 6.5 Optical characterization.....                    | 65 |
| 6.6 Conclusions .....                                | 67 |
| Bibliography .....                                   | 68 |

## Chapter 7

### **Growth of Wurtzite InP/AlInP Core-Multishell Nanowires ..... 71**

|                                                     |    |
|-----------------------------------------------------|----|
| 7.1 Introduction .....                              | 71 |
| 7.2 Experimental procedure .....                    | 73 |
| 7.3 Nanowire growth.....                            | 74 |
| 7.4 Structural characterization.....                | 75 |
| 7.5 Compositional and strain characterization ..... | 78 |
| 7.6 Optical characterization.....                   | 80 |
| 7.7 Conclusions .....                               | 83 |
| Bibliography .....                                  | 84 |

## **Chapter 8**

### **Conclusion ..... 87**

8.1 Summary ..... 87

8.2 Outlook for nanowire fabrication and application..... 89

## **Appendix**

### **Nanowire Device Fabrication ..... 91**

### **List of Publications ..... 95**

## List of Figures

|                 |                                                                                                                                                                                                                                                                                                                                                               |    |
|-----------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| <b>Fig. 1-1</b> | External quantum efficiency of InGaN- and AlGaInP-based light-emitting diodes as a function of wavelength, taken from ref [5] .....                                                                                                                                                                                                                           | 1  |
| <b>Fig. 1-2</b> | III-V compound semiconductors and their emission spectral regions for light-emitting diodes.....                                                                                                                                                                                                                                                              | 3  |
| <b>Fig. 2-1</b> | Number of published papers regarding nanowires. It has significantly increased since 2000 and reached 10000 published papers per year since 2013. Data was obtained from the Web-of-Science database with the following keywords, “topic = nanowire OR nanorod OR nanocolumn OR nanowhisker” and their plural forms .....                                     | 10 |
| <b>Fig. 2-2</b> | Schematic view of VLS growth of Si nanowires using Au catalyst. (a) Au particle is deposited on a Si (111) substrate. (b) The Au particle is heated above a melting point and becomes a liquid alloy droplet. (c) Nucleation occurs at the interface between the droplet and crystal, and then the nanowire begins to grow in the (111) direction .....       | 12 |
| <b>Fig. 2-3</b> | Schematic view of catalyst-free SA-MOVPE growth of GaAs nanowires. (a) Thin SiO <sub>2</sub> mask layer is deposited on a GaAs (111)B substrate. (b) Opening pattern on the SiO <sub>2</sub> mask is fabricated by lithography and etching. (c) Nucleation occurs on the mask opening area, and then the nanowire begins to grow in the (111)B direction..... | 13 |
| <b>Fig. 2-4</b> | Schematic views of (a) zinc blende (ZB) and (b) wurtzite (WZ) crystal structures, and stacking sequences of the (c) ZB and (d) WZ crystal structures .....                                                                                                                                                                                                    | 14 |
| <b>Fig. 2-5</b> | (a) Energy difference between the WZ and ZB structures, showing that the energy difference of InP is a minimum among non-nitride III-V compound semiconductors [51]. Typical InP nanowires in (b) ZB and (c) WZ structures [23] .....                                                                                                                         | 17 |
| <b>Fig. 2-6</b> | Brillouin zones in (a) ZB and (b) WZ. Band structures of (c) ZB GaP [65] and (d) WZ GaP [61] .....                                                                                                                                                                                                                                                            | 18 |
| <b>Fig. 2-7</b> | Band gap of wurtzite AlGaInP on the basis of the prediction [61].....                                                                                                                                                                                                                                                                                         | 19 |
| <b>Fig. 2-8</b> | (a) Schematic view of atomic arrangements in InP/GaP core-shell nanowires in the case of crystal structure transfer method is applied. (b) TEM image of the                                                                                                                                                                                                   |    |

|                 |                                                                                                                                                                                                                                                                                                                              |    |
|-----------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
|                 | core-shell interface .....                                                                                                                                                                                                                                                                                                   | 20 |
| <b>Fig. 3-1</b> | Schematic view of growth mechanism in the selective-area MOVPE process ....                                                                                                                                                                                                                                                  | 26 |
| <b>Fig. 3-2</b> | Schematic view of the MOVPE system used in this study. The reactor is maintained at a working pressure of 0.1 atm with a total flow of 5.75 SLM .....                                                                                                                                                                        | 28 |
| <b>Fig. 3-3</b> | Schematic view of the lines for a MO source provide by a bubbler. The red valves are opened and the blue valve is closed when the MO source is used. The green valve shows a pressure control valve, maintaining the pressure in the bubbler at 760 Torr .....                                                               | 28 |
| <b>Fig. 3-4</b> | Schematic view of PL measurement system used in this study. A He-Ne laser (632.8 nm) is used as an excitation source, and the laser spot size is about 2 $\mu\text{m}$ .....                                                                                                                                                 | 31 |
| <b>Fig. 3-5</b> | Schematic views of reciprocal spaces from the [0001]/[111] incident in (a) wurtzite and (b) zinc blende crystal structures, and (c) from the [10-10]/[11-2] incident that contains both wurtzite and zinc blende crystal structures.....                                                                                     | 32 |
| <b>Fig. 4-1</b> | SEM images of InP and InGaP NWs for $Ga_{\text{supply}} =$ (a) 0%, (b) 5%, and (c) 10% with a V/III ratio of 28. Each inset shows a top view of the NWs, showing the difference in orientation of hexagonal side facets. The mask opening $d_0$ and pattern pitch $a$ were 100 nm and 1.0 $\mu\text{m}$ , respectively ..... | 38 |
| <b>Fig. 4-2</b> | Dependence of NW height and diameter on $Ga_{\text{supply}}$ . All error bars denote standard deviations .....                                                                                                                                                                                                               | 38 |
| <b>Fig. 4-3</b> | SEM images of InGaP NWs for $Ga_{\text{supply}} = 10\%$ with V/III ratios of (a) 5.6, (b) 28, and (c) 84. The mask opening $d_0$ and pattern pitch $a$ were 100 nm and 1.0 $\mu\text{m}$ , respectively.....                                                                                                                 | 40 |
| <b>Fig. 4-4</b> | Dependence of NW height and diameter on pitch. All error bars denote standard deviations .....                                                                                                                                                                                                                               | 41 |
| <b>Fig. 4-5</b> | (a) PL spectra of InP and InGaP NWs for various $Ga_{\text{supply}}$ . (b) PL spectra of InGaP NWs with various $d_0$ . The base of each spectrum is shifted along the vertical direction for clarity .....                                                                                                                  | 42 |
| <b>Fig. 5-1</b> | 15°-tilted SEM image of InP/GaP core-shell nanowires, which have {10-10} side facets. The inset shows a magnified image of one nanowire .....                                                                                                                                                                                | 50 |
| <b>Fig. 5-2</b> | Crystal structures at the side of an InP/GaP core-shell nanowire. (a) TEM image of the InP/GaP interface. (b) and (c) Magnified TEM image of InP core and the                                                                                                                                                                |    |

- corresponding FFT image, showing a pure WZ structure. (d) and (e) Magnified TEM image at the InP/GaP interface and the corresponding FFT image, showing the existence of WZ GaP. (f) EDX line scans along the lateral direction of a core-shell nanowire and corresponding HAADF image. Black arrows in (a) and (d) indicate the positions of misfit dislocations..... 51
- Fig. 5-3** Crystal structures at the top of an InP/GaP core-shell nanowire. (a) Overall TEM image at the top of the core-shell nanowire. (b) EDX line scans of the GaP top shell along the lateral direction and corresponding HAADF image. (c) and (d) Magnified TEM image of GaP top shell and the corresponding FFT image, showing a pure ZB structure. (e) Magnified TEM image at the interface of WZ and ZB phases ..... 52
- Fig. 5-4** (a) Schematic illustration of grown crystal structures of InP/GaP core-shell nanowires. (b) Atomistic models for structural transition of the GaP shell. The stacking sequence of the WZ phase of “ABAB...” is strongly fixed in the  $\langle -211 \rangle_A$  direction (fixed stacking axis), while both WZ and ZB phases are geometrically possible in the  $\langle 111 \rangle_A$  direction (variable stacking axis)..... 53
- Fig. 6-1** (a) 30°-tilted view SEM image of InP/AlGaP CMS NWs. (b) Schematic illustration of grown layers of the CMS NW ..... 59
- Fig. 6-2** Cross-sectional HAADF STEM image of a CMS NW and corresponding EDX mappings of (b) In, (c) P, (d) Al, and (e) Ga, showing the existence of a QW structure ..... 60
- Fig. 6-3** EDX line scan of a CMS NW along the lateral direction and corresponding HAADF STEM image (inset)..... 61
- Fig. 6-4** Cross-sectional TEM images of an InP/AlGaP CMS NW. The incident of the electron beam was parallel to the  $\langle -110 \rangle$  direction of the substrate. (a) Overall TEM image of the NW. (b) and (c) Enlarged TEM images at the top and side of the NW shown in (a). (d)–(i) High-resolution TEM images and corresponding FFT images of the top AlGaP shell, side AlGaP shell, and InP core ..... 62
- Fig. 6-5** Schematic illustration of the formation of stacking faults at the InP/AlGaP core-shell interface ..... 63
- Fig. 6-6** XRD RSM of InP/AlGaP CMS NWs recorded around the ZB (331) reflection of the InP (111)A substrate ..... 64
- Fig. 6-7** CL spectra of a single InP/AlGaP CMS NW measured at 34 K. The electron beam was scanned along the NW axis. (a) Measured points and (b)

|                 |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |    |
|-----------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
|                 | corresponding CL spectra of the NW. (c) Representative CL spectra at the top and middle of the NW shown in a logarithmic scale.....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | 66 |
| <b>Fig. 7-1</b> | Schematic views from the (a) side and (b) top of the CMS NW .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 74 |
| <b>Fig. 7-2</b> | 30°-Tilted SEM images of the CMS NWs for $X_{\text{TMAI}} = 0.20\text{--}0.57$ . The insets show top-view SEM images, indicating the $\{-110\}$ side facets.....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | 74 |
| <b>Fig. 7-3</b> | Cross-sectional TEM images of an InP/AlInP CMS NW for $X_{\text{TMAI}} = 0.30$ . The incident of the electron beam was parallel to the $\langle -110 \rangle$ direction of the substrate. (a) Overall TEM image of the CMS NW. (b) High-resolution TEM image of the AlInP shell on the side of the InP NW, which was obtained from the area marked in a yellow rectangle in (a). The interfaces of InP, the AlInP barrier, and the AlInP active layers can be clearly observed. (c, d) Enlarged TEM images of the orange and pink rectangles in (b), showing the WZ structures. Misfit dislocation was observed at the core-shell interface, as indicated by a red arrow in (d). (e) High-resolution TEM image of the AlInP shell on top of the InP NW marked in a green rectangle in (a), showing a ZB structure. The insets in (c) and (e) show the SAED patterns of each area. (f) EDX line scan along the lateral direction of the NW with a HAADF-STEM image, showing the Al-rich AlInP barrier layers around the InP core NW ..... | 76 |
| <b>Fig. 7-4</b> | XRD RSMs of the InP/AlInP CMS NWs with different $X_{\text{TMAI}}$ values, which were recorded around the ZB (331) reflection of the InP (111)A substrate. In this area, the Bragg peaks between WZ and ZB as well as between InP and AlInP can be distinguished. The WZ AlInP (10-15) peaks become broader along $c$ -axis as $X_{\text{TMAI}}$ becomes larger.....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 77 |
| <b>Fig. 7-5</b> | (a) Schematic view of grown crystal structures. $c$ and $a$ indicate the axial and radial directions of the NW. (b,c) $c$ -axis and $a$ -axis lattice constants of the WZ InP core NW and AlInP shell calculated from the maximum peak positions of the (10-15) reflections. Blue and red solid lines represent the WZ lattice constants of relaxed InP and AlInP calculated from their ZB lattice constants when they were converted from ZB structures to ideal WZ structures .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | 80 |
| <b>Fig. 7-6</b> | (a) Average CL spectrum and (b) original CL spectra obtained from the WZ part of a single InP/AlInP CMS NW for $X_{\text{TMAI}} = 0.57$ . The average spectrum of spectra in (b) was used in (a). The electron beam was scanned along the NW axis .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | 81 |
| <b>Fig. 7-7</b> | (a) Average CL spectra of the WZ AlInP shells of all samples, together with the calculated Al compositions. The emission peaks of the InP core NW were                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |    |

omitted for clarity. (b) Energy gap for WZ AlInP shells as a function of the Al composition. Experimental values obtained from panel (a) are plotted as green dots. Vertical and horizontal error bars denote energy gaps at the emission maxima and minima and Al composition fluctuation estimated from EDX, respectively. Red and blue solid lines represent calculated energy gaps for WZ AlInP at the  $\Gamma_{7C}-\Gamma_{9V}$  and  $\Gamma_{8C}-\Gamma_{9V}$  transitions, respectively, in which the parameters are taken from ref [17] .....82

- Fig. A-1** (a) Schematic illustration of grown layers of the core-multishell nanowire. (b) 30° Tilted SEM image of the as-grown core-multishell nanowires.....91
- Fig. A-2** Schematic illustration of fabrication procedure for nanowire LEDs.....92
- Fig. A-3** Current-voltage (I-V) characteristics of an InP/AlInP core-multishell nanowire LED in (a) linear and (b) logarithmic scales .....93



## List of Tables

|                  |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |    |
|------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| <b>Table 2-1</b> | Lattice constants of III-V compound semiconductors in ZB and WZ structures. The ZB parameters are taken from ref [45], and the WZ parameters are converted from the ZB parameters using the relations $a_{WZ} = 1/\sqrt{2} a_{ZB}$ and $c_{WZ} = \sqrt{8/3} a_{WZ}$ . Experimental values are taken from refs [46-49].....                                                                                                                                                                                                                                                   | 16 |
| <b>Table 2-2</b> | Elastic constants of III-V compound semiconductors in ZB structures [45].....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 16 |
| <b>Table 2-3</b> | Elastic constants of III-V compound semiconductors in WZ structures. The WZ parameters are converted from the ZB parameters using the Martin transformation [50].....                                                                                                                                                                                                                                                                                                                                                                                                        | 16 |
| <b>Table 2-4</b> | Band gaps of III-V compound semiconductors in ZB and WZ structures [45,61] .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | 18 |
| <b>Table 4-1</b> | Ga composition of InGaP planar and NWs .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | 42 |
| <b>Table 6-1</b> | WZ lattice constants of the InP core and AlGaP shell .....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | 64 |
| <b>Table 7-1</b> | Al compositions, lattice constants and strain calculated from XRD measurements. $X_{TMAI}$ is the Al composition in the vapor phase. $X_{Al-planar}$ and $X_{Al-NW}$ are the Al compositions calculated from the AlInP planar on the InP (001) and AlInP shells, respectively. $a$ and $c$ are the radial and axial lattice constants calculated from the maximum peak positions of the (10-15) reflections in the RSMs. $\varepsilon_{xx}$ and $\varepsilon_{zz}$ are the radial and axial strain of the AlInP shells calculated using Vegard's law and elastic theory..... | 79 |



# Chapter 1

## Introduction

---

### 1.1 Background

In recent years, electronic and optical devices using III-V compound semiconductors have been providing the key to addressing urgent global issues such as energy resource depletion and global warming. In particular, light-emitting diodes (LEDs) have been widely used as solid-state lighting and display backlights all over the world owing to their long operating lifetime and low power consumption [1,2]. With visible LEDs, however, achieving high efficiency in the green and yellow spectral regions is challenging due to a lack of suitable semiconductor materials, which is referred to as the “green gap” [3,4].

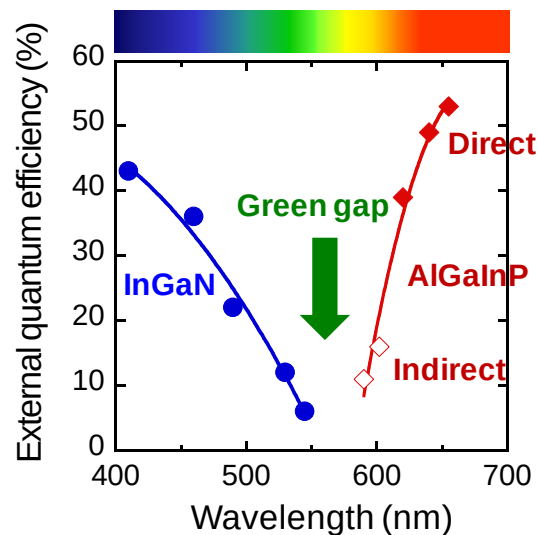


**Fig. 1-1** External quantum efficiency of InGaN- and AlGaInP-based light-emitting diodes as a function of wavelength, taken from ref [5].

Fig. 1-1 shows external quantum efficiency as a function of the wavelength [5]. The low efficiency in the green and yellow spectral regions lies between InGaN and AlGaInP materials. InGaN can cover all visible spectral regions if the alloy composition is changed, and it is usually used as blue and green LEDs. Although InGaN is suitable material for ultraviolet (UV) and blue LEDs, the quantum efficiency rapidly drops in the longer wavelength regions such as the green, yellow, and red spectral regions because it is difficult to fabricate InGaN with high crystal quality at higher In composition [6,7]. Among phosphide-based materials, GaP is used as green LEDs and AlGaInP is used as yellow and red LEDs. The efficiency of GaP-based green LEDs is enhanced by incorporating a small amount of optically active nitrogen (N) into GaP, and the external quantum efficiency achieves approximately 1%; however, further enhancement of the efficiency cannot be expected because GaP originally has an indirect band gap [8]. AlGaInP has a direct band gap in the range of 1.9–2.3 eV (539–652 nm), which covers the red, amber, yellow, and green spectral regions. However, the efficiency of  $(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}\text{P}$  rapidly drops at a wavelength less than 600 nm (yellow and green spectral regions) because the band structure of  $(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}\text{P}$  changes from direct to indirect when  $x > 0.53$  [9,10]. In both cases, the direct-indirect band transition limits the efficiency enhancement of GaP- and AlGaInP-based materials. In order to overcome this limitation and achieve high-efficiency LEDs in the yellow and green spectral regions, a new technology that can overcome the direct-indirect band transition is required.

## 1.2 Phosphide-based III-V semiconductor nanowires

As shown in Fig. 1-2, the conventional phosphide-based III-V semiconductors such as AlGaInP, GaP, and GaAsP have band gap energies in the green-red spectral regions, which are important spectra for the visible LEDs. Recently, band structure calculations have predicted that when the crystal structure of indirect-band-gap GaP is changed from stable zinc blende (ZB) to meta-stable wurtzite (WZ), its band gap also changes from indirect to direct with a gap energy of 2.18–2.25 eV [11-14]. Similarly, WZ AlP is predicted to have a direct band gap with a gap energy of 2.97 eV [12], in contrast to the conventional ZB AlP with an indirect band gap. The indirect-direct band transitions occur due to the zone folding effects, where the L point in

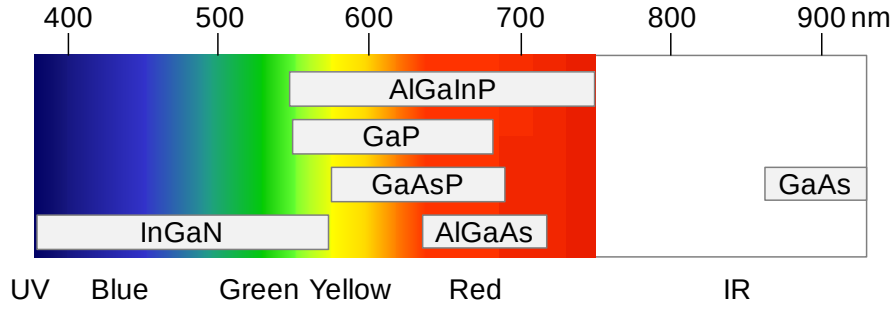


**Fig. 1-2** III-V compound semiconductors and their emission spectral regions for light-emitting diodes.

ZB is folded into the  $\Gamma$  point in WZ [11]. In addition to the theoretical calculations, experimental studies have confirmed by optical measurements the direct band gap transitions of WZ GaP [15] and WZ  $\text{Al}_{0.58}\text{In}_{0.42}\text{P}$  [16]. Therefore, phosphide-based III-V semiconductors with WZ crystal structures are considered promising materials for achieving high-efficiency LEDs.

However, it is not easy to fabricate meta-stable WZ structures using phosphide-based III-V semiconductors, which usually have stable ZB structures in bulk forms. A mainstream approach to meta-stable WZ structures is the use of semiconductor nanowires (NWs), which have a one-dimensional structure with a nm-sized diameter. High-quality WZ InP nanowires [17-19] and WZ GaP nanowires [15,20] have already been reported, but since such WZ III-phosphide nanowires are grown only under a particular kind of growth conditions such as high growth temperature and low V/III ratio [18,21], fabrication methods for high-quality WZ structures in ternary alloy semiconductors such as WZ AlGaP and WZ AlInP have not yet been established.

A key technology to fabricate high-quality WZ structures is the crystal structure transfer method, in which the arrangement of the crystal structure is copied from the substrate to the grown layer. For example, in planar structures, ZB ZnS is grown on ZB GaAs substrates (lattice mismatch: 4.3%) [22], ZB GaN is grown on ZB GaAs substrates (lattice mismatch: 20%) [23], and WZ  $\text{Al}_{0.58}\text{In}_{0.42}\text{P}$  is grown on WZ GaN substrates (lattice mismatch: 25%) [16]. However, since the planar structures usually have a significant lattice mismatch effect on defect formation, they have a very limited selection when it comes to material combinations

for high-quality WZ structures. In contrast to the planar structures, nanowires are expected to cause less defect formation by accommodation of the lattice mismatch due to their unique structure and small diameter [24,25]. Furthermore, binary nanowires can be grown directly with a WZ structure, as mentioned in the previous paragraph, and WZ GaP and WZ InP nanowires can be used as a WZ substrate [26,27]. Therefore, nanowires have far more freedom of material combinations than planar structures. In the crystal structure transfer method using nanowires, the core-shell nanowire growth is usually used and the crystal structure is transferred in the lateral direction of the nanowires. In 2012, the year this study started, crystal structure transfers in InP/InAs core-shell nanowires [28] and GaP/Si core-shell nanowires [26] had already been reported. However, an understanding of the mechanism behind the crystal structure transfer in core-shell nanowires is still lacking from the viewpoint of growth direction. An investigation of WZ ternary III-phosphides such as WZ AlGaP and WZ AlInP is also missing.

Recently, the number of reports on the crystal structure transfer in core-shell or core-multishell nanowires has been increasing. As of 2017, GaP/Si core-shell nanowires [26,29,30], GaP/Si/SiGe core-multishell nanowires [31], GaP/InGaP core-shell nanowires [32], GaP/AlGaP core-multishell nanowires [33], InP/GaP core-shell nanowires [27], InP/AlGaP core-multishell nanowires [34], InP/AlInP core-multishell nanowires [35], and InP/InGaAs core-multishell nanowires [36] have been reported.

### 1.3 Objective

Against the background described in the previous section, the broad purpose of this research is to develop key technology for improving the efficiency of visible light-emitting diodes, especially in the green and yellow spectral regions, by using phosphide-based III-V compound semiconductors. The main purpose of this study is to fabricate phosphide-based III-V compound semiconductor nanowires with high crystal quality in wurtzite structures and to understand their structural and optical properties. To this end, we propose a novel method for fabricating the wurtzite structures with high crystal quality, with a focus on the following points:

- 
- (i) To understand the growth and the structural and optical properties of ternary InGaP nanowires.
  - (ii) To demonstrate a crystal structure transfer in InP/GaP core-shell nanowires and understand the transfer mechanism.
  - (iii) To investigate the growth and the structural and optical properties of wurtzite InP/AlGaP core-multishell nanowires with AlGaP quantum well structures.
  - (iv) To investigate the relation among the chemical composition and the structural and optical properties of wurtzite AlInP using InP/AlInP core-multishell nanowires with AlInP double heterostructures.

## 1.4 Outline of this thesis

This thesis describes a series of experiments aimed at the growth and characterization of phosphide-based III-V semiconductor nanowires by selective-area MOVPE. This thesis is divided into eight chapters.

Chapter 2 describes the history, advantage, and growth method of semiconductor nanowires. In addition, the fundamental properties of phosphide-based III-V semiconductor nanowires are given, including the crystal structures, band structures, and basic parameters in wurtzite structures. One of the most effective growth techniques for wurtzite structures, which is known as crystal structure transfer method, is also introduced in this chapter.

Chapter 3 introduces the principles and basic growth characteristics of selective-area metal organic vapor phase epitaxy, which is used in this study in order to grow semiconductor nanowires. The characterization methods and equipments of semiconductor nanowires are also explained.

Chapter 4 discusses the growth of indium-rich InGaP nanowires formed on InP (111)A substrates by selective-area metal organic vapor phase epitaxy. The indium-rich InGaP nanowires are fabricated by adding gallium into wurtzite InP nanowires. As the gallium composition increased, the lateral growth is drastically enhanced, and structural transition from

wurtzite to zinc blende occurs. It is also found that the emission wavelength can be controlled by properly adjusting the diameter and pitch of the InGaP nanowires. Vertically aligned InGaP nanowires can be achieved by optimizing growth temperature and V/III ratio.

Chapter 5 examines the crystal structure transfer in InP/GaP core-shell nanowires. We attempt the transfer of the wurtzite crystal structure from the InP core to the GaP shell by using pure wurtzite InP core nanowires as a template. Transmission electron microscopy reveals that the wurtzite GaP is grown on the sidewall of the InP core in the lateral  $\langle -211 \rangle$  direction, while zinc blende GaP is grown on the top of the InP core in the axial  $\langle 111 \rangle$  direction. A growth model for the different crystal structures of the GaP shell is proposed from the viewpoint of the growth direction.

Chapter 6 investigates the growth of wurtzite InP/AlGaP core-multishell nanowires for the green spectral region. Wurtzite  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{P}/\text{Al}_{0.2}\text{Ga}_{0.8}\text{P}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{P}$  quantum wells are fabricated around InP nanowire sidewalls by changing the Al composition. Misfit location density in the wurtzite AlGaP shell is lower than estimated from the lattice mismatch, indicating that high-quality wurtzite structures with a low defect density can be fabricated by using small-diameter nanowires. In addition, wurtzite  $\text{Al}_{0.2}\text{Ga}_{0.8}\text{P}$  quantum well exhibits green emissions at 2.37 eV, which is the shortest wavelength among the wurtzite phosphide materials that has been reported so far.

Chapter 7 demonstrates the growth of wurtzite AlInP, which has a band gap in the entire visible regions. Wurtzite  $\text{Al}_y\text{In}_{1-y}\text{P}/\text{Al}_x\text{In}_{1-x}\text{P}/\text{Al}_y\text{In}_{1-y}\text{P}$  double heterostructures are fabricated around InP nanowire sidewalls by changing the Al composition ( $y > x$ ). The emission wavelength of wurtzite AlInP can be tuned from 590 nm to 750 nm, covering the red, amber, yellow spectral regions. An analytical technique for simultaneous investigation of the composition, strain, and crystal structures of the nanowires using X-ray diffraction is also developed through this study. These results provide experimental evidence of the structural and optical properties of WZ AlInP that could be applied in visible light-emitting diodes.

Finally, conclusions and outlook for nanowire fabrication and applications are given in Chapter 8.

## Bibliography

- [1] Y. H. Ra, R. Wang, S. Y. Woo, M. Djavid, S. Sadaf, J. Lee, G. A. Botton, and Z. Mi, *Nano Lett.* **16**, 4608 (2016).
- [2] J. Y. Tsao, M. E. Coltrin, M. H. Crawford, and J. A. Simmons, *Proc. IEEE* **98**, 1162 (2010).
- [3] M. Auf der Maur, A. Pecchia, G. Penazzi, W. Rodrigues, and A. Di Carlo, *Phys. Rev. Lett.* **116**, 027401 (2016).
- [4] M. R. Krames, O. B. Shchekin, R. Mueller-Mach, G. O. Mueller, L. Zhou, G. Harbers, and M. G. Craford, *J. Disp. Technol.* **3**, 160 (2007).
- [5] M. Ueno, *Oyo Buturi* **81**, 497 (2012).
- [6] M. Funato, M. Ueda, Y. Kawakami, Y. Narukawa, T. Kosugi, M. Takahashi, and T. Mukai, *Jpn. J. Appl. Phys.* **45**, L659 (2006).
- [7] S. Saito, R. Hashimoto, J. Hwang, and S. Nunoue, *Appl. Phys. Express* **6**, 111004 (2013).
- [8] D. G. Thomas and J. J. Hopfield, *Phys. Rev.* **150**, 680 (1966).
- [9] D. A. Vanderwater, I.-H. Tan, G. E. Höfler, D. C. Defever, and F. A. Kish, *Proc. IEEE* **85**, 1752 (1997).
- [10] E. F. Schubert, *Light-Emitting Diodes* (Cambridge University Press, 2006) second edition.
- [11] M. Murayama and T. Nakayama, *Phys. Rev. B* **49**, 4710 (1994).
- [12] A. De and C. E. Pryor, *Phys. Rev. B* **81**, 155210 (2010).
- [13] F. Bechstedt and A. Belabbes, *J. Phys.: Condens. Matter* **25**, 273201 (2013).
- [14] T. Akiyama, K. Nakamura, T. Ito, and A. J. Freeman, *Appl. Phys. Lett.* **104**, 132101 (2014).
- [15] S. Assali, I. Zardo, S. Plissard, D. Kriegner, M. A. Verheijen, G. Bauer, A. Meijerink, A. Belabbes, F. Bechstedt, J. E. M. Haverkort, and E. P. A. M. Bakkers, *Nano Lett.* **13**, 1559 (2013).
- [16] Y. Hiraya, F. Ishizaka, K. Tomioka, and T. Fukui, *Appl. Phys. Express* **9**, 035502 (2016).
- [17] P. Mohan, J. Motohisa, and T. Fukui, *Nanotechnology* **16**, 2903 (2005).
- [18] Y. Kitauchi, Y. Kobayashi, K. Tomioka, S. Hara, K. Hiruma, T. Fukui, and J. Motohisa, *Nano Lett.* **10**, 1699 (2010).
- [19] Q. Gao, D. Saxena, F. Wang, L. Fu, S. Mookapati, Y. Guo, L. Li, J. W.-Leung, P. Caroff, H. H. Tan, and C. Jagadish, *Nano Lett.* **14**, 5206 (2014).
- [20] Berg, S. Lehmann, N. Vainorius, A. Gustafsson, M-E. Pistol, L. R. Wallenberg, L.

- Samuelson, and M. T. Borgström, *J. Cryst. Growth* **386**, 47 (2014).
- [21] F. Ishizaka, K. Ikejiri, K. Tomioka, and T. Fukui, *Jpn. J. Appl. Phys.* **52**, 04CH05 (2013).
- [22] C.-Y. Yeh, Z.W. Lu, S. Froyen, and A. Zunger, *Phys. Rev. B* **46**, 10086 (1992).
- [23] A. Nakadaira and H. Tanaka, *J. Electron. Mater.* **26**, 320 (1996).
- [24] F. Glas, *Phys. Rev. B* **74**, 121302 (2006).
- [25] K. L. Kavanagh, *Semicond. Sci. Technol.* **25**, 024006 (2010).
- [26] R. E. Algra, M. Hocevar, M. A. Verheijen, I. Zardo, G. G. W. Immink, W. J. P. van Enckevort, G. Abstreiter, L. P. Kouwenhoven, E. Vlieg, and E. P. A. M. Bakkers, *Nano Lett.* **11**, 1690 (2011).
- [27] F. Ishizaka, Y. Hiraya, K. Tomioka, and T. Fukui, *J. Cryst. Growth* **411**, 71 (2015).
- [28] P. Mohan, J. Motohisa, and T. Fukui, *Appl. Phys. Lett.* **88**, 013110 (2006).
- [29] S. Conesa-Boj, H. I. T. Hauge, M. A. Verheijen, S. Assali, A. Li, E. P. A. M. Bakkers, and A. Fontcuberta i Morral, *Nano Lett.* **15**, 2974 (2015).
- [30] H. I. T. Hauge, M. A. Verheijen, S. Conesa-Boj, T. Etzelstorfer, M. Watzinger, D. Kriegner, I. Zardo, C. Fasolato, F. Captitani, P. Postorino, S. Kölling, A. Li, S. Assali, J. Stangl, and E. P. A. M. Bakkers, *Nano Lett.* **15**, 5855 (2015).
- [31] H. I. T. Hauge, S. Conesa-Boj, M. A. Verheijen, S. Koelling, and E. P. A. M. Bakkers, *Nano Lett.* **17**, 85 (2017).
- [32] L. Gagliano, A. Belabbes, M. Albani, S. Assali, M. A. Verheijen, L. Miglio, F. Bechstedt, J. E. M. Haverkort, and E. P. A. M. Bakkers, *Nano Lett.* **16**, 7930 (2016).
- [33] A. Berg, M. Heurlin, S. Tsopanidis, M.-E. Pistol, and M. T. Borgström, *Nanotechnology* **28**, 035706 (2017).
- [34] F. Ishizaka, Y. Hiraya, K. Tomioka, J. Motohisa, and T. Fukui, *Jpn. J. Appl. Phys.* **56**, 010311 (2017).
- [35] F. Ishizaka, Y. Hiraya, K. Tomioka, J. Motohisa, and T. Fukui, *Nano Lett.* (2017). doi: 10.1021/acs.nanolett.6b03727
- [36] M. Heurlin, T. Stankevič, S. Mickevičius, S. Yngman, D. Lindgren, A. Mikkelsen, R. Feidenhans'l, M. T. Borgström, and L. Samuelson, *Nano Lett.* **15**, 2462 (2015).

## Chapter 2

# Semiconductor Nanowires

---

## 2.1 Introduction

Semiconductor nanowires (NWs) have attracted considerable attention since the 1960s because of their unique structural and physical properties compared to their planar counterparts. This chapter reviews the research history of semiconductor nanowires, their advantages, and the growth method. It also describes the structural and optical properties of phosphide-based III-V semiconductor nanowires. In addition, recent research on the crystal structure transfer method, which is one of the most effective ways to fabricate high quality wurtzite structures, is explained in this chapter.

### 2.1.1 History of nanowire growth

Semiconductor nanowires have a long history and reach as far back as the 1960s. The “nanowire” was called as “whisker” until the late 1990s, and then it was called as “nano-pillar”, “nano-rods”, “nano-column” or “nano-wires”. In 1964, Wagner and Ellis at Bell Laboratory reported that Si whiskers were synthesized by vapor-liquid-solid (VLS) growth using gold catalysts [1]. In the 1990s, the Hiruma’s group at Central Research Laboratory, Hitachi Ltd., demonstrated the fabrication of light-emitting devices with pn junctions using GaAs whiskers for the first time [2]. After that, Si nanowire bipolar transistors and biosensors [3] and InP nanowire diodes [4] were reported by the Lieber’s group at Harvard University, ZnO nanowire ultraviolet lasers operating at room temperature were reported by the Yang group at University of California, Berkley [5], and single electron transistors using InP/InAs/InP heterostructure

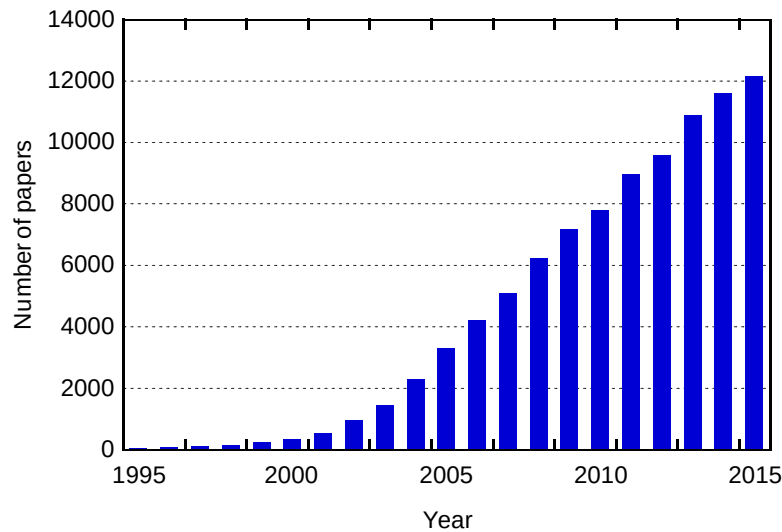


**Fig. 2-1** Number of published papers regarding nanowires. It has significantly increased since 2000 and reached 10000 published papers per year since 2013. Data was obtained from the Web-of-Science database with the following keywords, “topic = nanowire OR nanorod OR nanocolumn OR nanowhisker” and their plural forms.

nanowires were reported by the Samuleson’s group at Lund University [6]. Although all these nanowires were grown by VLS growth method, the first formation of InGaAs nanowire array using catalyst-free selective-area metal organic vapor phase epitaxy (SA-MOVPE) was reported by the Fukui’s group at Hokkaido University in 2003 [7]. These works on nanowire growth and device applications have become one of the most active research areas among the nanoscience fields. Fig. 2-1 shows the number of the published papers regarding nanowires over the past two decades. The number of papers has rapidly increased since 2000 and has been still increasing in 2016.

## 2.1.2 Advantages of nanowires

Semiconductor nanowires are one-dimensional wire-like nanostructures with a nm-sized diameter. The high aspect ratio (height/diameter) of nanowires gives much larger surface areas than planar structures. If the nanowires have a height of 4  $\mu\text{m}$  and a diameter of 100 nm with a pitch of 400 nm, the surface area of the nanowires is 10 times larger than that of the

conventional planar structures. Thanks to this geometrical property, lateral core-shell or core-multishell nanowires with a large area of p-n junctions are promising candidates for high-efficiency light-emitting diodes (LEDs).

The small diameter also gives the effect of strain relaxation without the formation of defects such as misfit dislocations because nanowires have free surfaces toward both the axial and lateral directions. Therefore, nanowires can be grown on lattice-mismatched substrates with no defects or a smaller amount of defects, beyond the limit of critical thicknesses in planar structures. The relation between the critical nanowire diameters and the lattice mismatch is calculated by Glas [8], and the allowable value of lattice mismatch increases as the critical nanowire diameter decreases. This gives a wider selection of heteroepitaxial material combinations, leading to III-V integration on Si or Ge substrates. For example, the heteroepitaxial growth of InAs and GaAs nanowires on Si substrates (lattice mismatch: 11.6 and 4.1%) [9,10] and InAs nanowires on Ge substrates (lattice mismatch: 6.7%) [11] are successfully achieved.

Another advantage of small diameter of nanowires is a great ease in forming wurtzite structures. Akiyama et al. calculated the structure stability in nanowires by comparing the bulk cohesive energy and the surface energy of the nanowire sidewall, and the result indicated that wurtzite structures are more likely to form as the nanowire diameter decreases [12].

## 2.2 Nanowire growth method

### 2.2.1 Catalyst-assisted vapor-liquid-solid growth

As described in the previous section, Wagner and Ellis first demonstrated the growth of Si whiskers by vapor-liquid-solid (VLS) growth using gold catalysts in 1964 [1]. In recent years, VLS growth method has been one of the major approaches for the nanowire formation. Fig. 2-2 shows a schematic view of catalyst-assisted VLS procedure of nanowire growth. When gas source materials flow over the substrate, precursor atoms preferentially deposit on the surface of liquid droplets, thereby forming an alloy with a lower melting temperature. Further

incorporation of the precursor atoms into the liquid droplets continues until the alloy becomes supersaturated. Consequently, crystal growth takes place at the solid-liquid interface and nanowire growth begins with a diameter as large as the size of the droplet, which means that the nanowire diameter can be control by the size of the droplet. After nanowire growth, the droplet usually remains at the tip of the nanowire, which becomes a sticky problem when growing core-shell structures. Another problem in VLS growth method is the contamination of the metal catalysts. For instance, the incorporation of gold catalysts into Si nanowires leads to deep level defects near the mid gap of Si, which reduces the performance of the device [13].

Alternatively, nanowires can be also grown without gold or other metal catalysts, which is known as “self-catalyzed growth”. In this method, one component of the nanowire materials acts as a catalytic droplet and nanowire growth proceeds based on VLS mechanism so that there are no contaminations originated from catalyst materials. For example, GaAs/AlGaAs core-shell [14] and InP/InAs axial heterostructures [15] have been reported using the self-catalyzed growth method.

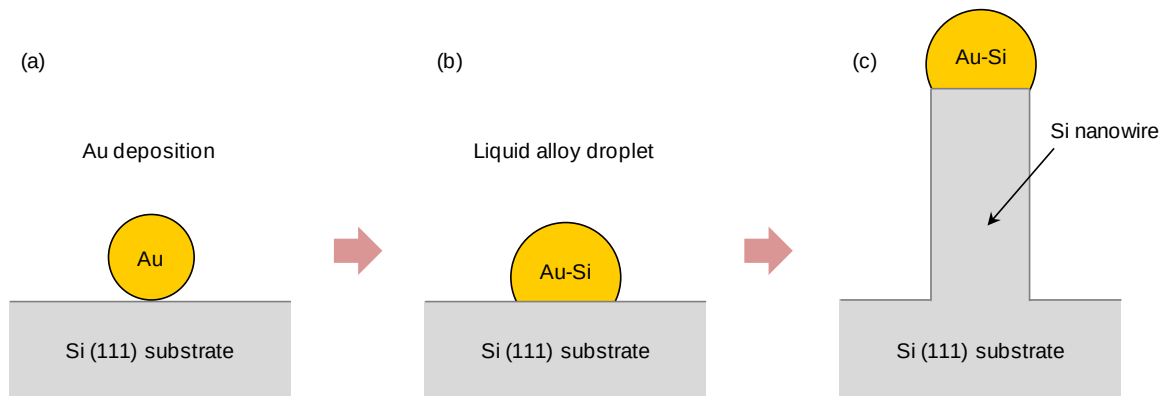


**Fig. 2-2** Schematic view of VLS growth of Si nanowires using Au catalyst. (a) Au particle is deposited on a Si (111) substrate. (b) The Au particle is heated above a melting point and becomes a liquid alloy droplet. (c) Nucleation occurs at the interface between the droplet and crystal, and then the nanowire begins to grow in the (111) direction.

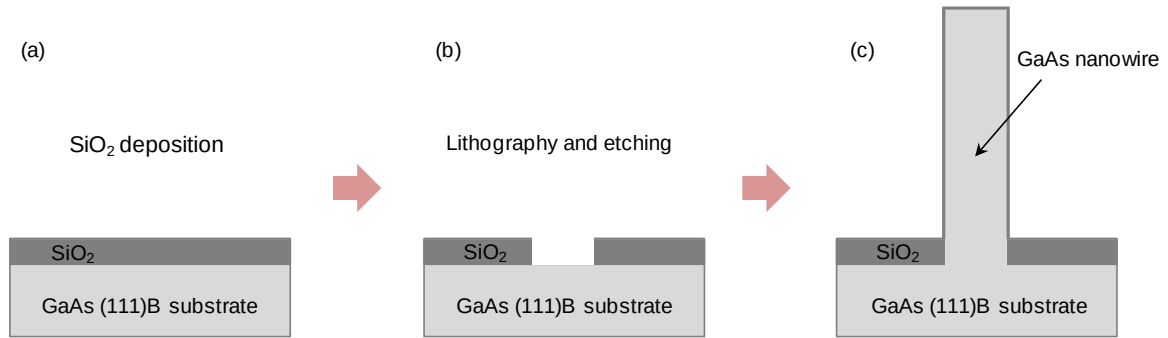


**Fig. 2-3** Schematic view of catalyst-free SA-MOVPE growth of GaAs nanowires. (a) Thin SiO<sub>2</sub> mask layer is deposited on a GaAs (111)B substrate. (b) Opening pattern on the SiO<sub>2</sub> mask is fabricated by lithography and etching. (c) Nucleation occurs on the mask opening area, and then the nanowire begins to grow in the (111)B direction.

## 2.2.2 Selective-area metal organic vapor phase epitaxy

Selective-area metal organic vapor phase epitaxy (SA-MOVPE) is a template growth method with a combination of top-down and bottom-up approaches. This method needs no catalysts, which is different from VLS growth method, and enables us to fabricate nanowires with a precise control of the size and position by using a mask substrate as a template for nanowire growth, in which amorphous films such as SiO<sub>2</sub> and SiN<sub>x</sub> are used as a mask material. The selective-area growth was demonstrated in 1962 by using chloride phase epitaxy of Si for the first time [16], and subsequently, in 1965, Tausch et al. reported the selective-area growth of GaAs with an SiO<sub>2</sub> mask layer [17]. After that, in 1987, H. Asai et al. reported that the narrow two-dimensional electron gas channels were fabricated in a GaAs/AlGaAs sidewall interface [18]. Since then, SA-MOVPE has been widely used as electronic and optical device applications.

The first formation of  $\{-110\}$  vertical facets on the (111)B-orientated substrate was reported by Fukui et al. in 1990 [19]. The formation of these  $\{-110\}$  vertical facets are of significant importance for the nanowire growth because the nanowire structures consist of six  $\{-110\}$  side facets and their preferential growth directions are usually  $\langle 111 \rangle_B$  or  $\langle 111 \rangle_A$ . In 1993, Ando et al. demonstrated the growth of micro-scale hexagonal pillar structures with  $\{-110\}$  side facets vertical to the substrate, and applied these structures to the photonic crystals [20]. After that, Hamano et al. reported in 1997 that GaAs nanowires along the axial  $\langle 111 \rangle_B$

direction were grown on a GaAs (111)B substrate with a lithography-defined SiO<sub>2</sub> mask layer [21]. Fig. 2-3 shows a schematic view of catalyst-free SA-MOVPE procedure of nanowire growth. These studies have been the basis for today's nanowire growth techniques. Our group has focused on the growth of III-V semiconductor nanowires by SA-MOVPE over the past decades. Selective-area growths of InP [22-26], GaP [27], InGaP [28,29], InAs [9,11,30], GaAs [10,31-33], InGaAs [34-42], GaAsP [43], AlGaAs [44] nanowires have been reported so far.

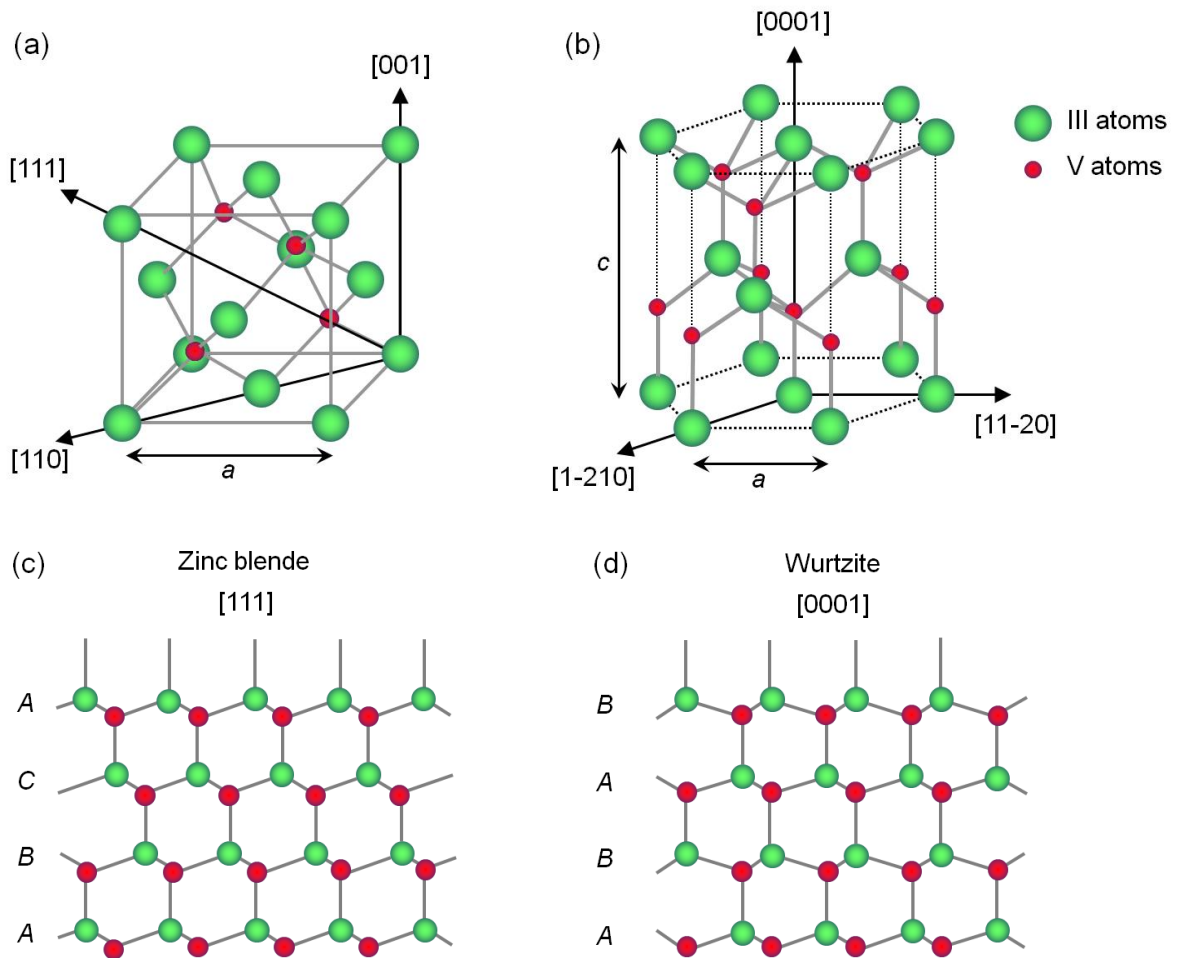


**Fig. 2-4** Schematic views of (a) zinc blende (ZB) and (b) wurtzite (WZ) crystal structures, and stacking sequences of the (c) ZB and (d) WZ crystal structures.

## 2.3 Phosphide-based nanowires

### 2.3.1 Wurtzite and zinc blende

Phosphide- and arsenide-based III-V semiconductors have zinc blende (ZB) crystal structures in bulk forms, whereas nitride-based III-V semiconductors have wurtzite (WZ) crystal structures. As shown in Figs. 2-4(a) and 2-4(b), the ZB and WZ crystal structures have cubic and hexagonal symmetries, respectively. Figs. 2-4(c) and 2-4(d) show schematic views of stacking sequences of the ZB and WZ phases. The ZB phase has a three-period stacking sequence of “ABCABC...”, whereas the WZ phase has a two-period stacking sequence of “ABABAB...”. This peculiarity gives rise to unique physical properties in the WZ structures such as energy band structure transitions, as described in the following section. Usually, basic parameters of the WZ structures can be obtained by converting ZB parameters to WZ counterparts. Lattice constants and elastic constants of the WZ structures are converted from ZB parameters found in the literature [45], which are summarized in Tables 2-1, 2-2, and 2-3. Experimental values of WZ lattice constants of InP [46], GaP [47], InAs [48], and GaAs [49] are also described in Table 2-1. The WZ elastic constants are converted using the Martin transformation [50].

Preferred crystal structures in III-V semiconductors are estimated by the calculation of the energy difference between the WZ and ZB phases ( $\Delta E_{\text{WZ-ZB}}$ ), as shown in Fig. 2-5(a) [51]. Among non-nitride III-V semiconductors, phosphide materials have smaller WZ-ZB energy differences  $\Delta E_{\text{WZ-ZB}}$ , and in particular, that of InP is a minimum. This tendency suggests that InP has high sensitivity to crystal structure transitions from ZB to WZ phases with respect to the growth conditions. In the case of InP nanowires grown by SA-MOVPE, both ZB and WZ structures (and also mixing of two phases) are observed [23,24], unlike GaAs or InAs nanowires. Figs. 2-5 (b) and 2-5(c) show typical ZB and WZ InP nanowires. The crystal structures can be controlled by properly adjusting the growth conditions such as growth temperature, V/III ratio, mask opening size, and nanowire pitch [23]. Usually, pure WZ structures are grown under the high growth temperature and low V/III ratio, whereas ZB structures are grown under the low growth temperature and high V/III ratio. This tendency is generally the same as other nanowires, for example, GaP nanowires grown by VLS method [52].

**Table 2-1** Lattice constants of III-V compound semiconductors in ZB and WZ structures. The ZB parameters are taken from ref [45], and the WZ parameters are converted from the ZB parameters using the relations  $a_{WZ} = 1/\sqrt{2} a_{ZB}$  and  $c_{WZ} = \sqrt{8/3} a_{WZ}$ . Experimental values are taken from refs [46-49].

|      | $a_{ZB}$ (Å) | $a_{WZ}$ (Å)<br>Conversion | $c_{WZ}$ (Å)<br>Conversion | $a_{WZ}$ (Å)<br>Experimental | $c_{WZ}$ (Å)<br>Experimental |
|------|--------------|----------------------------|----------------------------|------------------------------|------------------------------|
| InP  | 5.8697       | 4.1505                     | 6.7777                     | 4.1423                       | 6.8013                       |
| GaP  | 5.4505       | 3.8541                     | 6.2937                     | 3.8419                       | 6.3353                       |
| AlP  | 5.4672       | 3.8659                     | 6.3130                     | -                            | -                            |
| InAs | 6.0583       | 4.2839                     | 6.9955                     | 4.2742                       | 7.0250                       |
| GaAs | 5.6533       | 3.9975                     | 6.5278                     | 3.9975                       | 6.5759                       |
| AlAs | 5.6611       | 4.0030                     | 6.5369                     | -                            | -                            |

**Table 2-2** Elastic constants of III-V compound semiconductors in ZB structures [45].

|      | $C_{11}^{ZB}$ (GPa) | $C_{12}^{ZB}$ (GPa) | $C_{44}^{ZB}$ (GPa) |
|------|---------------------|---------------------|---------------------|
| InP  | 101.1               | 56.1                | 45.6                |
| GaP  | 140.5               | 62.0                | 70.3                |
| AlP  | 133.0               | 63.0                | 61.5                |
| InAs | 83.3                | 45.3                | 39.6                |
| GaAs | 122.1               | 56.6                | 60.0                |
| AlAs | 125.0               | 53.4                | 54.2                |

**Table 2-3** Elastic constants of III-V compound semiconductors in WZ structures. The WZ parameters are converted from the ZB parameters using the Martin transformation [50].

|      | $C_{11}^{WZ}$ (GPa) | $C_{12}^{WZ}$ (GPa) | $C_{13}^{WZ}$ (GPa) | $C_{33}^{WZ}$ (GPa) | $C_{44}^{WZ}$ (GPa) | $C_{66}^{WZ}$ (GPa) |
|------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| InP  | 120.3               | 52.3                | 40.7                | 131.9               | 27.1                | 34.0                |
| GaP  | 167.2               | 56.0                | 41.3                | 181.9               | 46.0                | 55.6                |
| AlP  | 164.3               | 62.4                | 43.3                | 183.3               | 40.1                | 51.0                |
| InAs | 100.3               | 42.2                | 31.7                | 110.7               | 23.0                | 29.1                |
| GaAs | 145.4               | 51.5                | 38.4                | 158.4               | 38.6                | 47.0                |
| AlAs | 141.6               | 49.1                | 41.1                | 149.5               | 40.4                | 46.3                |

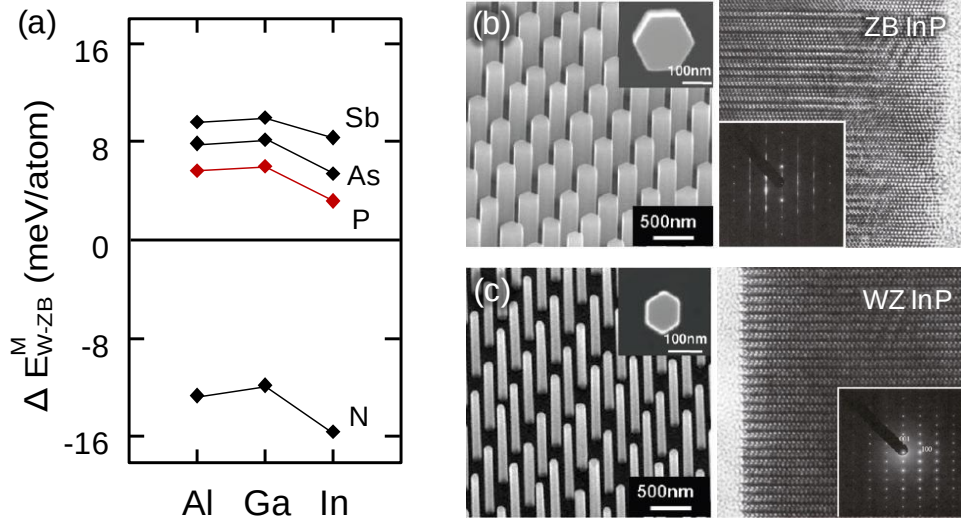


**Fig. 2-5** (a) Energy difference between the WZ and ZB structures, showing that the energy difference of InP is a minimum among non-nitride III-V compound semiconductors [51]. Typical InP nanowires in (b) ZB and (c) WZ structures [23].

While only InP nanowires can be grown with a WZ structure by SA-MOVPE, WZ InP [53,54], WZ GaP [52,55], WZ InAs [56,57], and WZ GaAs [58,59] nanowires can be grown by catalyst-assisted VLS method because catalysts are considered to decrease the WZ-ZB energy difference.

### 2.3.2 Energy band structure

The WZ crystal structures usually have energy band structures that are different from those of ZB materials. In 1994, Murayama and Nakayama at Chiba University calculated the band structures of semiconductors in both WZ and ZB phases using the first-principles pseudopotential method, and suggested that GaP in the WZ phase have a direct band gap for the first time [60]. The same results for WZ GaP have been recently reported by De and Pryor at University of Iowa [61], Belabbes et al. at Friedrich Schiller University Jena [62,63], and Akiyama et al. at Mie University [64]. Similarly, WZ AlP is suggested to have a direct band gap with a gap energy of 2.97 eV [61]. The energy band gaps for WZ and ZB structures are summarized Table 2-4, according to the literatures [45,61].

**Table 2-4** Band gaps of III-V compound semiconductors in ZB and WZ structures [45,61].

|      | $\Gamma^{\text{ZB}}$ (eV) | $X^{\text{ZB}}$ (eV) | $L^{\text{ZB}}$ (eV) | $\Gamma_{7C}^{\text{WZ}}$ (eV) | $\Gamma_{8C}^{\text{WZ}}$ (eV) |
|------|---------------------------|----------------------|----------------------|--------------------------------|--------------------------------|
| InP  | 1.424                     | 2.384                | 2.014                | 1.474                          | 1.712                          |
| GaP  | 2.886                     | 2.35                 | 2.72                 | 2.877                          | 2.251                          |
| AlP  | 3.63                      | 2.52                 | 3.57                 | 3.775                          | 2.969                          |
| InAs | 0.417                     | 1.433                | 1.133                | 0.481                          | 1.222                          |
| GaAs | 1.519                     | 1.981                | 1.815                | 1.588                          | 1.503                          |
| AlAs | 3.099                     | 2.24                 | 2.46                 | 3.153                          | 1.971                          |

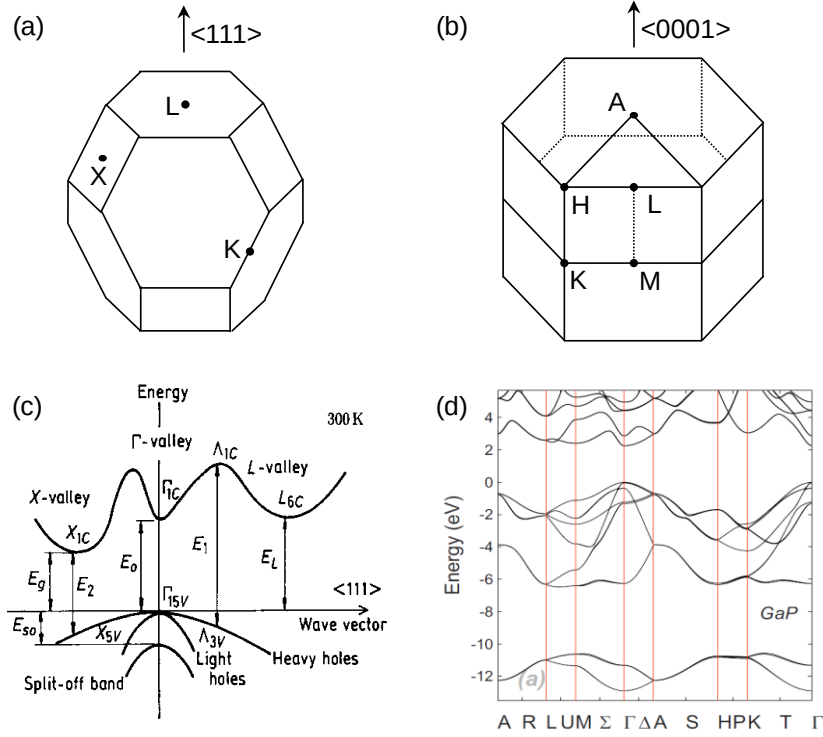
**Fig. 2-6** Brillouin zones in (a) ZB and (b) WZ. Band structures of (c) ZB GaP [65] and (d) WZ GaP [61].

Fig. 2-6 shows Brillouin zones and band structures of GaP for ZB [65] and WZ [61] structures. The high symmetry points in the Brillouin zones of ZB and WZ structures give rise to the indirect-direct band transitions, where the L point in ZB is zone-folded to the  $\Gamma$  point in WZ. The Ga- and Al-containing materials (GaP, GaAs, AlP, and AlAs) have  $\Gamma_{8C}$ - $\Gamma_{9V}$  transitions, whereas the In-containing materials (InP and InAs) have the  $\Gamma_{7C}$ - $\Gamma_{9V}$  transitions.

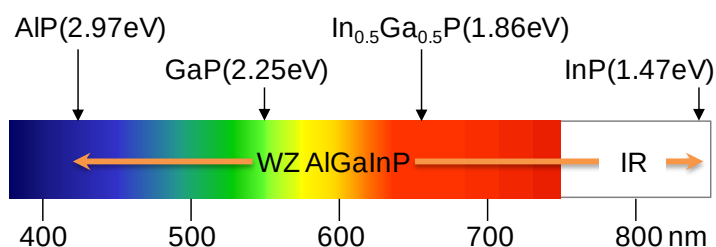


**Fig. 2-7** Band gap of wurtzite AlGaInP on the basis of the prediction [61].

In addition to the theoretical calculations, experimental studies have recently reported that the direct band gap transitions of WZ GaP [52] and WZ  $\text{Al}_{0.58}\text{In}_{0.42}\text{P}$  [66] have been confirmed by optical measurements. As a matter of fact, although some theory suggests that WZ AlP has an indirect band gap [64], it is at least possible to conclude that WZ AlInP with an Al composition below 58% has a direct band gap. Thus, phosphide-based III-V semiconductors with WZ crystal structures are the novel promising materials for achieving high-efficiency LEDs. Fig. 2-7 shows an example of WZ AlInGaP that can cover all visible spectral range including blue, green, yellow, and red.

### 2.3.3 Crystal structure transfer method

Crystal structure transfers in epitaxial growth have been observed in planar structures since early times [51]. For instance, Nakadaira and Tanaka reported that meta-stable ZB GaN planar is grown on ZB GaAs (100) substrates [67]. In this case, atomic arrangements of the ZB structure are copied from the GaAs substrate to the grown GaN layer. This crystal structure transfer technique is also adopted for nanowire structures. In 2011, Algra et al. at Eindhoven University (the Bakkers's group) reported that the WZ structure and twinning superlattice with the ZB structures are successfully transferred from VLS-grown GaP core nanowires to Si shells [68]. After that, using VLS-grown WZ GaP nanowires as a template for WZ structures, WZ Si shells [69,70], WZ Si/Ge multishells [71], and WZ InGaP shells [72] have been demonstrated. Similarly, the Samuelson's group at Lund University reported that WZ InGaAs shells are grown using VLS-grown WZ InP nanowires [73], and WZ AlGaP multishells are grown using

VLS-grown WZ GaP nanowires [74]. Our group also reported that WZ GaP shells [75], WZ AlGaP multishells [76], and AlInP multishells [77] are grown using selectively-grown WZ InP nanowires.

Fig. 2-8 shows schematic view and TEM image of the crystal structure transfer. The key point of the transfer is that the growth direction should be perpendicular to the WZ stacking direction. This is because the stacking sequence of the WZ phase (ABAB...) is strongly fixed in the lateral direction of the nanowire, while the stacking sequences of the WZ phase and the ZB phase (ABCABC...) are geometrically variable to each other in the axial direction. The detailed growth model is discussed in Chapter 5.

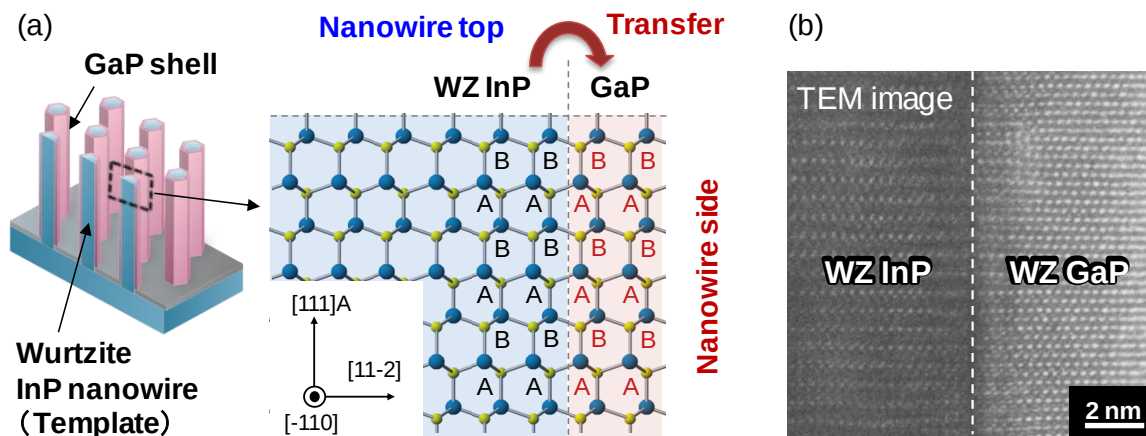


**Fig. 2-8** (a) Schematic view of atomic arrangements in InP/GaP core-shell nanowires in the case of crystal structure transfer method is applied. (b) TEM image of the core-shell interface.

## Bibliography

- [1] R.S. Wagner and W.C. Ellis, *Appl. Phys. Lett.* **4**, 89 (1964).
- [2] K. Hiruma, T. Katsuyama, K. Ogawa, M. Koguchi, H. Kakibayashi, and G. Morgan, *Appl. Phys. Lett.* **59**, 431 (1991).
- [3] Y. Cui, Q. Wei, H. Park, and C. M. Lieber, *Science* **293**, 1289 (2001).
- [4] X. Duan, Y. Huang, Y. Cui, J. Wang, and C. M. Lieber, *Nature* **409**, 66 (2001).
- [5] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, *Science* **292**, 1897 (2001).
- [6] C. Thelander, T. Martensson, M. T. Bjork, B. J. Ohlsson, M. W. Larsson, L. R. Wallenberg, and L. Samuelson, *Appl. Phys. Lett.* **83**, 2052 (2003).
- [7] M. Akabori, J. Takeda, J. Motohisa, and T. Fukui, *Nanotechnology* **14**, 1071 (2003).
- [8] F. Glas, *Phys. Rev. B* **74**, 121302 (2006).
- [9] K. Tomioka, J. Motohisa, S. Hara, and T. Fukui, *Nano Lett.* **8**, 3475 (2008).
- [10] K. Tomioka, Y. Kobayashi, J. Motohisa, S. Hara, and T. Fukui, *Nanotechnology* **20**, 145302 (2009).
- [11] K. Tomioka, F. Ishizaka, and T. Fukui, *Nano Lett.* **15**, 7253 (2015).
- [12] T. Akiyama, K. Sano, K. Nakamura, and T. Ito, *Jpn. J. Appl. Phys.* **45**, L275 (2006).
- [13] J. E. Allen, E. R. Hemesath, D. E. Perea, J. L. Lensch-Falk, Z. Y. Li, F. Yin, M. H. Gass, P. Wang, A. L. Bleloch, R. E. Palmer, and L. J. Lauhon, *Nat. Nanotechnol.* **3**, 168 (2008).
- [14] A. Fontcuberta i Morral, D. Spirkoska, J. Arbiol, M. Heigoldt, J. R. Morante, and G. Abstreiter, *Small* **4**, 899 (2008).
- [15] G. Zhang, S. Sasaki, K. Tateno, H. Gotoh, and T. Sogawa, *ALP Adv.* **3**, 052107 (2013).
- [16] B. D. Joyce and J. A. Baldrey, *Nature* **195**, 485 (1962).
- [17] F. W. Tausch, and G. Lapierre, *J. Electrochem. Soc.* **112**, 706 (1965).
- [18] H. Asai, S. Yamada, and T. Fukui, *Appl. Phys. Lett.* **51**, 1518 (1987).
- [19] T. Fukui, S. Ando, and Y. K. Fukai, *Appl. Phys. Lett.* **57**, 1209 (1990).
- [20] S. Ando, N. Kobayashi, and H. Ando, *Jpn. J. Appl. Phys.* **32**, L1293 (1993).
- [21] T. Hamano, H. Hirayama, and Y. Aoyagi, *Jpn. J. Appl. Phys.* **36**, L286 (1997).
- [22] P. Mohan, J. Motohisa, and T. Fukui, *Nanotechnology* **16**, 2903 (2005).

- [23] Y. Kitauchi, Y. Kobayashi, K. Tomioka, S. Hara, K. Hiruma, T. Fukui, and J. Motohisa, *Nano Lett.* **10**, 1699 (2010).
- [24] K. Ikejiri, F. Ishizaka, K. Tomioka, J. Motohisa, and T. Fukui, *Nano Lett.* **11**, 4314 (2011).
- [25] K. Ikejiri, F. Ishizaka, K. Tomioka, and T. Fukui, *Nano Lett.* **12**, 4770 (2012).
- [26] Q. Gao, D. Saxena, F. Wang, L. Fu, S. Mokkaapati, Y. Guo, L. Li, J. W.-Leung, P. Caroff, H. H. Tan, and C. Jagadish, *Nano Lett.* **14**, 5206 (2014).
- [27] K. Tomioka, K. Ikejiri, T. Tanaka, J. Motohisa, S. Hara, K. Hiruma, and T. Fukui, *J. Mater. Res.* **26**, 2127 (2011).
- [28] F. Ishizaka, K. Ikejiri, K. Tomioka, and T. Fukui, *Jpn. J. Appl. Phys.* **52**, 04CH05 (2013).
- [29] A. Berg, P. Caroff, N. Shahid, M. N. Lockrey, X. Yuan, M. T. Borgstrom, H. H. Tan, and C. Jagadish, *Nano Res.* (2016). doi:10.1007/s12274-016-1325-1
- [30] K. Tomioka, P. Mohan, J. Noborisaka, S. Hara, J. Motohisa, and T. Fukui, *J. Cryst. Growth* **298**, 644 (2007).
- [31] J. Noborisaka, J. Motohisa, and T. Fukui, *Appl. Phys. Lett.* **86**, 213102 (2005).
- [32] K. Ikejiri, J. Noborisaka, S. Hara, J. Motohisa, and T. Fukui, *J. Cryst. Growth* **298**, 616 (2007).
- [33] H. Yoshida, K. Ikejiri, T. Sato, S. Hara, K. Hiruma, J. Motohisa, and T. Fukui, *J. Cryst. Growth* **312**, 3592 (2009).
- [34] T. Sato, J. Motohisa, J. Noborisaka, S. Hara, and T. Fukui, *J. Cryst. Growth* **310**, 2359 (2008).
- [35] T. Sato, Y. Kobayashi, J. Motohisa, S. Hara, and T. Fukui, *J. Cryst. Growth* **310**, 5111 (2008).
- [36] M. Yoshimura, K. Tomioka, K. Hiruma, S. Hara, J. Motohisa, and T. Fukui, *Jpn. J. Appl. Phys.* **49**, 04DH08 (2010).
- [37] M. Yoshimura, K. Tomioka, K. Hiruma, S. Hara, J. Motohisa, and T. Fukui, *J. Cryst. Growth* **315**, 148 (2011).
- [38] Y. Kohashi, T. Sato, K. Ikejiri, K. Tomioka, S. Hara, and J. Motohisa, *J. Cryst. Growth* **338**, 47 (2012).
- [39] Y. Kohashi, S. Sakita, S. Hara, and J. Motohisa, *Appl. Phys. Express* **6**, 025502 (2013).
- [40] Y. Kohashi, S. Hara, and J. Motohisa, *Mater. Res. Express* **1**, 015036 (2014).
- [41] A. Yoshida, K. Tomioka, F. Ishizaka, K. Chiba, and J. Motohisa, *ECS Trans.* **75**, 265 (2016).
- [42] A. Yoshida, K. Tomioka, F. Ishizaka, and J. Motohisa, *J. Cryst. Growth* (2017). doi:

10.1016/j.jcrysgro.2016.10.083

- [43] S. Fujisawa, T. Sato, S. Hara, J. Motohisa, K. Hiruma, and T. Fukui, *Jpn. J. Appl. Phys.* **50**, 04DH03 (2011).
- [44] A. Hayashida, T. Sato, S. Hara, J. Motohisa, K. Hiruma, and T. Fukui, *J. Cryst. Growth* **312**, 3592 (2010).
- [45] Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, *J. Appl. Phys.* **89**, 5815 (2001).
- [46] D. Kriegner, E. Wintersberger, K. Kawaguchi, J. Wallentin, M. T. Borgström, and J. Stangl, *Nanotechnology* **22**, 425704 (2011).
- [47] D. Kriegner, S. Assali, A. Belabbes, T. Etzelstorfer, V. Holý, T. Schüllli, F. Bechstedt, E. P. A. M. Bakkers, G. Bauer, and J. Stangl, *Phys. Rev. B* **88**, 115315 (2013).
- [48] D. Kriegner, C. Panse, B. Mandl, K. A. Dick, M. Keplinger, J. M. Persson, P. Caroff, D. Ercolani, L. Sorba, F. Bechstedt, and J. Stangl, G. Bauer, *Nano Lett.* **11**, 1483 (2011).
- [49] A. Biermanns, S. Breuer, A. Davydok, L. Geelhaar, and U. Pietsch, *Phys. Status Solidi RRL* **5**, 156 (2011).
- [50] R. M. Martin, *Phys. Rev. B* **6**, 4546 (1972).
- [51] C.-Y. Yeh, Z.W. Lu, S. Froyen, and A. Zunger, *Phys. Rev. B* **46**, 10086 (1992).
- [52] S. Assali, I. Zardo, S. Plissard, D. Kriegner, M. A. Verheijen, G. Bauer, A. Meijerink, A. Belabbes, F. Bechstedt, J. E. M. Haverkort, and E. P. A. M. Bakkers, *Nano Lett.* **13**, 1559 (2013).
- [53] R. E. Algra, M. A. Verheijen, M. T. Borgstrom, L.-F. Feiner, G. Immink, W. J. P. van Enckevort, E. Vlieg, and E. P. A. M. Bakkers, *Nature* **456**, 369 (2008).
- [54] K. Pemasiri, M. Montazeri, R. Gass, L. M. Smith, H. E. Jackson, J. Yarrison-Rice, S. Paiman, Q. Gao, H. H. Tan, C. Jagadish, X. Zhang, and J. Zou, *Nano Letters* **9**, 648 (2009).
- [55] S. Assali, L. Gagliano, D. S. Oliveira, M. A. Verheijen, S. R. Plissard, L. F. Feiner, and E. P. A. M. Bakkers, *Nano Lett.* **15**, 8062 (2015).
- [56] H. J. Joyce, J. Wong-Leung, Q. Gao, H. H. Tan, and C. Jagadish, *Nano Lett.* **10**, 908 (2010).
- [57] K. A. Dick, C. Thelander, L. Samuelson, and P. Caroff, *Nano Lett.* **10**, 3494 (2010).
- [58] D. Spirkoska, J. Arbiol, A. Gustafsson, S. Conesa-Boj, F. Glas, I. Zardo, M. Heigoldt, M. H. Gass, A. L. Bleloch, S. Estrade, M. Kaniber, J. Rossler, F. Peiro, J. R. Morante, G. Abstreiter, L. Samuelson, and A. Fontcuberta i Morral, *Phys. Rev. B* **80**, 245325 (2009).
- [59] S. Lehman, D. Jacobsson, and K. A. Dick, *Nanotechnology* **26**, 301001 (2015).
- [60] M. Murayama and T. Nakayama, *Phys. Rev. B* **49**, 4710 (1994).

- [61] A. De and C. E. Pryor, *Phys. Rev. B* **81**, 155210 (2010).
- [62] A. Belabbes, C. Panse, J. Furthmüller, and F. Bechstedt, *Phys. Rev. B* **86**, 075208 (2012).
- [63] F. Bechstedt and A. Belabbes, *J. Phys.: Condens. Matter* **25**, 273201 (2013).
- [64] T. Akiyama, K. Nakamura, T. Ito, and A. J. Freeman, *Appl. Phys. Lett.* **104**, 132101 (2014).
- [65] M. Levinshtein, S. Rumyantsev, and M. Shur, *Handbook Series on Semiconductor Parameters* (Word Scientific Publishing, 1999) Vol. 2.
- [66] Y. Hiraya, F. Ishizaka, K. Tomioka, and T. Fukui, *Appl. Phys. Express* **9**, 035502 (2016).
- [67] A. Nakadaira and H. Tanaka, *J. Electron. Mater.* **26**, 320 (1996).
- [68] R. E. Algra, M. Hoeser, M. A. Verheijen, I. Zardo, G. G. W. Immink, W. J. P. van Enckevort, G. Abstreiter, L. P. Kouwenhoven, E. Vlieg, and E. P. A. M. Bakkers, *Nano Lett.* **11**, 1690 (2011).
- [69] S. Conesa-Boj, H. I. T. Hauge, M. A. Verheijen, S. Assali, A. Li, E. P. A. M. Bakkers, and A. Fontcuberta i Morral, *Nano Lett.* **15**, 2974 (2015).
- [70] H. I. T. Hauge, M. A. Verheijen, S. Conesa-Boj, T. Etzelstorfer, M. Watzinger, D. Kriegner, I. Zardo, C. Fasolato, F. Capitanì, P. Postorino, S. Kölling, A. Li, S. Assali, J. Stangl, and E. P. A. M. Bakkers, *Nano Lett.* **15**, 5855 (2015).
- [71] H. I. T. Hauge, S. Conesa-Boj, M. A. Verheijen, S. Kölling, and E. P. A. M. Bakkers, *Nano Lett.* **17**, 85 (2017).
- [72] L. Gagliano, A. Belabbes, M. Albani, S. Assali, M. A. Verheijen, L. Miglio, F. Bechstedt, J. E. M. Haverkort, and E. P. A. M. Bakkers, *Nano Lett.* **16**, 7930 (2016).
- [73] M. Heurlin, T. Stankevič, S. Mickevičius, S. Yngman, D. Lindgren, A. Mikkelsen, R. Feidenhans'l, M. T. Borgström, and L. Samuelson, *Nano Lett.* **15**, 2462 (2015).
- [74] A. Berg, M. Heurlin, S. Tsopanidis, M.-E. Pistol, and M. T. Borgström, *Nanotechnology* **28**, 035706 (2017).
- [75] F. Ishizaka, Y. Hiraya, K. Tomioka, and T. Fukui, *J. Cryst. Growth* **411**, 71 (2015).
- [76] F. Ishizaka, Y. Hiraya, K. Tomioka, J. Motohisa, and T. Fukui, *Jpn. J. Appl. Phys.* **56**, 010311 (2017).
- [77] F. Ishizaka, Y. Hiraya, K. Tomioka, J. Motohisa, and T. Fukui, *Nano Lett.* (2017). doi: 10.1021/acs.nanolett.6b03727

# Chapter 3

## Experimental Techniques

---

### 3.1 Introduction

This chapter describes the nanowire fabrication and characterization methods used in this study. III-V semiconductor nanowires are formed by selective-area metalorganic vapor phase epitaxy (SA-MOVPE), which is a self-organized formation method based on pure vapor phase growth. A partially masked substrate is used as a template of crystal growth in SA-MOVPE. This growth method enables us to precisely control the position and size of the nanowires. First, the principles of MOVPE and the nanowire fabrication procedure by SA-MOVPE are described, and then the structural and optical characterization methods for the grown nanowires are explained (refer to the previous study [1]).

### 3.2 Principles of MOVPE

#### 3.2.1 Overview

Metal organic vapor phase epitaxy (MOVPE) is one of the growth techniques to form single-crystal or poly-crystal thin films on substrates by using metal organic sources and gas sources with  $H_2$  or  $N_2$  carrier gas. Other representative growth techniques are liquid phase epitaxy (LPE), vapor phase epitaxy (VPE), hydride vapor phase epitaxy (HVPE), and molecular beam epitaxy (MBE). Among these growth techniques, MOVPE is suitable for high-volume production, and can produce all of the III/V materials and structures required for electronic and optical devices such as AlGaInP for red or yellow light-emitting diodes (LEDs), III-V nitrides for blue or green LEDs, and III-V highest efficiency tandem solar cells.

### 3.2.2 MOVPE growth process

The key processes during MOVPE growth are generally four phases including (i) mass transport, (ii) physical processes, (iii) chemical reactions, and (iv) thermodynamics [2].

- (i) When the carrier gas carries the source materials to the reactor, the laminar flow of the vapor forms a boundary layer above the substrate surface. Then, precursors diffuse through the boundary layer toward the substrate surface.
- (ii) While precursors diffuse at the substrate surface, adatoms adsorb into appropriate lattice positions at kinks and steps, or desorb into the vapor phase. Two- or three-dimensional nucleation can take place at the substrate surface.
- (iii) Chemical reactions strongly affect the surface reconstruction, adsorption or desorption processes of precursors, and density of step, kink or other defects. Thermal decomposition of precursors under certain growth conditions should be considered.
- (iv) Thermodynamics, which is the driving force for overall growth, dominates the grow rate because it defines the deviation from equilibrium. Thus, it also affects the incorporation of native defects or dopants and surface stoichiometry.

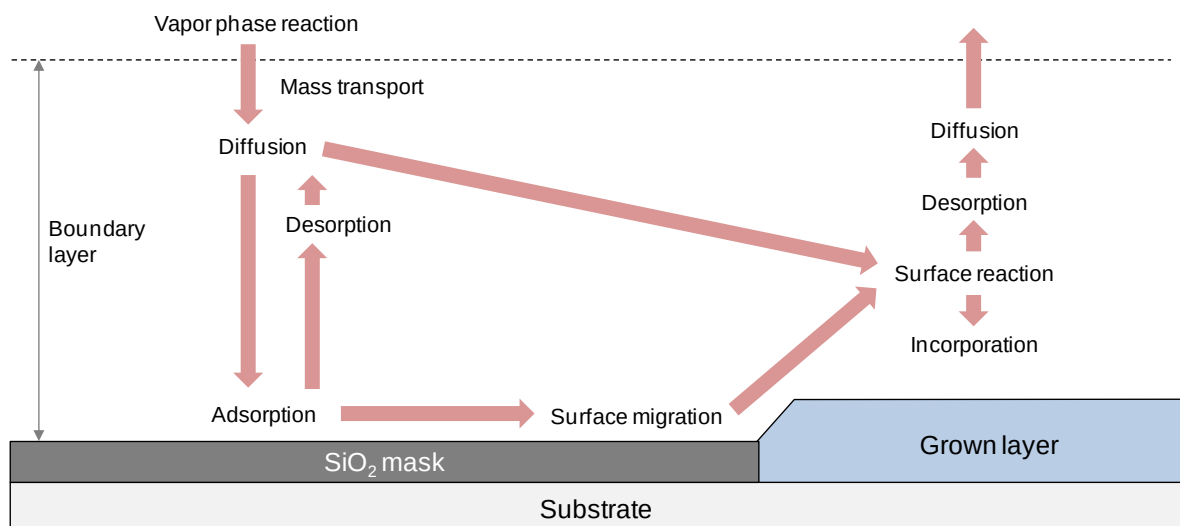


**Fig. 3-1** Schematic view of growth mechanism in the selective-area MOVPE process.

Fig. 3-1 shows schematic view of the mechanisms in the selective-area MOVPE process. The growth rate is affected by the diffusion of growth species from the  $\text{SiO}_2$  mask region and desorption to the outside of the boundary layer. In selective-area growth, the longer diffusion length of growth precursors is needed to improve the flatness of grown surfaces because the growth species dominantly diffuse from mask region to the opening area of the substrate surface. Accordingly, the selective-area growth needs higher growth temperatures than the conventional planar growth. In order to avoid the depositions of poly-crystals on the mask surfaces, the high growth temperature and low working pressure are also needed because the poly-crystals prefer to deposit under the conditions where the high probability of encountering group-III species caused by the long resident time of the precursors on the surface.

### 3.2.3 MOVPE system

Fig. 3-2 shows schematic view of the MOVPE system used in this study. The MOVPE system has three essential components: the gas delivery system, the horizontal reactor system with a temperature controller, and the exhaust disposal system with a low pressure pumping.

The MOVPE system uses palladium diffused purified hydrogen ( $\text{H}_2$ ) as a carrier gas, which transports the source materials to the reactor. The source materials flow to the reactor in separate lines for the metal organic (MO) sources and gas sources. The gas sources are supplied from gas cylinders. As shown in Fig. 3-3, the MO sources are supplied from the bubblers, which are kept at a constant temperature to control the amount of material supply. The partial pressure of MO sources is controlled by mass-flow controllers (MFCs). Pressure control valves (PCVs) keep the pressure constant in the bubbler.

The MOVPE reactor used in this study is a horizontal quartz ( $\text{SiO}_2$ ) tube. The substrate for nanowire growth is put on a graphite susceptor in the reactor, and the graphite susceptor is heated by a radio frequency (RF) coil. The substrate temperature is monitored by a thermocouple inserted into the susceptor. The total gas flow to the reactor is maintained at 5.75 standard liters per minute (SLM). The working pressure is kept constant at 0.1 atm by using a vacuum pumping during the growth. Since the MOVPE system uses toxic materials, the exhaust gases that contains non-reacted precursors are safely transported away though the

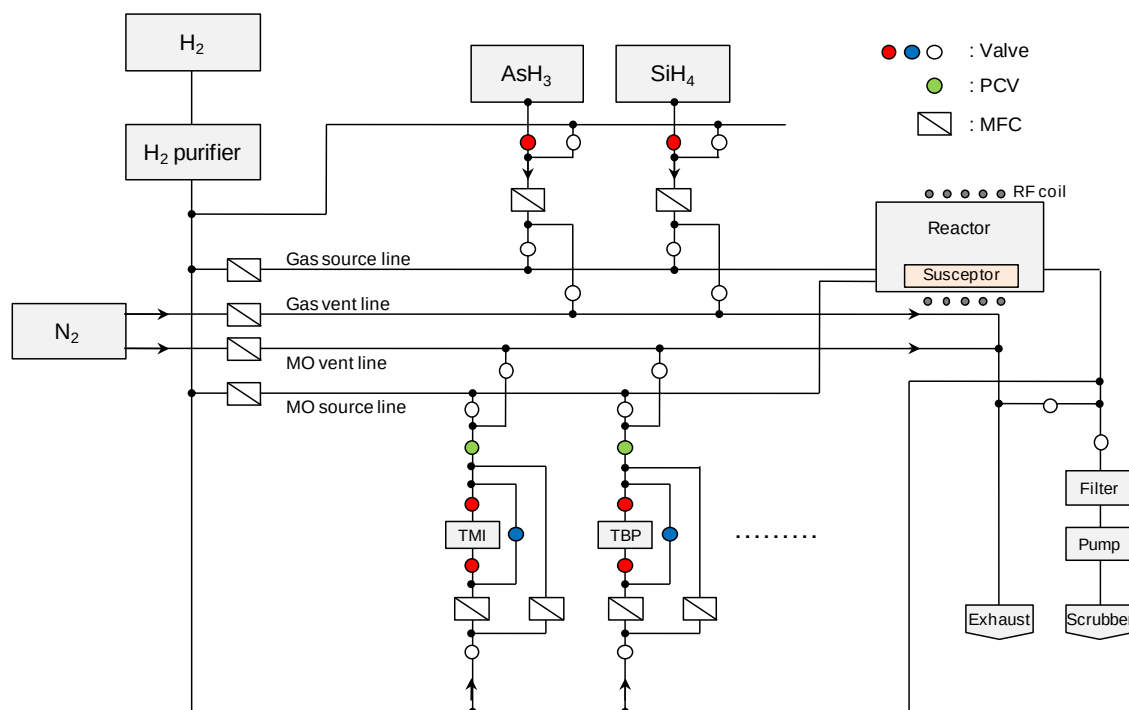


**Fig. 3-2** Schematic view of the MOVPE system used in this study. The reactor is maintained at a working pressure of 0.1 atm with a total flow of 5.75 SLM.

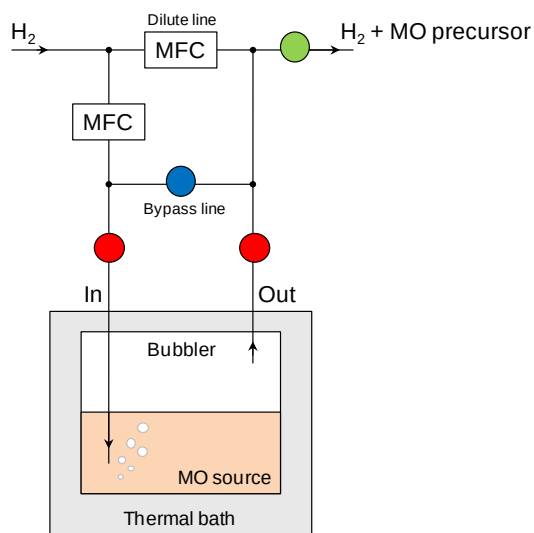


**Fig. 3-3** Schematic view of the lines for a MO source provide by a bubbler. The red valves are opened and the blue valve is closed when the MO source is used. The green valve shows a pressure control valve, maintaining the pressure in the bubbler at 760 Torr.

exhaust system. The MO and gas source materials equipped in this MOVPE system are tertiarybutylphosphine (TBP), trimethylindium (TMIn), trimethylgallium (TMGa), trimethylaluminum (TMAI), diethylzinc (DEZn), 50 ppm silane ( $\text{SiH}_4$ ) diluted in  $\text{H}_2$ , and 5% arsine ( $\text{AsH}_3$ ) diluted in  $\text{H}_2$ .

### 3.3 Nanowire fabrication by selective-area MOVPE

In this study, semiconductor nanowires are fabricated by selective-area metalorganic vapor phase epitaxy (SA-MOVPE), which is a bottom-up crystal growth technique combined with a top-down technique for fabricating the  $\text{SiO}_2$  mask. The nanowire fabrication procedure is as follows. First, approximately 20-nm-thick  $\text{SiO}_2$  films are deposited by plasma sputtering system (Shibaura Mechatronics Corporation, CFS-4EP-LL). The thickness of  $\text{SiO}_2$  film is measured by ellipsometry (ULVAC, ESM-1AT). After ultrasonic cleanings in acetone, ethanol, and ultrapure water for 5 min in each, an EB resist (Nippon Zeon: ZEP520A-7) is coated on the substrate by a spin-coater. The substrates are pre-baked at 170 °C for 2 min and 90 °C for 10 min, and then they are cooled to room temperature in order to prevent from surface cracks of the resist by a heat contraction.

The EB lithography system (JEOL, JBX-6300SF) using a ZrO/W field emitter with an accelerating voltage of 100 kV is used for making periodical hexagonal opening patterns on the EB resist. The opening patterns are defined by a small EB size of about 2 nm. After EB exposure, the substrates are developed with xylene or ZED-N50 for 90 sec, and rinsed with isopropyl alcohol (IPA) for 60 sec. The substrates are then post-baked at 140 °C for 10 min and cooled at room temperature. Next, wet chemical etching of  $\text{SiO}_2$  films is carried out using buffered hydrofluoric acid (BHF) solution, and the resist films are removed by methyl-ethyl-ketone (MEK) and 1165 remover (Rohm and Haas). Before loading samples to the reactor, the substrates are cleaned with organic solvents in an ultrasonic bath, and the native oxide on the surface of the substrates are removed by alkali solution (Furuuchi Chemical, Semicoclean) for 10 min in an ultrasonic bath.

## 3.4 Characterizations

### 3.4.1 Scanning electron microscopy

Scanning electron microscopy (SEM) is used for structural characterization of grown nanowires (Hitachi High-Tech, S-4100). The accelerating voltage of 30 kV is used in this study. The SEM system consists of an electron column with an electron source, condenser lenses, apertures, scanning coils, an objective lens and a specimen chamber. The column is kept at a high vacuum in order to prevent from an electrical discharge, to extend the lifetime of the electron gun, and to reduce undesirable collisions between electrons and air molecules. The spatial resolution of SEM is generally much higher than that of optical microscopy because the wavelength of the electrons is significantly shorter than that of visible light.

### 3.4.2 Transmission electron microscopy

Transmission electron microscopy (TEM) is used for structural characterization of grown nanowires on an atomic scale in order to obtain more detailed information. The TEM has enough a high resolution to characterize not only the crystallinity and crystal structure of materials but also the interface quality between two materials in a heterostructure. In the TEM system, since electrons are transmitted and scattered through the sample, the sample in this study is sliced as thin as about 10 nm using a milling during focused ion beam (FIB). The accelerating voltage of 300 kV is used in this study.

### 3.4.3 Photoluminescence

Photoluminescence (PL) is used for optical characterization of the nanowires. A He–Ne laser (632.8 nm) in cw operation is used as an excitation source, and the laser light was focused to 2  $\mu\text{m}$  in diameter with  $\times 50$  microscope objectives and onto samples placed in a cryostat. Fig. 3-4 shows a schematic view of the PL measurement system used in this study. The PL emissions are guided into a monochromator (Acton SP-2300i; wavelength resolution of 0.1 or

0.4 nm) and detected with a charge-coupled-device (CCD) camera, which is also used to monitor images of the sample surface. The number of nanowires within the laser spot is depending on the nanowire pitch.

### 3.4.4 Cathodoluminescence

Cathodoluminescence (CL) is used for optical characterization of an individual nanowire. The CL measurement system used in this study consists of SEM (Hitachi High-Tech, S-4300SE) combined with the spectrometer and CCD detector. CL measurements are performed at low temperature (34-36 K) with an acceleration voltage of 7 kV. On the basis of the calculation by Kanaya and Okayama [3], the penetration depth of electrons is about 500 nm under this condition, whereas most of the electrons are generated within a fraction of the penetration depth. The electron beam is irradiated in the direction perpendicular to the nanowire sidewalls, and scanned along the nanowire axis from the top to the bottom.

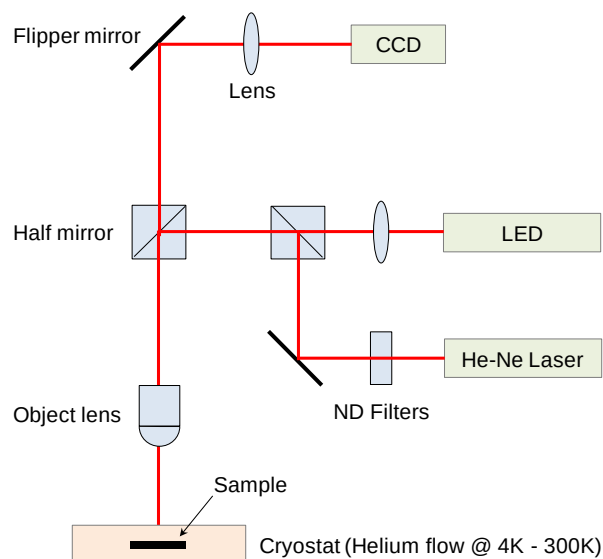


**Fig. 3-4** Schematic view of PL measurement system used in this study. A He-Ne laser (632.8 nm) is used as an excitation source, and the laser spot size is about 2  $\mu\text{m}$ .

### 3.4.5 X-ray diffraction

X-ray diffraction (XRD) measurements are used for structural, compositional, and strain characterizations of the nanowire assembly (Rigaku, SmartLab). The output power of X-ray is 9 kW with the voltage of 45 kV and current of 200 mA. The investigated sample area is about 4 mm<sup>2</sup>, in which more than one million nanowires are usually included since the nanowire pitch is 1000-1600 nm. Reciprocal space mappings (RSMs) are recorded in order to simultaneously investigate the crystal structure, chemical composition, and strain of the nanowires. Fig. 3-5 shows schematic views of reciprocal spaces from the [0001]/[111] and [10-10]/[11-2] incidents. In this study, the area around the ZB (331) reflection is usually analyzed to distinguish between the WZ and ZB Bragg peaks, where the WZ (10-15) peaks appear at the midpoint between the ZB (331) and ZB (224) twin peaks.

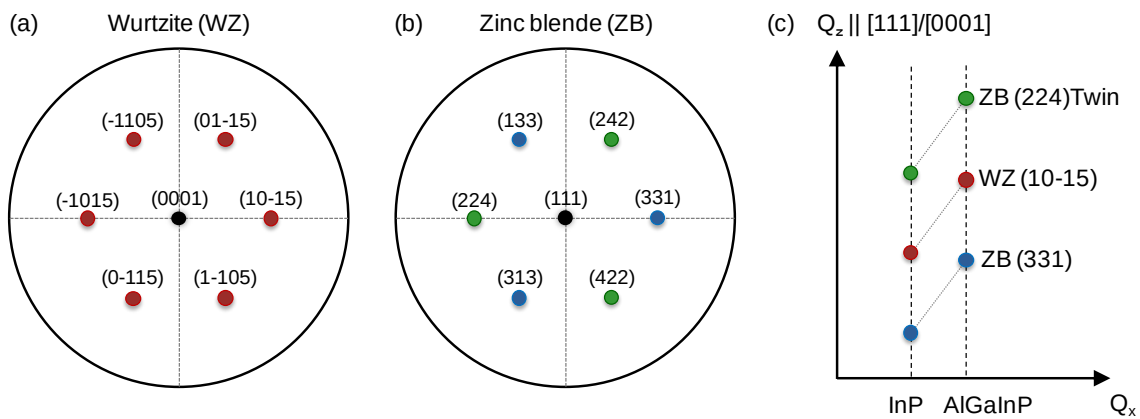


**Fig. 3-5** Schematic views of reciprocal spaces from the [0001]/[111] incident in (a) wurtzite and (b) zinc blende crystal structures, and (c) from the [10-10]/[11-2] incident that contains both wurtzite and zinc blende crystal structures.

## Bibliography

- [1] K. Ikejiri, Growth Mechanism of III-V Semiconductor Nanowires by Selective Area Metal organic Vapor Phase Epitaxy, PhD Thesis, Hokkaido University, Japan (2013).
- [2] G. B. Stringfellow, Organometallic Vapor-Phase Epitaxy: Theory and Practice (Academic Press, Inc.) second edition (1999).
- [3] K. Kanaya and S. Okayama, J. Phys. D: Appl. Phys. 5, 43 (1972).



## Chapter 4

### Growth of InGaP Nanowires on InP (111)A

---

We studied the growth of indium-rich InGaP nanowires (NWs) on InP (111)A substrates by selective-area metal organic vapor phase epitaxy (SA-MOVPE). We obtained vertically aligned InGaP NWs by optimizing growth conditions, such as group III supply ratio and V/III ratio. We found that the height, diameter, shape, and composition of InGaP NWs depended significantly on the supply ratios of trimethylgallium (TMGa) and trimethylindium (TMIn). As the supply ratio of TMGa was increased, the lateral growth was drastically enhanced, and the uniformity of NWs deteriorated. Furthermore, the sidewall facets of NWs changed from  $\{-211\}$  to  $\{-110\}$  as the supply ratio of TMGa was increased, indicating the possibility of structural transition from wurtzite (WZ) to zinc blende (ZB). We propose a possible growth model for such lateral growth, uniformity, and structural transition. Photoluminescence (PL) measurements revealed that the Ga compositions ranged approximately from 0 to 15%. Our results show that highly uniform InGaP NWs can be grown by controlling the growth conditions.

#### 4.1 Introduction

Over the past decade, semiconductor nanowires (NWs) have attracted a great deal of attention for the revolutionary advances that have been achieved for them in fields including nanotechnology-based electronics, optoelectronics, and biotechnology. Accordingly, extensive studies are being carried out to investigate their application in field-effect transistors [1,2], ultrasmall light-emitting diodes [3-5], solar cells [6-8], high-sensitivity chemical sensors [9,10], and other such devices. Until now, most semiconductor NWs have been fabricated by

catalyst-assisted vapor–liquid–solid (VLS) growth. This method entails growing NWs on substrates where alloys of catalyst metals, for instance, Au or Ni, and constituent atoms of the semiconductor are formed. As an alternative method, we have reported on the catalyst-free growth of III–V semiconductor NWs by selective-area metal organic vapor phase epitaxy (SA-MOVPE) [11]. This method has a great advantage in the controllability of the size and position of NWs. It is also noted that semiconductor alloys are essential for achieving various kinds of heterostructured NWs. Furthermore, with NWs, lattice-matching issues are expected to be insignificant owing to their geometrical sizes and shapes, which enhance the possibilities for the choice of materials and the controllability of bandgap energy.

Among alloy semiconductors, InGaP is considered to be a suitable material for light-emitting diodes in the visible red region and for multi-junction solar cells because of its bandgap in the range from 1.35 to 2.26 eV, depending on the alloy composition. InGaP NWs formed by VLS growth have been reported [12–14]. However, few investigations of SA-MOVPE of InGaP NWs have been carried out, although much research has been carried out on other materials, for example, InAs [15,16], InGaAs [17–19], GaAs [11,20,21], and InP [22–25]. Here, we report on the growth of InGaP NWs on InP(111)A substrates by SA-MOVPE and discuss their structural characterization and composition measured by scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, and micro-photoluminescence ( $\mu$ -PL) analysis.

## 4.2 Experimental procedure

The fabrication of NWs consisted of first preparing patterned InP (111)A substrates partially covered with a SiO<sub>2</sub> mask. A 25-nm-thick SiO<sub>2</sub> film was deposited on InP(111)A by plasma sputtering, and hexagonal-opening patterns were defined by electron beam (EB) lithography and wet chemical etching based on buffered hydrofluoric acid (BHF). The SiO<sub>2</sub> patterns were designed to be a periodic array of openings with the diameter  $d_0$  in the range from 30 to 200 nm and the pitch  $a$  in the range from 0.5 to 5.0  $\mu$ m. The SA-MOVPE of NWs was carried out in a horizontal-low-pressure MOVPE system, in which trimethylgallium

(TMGa), trimethylindium (TMIn), and tertiarybutylphosphine (TBP) were used as source materials. The total of the partial pressures of TMGa, [TMGa], and TMIn, [TMIn], remained constant at  $2.86 \times 10^{-6}$  atm. The TMGa partial pressure ratio,  $Ga_{supply} = [TMGa]/([TMGa]+[TMIn])$ , was changed to 0, 5, or 10%. The partial pressures of TBP, [TBP], ranged from 0.16 to  $2.40 \times 10^{-4}$  atm, and the V/III ratio was changed to 5.6, 28, and 84 with a constant group III supply. The typical condition for InP NWs with wurtzite structures was  $Ga_{supply} = 0\%$  and V/III ratio = 28. The growth temperature ( $T_g$ ) and growth time were 650 °C and 20 min, respectively.

XRD measurements were carried out using Cu  $K\alpha_1$  radiation ( $\lambda = 1.54059$  Å) with a Ge(400) double-crystal monochromator.  $\mu$ -PL was measured at 4.2 K. The excitation light from a He-Ne laser with a wavelength of 632.8 nm was focused on the NW arrays using the  $\times 50$  microscope objectives with a 0.42 numerical aperture, which were also used to collect the PL from the NWs. The excitation power density was 1.0 kW/cm<sup>2</sup>, and the laser spot was less than 2  $\mu$ m in diameter.

### 4.3 Group III supply ratio dependence

Fig. 4-1 shows 45° tilted SEM images of InP and InGaP NWs with various  $Ga_{supply}$  values. The mask opening  $d_0$  and the pattern pitch  $a$  are 100 nm and 1.0  $\mu$ m, respectively. For  $Ga_{supply} = 0\%$  [Fig. 4-1(a)], uniform hexagonal pillar structures were formed in the mask openings. The sidewalls of the hexagonal structures are  $\{-211\}$  facets vertical to the InP (111)A substrate. However, as  $Ga_{supply}$  increased [Figs. 4-1(b) and 4-1(c)], the lateral growth was drastically enhanced, and the uniformity and surface flatness of NWs deteriorated. Furthermore, the sidewall facets of NWs changed from  $\{-211\}$  to  $\{-110\}$  as  $Ga_{supply}$  increased, as shown in the insets of Figs. 4-1(a)-4-1(c). The average heights and diameters of NWs as a function of  $Ga_{supply}$  are plotted in Fig. 4-2. NW height decreased and NW diameter increased with increasing  $Ga_{supply}$ . These tendencies are almost the same as those observed in InP NWs when  $T_g$  decreases. That is, the increase in  $Ga_{supply}$  can cause the reduction in apparent  $T_g$ .

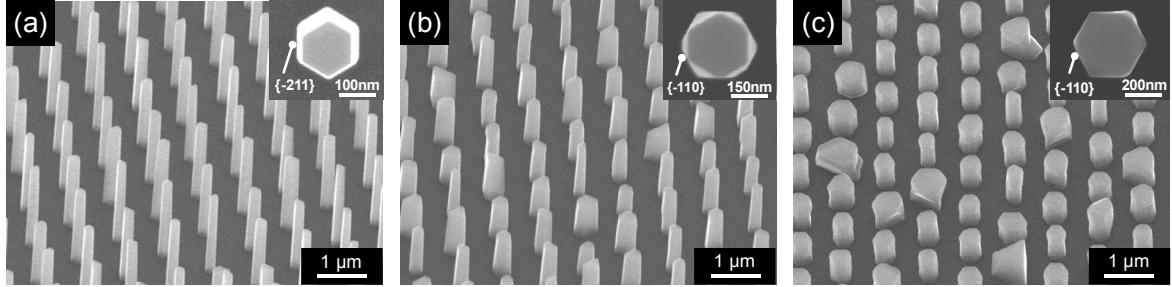


**Fig. 4-1** SEM images of InP and InGaP NWs for  $Ga_{supply} =$  (a) 0%, (b) 5%, and (c) 10% with a V/III ratio of 28. Each inset shows a top view of the NWs, showing the difference in orientation of hexagonal side facets. The mask opening  $d_0$  and pattern pitch  $a$  were 100 nm and 1.0  $\mu\text{m}$ , respectively.

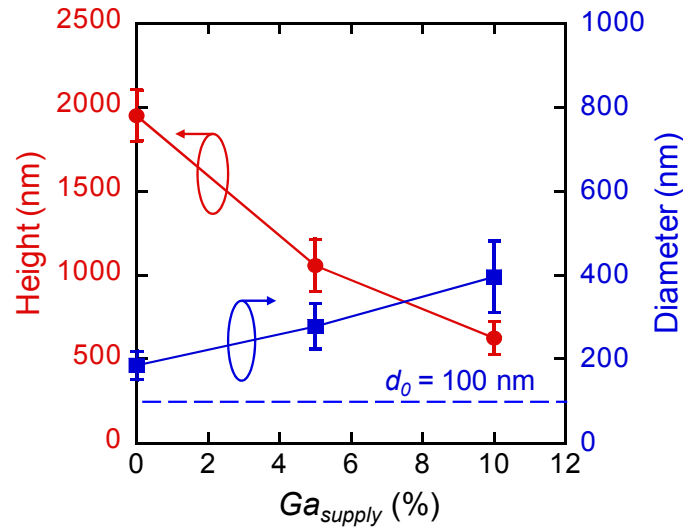


**Fig. 4-2** Dependence of NW height and diameter on  $Ga_{supply}$ . All error bars denote standard deviations.

Next, we discuss the enhancement of lateral growth and suppression of vertical growth. With SA-MOVPE, in general, the lateral growth is enhanced under low  $T_g$  and high V/III ratio conditions. This is because these conditions lead to a decrease in the amount of group V atoms desorbed from the  $\{-110\}$  surface and an increase in group V coverage, thereby increasing the adsorbed amount of group III atoms [20,22]. As a result, the lateral growth is enhanced.

With InGaP NWs, the lateral growth was enhanced as  $Ga_{supply}$  increased, as shown in Fig. 4-2, which agreed with InGaAs NWs reported by Sato *et al.* [17]. The optimum growth temperature ( $T_{op}$ ) empirically has a relationship with the melting temperature ( $T_m$ ) for III–V NW growth by SA-MOVPE. According to the melting temperature difference [ $T_m(\text{InP}) = 1330$  K, and  $T_m(\text{GaP}) = 1750$  K] [26], the  $T_{op}$  required to obtain vertical pillar growth also increases as  $Ga_{supply}$  increases. The present  $T_g$  is much more preferable for the growth of  $\{-110\}$  surfaces owing to its being lower than the  $T_{op}$  for GaP NWs without any lateral growth. Thus, as  $Ga_{supply}$  increases, the  $T_{op}$  for InGaP NWs increased; that is, the  $T_g$  decreased to a value below  $T_{op}$ . Hence, lateral growth was enhanced owing to the increase in P coverage. Under this high P coverage condition, the P trimers are formed on the (111)A surface [27,28], which prevents the group III atoms from adsorbing onto the (111)A growth interface, thereby suppressing the vertical growth.

Next, we discuss the change in the sidewall facets from  $\{-211\}$  to  $\{-110\}$ . Our previous study [23] revealed that two types of InP NW can be grown by controlling the growth conditions. One is the WZ structure with  $\{-211\}$  sidewall facets under high  $T_g$  and low V/III ratio (low P coverage) conditions, and the other is the ZB structure with  $\{-110\}$  sidewall facets under low  $T_g$  and high V/III ratio (high P coverage) conditions. Also, since the density of dangling bonds, or surface energy, is different between  $\{-211\}$  and  $\{-110\}$  facets, WZ nanowires with  $\{-211\}$  facets and ZB nanowires with  $\{-110\}$  facets are more stable and are more likely to be formed.

As a result of growing InGaP NWs,  $T_{op}$  tended to increase with increasing Ga composition, and the growth condition was shifted relatively to the lower temperature, that is, a high P coverage condition, as we mentioned in the previous paragraph. Hence, the increase in Ga composition contributes to the condition under which the crystal structures of InGaP NWs are more likely to be ZB structures because of the increased P coverage. Therefore, we consider that the change in the sidewall facets from  $\{-211\}$  to  $\{-110\}$  occurred owing to the structural transition from WZ to ZB.

In addition to the influence of P coverage, we describe a possible reason for the structural transition from the viewpoint of ionicity. The ionicity of InP (0.421) is larger than that of GaP (0.327) [29]. Therefore, with the second nearest pair of groups III and V atoms in WZ stacking,

the Coulomb interaction of In-P pairs is much larger than that of Ga-P pairs. This indicates that In-P pairs favor WZ stacking, whereas Ga-P pairs have less preference for WZ stacking. Hence, even under the same growth conditions, InGaP NWs can be shifted to have ZB structures with a small amount of Ga.

## 4.4 V/III ratio dependence

Fig. 4-3 shows SEM images of InGaP NWs for  $Ga_{supply} = 10\%$  at various V/III ratios. At a low V/III ratio, tetrahedron-like structures are formed in the mask openings [Fig. 4-3(a)]. In contrast, at a high V/III ratio, hexagonal structures with clear  $\{-110\}$  sidewall facets are formed, and their uniformity is improved as compared with those produced at a V/III ratio of 28 [Fig. 4-1(c)]. This result indicates that a higher V/III ratio contributes to the growth of hexagonal structures with clear  $\{-110\}$  sidewall facets. In addition, InGaP NWs grown at a V/III ratio of 28 are thought to be ZB mixed with a small number of WZ crystal phases. This instability of the crystal structures results in nonuniform NWs. In contrast, InGaP NWs grown at a V/III ratio of 84 are considered to be a result of the condition under which the ZB crystal structure is stably formed because of a higher P coverage obtained by increasing the V/III ratio, as mentioned in the previous section, thereby improving the uniformity.

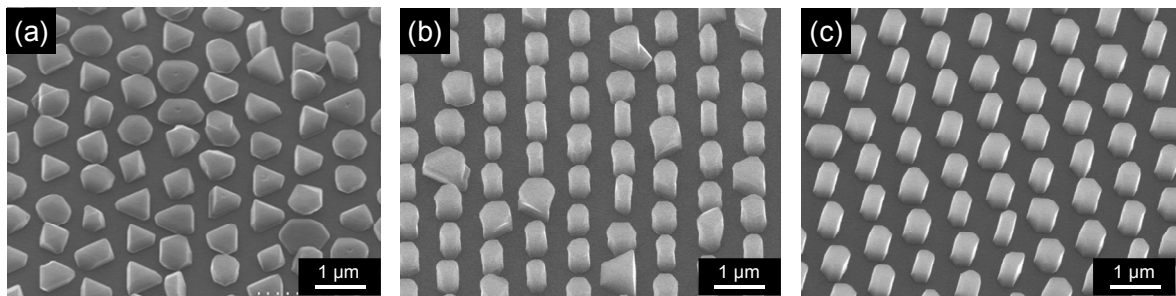


**Fig. 4-3** SEM images of InGaP NWs for  $Ga_{supply} = 10\%$  with V/III ratios of (a) 5.6, (b) 28, and (c) 84. The mask opening  $d_0$  and pattern pitch  $a$  were 100 nm and 1.0  $\mu\text{m}$ , respectively.

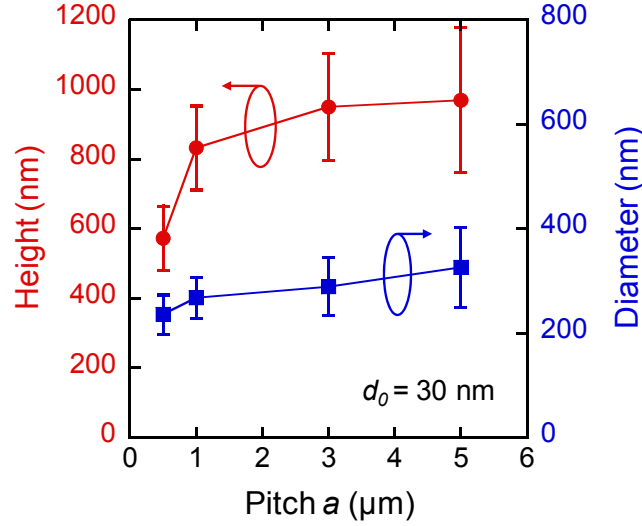


**Fig. 4-4** Dependence of NW height and diameter on pitch. All error bars denote standard deviations.

For InGaP NWs grown at a V/III ratio of 84 [Fig. 4-3(c)], the dependence of the average height and diameter of NWs on pattern pitch is plotted in Fig. 4-4. As pitch increases, NW height increased and tended to saturate at approximately 3  $\mu\text{m}$ . NW diameter linearly increases with increasing pitch. These results agree very well with those of the ZB InP NWs reported by Kitauchi *et al.* [23] The increase in both height and diameter can be explained by the diffusion of growth species in the gas phase and on the surface. If the supply of source materials per unit area is constant, the amount of materials to be incorporated into both the top and sidewall of a single NW increases as pitch increases, resulting in the increase in both NW height and diameter.

## 4.5 Compositional characterization

In order to estimate the Ga composition of InGaP, XRD measurements were carried out with reference InGaP planar layers on InP(001) substrates, which were grown simultaneously with InGaP NWs for each  $Ga_{\text{supply}}$ . The calculated Ga compositions of the planar layers for  $Ga_{\text{supply}} = 5$  and 10% were 8 and 11%, respectively.

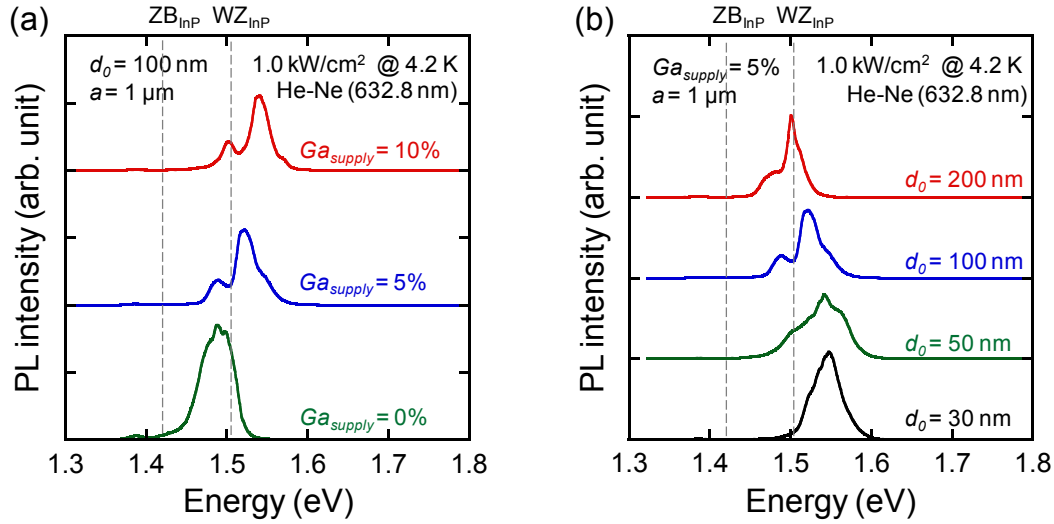


**Fig. 4-5** (a) PL spectra of InP and InGaP NWs for various  $Ga_{supply}$ . (b) PL spectra of InGaP NWs with various  $d_0$ . The base of each spectrum is shifted along the vertical direction for clarity.

**Table 4-1** Ga composition of InGaP planar and NWs.

| $Ga_{supply}$ | Planar (XRD) | NW (PL) |
|---------------|--------------|---------|
| 5%            | 8%           | 12.2%   |
| 10%           | 11%          | 14.3%   |

The PL spectra of InP and InGaP NWs are plotted in Fig. 4-5(a). The number of NWs with  $a = 1.0 \mu\text{m}$  was approximately 5 within the laser spot. The InP NWs had a peak energy of 1.48 eV, which was slightly redshifted from the bandgap energy of WZ InP. As we discussed in detail in our previous work [24], mixing ZB segments into WZ NWs gives rise to a redshift in InP NWs. In the present case, we assume that the InP NWs had WZ structures mixed with a small number of ZB segments. As for the two peak energies of InGaP NWs, we think that the low and high peak energies correspond to donor-acceptor and band-to-band emissions, respectively. The high peak energy led to the estimated Ga compositions of NWs for  $Ga_{supply} = 5$  and 10% of 12.2 and 14.3%, respectively, assuming that these NWs are completely ZB. Fig.

4-5(b) shows plot of the PL spectra of InGaP NWs with various  $d_0$  values. The observed PL peak energy shifted slightly to a higher energy region as  $d_0$  decreased from 200 to 30 nm, indicating that the Ga composition increased by approximately 5%. This phenomenon can be explained by the difference in desorption rate between Ga and In precursors on the mask surface. The desorption rate of Ga is lower than that of In. [17,18] Therefore, the decrease in  $d_0$ , which is equivalent to the increase in the mask surface area, leads to the increase in Ga composition.

The estimated Ga compositions of InGaP NWs with  $d_0 = 100$  nm and  $a = 1.0$   $\mu\text{m}$  are summarized in Table I. We think that the Ga compositions of InGaP NWs are slightly higher than those of the planar layers because selective-area growth enhances the adsorption of Ga atoms owing to the difference in desorption rate between Ga and In, as mentioned in the previous paragraph. Also, the Ga compositions estimated from the PL spectra of the NWs are higher than those determined by XRD analysis of the planar layers. This is probably due to the effect of ZB and WZ phase mixing. [24] We require more detailed analysis of the correlation between the crystal phase and PL peak energy in order to clarify the mixing ratio of ZB and WZ.

## 4.6 Conclusions

We fabricated InGaP NWs on InP(111)A substrates by SA-MOVPE under various  $Ga_{\text{supply}}$  and V/III ratio conditions. The lateral growth was drastically enhanced, and the uniformity of NWs deteriorated as  $Ga_{\text{supply}}$  increased. Furthermore, the sidewall facets of NWs changed from  $\{-211\}$  to  $\{-110\}$  with increasing  $Ga_{\text{supply}}$ , indicating the possibility of a structural transition from WZ to ZB. In addition, we successfully improved the uniformity of NWs by increasing the V/III ratio. We also estimated the compositions of the InGaP NWs from XRD and PL measurements. The Ga compositions ranged approximately from 0 to 15% and increased with increasing  $Ga_{\text{supply}}$  and decreasing mask opening diameter. These results indicate that the height, diameter, shape, uniformity, and composition of InGaP NWs depend on V/III ratio as well as  $Ga_{\text{supply}}$ . Further studies are needed to obtain InGaP NWs over the entire composition range.

## Bibliography

- [1] K. Tomioka, M. Yoshimura, and T. Fukui: *Nature* **488** (2012) 189.
- [2] H.T. Ng, J. Han, T. Yamada, P. Nguyen, Y.P. Chen, and M. Meyyappan: *Nano Lett.* **4** (2004) 1247.
- [3] H. Sekiguchi, K. Kishino, and A. Kikuchi: *Appl. Phys. Lett.* **96** (2010) 231104.
- [4] L.K. van Vugt, S. Rühle, and D. Vanmaekelbergh: *Nano Lett.* **6** (2006) 2707.
- [5] K. Tomioka, J. Motohisa, S. Hara, K. Hiruma, and T. Fukui: *Nano Lett.* **10** (2010) 1639.
- [6] M. Law, L.E. Greene, J.C. Johnson, R. Saykally, and P. Yang: *Nat. Mater.* **4** (2005) 455.
- [7] E. Garnett and P. Yang: *Nano Lett.* **10** (2010) 1082.
- [8] H. Goto, K. Nosaki, K. Tomioka, S. Hara, K. Hiruma, J. Motohisa, and T. Fukui: *Appl. Phys. Express* **2** (2009) 035004.
- [9] C. Li, D. Zhang, X. Liu, S. Han, T. Tang, J. Han, and C. Zhou: *Appl. Phys. Lett.* **82** (2003) 1613.
- [10] Z. Fan, D. Wang, P.-C. Chang, W.-Y. Tseng, and J.G. Lu: *Appl. Phys. Lett.* **85** (2004) 5923.
- [11] J. Noborisaka, J. Motohisa, and T. Fukui: *Appl. Phys. Lett.* **86** (2005) 213102.
- [12] D. Jacobsson, J.M. Persson, D. Kriegner, T. Etzelstorfer, J. Wallentin, J.B. Wagner, J. Stangl, L. Samuelson, K. Deppert, and M.T. Borgström: *Nanotechnology* **23** (2012) 245601.
- [13] A Fakhr, Y.M. Haddara, and R.R. Lapierre: *Nanotechnology* **21** (2010) 165601.
- [14] C.P.T. Svensson, T. Mårtensson, J. Trägårdh, C. Larsson, M. Rask, D. Hessman, L. Samuelson, and J. Ohlsson: *Nanotechnology* **19** (2008) 305201.
- [15] K. Tomioka, P. Mohan, J. Noborisaka, S. Hara, J. Motohisa, and T. Fukui: *J. Cryst. Growth* **298** (2007) 644.
- [16] K. Tomioka, J. Motohisa, S. Hara, and T. Fukui: *Nano Lett.* **8** (2008) 3475.
- [17] T. Sato, J. Motohisa, J. Noborisaka, S. Hara, and T. Fukui: *J. Cryst. Growth* **310** (2008) 2359.
- [18] M. Yoshimura, K. Tomioka, K. Hiruma, S. Hara, J. Motohisa, and T. Fukui: *Jpn. J. Appl. Phys.* **49** (2010) 04DH08.

- [19] Y. Kohashi, T. Sato, K. Ikejiri, K. Tomioka, S. Hara, and J. Motohisa: J. Cryst. Growth **338** (2012) 47.
- [20] K. Ikejiri, J. Noborisaka, S. Hara, J. Motohisa, and T. Fukui: J. Cryst. Growth **298** (2007) 616.
- [21] H. Yoshida, K. Ikejiri, T. Sato, S. Hara, K. Hiruma, J. Motohisa, and T. Fukui: J. Cryst. Growth **312** (2009) 3592.
- [22] P. Mohan, J. Motohisa, and T. Fukui: Nanotechnology **16** (2005) 2903.
- [23] Y. Kitauchi, Y. Kobayashi, K. Tomioka, S. Hara, K. Hiruma, T. Fukui, and J. Motohisa: Nano Lett. **10** (2010) 1699.
- [24] K. Ikejiri, Y. Kitauchi, K. Tomioka, J. Motohisa, and T. Fukui: Nano Lett. **11** (2011) 4314.
- [25] K. Ikejiri, F. Ishizaka, K. Tomioka, and T. Fukui: Nano Lett. **12** (2012) 4770.
- [26] V. Kumar, V. Jha, and A. K. Shrivastava: Cryst. Res. Technol. **45** (2010) 920.
- [27] C. H. Li, Y. Sun, D. C. Law, S. B. Visbeck, and R. F. Hicks: Phys. Rev. B **68** (2003) 085320.
- [28] T. Akiyama, T. Kondo, H. Tatematsu, K. Nakamura, and T. Ito: Phys. Rev. B **78** (2008) 205318.
- [29] N. Christensen, S. Satpathy, and Z. Pawlowska: Phys. Rev. B **36** (1987) 1032.



## Chapter 5

# Crystal Structure Transfer in InP/GaP Core-Shell Nanowires

---

A GaP nanowire is promising from the viewpoint of device applications because when its crystal phase is changed from zinc blende (ZB) to wurtzite (WZ), its band gap changes from indirect to direct. GaP in the WZ phase is theoretically and experimentally shown to have the possibility of “green” emission. Here we report on the growth of WZ GaP in InP/GaP core-shell nanowires by selective-area metal-organic vapor-phase epitaxy (SA-MOVPE). WZ InP nanowires were used as a template for transferring the WZ structure to GaP. Transmission electron microscopy revealed that WZ GaP was grown on the sidewalls of the InP core in the lateral  $\langle -211 \rangle$  direction and that ZB GaP was grown on the top of the InP core in the axial  $\langle 111 \rangle$  direction. A growth model for the different crystal structures of the GaP shell is proposed from the viewpoint of the growth direction. The WZ structure is “transferred” from the InP core to the GaP shell only when GaP grows in the direction perpendicular to the WZ stacking direction of the InP core. This so-called “crystal structure transfer” can also be applied to p- and n-doped GaP and is therefore promising for fabricating WZ-GaP-based light-emitting diodes.

### 5.1 Introduction

Semiconductor nanowires (NWs) have attracted considerable interest in recent years because of their potential applications in devices such as field-effect transistors [1,2], light-emitting diodes [3-6], and solar cells [7,8]. The most-surprising feature of nanowires is

that they can be grown with a wurtzite (WZ) crystal structure by appropriately adjusting the growth conditions such as growth temperature, V/III ratio, and doping amount [9-16], even though they are stable in the zinc blende (ZB) phase of the bulk crystal. This crystal structure engineering opens up a new possibility for the device applications of nanowires because the crystal structure has a significant effect on the physical properties of semiconductor materials. Interestingly, band-structure calculations suggest that GaP in the WZ phase has a direct band gap [17-21], although that in the ZB phase has an indirect band gap. Recently, this suggestion has been experimentally confirmed by using WZ GaP nanowires fabricated by vapor-liquid-solid (VLS) growth, suggesting the direct-band-gap transition at 2.09 eV [14]. This direct-band-gap WZ GaP may increase the efficiency of green light-emitting diodes and close the “green gap” issue.

We have grown III–V compound semiconductor nanowires by selective-area metal-organic vapor-phase epitaxy (SA-MOVPE) [1,4,8-11,22-26]. The crystal structures of InP nanowires can be controlled by adjusting the growth conditions of SA-MOVPE, and pure WZ InP nanowires can be obtained at high growth temperature and low V/III ratio [9,10]. However, this type of control is not yet possible with other III–V compounds, such as GaP, GaAs, and InAs. To promote the crystal-phase change of those compounds, it is necessary to transfer the WZ structure from the core to the shell. We have already reported pure WZ InAs nanotubes based on InP/InAs core-shell nanowires, in which the WZ structure of the InP core is transferred to the InAs shell [22]. In this study, we demonstrate the growth of WZ GaP by using WZ InP nanowires as a template for transferring the WZ structure to GaP, and propose a possible growth model for the crystal structure transfer. InP was chosen as a template because the WZ structures can be easily obtained. From the calculation, the energy difference between the WZ and ZB structures of InP is a minimum in the case of typical III-V compounds including aluminum, gallium, and indium as group-III elements and phosphorus, arsenic, and antimony as group-V elements [27].

## 5.2 Experimental procedure

As for the process for fabricating the nanowires, a 25-nm-thick SiO<sub>2</sub> film was first deposited on an InP (111)A substrate by plasma sputtering, and hexagonal-opening patterns

were defined by electron-beam (EB) lithography and wet chemical etching using buffered hydrofluoric acid (BHF). The SiO<sub>2</sub> patterns were designed to be a periodic array of openings with a diameter of 90 nm and a pitch of 400 nm. The SA-MOVPE of nanowires was carried out in a horizontal low-pressure MOVPE system using trimethylgallium (TMGa), trimethylindium (TMIn), and tertiarybutylphosphine (TBP) as source materials. The partial pressures of TMIn and TBP were respectively  $2.7 \times 10^{-6}$  and  $4.9 \times 10^{-5}$  atm for InP core growth, and the partial pressures of TMGa and TBP were respectively  $4.8 \times 10^{-7}$  and  $3.1 \times 10^{-4}$  for GaP shell growth. Prior to the growth, the native oxide on the openings was removed by thermal cleaning at 600°C under a hydrogen and TBP ambient. WZ InP nanowires were grown for 20 min at 660°C with a V/III ratio of 18, which is the typical condition for growing WZ structures [9,10]. GaP shells were then grown for 3 min at 600°C with a V/III ratio of 646. This low-temperature and high-V/III-ratio condition was chosen to promote lateral growth of the shell [23,28]. The grown structures were characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM). As for the TEM characterization, the electron-beam projection was parallel to the  $\langle -110 \rangle$  direction.

### 5.3 Growth of InP/GaP core-shell nanowires

Fig. 5-1 shows a 15°-tilted SEM image of the grown InP/GaP core-shell nanowires, which have hexagonal {10-10} vertical sidewall facets with average diameter and height of 100 nm and 1.6 μm, respectively. Sidewalls of InP nanowires with WZ structures are typically {10-10} facets (which correspond to {-211} facets in cubic ZB notation), but those with ZB structures are {-110} facets. SEM studies revealed that growth of the GaP shell was always non-uniform and that three-dimensional growth was partially observed, probably due to the large lattice mismatch of the InP/GaP material system (7.1%). In the case of InP/InAs core-shell nanowires (with lattice mismatch of 3.2%) [22], a uniform InAs shell can be obtained at low growth temperature and a small supply of group-III precursors. Accordingly, to improve the uniformity of the shell, it is necessary to further optimize the growth condition and/or the buffer layer between the core and shell.

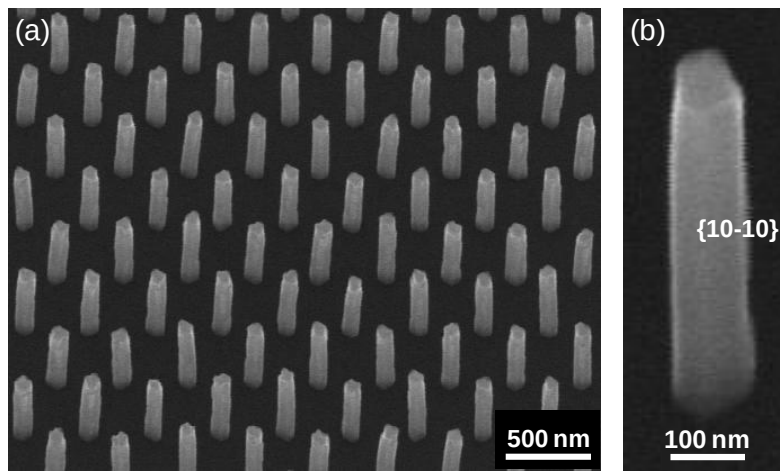


**Fig. 5-1** 15°-tilted SEM image of InP/GaP core-shell nanowires, which have {10-10} side facets. The inset shows a magnified image of one nanowire.

The crystal structure of core-shell nanowires was clarified by high-resolution TEM. Fig. 5-2(a) shows a TEM image of the InP/GaP interface at the sidewall of a core-shell nanowire. As shown in Figs. 5-2(b) and 5-2(c), the TEM image of the InP core and the corresponding fast-Fourier-transform (FFT) image revealed that the template InP nanowires had a WZ structure with a few stacking faults per micrometer. From the magnified TEM image and the corresponding FFT image in Figs. 5-2(d) and 5-2(e), it is confirmed that WZ GaP was grown laterally on the sidewalls of the WZ InP nanowires. The thickness of the GaP shell was about 5 nm. The spot splitting in the FFT image was caused by two different lattice spacings, which indicates the existence of the GaP shell. The GaP shell was also confirmed by energy-dispersive X-ray spectroscopy (EDX) line scans along the lateral direction of an InP/GaP core-shell nanowire, with a corresponding high-angle annular dark-field (HAADF) image, as shown in Fig. 5-2(f). Misfit dislocations are also observed in Figs. 5-2(a) and 5-2(d). The correlation between misfit dislocations and strain at the InP/GaP interface was investigated. Under the assumption of complete relaxation of the InP/GaP core-shell nanowires, the spacing between misfit dislocations is calculated from its lattice mismatch of 7.1% to be 4.4 nm by using the ZB lattice parameters of InP and GaP. The measured average spacing was 10.6 nm, which differs from the calculated value. This result means that 40% of interface stress was accommodated by misfit dislocations and the rest was maintained in the InP/GaP interface.

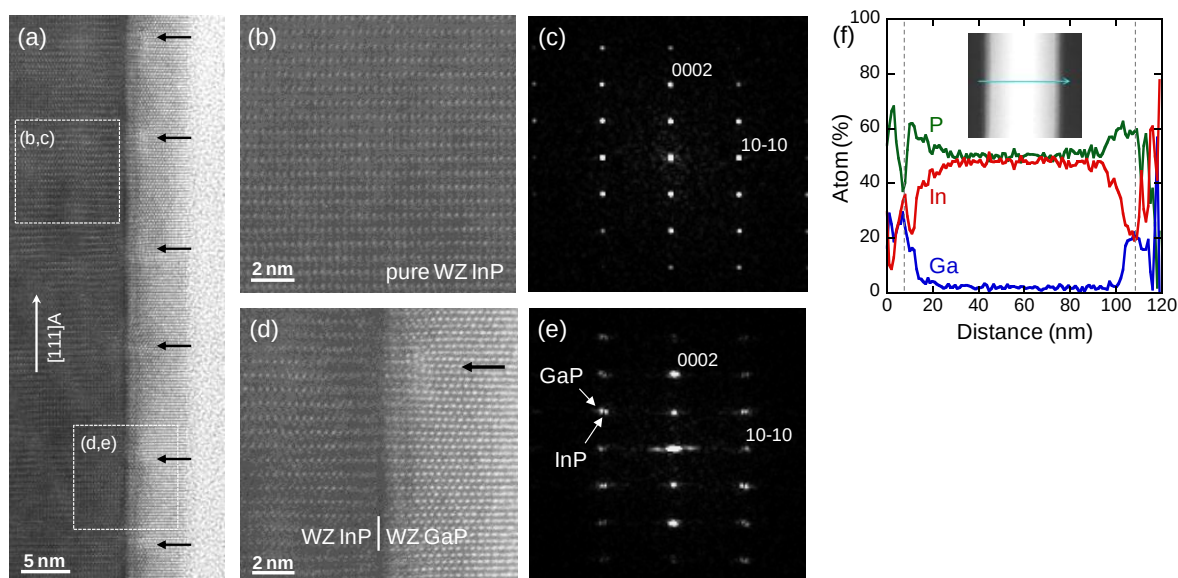


**Fig. 5-2** Crystal structures at the side of an InP/GaP core-shell nanowire. (a) TEM image of the InP/GaP interface. (b) and (c) Magnified TEM image of InP core and the corresponding FFT image, showing a pure WZ structure. (d) and (e) Magnified TEM image at the InP/GaP interface and the corresponding FFT image, showing the existence of WZ GaP. (f) EDX line scans along the lateral direction of a core-shell nanowire and corresponding HAADF image. Black arrows in (a) and (d) indicate the positions of misfit dislocations.

Fig. 5-3(a) shows a high-resolution TEM image of the top of an InP/GaP core-shell nanowire. The EDX line scans of the GaP top shell in Fig. 5-3(b) shows that indium at a composition of 20% was incorporated into GaP, probably due to surface segregation of indium during growth of GaP. Magnified TEM and FFT images of GaP grown on the top of an InP nanowire are shown in Figs. 5-3(c) and 5-3(d), which indicate that GaP has a ZB structure. A magnified TEM image of the interface of WZ InP and ZB GaP is shown in Fig. 5-3(e). The crystal structures of nanowires completely changed from WZ to ZB after growth of a monolayer of GaP, and stacking faults and twins did not appear near the interface except for the phase transition boundary. In other words, when GaP growth started in the  $\langle 111 \rangle_A$  direction, the growth mode immediately changed to the same situation as the selective-area growth of GaP on a planar (111)A substrate. In growth of GaP by SA-MOVPE on GaP(111)A

and B substrates [25], although hexagonal nanowires are grown in the  $\langle 111 \rangle_B$  direction, tetrahedral structures with (111)B facets are formed in the  $\langle 111 \rangle_A$  direction. In addition, these tetrahedral GaP structures formed on the (111)A plane are thought to have ZB phase because the corners of all tetrahedrons are pointed in one direction [24]. In the present study, tetrahedral-like GaP structures, in which (111)B facets partially appeared, were formed on the top of InP nanowires and had ZB phase. Note that the InP nanowires, as well as the GaP top shell, were grown in the  $\langle 111 \rangle_A$  direction. The present result is consistent with our previous study on growth of GaP by SA-MOVPE.

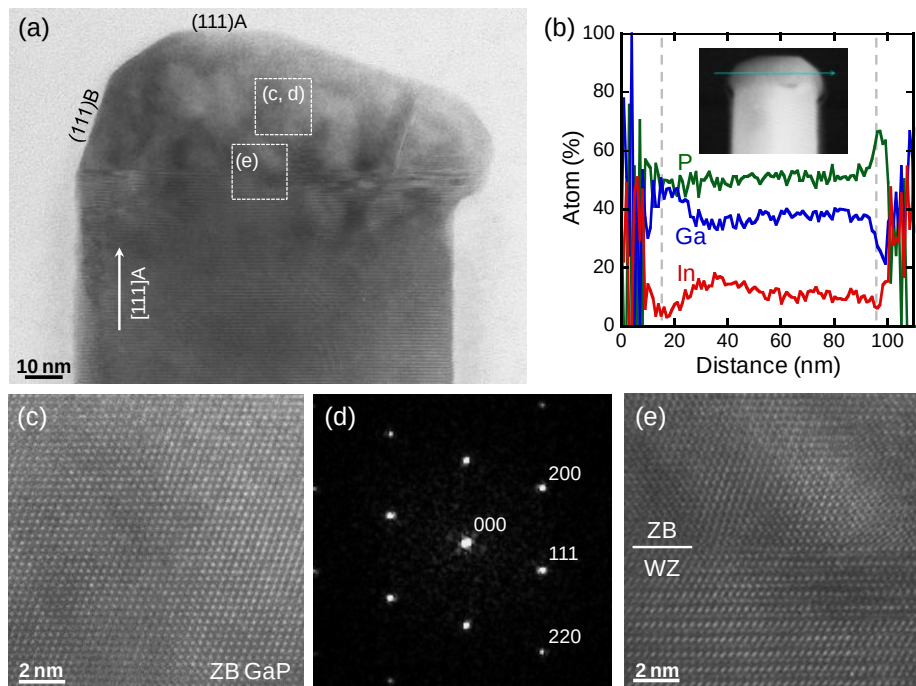


**Fig. 5-3** Crystal structures at the top of an InP/GaP core-shell nanowire. (a) Overall TEM image at the top of the core-shell nanowire. (b) EDX line scans of the GaP top shell along the lateral direction and corresponding HAADF image. (c) and (d) Magnified TEM image of GaP top shell and the corresponding FFT image, showing a pure ZB structure. (e) Magnified TEM image at the interface of WZ and ZB phases.

## 5.4 Crystal structure transfer in core-shell nanowires

Crystal structures of InP/GaP core-shell nanowires are summarized schematically in Fig. 5-4(a). The reason that different crystal structures were grown on the top and side of the InP nanowires is discussed in the following from the viewpoint of the stacking direction of a WZ InP template. Atomistic models for structural transition in InP/GaP core-shell nanowires are shown in Fig. 5-4(b). In the axial  $\langle 111 \rangle_A$  direction, the stacking sequences of the WZ phase (ABAB...) and the ZB phase (ABCABC...) are geometrically variable to each other without introducing mis-coordinated atoms because the growth direction of the top shell is the same as the WZ stacking direction. The crystal structure of the GaP top shell can therefore be changed in accordance with the materials of the shell and growth conditions. In our previous study on InGaP nanowires on InP(111)A substrates [26], the crystal phase transition from WZ to ZB occurred when a small amount of gallium was added to WZ InP nanowires, indicating that GaP has a strong tendency to form ZB phase. In addition, in this study, the GaP shell was grown under the condition of low growth temperature and high V/III ratio, at which ZB structures are likely to form [13,28]. Hence, ZB GaP was formed on the top of the InP nanowires.

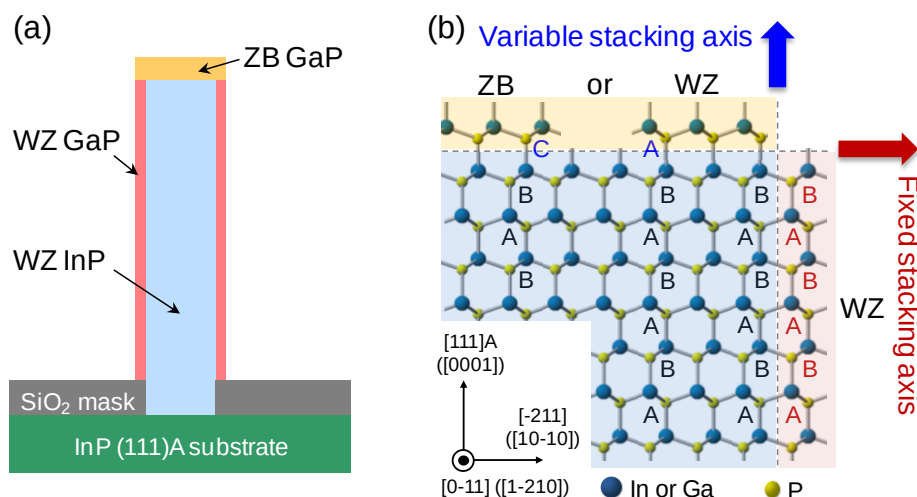


**Fig. 5-4** (a) Schematic illustration of grown crystal structures of InP/GaP core-shell nanowires. (b) Atomistic models for structural transition of the GaP shell. The stacking sequence of the WZ phase of “ABAB...” is strongly fixed in the  $\langle -211 \rangle_A$  direction (fixed stacking axis), while both WZ and ZB phases are geometrically possible in the  $\langle 111 \rangle_A$  direction (variable stacking axis).

In the lateral  $\langle -211 \rangle$  direction, however, the WZ stacking sequence “ABAB...” is strongly fixed because the growth direction of the shell is perpendicular to the WZ stacking direction. In this situation, crystal structures can be transferred in accordance with the energy balance for the core and shell materials. Major factors affecting this balance are the defect-formation energy and the energy difference between the WZ and ZB structures, which was calculated by Yeh et al. [27] When the WZ–ZB energy difference is larger than the defect-formation energy, ZB structures are formed by introducing many misfit dislocations between core and shell layers. When the WZ–ZB energy difference is small enough, however, WZ structures are maintained during shell growth. In this study, according to the TEM image in Fig. 5-2(d), the GaP side shell was grown coherently with a few monolayers before the misfit dislocations were introduced, and this coherent growth of the shell indicates a relatively large defect-formation energy. The WZ–ZB energy difference was therefore probably much smaller than the defect-formation energy, resulting in the sequence “ABAB...” being transferred from the InP core to the GaP shell regardless of the growth conditions. The key requirements concerning this technique for transferring the crystal structure are the twofold: first, growth direction is perpendicular to the WZ stacking direction; second, the WZ–ZB energy difference is smaller than the defect-formation energy.

## 5.5 Conclusions

We demonstrated the growth of WZ GaP in InP/GaP core-shell nanowires by SA-MOVPE, in which the WZ InP nanowires were used as a template for transferring the WZ structure to the GaP shell. TEM and FFT analyses revealed that WZ GaP was grown on the sidewalls of the InP core in the lateral  $\langle -211 \rangle$  direction and that ZB GaP was also grown on the top of the InP core in the axial  $\langle 111 \rangle_A$  direction. Next, we showed a growth model for the different crystal structures of GaP. The “ABAB...” stacking sequence of WZ phase is strongly fixed in the  $\langle -211 \rangle$  direction, while both the WZ and ZB phases are geometrically possible in the  $\langle 111 \rangle_A$  direction. A WZ structure is transferred from the InP core to the GaP shell in the  $\langle -211 \rangle$  direction because the WZ–ZB energy difference is relatively small. This crystal structure transfer can be applied to p- and n-doped GaP and is therefore promising for fabricating WZ-GaP-based light-emitting diodes.

## Bibliography

- [1] K. Tomioka, M. Yoshimura, and T. Fukui, *Nature* **488**, 189 (2012).
- [2] H. T. Ng, J. Han, T. Yamada, P. Nguyen, Y. P. Chen, and M. Meyyappan, *Nano Lett.* **4**, 1247 (2004).
- [3] E. Dimakis, U. Jahn, M. Ramsteiner, A. Tahraoui, J. Grandal, X. Kong, O. Marquardt, A. Trampert, H. Riechert, and L. Geelhaar, *Nano Lett.* **14**, 2604 (2014).
- [4] K. Tomioka, J. Motohisa, S. Hara, K. Hiruma, and T. Fukui, *Nano Lett.* **10**, 1639 (2010).
- [5] C. P. T. Svensson, T. Mårtensson, J. Trägårdh, C. Larsson, M. Rask, D. Hessman, L. Samuelson, and J. Ohlsson, *Nanotechnology* **19**, 305201 (2008).
- [6] K. Hiruma, M. Yazawa, T. Katsuyama, K. Ogawa, K. Haraguchi, M. Koguchi, and H. Kakibayashi, *J. Appl. Phys.* **77**, 447 (1995).
- [7] J. Wallentin, N. Anttu, D. Asoli, M. Huffman, I. Åberg, M. H. Magnusson, G. Siefert, P. Fuss-Kailuweit, F. Dimroth, B. Witzigmann, H. W. Xu, L. Samuelson, K. Deppert, and M. T. Borgström, *Science* **339**, 1057 (2013).
- [8] M. Yoshimura, E. Nakai, K. Tomioka, and T. Fukui, *Appl. Phys. Lett.* **103**, 243111 (2013).
- [9] Y. Kitauchi, Y. Kobayashi, K. Tomioka, S. Hara, K. Hiruma, T. Fukui, and J. Motohisa, *Nano Lett.* **10**, 1699 (2010).
- [10] K. Ikejiri, Y. Kitauchi, K. Tomioka, J. Motohisa, and T. Fukui, *Nano Lett.* **11**, 4314 (2011).
- [11] K. Ikejiri, F. Ishizaka, K. Tomioka, and T. Fukui, *Nano Lett.* **12**, 4770 (2012).
- [12] Q. Gao, D. Saxena, F. Wang, L. Fu, S. Mokkapati, Y. Guo, L. Li, J. W.-Leung, P. Caroff, H. H. Tan, and C. Jagadish, *Nano Lett.* **14**, 5206 (2014).
- [13] R. E. Algra, M. Hocevar, M. A. Verheijen, I. Zardo, G. G. W. Immink, W. J. P. van Enkevort, G. Abstreiter, L. P. Kouwenhoven, E. Vlieg, and E. P. A. M. Bakkers, *Nano Lett.* **11**, 1690 (2011).
- [14] S. Assali, I. Zardo, S. Plissard, D. Kriegner, M. A. Verheijen, G. Bauer, A. Meijerink, A. Belabbes, F. Bechstedt, J. E. M. Haverkort, and E. P. A. M. Bakkers, *Nano Lett.* **13**, 1559 (2013).
- [15] A. Berg, S. Lehmann, N. Vainorius, A. Gustafsson, M.-E. Pistol, L. R. Wallenberg, L. Samuelson, and M. T. Borgström, *J. Cryst. Growth* **386**, 47 (2014).
- [16] E. Husanu, D. Ercolani, M. Gemmi, and L. Sorba, *Nanotechnology* **25**, 205601 (2014).
- [17] M. Murayama and T. Nakayama, *Phys. Rev. B* **49**, 4710 (1994).

- [18] C.-Y. Yeh, S.-H. Wei, and A. Zunger, *Phys. Rev. B* **50**, 2715 (1994).
- [19] A. De and C. E. Pryor, *Phys. Rev. B* **81**, 155210 (2010).
- [20] A. Belabbes, C. Panse, J. Furthmüller, and F. Bechstedt, *Phys. Rev. B* **86**, 075208 (2012).
- [21] T. Akiyama, K. Nakamura, T. Ito, and A. J. Freeman, *Appl. Phys. Lett.* **104**, 132101 (2014).
- [22] P. Mohan, J. Motohisa, and T. Fukui, *Appl. Phys. Lett.* **88**, 013110 (2006).
- [23] P. Mohan, J. Motohisa, and T. Fukui, *Nanotechnology* **16**, 2903 (2005).
- [24] H. Yoshida, K. Ikejiri, T. Sato, S. Hara, K. Hiruma, J. Motohisa, and T. Fukui, *J. Cryst. Growth* **312**, 52 (2009).
- [25] K. Tomioka, K. Ikejiri, T. Tanaka, J. Motohisa, S. Hara, K. Hiruma, and T. Fukui, *J. Mater. Res.* **26**, 2127 (2011).
- [26] F. Ishizaka, K. Ikejiri, K. Tomioka, and T. Fukui, *Jpn. J. Appl. Phys.* **52**, 04CH05 (2013).
- [27] C.-Y. Yeh, Z.W. Lu, S. Froyen, and A. Zunger, *Phys. Rev. B* **46**, 10086 (1992).
- [28] M. A. Verheijen, R. E. Algra, M. T. Borgström, G. Immink, E. Sourty, W. J. P. van Enckevort, E. Vlieg, and E. P. A. M. Bakkers, *Nano Lett.* **7**, 3051 (2007).

## Chapter 6

# Growth of Wurtzite InP/AlGaP Core-Multishell Nanowires

---

We report on the selective-area growth and characterization of wurtzite (WZ) InP/AlGaP core-multishell nanowires. Quantum well (QW) structures were fabricated in AlGaP multishells by changing the alloy composition. Transmission electron microscopy revealed that the AlGaP multishells were grown with a WZ structure on the side of the WZ InP core. The lattice constants of the WZ InP core and WZ AlGaP shell were determined by X-ray diffraction. Cathodoluminescence studies showed that the WZ AlGaP QW with an Al composition of 20% exhibited green emissions at 2.37 eV. These results open the possibility of fabricating green light-emitting diodes using WZ AlGaP-based materials.

### 6.1 Introduction

Color-mixed red-green-blue (RGB) light-emitting diodes (LEDs) are promising candidates for future solid-state lighting and display technology owing to their potential advantages in terms of energy conversion efficiency and color rendering index (CRI) [1,2]. However, achieving high-efficiency LEDs in the green region is challenging owing to a lack of suitable semiconductor materials; this region is known as the “green gap” [3,4]. Non-nitride III-V materials having wurtzite (WZ) structures have recently provided a new approach to overcoming this problem. Some theories predict that GaP and AlP in WZ structures have direct band gaps in contrast to conventional zinc blende (ZB) structures that have indirect band gaps [5-7]. Although this new approach has been experimentally demonstrated in WZ GaP [8,9] and

WZ AlInP [10],<sup>1</sup> such WZ materials with the quantum well (QW) structures required for LED applications have not been reported so far. In nanowire (NW) structures, radial core-multishell (CMS) NWs with QW structures are suitable for LED applications [11,12]. In this study, we report the growth and characterization of WZ InP/AlGaP CMS NWs with QW structures for the green spectral region. The WZ AlGaP with an Al composition of approximately 20% is expected to have a band gap energy in the green spectral region on the basis of the calculations of their band structures [6,7].

## 6.2 Experimental procedure

CMS NWs were synthesized by selective-area metal organic vapor phase epitaxy (SA-MOVPE). In SA-MOVPE, InP NWs can be grown with a pure WZ structure by properly adjusting the growth conditions [13-15]. The crystal structure transfer method [16-18] was applied to these WZ InP NWs for radial multishell growth. First, a 20-nm-thick SiO<sub>2</sub> layer was deposited on an InP (111)A substrate by plasma sputtering, and the SiO<sub>2</sub> layer was partially removed by electron-beam (EB) lithography and wet chemical etching. SiO<sub>2</sub> patterns were designed to be a periodic array of openings with a diameter of 130 nm. SA-MOVPE was performed in a low-pressure MOVPE reactor using trimethylaluminum (TMAI), trimethylgallium (TMGa), trimethylindium (TMIn), and tertiarybutylphosphine (TBP) as source materials. Prior to the growth, the native oxide on the openings was removed by thermal cleaning for 5 min at 600 °C in hydrogen and TBP ambient. After thermal cleaning, WZ InP NWs were grown for 15 min at 660 °C with a V/III ratio of 18, which is the typical condition for growing WZ structures [13]. The partial pressures of TMIn and TBP were  $2.7 \times 10^{-6}$  and  $4.9 \times 10^{-5}$  atm, respectively. Low-temperature (LT) AlGaP shells were then grown for 7 min at 600 °C with a V/III ratio of 650 to prevent P desorption from InP NWs. The respective partial pressures of TMAI, TMGa, and TBP were  $2.4 \times 10^{-7}$ ,  $2.4 \times 10^{-7}$ , and  $3.1 \times 10^{-4}$  atm, which correspond to the TMAI supply ratio,  $[\text{TMAI}]/([\text{TMAI}]+[\text{TMGa}])$ , of 0.50 in the vapor phase. After LT AlGaP shell growth, three AlGaP shell layers were grown to fabricate QW structures by changing the TMAI supply ratios. The inner barrier layer was grown for 20 min at 750 °C with a V/III ratio of 320. The respective partial pressures of TMAI, TMGa, and TBP were

$4.8 \times 10^{-7}$ ,  $4.8 \times 10^{-7}$ , and  $3.1 \times 10^{-4}$  atm, which correspond to the TMAI supply ratio of 0.50 in the vapor phase. The QW layer was grown for 3 min at 700 °C with a V/III ratio of 320. The respective partial pressures of TMAI, TMGa, and TBP were  $1.9 \times 10^{-7}$ ,  $7.7 \times 10^{-7}$ , and  $3.1 \times 10^{-4}$  atm, which correspond to the TMAI supply ratio of 0.20 in the vapor phase. The outer barrier layer was grown for 10 min at 700 °C with a V/III ratio of 320. The partial pressures of TMAI, TMIn, and TBP were the same as those of the inner barrier layer. Finally, the GaP shell was grown for 1 min at 700 °C with a V/III ratio of 650 as a capping layer to prevent oxidation of AlGaP. The partial pressures of TMGa and TBP were  $9.6 \times 10^{-7}$  and  $6.2 \times 10^{-4}$  atm, respectively.

The morphology, crystal structures, and compositions of CMS NWs were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDX) combined with scanning transmission electron microscopy (STEM). The electron-beam projection was parallel to the  $\langle -110 \rangle$  direction. X-ray diffraction (XRD) measurements were carried out to investigate the crystal structures of the NW assembly. The NW pitch was 1600 nm and the investigated sample area was about 4 mm<sup>2</sup>, in which more than one million NWs were included. Cathodoluminescence (CL) measurements were performed at 34 K on a single CMS NW with an acceleration voltage of 7 kV. On the basis of the calculation by Kanaya and Okayama [19], the penetration depth of electrons was about 500 nm under this condition, whereas most of the electrons were generated within a fraction of the penetration depth.

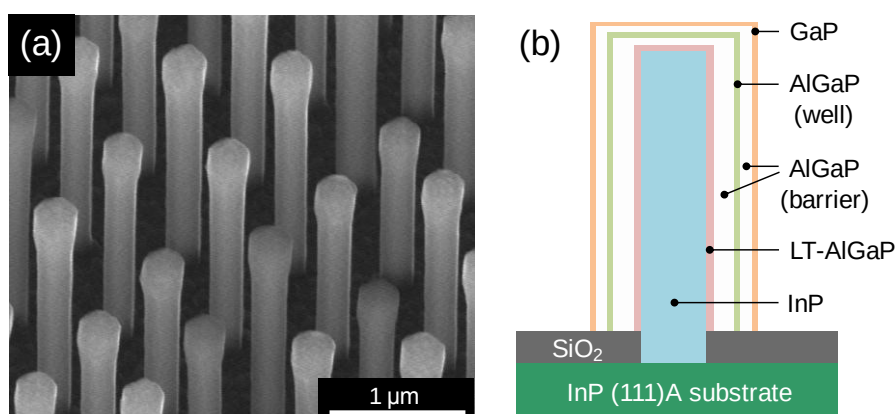


**Fig. 6-1** (a) 30°-tilted view SEM image of InP/AlGaP CMS NWs. (b) Schematic illustration of grown layers of the CMS NW.

### 6.3 Nanowire growth and quantum well structure

An SEM image and a schematic illustration of InP/AlGaP CMS NWs with QW structures are shown in Fig. 6-1. The NWs resembled hexagonal pillars with  $\{-110\}$  side facets. The NW pitch was 600 nm. The average height and total diameter of the CMS NWs were 2.6  $\mu\text{m}$  and 240 nm, respectively. A slightly larger diameter was found at the tip of the NWs, which corresponds to the AlGaP shell grown on top of the InP core. From the SEM image, no tapering or bending of the NWs were observed, while polycrystal deposition on  $\text{SiO}_2$  films was observed. The deposition began to appear when the AlGaP shell growth time was 20 min or more.

To confirm QW structures fabricated in the AlGaP shell, we investigated the compositions of the CMS NWs by EDX measurements. A high-angle annular dark-field (HAADF) STEM image of a NW cross section of the middle part and corresponding EDX mappings are shown in Fig. 6-2. From these images, the diameter of the InP core and the thickness of the AlGaP shell were determined to be approximately 125 and 50 nm, respectively. The QW thickness was about 3 nm. The two barrier layers had different thicknesses because the growth time of the outer barrier layer was shorter than that of the inner barrier layer. This is also because the growth rate of the outer AlGaP shell decreased as the growth time increased probably owing to the increasing amount of polycrystals deposited on the  $\text{SiO}_2$  mask area.

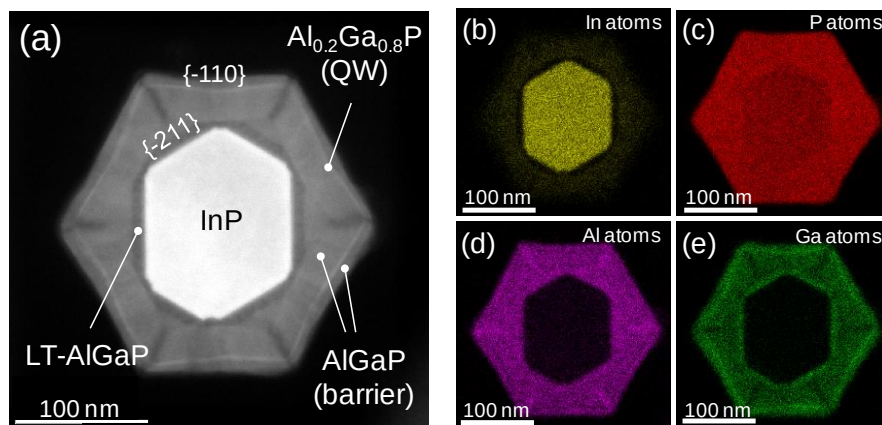


**Fig. 6-2** Cross-sectional HAADF STEM image of a CMS NW and corresponding EDX mappings of (b) In, (c) P, (d) Al, and (e) Ga, showing the existence of a QW structure.

Fig. 6-2(a) shows two types of black contrast. The black contrast around the InP core resulted from the low crystal quality of the LT AlGaP shell layer. The other black contrast along the  $\langle -211 \rangle$  radial directions was due to aluminum segregation, which commonly appears in aluminum-containing shell layers, such as GaAs/AlInP core-shell NWs [20]. Aluminum segregation was also found in EDX mappings in Figs. 6-2(d) and 6-2(e). In addition to aluminum segregation, indium diffusion appeared in the AlGaP shell, which can be seen in both the EDX mapping and the line scan in Fig. 6-2(b) and Fig. 6-3, respectively. The reason for this indium diffusion is that the growth temperature of the AlGaP shell is higher than that of the InP core. From Fig. 6-3, the aluminum and gallium compositions in the barrier layers were almost the same, excluding the effect of indium diffusion, which is equal to the supply ratio of TMAI and TMGa. Therefore, the aluminum and gallium compositions in the QW layer were estimated to be 20 and 80%, respectively.

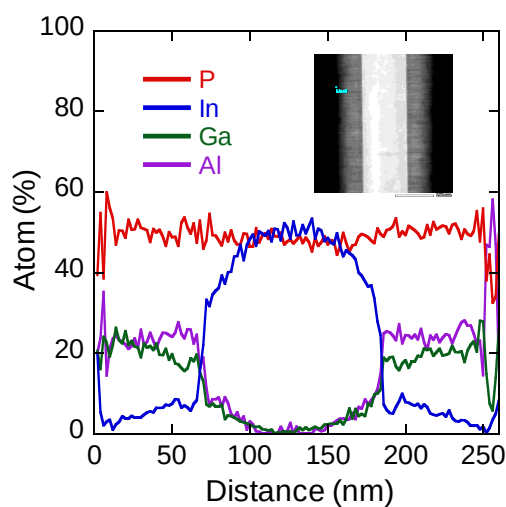


**Fig. 6-3** EDX line scan of a CMS NW along the lateral direction and corresponding HAADF STEM image (inset).

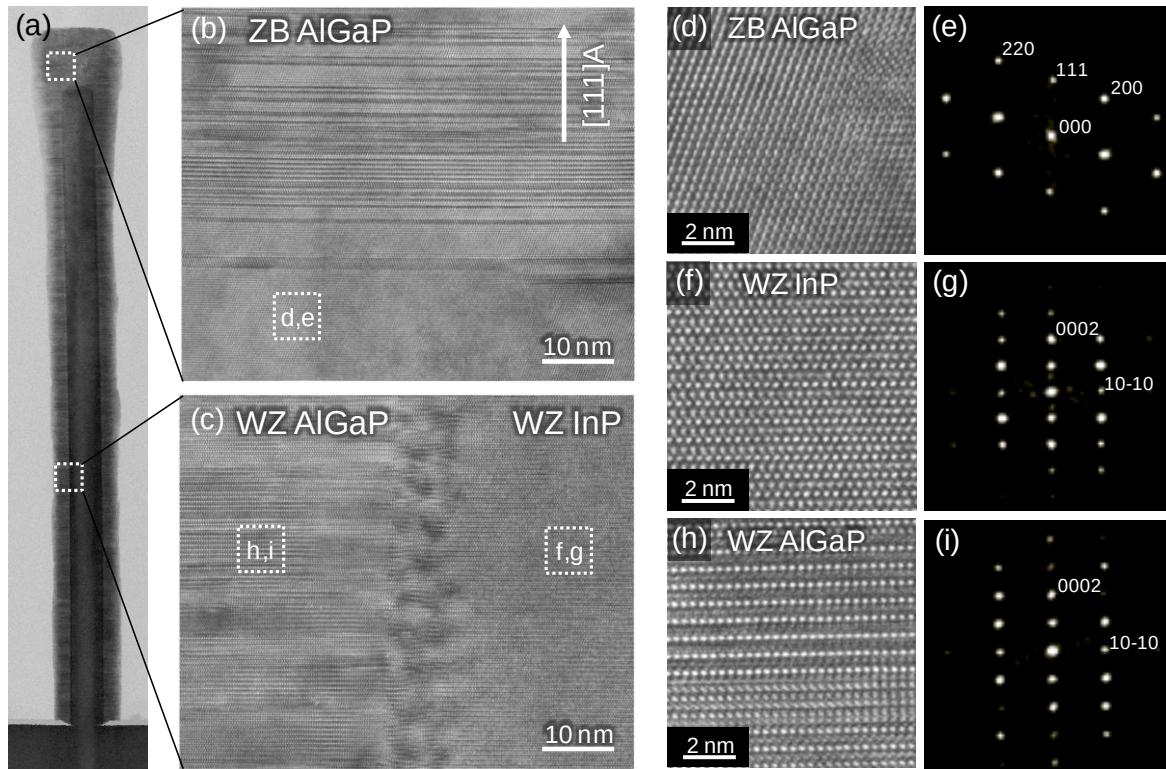


**Fig. 6-4** Cross-sectional TEM images of an InP/AlGaP CMS NW. The incident of the electron beam was parallel to the  $\langle -110 \rangle$  direction of the substrate. (a) Overall TEM image of the NW. (b) and (c) Enlarged TEM images at the top and side of the NW shown in (a). (d)–(i) High-resolution TEM images and corresponding FFT images of the top AlGaP shell, side AlGaP shell, and InP core.

## 6.4 Structural characterization

To confirm the crystal structures of a CMS NW, we performed TEM and fast-Fourier-transform (FFT) analyses of a NW, and the results are shown in Fig. 6-4. Three parts of the NW were investigated. First, the InP core had a WZ structure with a few stacking faults per micrometer. Second, the AlGaP shell on top of the InP core had a ZB structure with stacking faults. In Fig. 6-4(a), the diameter of the top part of the NW was larger than that of the middle part. This is another piece of evidence showing that the AlGaP shell on the top consists of ZB structures because stacking faults and lateral growth continuously occur until stable  $\{-110\}$  facets are formed in the case of selective-area growth of NWs with ZB structures

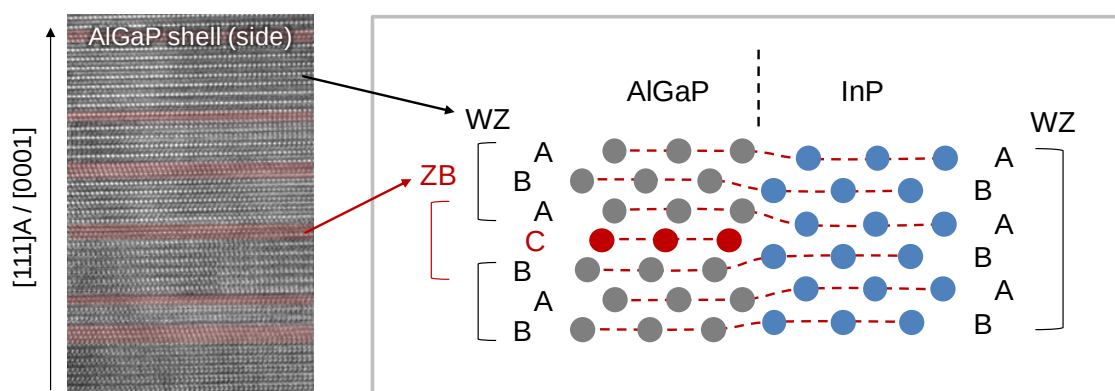


**Fig. 6-5** Schematic illustration of the formation of stacking faults at the InP/AlGaP core-shell interface.

[14,21]. Third, the AlGaP shell on the side of the InP core mainly had a WZ structure, but it partly had a ZB structure resulting from stacking faults. The appearance ratio of WZ segments in the AlGaP shell was calculated to be 84% by statistical analysis [22]. We consider that the stacking faults and ZB segments appeared at the interface of the InP core and AlGaP shell for the following reasons. For planar layers, the critical thickness is calculated to be less than 1 nm from the lattice mismatch of 7.0% between InP and  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{P}$ . When the AlGaP shell is grown on the InP core, it can be coherently grown on the InP core until it reaches a critical thickness, and then misfit dislocations appear in the AlGaP shell. As a result, additional layers are introduced in WZ layers of the AlGaP shell that has a smaller lattice constant, resulting in ZB segments such as “ABABCBCB...” and “ABACABAB...”, as shown in Fig. 6-5.

Fig. 6-6 shows an XRD reciprocal space mapping (RSM) around the ZB (331) reflection of the InP (111)A substrate. The WZ (10-15) and ZB (331) peaks were observed for the InP core and substrate, and the WZ (10-15), ZB (224) twin, and faint ZB (331) peaks were observed for the AlGaP shell. The strong intensity of the WZ InP (10-15) peak indicates that the InP core has a high crystal quality in the WZ structure. In contrast, the intensity of the WZ AlGaP (10-15) peak was relatively low and broad owing to the low crystal quality resulting from stacking faults. The ZB (224) twin peak and faint spot of ZB (331) for AlGaP were attributed to the ZB AlGaP shell with rotational twins grown on the top of the InP core, because no ZB (224) twin peak was observed for both the InP core and substrate. These results are in good agreement with those of TEM analysis.

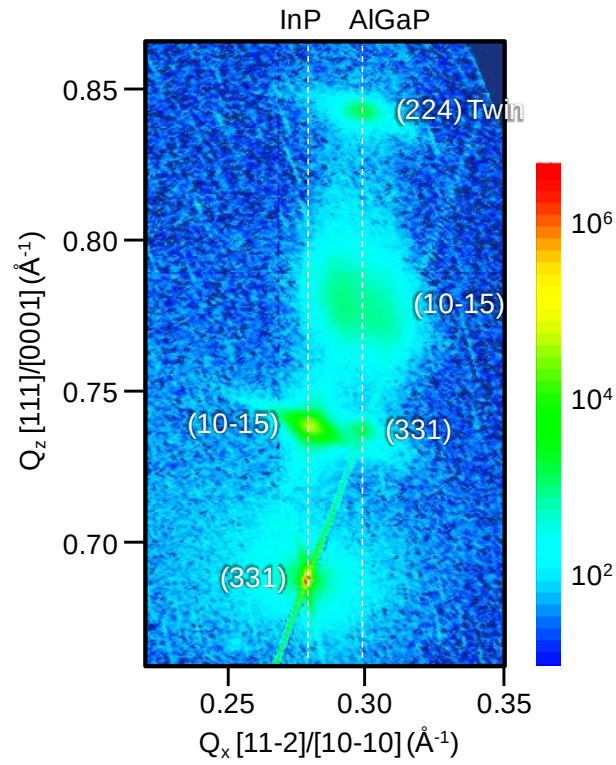


**Fig. 6-6** XRD RSM of InP/AlGaP CMS NWs recorded around the ZB (331) reflection of the InP (111)A substrate.

**Table 6-1** WZ lattice constants of the InP core and AlGaP shell.

| Material                                 | Method                    | $a$ (Å) | $c$ (Å) | $c/a$ |
|------------------------------------------|---------------------------|---------|---------|-------|
| WZ InP                                   | Conversion                | 4.1498  | 6.7766  | 1.633 |
|                                          | Experimental <sup>1</sup> | 4.1423  | 6.8013  | 1.642 |
|                                          | This work                 | 4.15    | 6.77    | 1.63  |
| WZ Al <sub>0.5</sub> Ga <sub>0.5</sub> P | Conversion                | 3.8587  | 6.3012  | 1.633 |
|                                          | This work                 | 3.93    | 6.43    | 1.64  |

<sup>1</sup> From ref 23.

Next, we measured the axial and radial lattice constants,  $c_{WZ}$  and  $a_{WZ}$ , of the WZ InP core and WZ AlGaP shell from the peak positions of WZ (10-15) reflections, and compared the measured values with relaxed WZ lattice constants geometrically converted from ZB lattice constants. For the conversion, the relations  $a_{WZ} = 1/\sqrt{2} a_{ZB}$  and  $c_{WZ} = \sqrt{8/3} a_{WZ}$  were used, and Vegard's law was applied to the calculations of AlGaP lattice constants. The calculation results are summarized in Table 6-1. For WZ InP, both the measured  $a_{WZ}$  and  $c_{WZ}$  values were almost the same as the converted  $a_{WZ}$  and  $c_{WZ}$  values. Kriegner et al. have reported that free-standing WZ InP is elongated in the  $c$ -axis direction and compressed in the  $a$ -axis direction as compared with the converted values [23]. These tendencies were also found in other III-V NWs [24,25]. However, in this study, no such tendency was found probably because the WZ InP core was surrounded by an AlGaP shell that has a smaller lattice constant and was therefore subject to compressive strain in the  $c$ -axis direction. For WZ AlGaP, both the measured  $a_{WZ}$  and  $c_{WZ}$  values were substantially larger than the converted  $a_{WZ}$  and  $c_{WZ}$  values. This implies the incorporation of InP, which has a larger lattice constant. The measured lattice constants of WZ AlGaP correspond to those of WZ AlGaInP with about 10% indium when they are geometrically converted using Vegard's law. This result is consistent with the EDX analysis results shown in Fig. 6-3.

## 6.5 Optical characterization

To understand the effects of WZ and ZB structures on optical properties, we carried out CL measurements of a single NW at 34 K. The electron beam was scanned along the NW axis with 16 measured points at intervals of about 150 nm, as shown in Fig. 6-7(a). The obtained CL spectra are shown in Fig. 6-7(b). For clarity of CL peak energies, representative CL spectra of the top and middle of the NW are shown in Fig. 6-7(c) in a logarithmic scale. The peaks at 1.42 and 1.62 eV correspond to emissions from the ZB InP substrate and WZ InP core NW. The peaks at 1.36–1.38 eV, observed at beam positions #15 and #16 in Fig. 6-7(b), correspond to bound exciton and donor-acceptor emissions of the InP substrate [26]. The peak energy for ZB InP is equivalent to the known value, whereas the peak energy for WZ InP is slightly higher than those previously reported [13]. The theoretical band gap energy of WZ InP is 1.502

eV, and the band gap energy of previously reported WZ InP NWs is 1.54 eV. In this study, the WZ InP core has compressive strain arising from the AlGaP shell, which can lead to an increase in band gap energy. If the band gap energy of the WZ InP NWs is the same as that previously reported, the effect of compressive strain will lead to an energy shift of 80 meV.

Regarding the AlGaP multishell, CL emissions were observed at 2.18 and 2.37 eV. From the electron beam spot, the former can be attributed to ZB AlGaP at the top of the InP core, and the latter can be attributed to WZ AlGaP on the side. We consider that these two emissions originated from the AlGaP QWs because we found in a similar material combination that simple core-shell NWs without QW structures exhibited no CL emissions from the shells. Although the origin of the peak at 2.30 eV observed at beam positions #3–#5 in Fig. 6-7(b) was unclear, it was probably related to WZ/ZB type II junctions at the interface of WZ and ZB AlGaP shells. The reason for the low emission intensity was that the generated electron-hole pairs were easily moved from the AlGaP shell to the InP core. The results indicate that green emissions at 2.37 eV (523 nm) were evident from the WZ AlGaP QW, which had a shorter wavelength than reported ones [8,10].

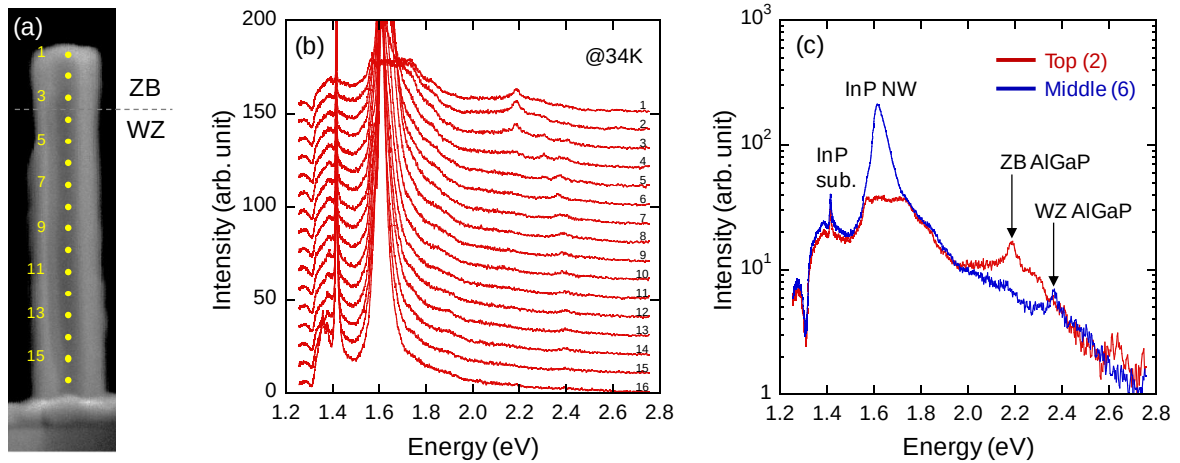


**Fig. 6-7** CL spectra of a single InP/AlGaP CMS NW measured at 34 K. The electron beam was scanned along the NW axis. (a) Measured points and (b) corresponding CL spectra of the NW. (c) Representative CL spectra at the top and middle of the NW shown in a logarithmic scale.

The band gap of WZ  $\text{Al}_{0.2}\text{Ga}_{0.8}\text{P}$  is estimated to be 2.394 eV by linear approximation from the values found in the literature [6,27]. WZ  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{P}/\text{Al}_{0.2}\text{Ga}_{0.8}\text{P}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{P}$  QW is predicted to show type I band alignment with the conduction and valence band offsets of 93 and 112 meV, and the quantum-confinement effect of 3-nm-thick QW leads to an energy blue shift of 111 meV. In addition, the effect of incorporating 10% indium, which was suggested from XRD and EDX measurements, leads to an energy red shift of 92 meV. Therefore, the emission energy of our WZ QW is estimated to be 2.413 eV. This estimation is consistent with the experimental result. Calculation based on a ZB QW gave similar confinement energy and red shift owing to indium incorporation; thus, this ZB QW is less likely. However, the analysis of the nature of these emissions in greater detail is difficult at present and strain effects and the variations in the composition and the QW thickness should be considered to achieve more accurate assessment. In this regard, other optical investigations, such as time-resolved measurements, are required to clarify whether WZ AlGaP QWs have direct band gaps.

## 6.6 Conclusions

We investigated the growth morphology, composition, and structural and optical properties of WZ InP/AlGaP CMS NWs grown by the crystal structure transfer method. Cross-sectional STEM and EDX images showed that the QW structures were formed in the AlGaP multishell. TEM analysis revealed that the InP core had a WZ structure with very few stacking faults and that the AlGaP multishell was grown with a WZ structure on the side of the InP core, whereas it was grown with a ZB structure at the top. From XRD measurements, the measured lattice constants of WZ InP were found to be almost the same as the calculated values, while those of WZ AlGaP were larger owing to indium outdiffusion. Finally, we observed green emissions at 2.37 eV from the WZ AlGaP QW and showed that a difference in crystal structure affects the CL emission energy in AlGaP QWs. Our results demonstrate a pathway for preparing green LEDs using WZ AlGaP-based materials.

## Bibliography

- [1] J. Y. Tsao, M. E. Coltrin, M. H. Crawford, and J. A. Simmons, *Proc. IEEE* **98**, 1162 (2010).
- [2] Y. H. Ra, R. Wang, S. Y. Woo, M. Djavid, S. Sadaf, J. Lee, G. A. Botton, and Z. Mi, *Nano Lett.* **16**, 4608 (2016).
- [3] M. R. Krames, O. B. Shchekin, R. Mueller-Mach, G. O. Mueller, L. Zhou, G. Harbers, and M. G. Craford, *J. Disp. Technol.* **3**, 160 (2007).
- [4] M. Auf der Maur, A. Pecchia, G. Penazzi, W. Rodrigues, and A. Di Carlo, *Phys. Rev. Lett.* **116**, 027401 (2016).
- [5] M. Murayama and T. Nakayama, *Phys. Rev. B* **49**, 4710 (1994).
- [6] A. De and C. E. Pryor, *Phys. Rev. B* **81**, 155210 (2010).
- [7] F. Bechstedt and A. Belabbes, *J. Phys.: Condens. Matter* **25**, 273201 (2013).
- [8] S. Assali, I. Zardo, S. Plissard, D. Kriegner, M. A. Verheijen, G. Bauer, A. Meijerink, A. Belabbes, F. Bechstedt, J. E. M. Haverkort, and E. P. A. M. Bakkers, *Nano Lett.* **13**, 1559 (2013).
- [9] Berg, S. Lehmann, N. Vainorius, A. Gustafsson, M-E. Pistol, L. R. Wallenberg, L. Samuelson, and M. T. Borgström, *J. Cryst. Growth* **386**, 47 (2014).
- [10] Y. Hiraya, F. Ishizaka, K. Tomioka, and T. Fukui, *Appl. Phys. Express* **9**, 035502 (2016).
- [11] K. Tomioka, J. Motohisa, S. Hara, K. Hiruma, and T. Fukui, *Nano Lett.* **10**, 1639 (2010).
- [12] Berg, S. Yazdi, A. Nowzari, K. Storm, V. Jain, N. Vainorius, L. Samuelson, J. B. Wagner, and M. T. Borgstrom, *Nano Lett.* **16**, 656 (2016).
- [13] Y. Kitauchi, Y. Kobayashi, K. Tomioka, S. Hara, K. Hiruma, T. Fukui, and J. Motohisa, *Nano Lett.* **10**, 1699 (2010).
- [14] K. Ikejiri, Y. Kitauchi, K. Tomioka, J. Motohisa, and T. Fukui, *Nano Lett.* **11**, 4314 (2011).
- [15] Q. Gao, D. Saxena, F. Wang, L. Fu, S. Mokkalapati, Y. Guo, L. Li, J. W.-Leung, P. Caroff, H. H. Tan, and C. Jagadish, *Nano Lett.* **14**, 5206 (2014).
- [16] R. E. Algra, M. Hocevar, M. A. Verheijen, I. Zardo, G. G. W. Immink, W. J. P. van Enkevort, G. Abstreiter, L. P. Kouwenhoven, E. Vlieg, and E. P. A. M. Bakkers, *Nano Lett.* **11**, 1690 (2011).
- [17] F. Ishizaka, Y. Hiraya, K. Tomioka, and T. Fukui, *J. Cryst. Growth* **411**, 71 (2015).
- [18] M. Heurlin, T. Stankevič, S. Mickevičius, S. Yngman, D. Lindgren, A. Mikkelsen, R. Feidenhans'l, M. T. Borgström, and L. Samuelson, *Nano Lett.* **15**, 2462 (2015).

- 
- [19] K. Kanaya and S. Okayama, *J. Phys. D: Appl. Phys.* **5**, 43 (1972).
- [20] J. B. Wagner, N. Sköld, L. R. Wallenberg, and L. Samuelson, *J. Cryst. Growth* **312**, 1755 (2010).
- [21] K. Ikejiri, T. Sato, H. Yoshida, K. Hiruma, J. Motohisa, S. Hara, and T. Fukui, *Nanotechnology* **19**, 265604 (2008).
- [22] K. Tomioka, J. Motohisa, S. Hara, and T. Fukui, *Jpn. J. Appl. Phys.* **46**, L1102 (2007).
- [23] D. Kriegner, E. Wintersberger, K. Kawaguchi, J. Wallentin, M. T. Borgström, and J. Stangl, *Nanotechnology* **22**, 425704 (2011).
- [24] D. Kriegner, C. Panse, B. Mandl, K. A. Dick, M. Keplinger, J. M. Persson, P. Caroff, D. Ercolani, L. Sorba, F. Bechstedt, and J. Stangl, *Nano Lett.* **11**, 1483 (2011).
- [25] D. Kriegner, S. Assali, A. Belabbes, T. Etzelstorfer, V. Holý, T. Schüllli, F. Bechstedt, E. P. A. M. Bakkers, G. Bauer, and J. Stangl, *Phys. Rev. B* **88**, 115315 (2013).
- [26] K. Kuriyama, K. Ushiyama, T. Tsunoda, M. Uchida, and K. Yokoyama, *J. Electron. Mater.* **27**, 462 (1998).
- [27] Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, *J. Appl. Phys.* **89**, 5815 (2001).



## Chapter 7

# Growth of Wurtzite InP/AlInP Core-Multishell Nanowires

---

We demonstrated a formation of all wurtzite (WZ) InP/AlInP core-multishell (CMS) nanowires (NWs) by selective-area growth with the crystal structure transfer method. The CMS NWs consisting of AlInP-based double heterostructure showed that the crystal structure of the multi-shell succeeded to the WZ phase from the WZ InP NW by the crystal structure transfer method. Transmission electron microscopy revealed that the core-shell interface had a few stacking faults due to lattice mismatch. In addition, lattice constants of WZ AlInP with a variation of Al content were determined by X-ray diffraction reciprocal space mappings, and the WZ AlInP shell had tensile strain along the *c*-axis. The WZ AlInP shells (Al content: 25–54%) showed cathode luminescence emissions at 1.6–2.1 eV, possibly related to In-rich domains due to composition fluctuation in the WZ AlInP shell.

### 7.1 Introduction

Semiconductor nanowires (NWs) have attracted considerable attention because of their potential applications such as field-effect transistors [1,2], light-emitting diodes (LEDs) [3-6], and solar cells [7,8]. In contrast, the unique phenomenon of NW material in terms of crystallography is that they can be grown with a pure wurtzite (WZ) structure by properly controlling supersaturations with the growth temperature, V/III ratio, and doping amount [9-16], even though their stable phase in bulk forms has a zincblende (ZB) structure. This crystal phase engineering enables fabrication of novel device applications of NWs due to

significant effect on the physical properties of semiconductor materials. It has been theoretically predicted that when the crystal phases of indirect band gap materials such as GaP and AlP are changed from ZB to WZ, their band gaps also change from indirect to direct due to zone folding effects [17,18]. These predictions have been experimentally proven by WZ  $\text{Al}_x\text{Ga}_{1-x}\text{P}$  NWs with  $0 \leq x \leq 0.46$ , and the efficiency of LEDs can be increased by the crystal phase transition [19].

In visible LEDs, the low efficiency in the green and yellow regions, known as the green gap, is an important issue. Although nitride materials have been extensively studied to achieve high-efficiency green LEDs, there are still no good candidates for high-efficiency yellow LEDs, which could be used as the fourth LED to realize four-color (red, yellow, green, and blue) white LEDs with a high color rendering index (CRI) [20]. Phosphide materials having the band gap in the yellow region, such as AlGaInP and AlInP, have a significant decrease in emission efficiency in the conventional ZB structure due to the transition from direct to indirect when increasing Al compositions. However, since phosphide materials (InP, GaP, and AlP) in the WZ structure have direct band gaps according to the calculation of their band structure [17], their ternary and quaternary alloys, such as AlInP, AlGaP, InGaP, and AlInGaP, are expected to have direct band gaps in the entire compositional range. Among these WZ materials, band gap of WZ AlInP can vary from 1.47 to 2.97 eV by changing the alloy composition and therefore can cover all visible regions. In addition, planar WZ  $\text{Al}_{0.58}\text{In}_{0.42}\text{P}$ , which is higher than that of the crossover point in ZB structure (Al composition of 40%), has recently been suggested to have a direct band gap transition in the green spectral region [21]. Thus, WZ AlInP opens up a new possibility of fabricating high-efficiency LEDs in the red, yellow, and green regions. In particular, WZ phosphide materials are more suitable for the yellow region than nitride materials that have a great difficulty in making high crystal quality at longer wavelength region. In NW structures, GaAs/AlInP core-shell NWs with a mixture of WZ and ZB structures have exhibited an emission of 1.9–2.1 eV from the  $\text{Al}_{0.5}\text{In}_{0.5}\text{P}$  shell [22]. However, both in NW and planar structures, relationships among the structural and optical properties and chemical composition of the WZ AlInP system have not been thoroughly investigated until now. Furthermore, understanding these relationships is of great importance to fabricate WZ AlInP or WZ AlGaInP based LEDs. In this study, we demonstrate the growth of WZ InP/AlInP core-multishell (CMS) NWs in which double heterostructures were fabricated in the AlInP

shell by changing the Al compositions and discuss their growth morphology, composition, and structural and optical properties.

Regarding fabrication methods, although WZ structures are obtained through NW growth under a particular set of conditions, another approach, known as the crystal structure transfer method, has been created for core-shell NW systems in which the crystal structure is transferred from the template core to the shell. For example, WZ Si shells were grown on WZ GaP NWs [23,24], and WZ InGaAs shells were grown on WZ InP NWs [25]. In case of selective-area metal-organic vapor-phase epitaxy (SA-MOVPE) [11], InP NWs can easily form WZ structures because of the small energy difference between the WZ and ZB structures [26]. In a previous study, we also grew WZ InP/GaP core-shell NWs using SA-MOVPE in which WZ InP NWs were used as a template for the WZ GaP shell [27]. The same approach was performed in this study.

## 7.2 Experimental procedure

The process for fabricating the NWs is as follows. SiO<sub>2</sub> layer with a thickness of 20 nm was deposited on an InP (111)A substrate by RF plasma sputtering, and hexagonal-opening patterns were defined by electron-beam lithography and wet chemical etching. The SiO<sub>2</sub> patterns were designed to be a periodic array of openings with diameters of approximately 200 nm and pitches of 1.0 μm. The SA-MOVPE of the NWs was carried out in a low-pressure MOVPE system using trimethylaluminum (TMAI), trimethylindium (TMIn), and tertiarybutylphosphine (TBP) as the source materials. Grown layers of the CMS NWs are shown in Fig. 7-1(a). For InP core growth, the growth temperature and growth time were 660°C and 15 min with a V/III ratio of 18. The partial pressures of TMIn and TBP were  $2.7 \times 10^{-6}$  and  $4.9 \times 10^{-5}$  atm, respectively. For AlInP shell growth, the active layer was grown at 600°C for 30 min, and the thin barrier layers were grown on both sides of the active layer at 600°C for 5 min for each layer. The Al content in vapor for the active layers,  $X_{\text{TMAI}} = [\text{TMAI}]/([\text{TMAI}]+[\text{TMIn}])$ , was changed to 0.20–0.57, and those for the barrier layers,  $Y_{\text{TMAI}}$ , was 0.40–0.75. The sum of the group III partial pressures was  $1.5 \times 10^{-6}$  atm, and the partial pressure of TBP was  $3.1 \times 10^{-4}$  atm. The grown structures were characterized using a scanning electron microscope (SEM) and transmission electron microscope (TEM). X-ray diffraction

(XRD) measurements were performed on an approximate  $4 \text{ mm}^2$  area, where more than one million NWs were included. Cathode luminescence (CL) measurements were carried out at 36 K for a single NW.

### 7.3 Nanowire growth

Schematic views of InP/AlInP CMS NWs are shown in Fig. 7-1. The InP core NW was used as a template for making WZ phase AlInP shell. The first AlInP barrier layer was to avoid electron-hole recombination inside the lower-bandgap InP. The InP cap layer was grown to suppress oxidation of the AlInP shell in ambient. Fig. 7-2 shows SEM images of InP/AlInP CMS NWs. The average height and total diameter of the CMS NWs were ranged from 2.5–2.8  $\mu\text{m}$  and 390–440 nm.

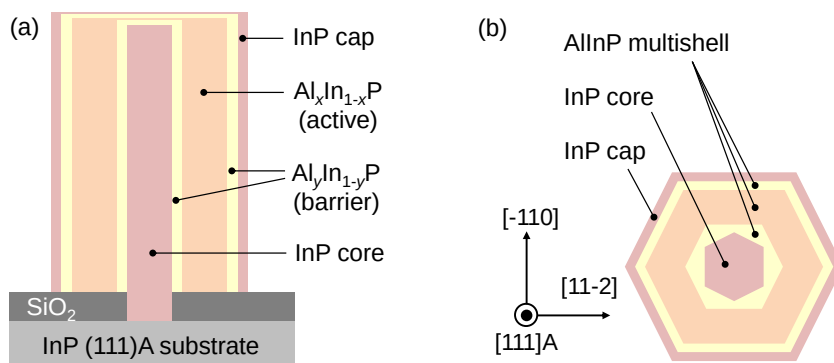


**Fig. 7-1** Schematic views from the (a) side and (b) top of the CMS NW.

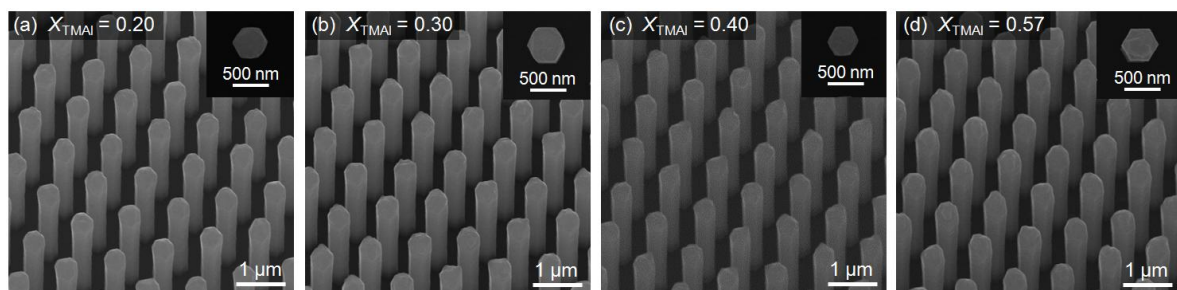


**Fig. 7-2** 30°-Tilted SEM images of the CMS NWs for  $X_{\text{TMAI}} = 0.20$ – $0.57$ . The insets show top-view SEM images, indicating the  $\{-110\}$  side facets.

In VLS growth using gold catalysts [6,25], the nanowire sample needs to be put out from the reactor and the gold catalysts are removed by wet chemical etching before the lateral shell growth because the gold catalysts enhance the axial growth. In contrast, such procedure is not required for selective-area growth, and growth direction can be switched from axial to lateral by changing only the growth conditions such as growth temperature and V/III ratio. As schematically shown in Fig. 7-1(b), the side facets of the AlInP shell were  $\{-110\}$  (equivalent to  $\{11-20\}$  in WZ notation) and  $30^\circ$  rotated from those of the InP core possessing  $\{11-2\}$  (equivalent to  $\{10-10\}$  in WZ notation) facets. The difference in facet orientation can be attributed to growth rates of  $\{-110\}$  and  $\{11-2\}$ . The  $\{11-2\}$  side facets become stable when vertical growth takes place without lateral growth, while  $\{-110\}$  become stable surface when lateral growth likely occurs. Therefore, the side facets of the CMS NWs were changed from  $\{11-2\}$  to  $\{-110\}$ . Similar facet rotations were also reported in GaP/AlGaP core-shell [19] and InP/InP core-shell [28] NWs.

## 7.4 Structural characterization

Fig. 7-3 shows high-resolution TEM images and selected area electron diffraction (SAED) patterns of a CMS NW for  $X_{\text{TMAI}} = 0.30$ . Both the template InP core and the AlInP shell had WZ structures, while the AlInP shell on top of the InP NW had a ZB structure with rotational twins around the  $\langle 111 \rangle$  axis. The difference indicates that the WZ structure can be transferred in the radial  $\langle 11-2 \rangle$  direction but was changed to a more stable ZB structure in the axial  $\langle 111 \rangle_A$  direction. The difference in Al compositions between the barrier and active layers were clearly observed in the TEM image and energy-dispersive X-ray (EDX) line scans, as shown in Figs. 7-3(b) and 7-3(f). The thicknesses of the AlInP barrier and active layers in Figs. 7-3(b) and 7-3(f) were approximately 13 nm and 74 nm. In Fig. 7-3(f), Al composition in the AlInP active layer was 0.29 on average, and inhomogeneous Al composition was possibly due to phase segregation [22]. In Fig. 7-3(d), a misfit dislocation due to lattice mismatch was observed at the interface of the InP core and AlInP barrier layer, indicating that lattice relaxation occurred across the core-shell interface. The misfit dislocation also leads to the introduction of an additional layer in the WZ AlInP shell, resulting in a stacking fault such as a

sequence of “ABCAB...”, because the lattice constant of AlInP is smaller than that of InP. It is noted that the stacking faults in the AlInP shell were originated from the core-shell interface and were not transferred from the InP core NW because it had virtually no stacking faults.

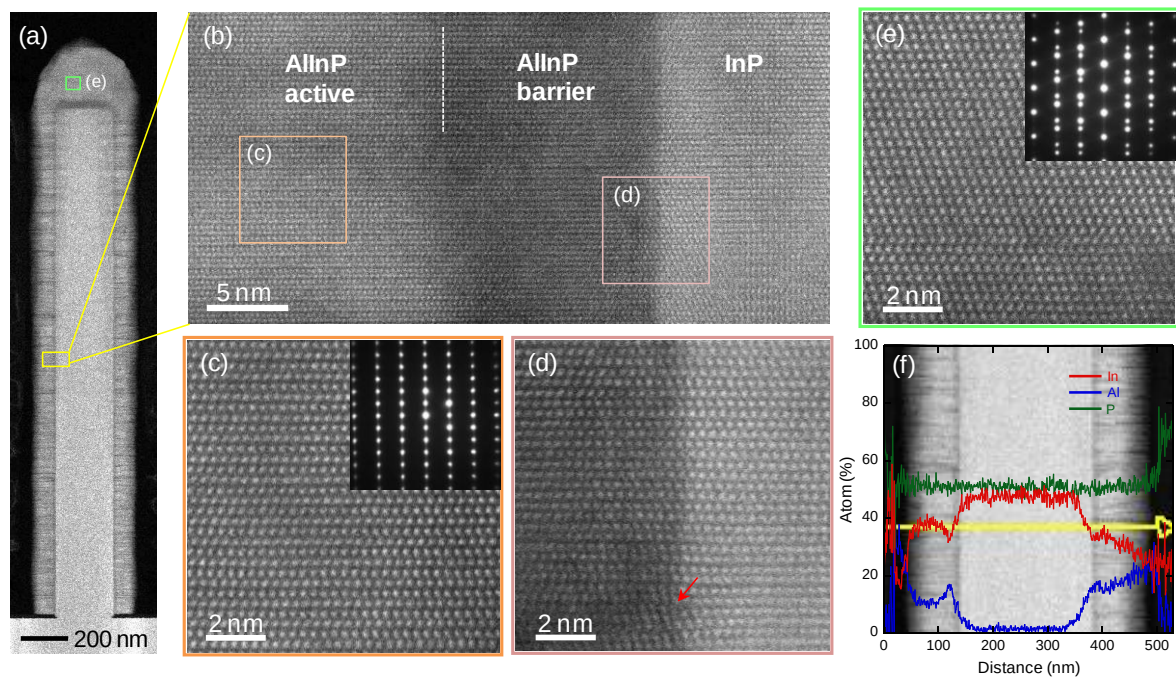


**Fig. 7-3** Cross-sectional TEM images of an InP/AlInP CMS NW for  $X_{\text{TMAI}} = 0.30$ . The incident of the electron beam was parallel to the  $\langle -110 \rangle$  direction of the substrate. (a) Overall TEM image of the CMS NW. (b) High-resolution TEM image of the AlInP shell on the side of the InP NW, which was obtained from the area marked in a yellow rectangle in (a). The interfaces of InP, the AlInP barrier, and the AlInP active layers can be clearly observed. (c, d) Enlarged TEM images of the orange and pink rectangles in (b), showing the WZ structures. Misfit dislocation was observed at the core-shell interface, as indicated by a red arrow in (d). (e) High-resolution TEM image of the AlInP shell on top of the InP NW marked in a green rectangle in (a), showing a ZB structure. The insets in (c) and (e) show the SAED patterns of each area. (f) EDX line scan along the lateral direction of the NW with a HAADF-STEM image, showing the Al-rich AlInP barrier layers around the InP core NW.

To characterize crystallinity of the CMS NWs, we characterized reciprocal space mappings (RSMs) of the CMS NWs from XRD measurements. The area around the ZB (331) reflection of the InP (111)A substrate was analyzed to distinguish between the WZ and ZB Bragg peaks. In this RSM, the WZ (10-15) peaks appear at the midpoint between the ZB (331) and ZB (224) twin peaks. Fig. 7-4 shows the RSMs of the InP/AlInP CMS NWs with different  $X_{\text{TMAI}}$  values. The WZ (10-15) and ZB (331) peaks were observed for the InP core NW and substrate, and the WZ (10-15) and ZB (224) twin peaks were observed for the AlInP shell. The strong WZ InP (10-15) peak indicates that the InP core NW has high crystal quality in the WZ structure, while the WZ AlInP (10-15) peak was slightly broader along the  $c$ -axis, implying that the WZ AlInP shell has a few stacking faults due to the lattice mismatch because the WZ AlInP (10-15) peaks become broader as  $X_{\text{TMAI}}$  becomes larger. The ZB (224) twin peak for AlInP was attributed to the ZB AlInP shell with twins grown on top of the InP core NW because the ZB (224) twin peak was not observed for either the InP core NW or substrate.

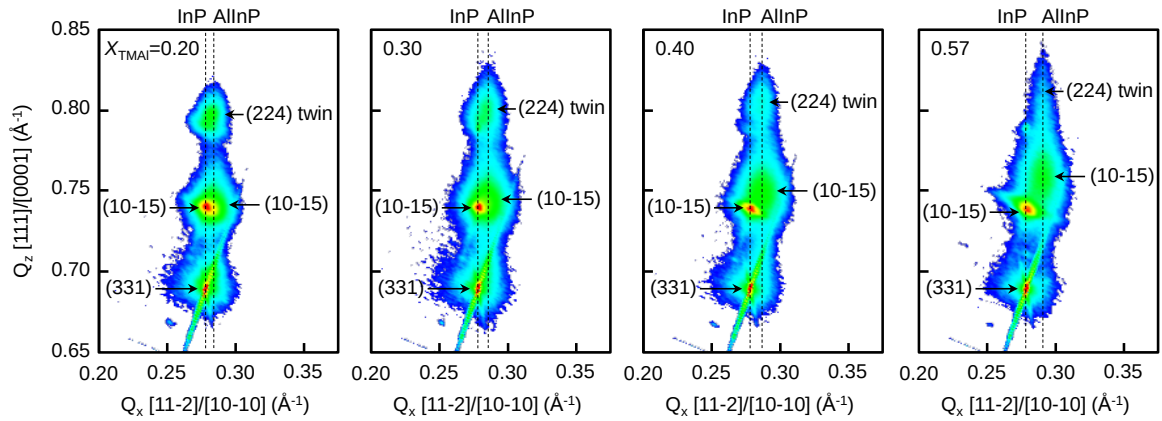


**Fig. 7-4** XRD RSMs of the InP/AlInP CMS NWs with different  $X_{\text{TMAI}}$  values, which were recorded around the ZB (331) reflection of the InP (111)A substrate. In this area, the Bragg peaks between WZ and ZB as well as between InP and AlInP can be distinguished. The WZ AlInP (10-15) peaks become broader along  $c$ -axis as  $X_{\text{TMAI}}$  becomes larger.

## 7.5 Composition and strain characterization

Next, we investigated the strain and composition of the WZ AlInP shell using Vegard's law and anisotropic elastic theory [25]. In the case of a uniaxial strain parallel to the  $c$ -axis, the strain tensor  $\varepsilon$  and stress tensor  $\sigma$  are given by

$$\varepsilon_{xx} = \varepsilon_{yy} = \frac{a - a_0}{a_0} \quad (1)$$

$$\varepsilon_{zz} = \frac{c - c_0}{c_0} \quad (2)$$

$$\sigma_{xx} = \sigma_{yy} = C_{11}\varepsilon_{xx} + C_{12}\varepsilon_{yy} + C_{13}\varepsilon_{zz} \quad (3)$$

where  $a$  and  $c$  are the strained lattice constants,  $a_0$  and  $c_0$  are the relaxed lattice constants, and  $C_{11}$ ,  $C_{12}$ , and  $C_{13}$  are elastic constants. Here, the  $z$ -axis is taken along the  $c$ -axis, and the  $x$ -axis normal to the shell layer. The strained lattice constants of WZ AlInP were determined from the maximum peak positions of the WZ (10-15) reflection in the RSMs, where we considered that the peaks from the AlInP active layers were dominant because the volume of the active layers was larger than that of the barrier layers. The relaxed lattice constants of WZ InP and AlP were geometrically converted from the lattice constants of ZB InP and AlP [29] using the relations  $a_{WZ} = 1/\sqrt{2} a_{ZB}$  and  $c_{WZ} = \sqrt{8/3} a_{WZ}$ . Then the relaxed lattice constants of WZ AlInP were calculated from the lattice constants of WZ InP and AlP using Vegard's law:

$$a_0^{\text{AlInP}} = X_{\text{Al}}a_0^{\text{AlP}} + (1 - X_{\text{Al}})a_0^{\text{InP}} \quad (4)$$

$$c_0^{\text{AlInP}} = X_{\text{Al}}c_0^{\text{AlP}} + (1 - X_{\text{Al}})c_0^{\text{InP}}. \quad (5)$$

When the WZ lattice is subjected to the uniaxial strain parallel to the  $c$ -axis,  $\sigma_{xx} = \sigma_{yy} = 0$  holds and Eq. (3) gives the relation  $\varepsilon_{xx} = -v\varepsilon_{zz}$  with the Poisson ratio:

$$v = \frac{C_{13}}{C_{11} + C_{12}}. \quad (6)$$

It is noted that the assumption for uniaxial strain ignores lattice matching conditions for the  $y$ -direction (the direction parallel to the shell layer and vertical to the  $c$ -axis) and freely strained in the  $x$  and  $y$ -directions so that Poisson effect is satisfied.

**Table 7-1** Al compositions, lattice constants and strain calculated from XRD measurements.  $X_{\text{TMAI}}$  is the Al composition in the vapor phase.  $X_{\text{Al-planar}}$  and  $X_{\text{Al-NW}}$  are the Al compositions calculated from the AlInP planar on the InP (001) and AlInP shells, respectively.  $a$  and  $c$  are the radial and axial lattice constants calculated from the maximum peak positions of the (10-15) reflections in the RSMs.  $\epsilon_{xx}$  and  $\epsilon_{zz}$  are the radial and axial strain of the AlInP shells calculated using Vegard's law and elastic theory.

| Sample | $X_{\text{TMAI}}$ | $X_{\text{Al-planar}}$ | $X_{\text{Al-NW}}$ | $a$ (Å) | $c$ (Å) | $c/a$ | $\epsilon_{xx}$ | $\epsilon_{zz}$ |
|--------|-------------------|------------------------|--------------------|---------|---------|-------|-----------------|-----------------|
| #1     | 0.20              | 0.16                   | 0.25               | 4.064   | 6.746   | 1.660 | -0.299%         | 1.355%          |
| #2     | 0.30              | 0.27                   | 0.28               | 4.056   | 6.712   | 1.665 | -0.280%         | 1.064%          |
| #3     | 0.40              | 0.37                   | 0.34               | 4.042   | 6.678   | 1.652 | -0.183%         | 0.995%          |
| #4     | 0.57              | 0.57                   | 0.54               | 3.981   | 6.591   | 1.656 | -0.239%         | 1.150%          |

The elastic constants of WZ InP and AlP can be converted from the elastic constants of ZB InP and AlP [32] using the Martin transformation [30,31]:

$$\begin{pmatrix} C_{11}^{WZ} \\ C_{12}^{WZ} \\ C_{13}^{WZ} \\ C_{33}^{WZ} \\ C_{44}^{WZ} \\ C_{66}^{WZ} \end{pmatrix} = \frac{1}{6} \begin{pmatrix} 3 & 3 & 6 \\ 1 & 5 & -2 \\ 2 & 4 & -4 \\ 2 & 4 & 8 \\ 2 & -2 & 2 \\ 1 & -1 & 4 \end{pmatrix} \begin{pmatrix} C_{11}^{ZB} \\ C_{12}^{ZB} \\ C_{44}^{ZB} \end{pmatrix} - \begin{pmatrix} \Delta^2/C_{44}^{-WZ} \\ -\Delta^2/C_{44}^{-WZ} \\ 0 \\ 0 \\ \Delta^2/C_{66}^{-WZ} \\ \Delta^2/C_{44}^{-WZ} \end{pmatrix} \quad (7)$$

where  $\Delta = \sqrt{2}/6(C_{11}^{ZB} - C_{12}^{ZB} - 2C_{44}^{ZB})$  and  $C_{ij}^{-WZ}$  was a pure rotation obtained by omitting the second term on the right-hand side. Then the elastic constants of WZ AlInP were approximated using Vegard's law:

$$C_{ij}^{\text{AlInP}} = X_{\text{Al}}C_{ij}^{\text{AlP}} + (1 - X_{\text{Al}})C_{ij}^{\text{InP}}. \quad (8)$$

Consequently, strain and composition can be numerically calculated and the results are summarized in Table 7-1. The measured Al compositions were 0.25, 0.28, 0.34, and 0.54 for  $X_{\text{TMAI}} = 0.20, 0.30, 0.40,$  and  $0.57$ , respectively. The value for  $X_{\text{TMAI}} = 0.30$  is consistent with the Al composition (0.29) obtained from EDX measurements. Fig. 7-5 shows the  $c$ -axis and  $a$ -axis lattice constants as a function of the Al composition in the AlInP active layers. The AlInP shells had tensile strain along the  $c$ -axis over a range of 1.00–1.36% and compressive strain along the  $a$ -axis over a range of 0.18–0.30%.

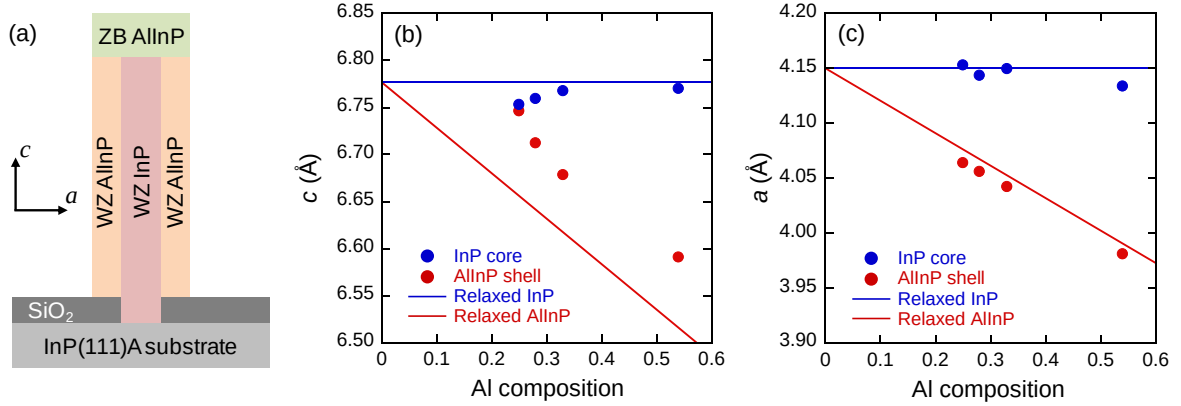


**Fig. 7-5** (a) Schematic view of grown crystal structures.  $c$  and  $a$  indicate the axial and radial directions of the NW. (b,c)  $c$ -axis and  $a$ -axis lattice constants of the WZ InP core NW and AlInP shell calculated from the maximum peak positions of the (10-15) reflections. Blue and red solid lines represent the WZ lattice constants of relaxed InP and AlInP calculated from their ZB lattice constants when they were converted from ZB structures to ideal WZ structures.

## 7.6 Optical characterization

To understand the optical properties of WZ AlInP, we carried out position-dependent CL measurements for a single NW at 36 K, where the electron beam was scanned along the NW axis. Fig. 7-6(a) shows the average CL spectrum obtained from the WZ part of an InP/AlInP CMS NW for  $X_{\text{TMAI}} = 0.57$ . The emission peaks for the WZ InP core were 1.53 and 1.49 eV, which correspond to the WZ InP band edge emission and staggered type II junctions between the WZ and ZB phases, respectively [12]. The multiple emission peaks for the WZ AlInP shell appeared at approximately 1.8–2.1 eV. Each original spectrum of the average CL spectrum in Fig. 7-6(a) is shown in Fig. 7-6(b). It seems that the linewidth of the CL spectrum originated from AlInP shell increases from the root to the tip regions of the WZ part. This may be related to the different irradiation position of the electron beam, because the generated electrons were diffused to the InP substrate at the root region of the WZ part, whereas they were diffused within the NW at the tip region of WZ part. The shift of the CL peak energy was not observed, thus, the composition of AlInP shell was macroscopically constant along the axial direction of the NW.

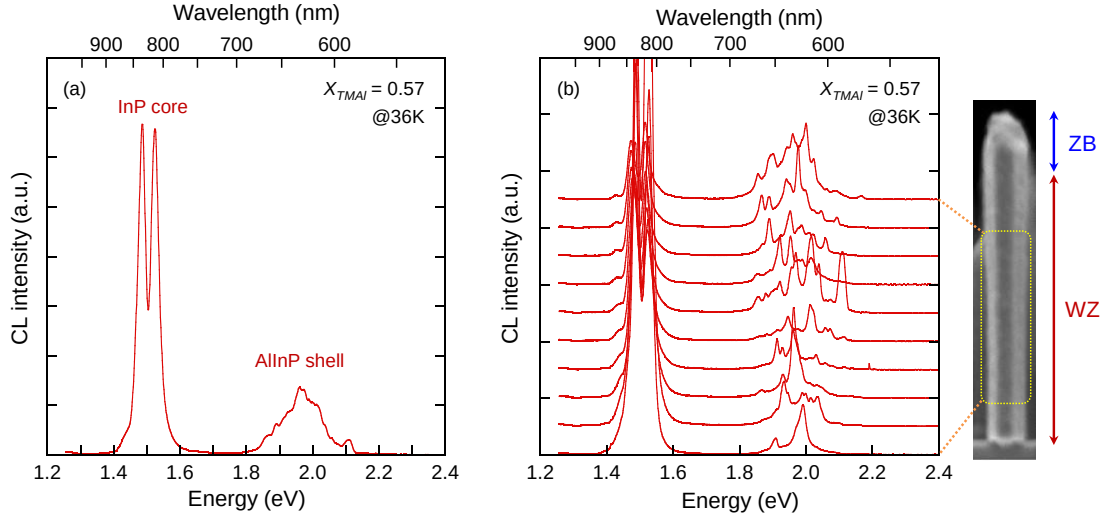


**Fig. 7-6** (a) Average CL spectrum and (b) original CL spectra obtained from the WZ part of a single InP/AlInP CMS NW for  $X_{\text{TMAI}} = 0.57$ . The average spectrum of spectra in (b) was used in (a). The electron beam was scanned along the NW axis.

Fig. 7-7(a) shows the average CL spectra of the WZ AlInP shells for all samples. The emission peaks were located at 1.6–1.8, 1.6–1.8, and 1.7–1.9 eV for WZ AlInP with Al compositions of 0.25, 0.28, and 0.34, respectively. These values are plotted as a function of Al composition in Fig. 7-7(b) and estimated to be approximately 300 meV lower than the theoretical band gaps of WZ AlInP using a linear approximation from WZ InP and AlP [17]. However, the emission energy for WZ  $\text{Al}_{0.54}\text{In}_{0.46}\text{P}$  ranged in the red-amber spectral region and could therefore potentially be applied in visible LEDs.

Three possible reasons can be considered for this energy difference between experimental and theoretical values. First, the WZ AlInP shells have tensile strain along the  $c$ -axis at a strain level of 1.00–1.36%, which was suggested from XRD measurements. This strain effect can decrease a band gap energy of 56–75 meV calculated using ZB parameters of hydrostatic deformation potential and elastic constants [29]. In a similar case of tensile strain along the  $c$ -axis, Greil et al. reported that uniaxial tensile strain in WZ GaP NWs leads to an energy shift of 250 meV toward lower energies at a strain level of 6% [32]. The strain effect on band gap energy is considered to be on the same order as our case. Second and most importantly, Sköld

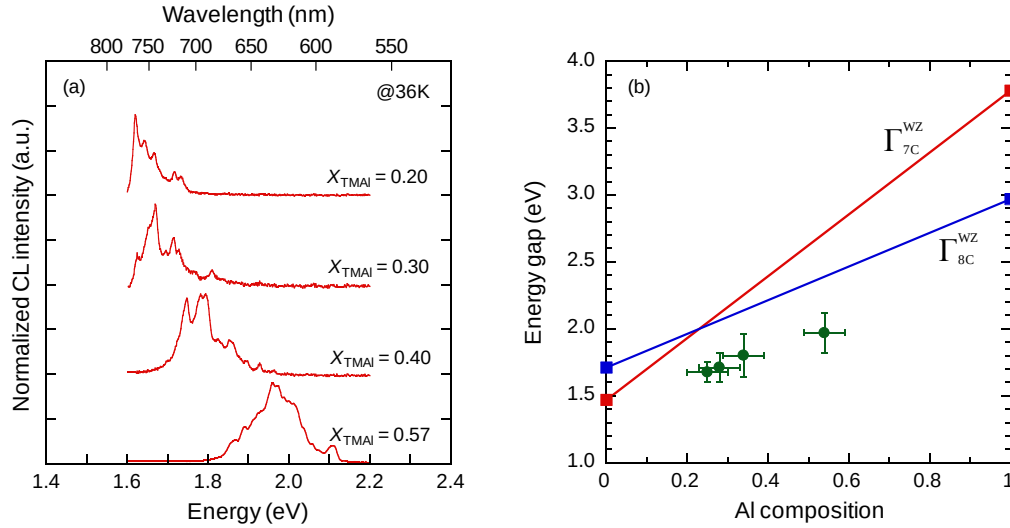


**Fig. 7-7** (a) Average CL spectra of the WZ AlInP shells of all samples, together with the calculated Al compositions. The emission peaks of the InP core NW were omitted for clarity. (b) Energy gap for WZ AlInP shells as a function of the Al composition. Experimental values obtained from panel (a) are plotted as green dots. Vertical and horizontal error bars denote energy gaps at the emission maxima and minima and Al composition fluctuation estimated from EDX, respectively. Red and blue solid lines represent calculated energy gaps for WZ AlInP at the  $\Gamma_{7C} - \Gamma_{9V}$  and  $\Gamma_{8C} - \Gamma_{9V}$  transitions, respectively, in which the parameters are taken from ref [17].

et al. reported that AlInP shells have local band gap potential minima in In-rich domains due to Al composition fluctuation, resulting in multiple emission peaks [22]. They also argued that alloy ordering of the AlInP shells decreased the band gap energy of approximately 200 meV. Such band gap reductions related to the composition fluctuation and alloy ordering were also observed in GaAs/InGaP cores-shell [33] and GaAs/AlGaAs core-shell [34] NWs. We believe the same phenomenon also occurs in our WZ AlInP shells. The multiple emission peaks were caused by the Al fluctuation in the WZ AlInP shells, which resulted in the broad peaks with approximately 300 meV. This tendency of broad peaks in AlInP is also observed in the planar structures [21]. The discrepancy between the experimental and theoretical band gap was mainly due to the alloy ordering. The alloy ordering of AlInP is commonly observed [35,36] and the theoretical band gap reduction is 270 meV at a maximum [37]. Third, stacking faults in the WZ AlInP shell may lead to a deep electron trap level because WZ/ZB heterojunctions have type II band lineup in which both the conduction band energy and valence band energy in

the ZB phase are lower than those in the WZ phase. The conduction band offset ranges from 183 meV ( $x=0$ , InP) to 271 meV ( $x=1$ , AlP) for  $\text{Al}_x\text{In}_{1-x}\text{P}$ .<sup>18</sup> This effect can be enhanced with increasing Al composition due to the increasing amount of stacking faults. Although it is difficult to distinguish precisely between the effects of Al fluctuation and stacking faults, these three effects could be major factors for the unexpected lower transition energies.

## 7.7 Conclusions

We investigated the composition and structural and optical properties of WZ InP/AlInP CMS NWs grown using the crystal structure transfer method. TEM and EDX studies showed that the WZ structure was transferred from InP core NW to the AlInP multishell and double heterostructures were formed in the AlInP multishell by changing Al compositions. The crystal structures and lattice constants of CMS NWs were analyzed by XRD RSMs, indicating that the WZ AlInP shells had tensile strain along  $c$ -axis within a range of 1.00–1.36%, depending on the Al composition. The WZ  $\text{Al}_{0.54}\text{In}_{0.46}\text{P}$  shell had a CL emission at 1.8–2.1 eV, located in the red-amber spectral region. Our study provides experimental evidence of the structural and optical properties of WZ  $\text{Al}_x\text{In}_{1-x}\text{P}$  that could be applied in visible LEDs.

## Bibliography

- [1] K. Tomioka, M. Yoshimura, and T. Fukui, *Nature* **488**, 189 (2012).
- [2] H. Rie., L.-E. Wernersson, M. Hong, and J. A. del Alamo, *MRS Bul.* **39**, 668 (2014).
- [3] K. Hiruma, M. Yazawa, T. Katsuyama, K. Ogawa, K. Haraguchi, M. Koguchi, and H. Kakibayashi, *J. Appl. Phys.* **77**, 447 (1995).
- [4] K. Tomioka, J. Motohisa, S. Hara, K. Hiruma, and T. Fukui, *Nano Lett.* **10**, 1639 (2010).
- [5] K. Kawaguchi, H. Sudo, M. Matsuda, M. Ekawa, T. Yamamoto, and Y. Arakawa, *Jpn. J. Appl. Phys.* **54**, 04DN02 (2015).
- [6] Berg, S. Yazdi, A. Nowzari, K. Storm, V. Jain, N. Vainorius, L. Samuelson, J. B. Wagner, and M. T. Borgstrom, *Nano Lett.* **16**, 656 (2016).
- [7] J. Wallentin, N. Anttu, D. Asoli, M. Huffman, I. Åberg, M. H. Magnusson, G. Siefert, P. Fuss-Kailuweit, F. Dimroth, B. Witzigmann, H. W. Xu, L. Samuelson, K. Deppert, and M. T. Borgström, *Science* **339**, 1057 (2013).
- [8] M. Yoshimura, E. Nakai, K. Tomioka, and T. Fukui, *Appl. Phys. Lett.* **103**, 243111 (2013).
- [9] R. E. Algra, M. A. Verheijen, M. T. Borgström, L.-F. Feiner, G. Immink, W. J. P. van Enckevort, E. Vlieg, and E. P. A. M. Bakkers, *Nature* **456**, 369 (2008).
- [10] H. J. Joyce, J. W.-Leung, Q. Gao, H. H. Tan, and C. Jagadish, *Nano Lett.* **10**, 908 (2010).
- [11] Y. Kitauchi, Y. Kobayashi, K. Tomioka, S. Hara, K. Hiruma, T. Fukui, and J. Motohisa, *Nano Lett.* **10**, 1699 (2010).
- [12] K. Ikejiri, Y. Kitauchi, K. Tomioka, J. Motohisa, and T. Fukui, *Nano Lett.* **11**, 4314 (2011).
- [13] K. Ikejiri, F. Ishizaka, K. Tomioka, and T. Fukui, *Nano Lett.* **12**, 4770 (2012).
- [14] Q. Gao, D. Saxena, F. Wang, L. Fu, S. Mookapati, Y. Guo, L. Li, J. W.-Leung, P. Caroff, H. H. Tan, and C. Jagadish, *Nano Lett.* **14**, 5206 (2014).
- [15] A. Berg, S. Lehmann, N. Vainorius, A. Gustafsson, M.-E. Pistol, L. R. Wallenberg, and L. Samuelson, M. T. Borgström, *J. Cryst. Growth* **386**, 47 (2014).
- [16] E. Husanu, D. Ercolani, M. Gemmi, and L. Sorba, *Nanotechnology* **25**, 205601 (2014).
- [17] A. De and C. E. Pryor, *Phys. Rev. B* **81**, 155210 (2010).
- [18] F. Bechstedt and A. Belabbes, *J. Phys.: Condens. Matter* **25**, 273201 (2013).
- [19] S. Assali, I. Zardo, S. Plissard, D. Kriegner, M. A. Verheijen, G. Bauer, A. Meijerink, A.

- 
- Belabbes, F. Bechstedt, J. E. M. Haverkort, and E. P. A. M. Bakkers, *Nano Lett.* **13**, 1559 (2013).
- [20] J. Y. Tsao, M. E. Coltrin, M. H. Crawford, and J. A. Simmons, *Proc. IEEE* **98**, 1162 (2010).
- [21] Y. Hiraya, F. Ishizaka, K. Tomioka, and T. Fukui, *Appl. Phys. Express* **9**, 035502 (2016).
- [22] N. Sköld, J. B. Wagner, G. Karlsson, T. Hernan, W. Seifert, M.-E. Pistol, and L. Samuelson, *Nano Lett.* **6**, 2743 (2006).
- [23] R. E. Algra, M. Hoes, M. A. Verheijen, I. Zardo, G. G. W. Immink, W. J. P. van Enckevort, G. Abstreiter, L. P. Kouwenhoven, E. Vlieg, and E. P. A. M. Bakkers, *Nano Lett.* **11**, 1690 (2011).
- [24] H. I. T. Hauge, M. A. Verheijen, S. Conesa-Boj, T. Etzelstorfer, M. Watzinger, D. Kriegner, I. Zardo, C. Fasolato, F. Capitani, P. Postorino, S. Kölling, A. Li, S. Assali, J. Stangl, and E. P. A. M. Bakkers, *Nano Lett.* **15**, 5855 (2015).
- [25] M. Heurlin, T. Stankevič, S. Mickevičius, S. Yngman, D. Lindgren, A. Mikkelsen, R. Feidenhans'l, M. T. Borgström, and L. Samuelson, *Nano Lett.* **15**, 2462 (2015).
- [26] C.-Y. Yeh, Z. W. Lu, S. Froyen, and A. Zunger, *Phys. Rev. B* **46**, 10086 (1992).
- [27] F. Ishizaka, Y. Hiraya, K. Tomioka, and T. Fukui, *J. Cryst. Growth* **411**, 71 (2015).
- [28] H. Goto, K. Nosaki, K. Tomioka, S. Hara, K. Hiruma, J. Motohisa, and T. Fukui, *Appl. Phys. Express* **2**, 035004 (2009).
- [29] Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, *J. Appl. Phys.* **89**, 5815 (2001).
- [30] R. M. Martin, *Phys. Rev. B* **6**, 4546 (1972).
- [31] M. W. Larsson, J. B. Wagner, M. Wallin, P. Hakansson, L. E. Froberg, L. Samuelson, and L. R. Wallenberg, *Nanotechnology* **18**, 015504 (2007).
- [32] J. Greil, S. Assali, Y. Isono, A. Belabbes, F. Bechstedt, F. O. V. Mackenzie, A. Y. Silov, E. P. A. M. Bakkers, and J. E. M. Haverkort, *Nano Lett.* **16**, 3703 (2016).
- [33] N. Sköld, L. S. Karlsson, M. W. Larsson, M.-E. Pistol, W. Seifert, J. Trägårdh, and L. Samuelson, *Nano Lett.* **5**, 1943 (2005).
- [34] D. Rudolph, S. Funk, M. Döblinger, S. Morkötter, S. Hertenberger, L. Schweickert, J. Becker, S. Matich, M. Bichler, D. Spirkoska, I. Zardo, J. J. Finley, G. Abstreiter, and G. Koblmüller, *Nano Lett.* **13**, 1522 (2013).
- [35] T. M. Christian, D. A. Beaton, K. Mukherjee, K. Alberi, E. A. Fitzgerald, and A. Mascarenhas, *Appl. Phys. Lett.* **114**, 074505 (2013).
- [36] J. Zhao, X. Tang, J. Teng, and A. M. Yong, *J. Cryst. Growth* **312**, 1015 (2010).

[37] S.-H. Wei and A. Zunger, Phys. Rev. B **57**, 8983 (1998).

# Chapter 8

## Conclusion

---

### 8.1 Summary

The purpose of this study is to fabricate phosphide-based III-V compound semiconductor nanowires with the high crystal quality in wurtzite structures, and characterize their structural and optical properties. Summary and conclusions are the following.

In Chapter 4, we fabricated InGaP NWs on InP(111)A substrates by SA-MOVPE under various  $Ga_{supply}$  and V/III ratio conditions. The lateral growth was drastically enhanced, and the uniformity of NWs deteriorated as  $Ga_{supply}$  increased. Furthermore, the sidewall facets of NWs changed from  $\{-211\}$  to  $\{-110\}$  with increasing  $Ga_{supply}$ , indicating the possibility of a structural transition from WZ to ZB. In addition, we successfully improved the uniformity of NWs by increasing the V/III ratio. We also estimated the compositions of the InGaP NWs from XRD and PL measurements. The Ga compositions ranged approximately from 0 to 15% and increased with increasing  $Ga_{supply}$  and decreasing mask opening diameter. These results indicate that the height, diameter, shape, uniformity, and composition of InGaP NWs depend on V/III ratio as well as  $Ga_{supply}$ .

In Chapter 5, we demonstrated the growth of WZ GaP in InP/GaP core-shell nanowires by SA-MOVPE, in which the WZ InP nanowires were used as a template for transferring the WZ structure to the GaP shell. TEM and FFT analyses revealed that WZ GaP was grown on the sidewalls of the InP core in the lateral  $\langle -211 \rangle$  direction and that ZB GaP was also grown on the top of the InP core in the axial  $\langle 111 \rangle_A$  direction. Next, we showed a growth model for the different crystal structures of GaP. The “ABAB...” stacking sequence of WZ phase is strongly fixed in the  $\langle -211 \rangle$  direction, while both the WZ and ZB phases are geometrically possible in

the  $\langle 111 \rangle_A$  direction. A WZ structure is transferred from the InP core to the GaP shell in the  $\langle -211 \rangle$  direction because the WZ–ZB energy difference is relatively small. This crystal structure transfer can be applied to p- and n-doped GaP and is therefore promising for fabricating WZ-GaP-based LEDs.

In Chapter 6, we investigated the growth morphology, composition, and structural and optical properties of WZ InP/AlGaP core-multishell nanowires grown by the crystal structure transfer method. Cross-sectional STEM and EDX images showed that the QW structures were formed in the AlGaP multishell. TEM analysis revealed that the InP core had a WZ structure with very few stacking faults and that the AlGaP multishell was grown with a WZ structure on the side of the InP core, whereas it was grown with a ZB structure at the top. From XRD measurements, the measured lattice constants of WZ InP were found to be almost the same as the calculated values, while those of WZ AlGaP were larger owing to indium outdiffusion. Finally, we observed green emissions at 2.37 eV from the WZ AlGaP QW and showed that a difference in crystal structure affects the CL emission energy in AlGaP QWs. These results demonstrate a pathway for preparing green LEDs using WZ AlGaP-based materials.

In Chapter 7, we investigated the composition and structural and optical properties of WZ InP/AlInP core-multishell nanowires grown using the crystal structure transfer method. TEM and EDX studies showed that the WZ structure was transferred from InP core NW to the AlInP multishell and double heterostructures were formed in the AlInP multishell by changing Al compositions. The crystal structures and lattice constants of core-multishell nanowires were analyzed by XRD RSMs, indicating that the WZ AlInP shells had tensile strain along  $c$ -axis within a range of 1.00–1.36%, depending on the Al composition. The WZ  $\text{Al}_{0.54}\text{In}_{0.46}\text{P}$  shell had a CL emission at 1.8–2.1 eV, located in the red-amber spectral region. This result provides experimental evidence of the structural and optical properties of WZ  $\text{Al}_x\text{In}_{1-x}\text{P}$  that could be applied in visible LEDs.

## 8.2 Outlook for nanowire fabrication and application

In the past few years, the number of reports on non-nitride III-V semiconductor nanowires with wurtzite crystal structures has been increasing. Understanding the physical, structural, and optical properties is an important issue facing such wurtzite III-V nanowires. Although binary alloy wurtzite nanowires such as GaP, InP, GaAs, and InAs have been extensively investigated so far, ternary alloy wurtzite nanowires such as AlGaP, AlInP, and InGaP have been less studied. The ternary wurtzite nanowires, which can tune wavelengths, are necessary for light-emitting device applications in the visible region. In light of this situation, this study provides useful insights into the growth and basic properties of ternary wurtzite nanowires. The next step is to demonstrate visible light-emitting diodes by combining the growth technique for phosphide-based wurtzite nanowires and the device fabrication technique for core-shell nanowire structures. It is hoped that the research on phosphide-based wurtzite nanowires makes continuous progress toward light-emitting device applications.



## Appendix

### Nanowire Device Fabrication

This appendix describes preliminary results of device fabrication toward light-emitting diodes (LEDs) using phosphide-based wurtzite nanowires developed in this study.

**Nanowire Growth.** The p-InP/p-AlInP/i-AlInP/n-AlInP/n-InP core-multishell nanowires were grown on p-type InP (111)A substrates partially covered with a thin SiO<sub>2</sub> mask. The SiO<sub>2</sub> patterns were designed to be a periodic array of openings with a pitch of 800 nm. The selective-area growth was carried out in a horizontal low-pressure MOVPE system using trimethylaluminum (TMAl), trimethylindium (TMIn), and tertiarybutylphosphine (TBP), diethylzinc (DEZn), and monosilane (SiH<sub>4</sub>) as the source materials. The DEZn and SiH<sub>4</sub> were used as the p- and n-type dopants, respectively. Fig. A-1(a) shows grown layers of the core-multishell nanowires. For p-type InP core growth, the growth temperature and growth time were 660°C and 10 min. The partial pressures of TMIn, TBP, and DEZn were  $2.7 \times 10^{-6}$ ,  $4.9 \times 10^{-5}$ , and  $8.6 \times 10^{-8}$  atm, respectively. For p- and n-type AlInP barrier layers, the growth

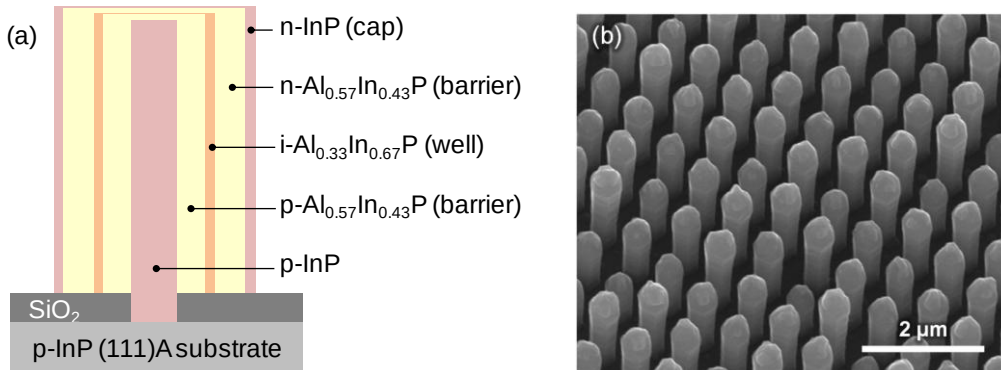


**Fig. A-1** (a) Schematic illustration of grown layers of the core-multishell nanowire. (b) 30°-Tilted SEM image of the as-grown core-multishell nanowires.

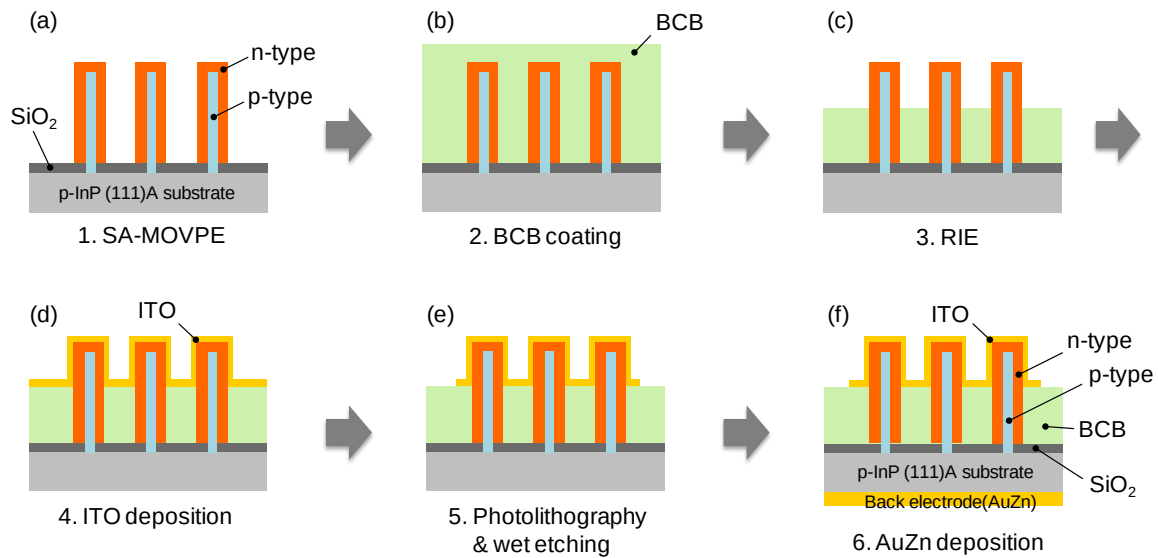


**Fig. A-2** Schematic illustration of fabrication procedure for nanowire LEDs.

temperature and growth time were 600°C and 20 min for each layer. The partial pressures of TMAI, TMIn, and TBP were  $1.2 \times 10^{-6}$ ,  $9.1 \times 10^{-7}$ , and  $3.1 \times 10^{-4}$  atm, respectively. The partial pressures of DEZn and  $\text{SiH}_4$  were  $8.6 \times 10^{-8}$  and  $2.5 \times 10^{-8}$  atm for the p- and n-type layers, respectively. For non-doped AlInP well layer, the growth temperature and growth time were 600°C and 1 min. The partial pressures of TMAI, TMIn, and TBP were  $6.0 \times 10^{-7}$ ,  $1.2 \times 10^{-6}$ , and  $3.1 \times 10^{-4}$  atm, respectively. For n-type InP cap layer, the growth temperature and growth time were 600°C and 1 min. The partial pressures of TMIn, TBP, and  $\text{SiH}_4$  were  $1.5 \times 10^{-6}$ ,  $3.1 \times 10^{-4}$ , and  $2.5 \times 10^{-8}$  atm, respectively. The Al contents in vapor,  $[\text{TMAI}]/([\text{TMAI}]+[\text{TMIn}])$ , were 0.33 and 0.57 for the active and barrier layers, respectively. Fig. A-1(b) shows a 30°-tilted view of the grown core-multishell nanowires. The average height and diameter of the core-multishell nanowires are 1.6  $\mu\text{m}$  and 420 nm, respectively.

**Device Fabrication Procedure.** Fig. A-2 shows a schematic illustration of fabrication procedure for nanowire LEDs. After the nanowire growth, the space between nanowires was filled by spin coating with polymer resin (benzocyclobutene, BCB) as a transparent electrical insulator. The overlaid excess resin was removed by reactive ion etching (RIE) using  $\text{CF}_4$  and  $\text{O}_2$  gases in order to expose the nanowire tips. Next, a transparent indium tin oxide (ITO) electrode was sputtered onto nanowire arrays. Then, the nanowire array was isolated by

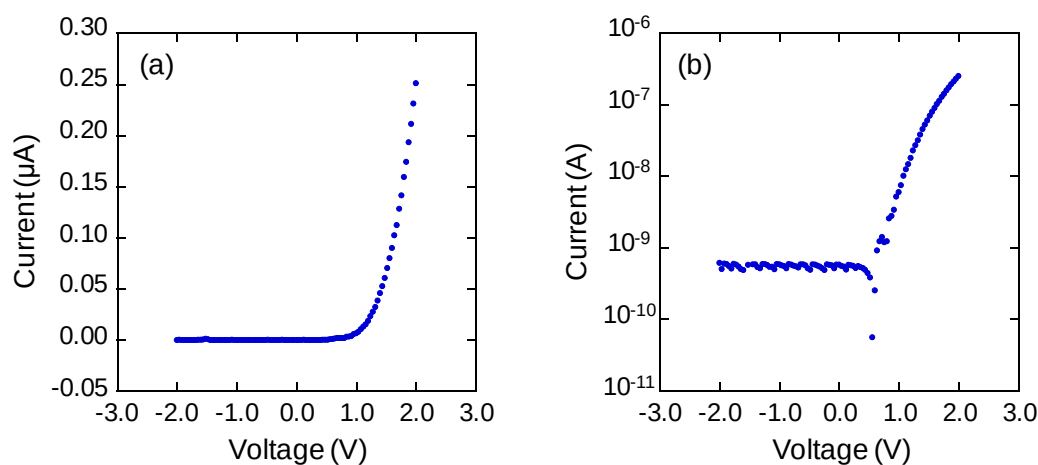


**Fig. A-3** Current-voltage (I-V) characteristics of an InP/AlInP core-multishell nanowire LED in (a) linear and (b) logarithmic scales.

photolithography and wet etching based on HCl. Finally, the backside electrode was formed by alloying Au-Zn. The whole sample was then annealed in N<sub>2</sub> ambient for 15 min at 400 °C.

**I-V Characteristics.** Fig. A-3 shows a result of the current-voltage (I-V) characteristics of the fabricated nanowire LED. The I-V curve exhibited clear rectifying behavior with small forward and reverse bias leakage. Thus, p-n junction was thought to be formed within the core-multishell nanowires. However, the turn-on voltage was about 1.4 V, which is somewhat different from the expected band gap of the non-doped Al<sub>0.33</sub>In<sub>0.67</sub>P well layer (about 1.7 eV). The current was 0.25 μA at a bias voltage of 2 V, which is smaller than that of the typical nanowire LEDs by several orders of magnitude. To improve the performance, the growth condition and device fabrication process need to be optimized.



# List of Publications

## 1. Publications related to this work

- [1] F. Ishizaka, K. Ikejiri, K. Tomioka, and T. Fukui, “Indium-rich InGaP Nanowires Formed on InP(111)A Substrates by Selective-area Metal Organic Vapor Phase Epitaxy”, Japanese Journal of Applied Physics, Vol. 52, No. 4, pp. 04CH05-1-4, 2013. (IF=1.122, Time Cited=3)
- [2] F. Ishizaka, Y. Hiraya, K. Tomioka, and T. Fukui, “Growth of wurtzite GaP in InP/GaP core-shell nanowires by Selective-area MOVPE”, Journal of Crystal Growth, Vol. 411, pp. 71-75, 2015. (IF=1.462, Time Cited=9)
- [3] F. Ishizaka, Y. Hiraya, K. Tomioka, J. Motohisa, and T. Fukui, “Growth and characterization of wurtzite InP/AlGaP core-multishell nanowires with AlGaP quantum well structures”, Japanese Journal of Applied Physics, Vol. 56, No. 1, pp. 010311-1-4, 2017. (IF=1.122, Time Cited=0)
- [4] F. Ishizaka, Y. Hiraya, K. Tomioka, J. Motohisa, and T. Fukui, “Growth of All-Wurtzite InP/AlInP Core-Multishell Nanowires”, Nano Letters, 2017. [doi: 10.1021/acs.nanolett.6b03727] (IF=13.779, Time Cited=0)

## 2. Publications related to other work

- [1] K. Ikejiri, F. Ishizaka, K. Tomioka, and T. Fukui, “Bidirectional Growth of Indium Phosphide Nanowires”, Nano Letters, Vol. 12, No. 9, pp. 4770-4774, 2012. (IF=13.779, Time Cited=14)
- [2] K. Ikejiri, F. Ishizaka, K. Tomioka, and T. Fukui, “GaAs nanowire growth on polycrystalline silicon thin films using selective-area MOVPE”, Nanotechnology, Vol. 24, No. 11, pp. 115304-1-6, 2013. (IF=3.573, Time Cited=17)
- [3] K. Tomioka, F. Ishizaka, and T. Fukui, “Selective-Area Growth of InAs Nanowires on Ge and Vertical Transistor Application”, Nano Letters, Vol. 15, No. 11, pp. 7253-7257, 2015. (IF=13.779, Time Cited=6)
- [4] Y. Hiraya, F. Ishizaka, K. Tomioka, and T. Fukui, “Crystal phase transition to green emission wurtzite AlInP by crystal structure transfer”, Applied Physics Express, Vol. 9, No. 3, pp. 035502-1-4, 2016. (IF=2.265, Time Cited=3)
- [5] A. Yoshida, K. Tomioka, F. Ishizaka, K. Chiba, and J. Motohisa, “Selective-Area Growth of

Vertical InGaAs Nanowires on Ge for Transistor Application”, ECS Transactions, Vol. 75, Issue 5, pp. 265-270, 2016. (Time Cited=0)

- [6] A. Yoshida, K. Tomioka, F. Ishizaka, and J. Motohisa, “Growth of InGaAs Nanowires on Ge(111) by Selective-Area Metal-Organic Vapor-Phase Epitaxy”, Journal of Crystal Growth, 2017. [doi: 10.1016/j.jcrysgro.2016.10.083] (IF=1.462, Time Cited=0)

### 3. Presentations related to this work

#### International conference

- [1] F. Ishizaka, K. Ikejiri, K. Tomioka, and T. Fukui, “Fabrication and Characterization of InGaP Nanowires by Selective-Area Metal Organic Vapor Phase Epitaxy”, 31st Electronic Materials Symposium (EMS31), Th5-5, Shizuoka, Japan, July 11-13, 2012.
- [2] F. Ishizaka, K. Ikejiri, K. Tomioka, and T. Fukui, “InGaP Nanowires grown by Selective-Area MOVPE”, 2012 International Conference on Solid State Devices and Materials (SSDM2012), I-4-3, Kyoto, Japan, September 25-27, 2012.
- [3] F. Ishizaka, K. Ikejiri, K. Tomioka, and T. Fukui, “Growth of Wurtzite InP/GaP Core-shell Nanowires by Selective-area Metal Organic Vapor Phase Epitaxy”, 32nd Electronic Materials Symposium (EMS32), Fr1-10, Shiga, Japan, July 10-12, 2013.
- [4] F. Ishizaka, K. Ikejiri, K. Tomioka, and T. Fukui, “Wurtzite InP/GaP core-shell nanowires toward direct band gap transition”, International Conference on One-dimensional Nanomaterials (ICON2013), P1.33, Annecy, France, September 23-26, 2013.
- [5] F. Ishizaka, K. Tomioka, and T. Fukui, “Wurtzite InP/AlGaP Core-shell Nanowires toward Direct Band Gap Transition”, 2014 Materials Research Society (MRS) Spring Meeting, UU3.05, San Francisco, USA, April 21-25, 2014.
- [6] F. Ishizaka, Y. Hiraya, K. Tomioka, and T. Fukui, “Selective-area growth of wurtzite InP/AlGaP core-shell nanowires”, 17th International Conference on Metalorganic Vapor Phase Epitaxy (IC-MOVPE17), Thu-Poster-2-21, Lausanne, Switzerland, July 13-18, 2014.
- [7] F. Ishizaka, Y. Hiraya, K. Tomioka, and T. Fukui, “Selective-area Growth of Wurtzite InP/AlGaP Core-shell Nanowires Toward Direct-band-gap Green Emission”, 42nd Conference on the Physics and Chemistry of Surfaces and Interfaces (PCSI-42), Mo1140, Salt Lake City, USA, January 18-22, 2015.
- [8] F. Ishizaka, Y. Hiraya, K. Tomioka, and T. Fukui, “Growth and Characterization of Wurtzite InP/AlInP Core-Shell Nanowires”, 2015 International Conference on Solid State Devices

and Materials (SSDM2015), PS-13-18, Sapporo, Japan, September 27-30, 2015.

- [9] F. Ishizaka, Y. Hiraya, K. Tomioka, and T. Fukui, “Structural and optical properties of wurtzite AlInP grown on wurtzite InP nanowires”, 2015 Materials Research Society (MRS) Fall Meeting, P5.08, Boston, USA, November 28 - December 4, 2015.
- [10] F. Ishizaka, Y. Hiraya, K. Tomioka, and T. Fukui, “Growth of Wurtzite AlInP in InP/AlInP Core-Shell Nanowires by Crystal Structure Transfer Method”, 18th International Conference on Metalorganic Vapor Phase Epitaxy (IC-MOVPE18), 4B-1.4, San Diego, USA, July 10-15, 2016.
- [11] F. Ishizaka, Y. Hiraya, K. Tomioka, J. Motohisa, and T. Fukui, “Structural and Optical Properties of Wurtzite InP/AlInP Core-Multishell Nanowires”, 2016 International Conference on Solid State Devices and Materials (SSDM2016), PS-13-11, Tsukuba, Japan, September 26-29, 2016.

## Domestic conference

- [1] 石坂文哉, 池尻圭太郎, 富岡克広, 福井孝志, 「MOVPE 選択成長法による InGaP ナノワイヤの作製と評価」, 第 59 回応用物理学関係連合講演会, 17p-DP3-21, 東京, 2012 年 3 月 15 日～3 月 18 日.
- [2] 石坂文哉, 池尻圭太郎, 富岡克広, 福井孝志, 「InGaP ナノワイヤの選択成長と組成評価」, 第 73 回応用物理学会学術講演会, 12a-J-3, 愛媛, 2012 年 9 月 11 日～9 月 14 日.
- [3] 石坂文哉, 池尻圭太郎, 富岡克広, 福井孝志, 「MOVPE 選択成長法によるウルツ鉱構造 InP/GaP コアシェルナノワイヤの作製」, 第 74 回応用物理学会秋季学術講演会, 18p-C11-10, 京都, 2013 年 9 月 16 日～9 月 20 日.
- [4] 石坂文哉, 富岡克広, 福井孝志, 「MOVPE 選択成長法によるウルツ鉱型 InP/AlGaP コアシェルナノワイヤ成長」, 第 61 回応用物理学会春季学術講演会, 19a-PA6-10, 神奈川, 2014 年 3 月 17 日～3 月 20 日.
- [5] 石坂文哉, 平谷佳大, 富岡克広, 福井孝志, 「InP/AlGaP コアシェルナノワイヤの結晶構造評価」, 第 62 回応用物理学会春季学術講演会, 12a-A20-2, 神奈川, 2015 年 3 月 11 日～3 月 14 日.
- [6] 石坂文哉, 平谷佳大, 富岡克広, 福井孝志, 「ウルツ鉱構造 InP/AlInP コアシェルナノワイヤの作製と評価」, 第 75 回応用物理学会秋季学術講演会, 14p-2Q-1, 名古屋, 2015 年 9 月 13 日～9 月 16 日. (講演奨励賞受賞記念講演)
- [7] 石坂文哉, 平谷佳大, 富岡克広, 本久順一, 福井孝志, 「ウルツ鉱構造 InP/AlInP コアマルチシェルナノワイヤの構造及び光学特性評価」, 第 77 回応用物理学会秋季学術講演会, 14p-D64-4, 新潟, 2016 年 9 月 13 日～9 月 16 日.

## 4. Presentations related to other work

### International conference

- [1] K. Ikejiri, F. Ishizaka, K. Tomioka, and T. Fukui, “Bi-directional Growth of InP Nanowires by Selective-area MOVPE”, 1st International Conference on Emerging Advanced Nanomaterials (ICEAN-2012), PII-57, Brisbane, Australia, October 22-25, 2012.
- [2] T. Fukui, M. Yoshimura, E. Nakai, F. Ishizaka, and K. Tomioka, “III-V semiconductor nanowires and their photovoltaic device applications”, 12th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-12), 6aC1-1, Tsukuba, Japan, November 4-8, 2013. (Invited)
- [3] T. Fukui, M. Yoshimura, E. Nakai, F. Ishizaka, and K. Tomioka, “Selective area growth of III-V semiconductor nanowires and their photovoltaic and electron device applications”, Nanowires 2013, Rehovot, Israel, November 12-15, 2013. (Invited)
- [4] K. Tomioka, M. Yoshimura, E. Nakai, F. Ishizaka, and T. Fukui, “Integration of III-V nanowires on Si: From high-performance vertical FET to steep-slop switch”, the 2013 IEEE International Electron Devices Meeting (IEDM), Washington, USA, December 9-11, 2013. (Invited)
- [5] K. Tomioka, F. Ishizaka, E. Nakai, and T. Fukui, “Selective-area growth of vertical InAs nanowires on Ge(111)”, 17th International Conference on Metalorganic Vapor Phase Epitaxy (IC-MOVPE17), Lausanne, Switzerland, July 13-18, 2014. (Invited)
- [6] K. Tomioka, F. Ishizaka, and T. Fukui, “Selective-area growth of InAs nanowire inside Si(100) and SOI substrates toward tunnel FET applications using InAs/Si heterojunctions”, 17th International Conference on Metalorganic Vapor Phase Epitaxy (IC-MOVPE17), Lausanne, Switzerland, July 13-18, 2014.
- [7] K. Tomioka, F. Ishizaka, E. Nakai, M. Chen and T. Fukui, “Integration of Vertical InAs Nanowires on Ge (111) by Selective-Area MOVPE”, 2014 International Conference on Solid State Devices and Materials (SSDM2014), P-3-3, Tsukuba, Japan, September 8-11, 2014.
- [8] T. Fukui, E. Nakai, F. Ishizaka, and K. Tomioka, “Vertically aligned III-V semiconductor nanowires and their applications”, 42nd Conference on the Physics and Chemistry of Surfaces and Interfaces (PCSI-42), Salt Lake City, USA, January 18-22, 2015. (Invited)
- [9] T. Fukui, E. Nakai, F. Ishizaka, and K. Tomioka, “III-V semiconductor hetero-structure nanowires and their photonic applications”, 582nd Wilhelm and Else Heraeus Seminar, III-V Nanowire Photonics, Bad Honnef, Germany, March 22-25, 2015. (Invited)
- [10] K. Tomioka, F. Ishizaka, E. Nakai, and T. Fukui, “Selective-area growth of vertical InAs nanowires on Ge(111)”, 2015 Materials Research Society (MRS) Spring Meeting, San

Francisco, USA, April 6-10, 2015.

- [11] T. Fukui, F. Ishizaka, and K. Tomioka, “Vertically Aligned Semiconductor Nanowire Array and Their Applications”, 42nd International Symposium on Compound Semiconductors, Santa Barbara, USA, June 28 – July 2, 2015. (Invited)
- [12] Y. Hiraya, F. Ishizaka, K. Tomioka, and T. Fukui, “Growth of AlGaP and AlInP on GaN Substrates Toward Transferring Wurtzite Structure”, 42nd International Symposium on Compound Semiconductors, Santa Barbara, USA, June 28 – July 2, 2015.
- [13] T. Fukui, F. Ishizaka, and K. Tomioka, “III-V Semiconductor Nanowires Grown by Selective Area MOVPE and Their Device Applications”, 5th International Workshop on Epitaxial Growth and Fundamental Properties of Semiconductor Nanostructures, Hsinchu, Taiwan, September 6–11, 2015. (Invited)
- [14] K. Tomioka, F. Ishizaka, J. Motohisa, and T. Fukui, “Steep-Slope Tunnel FET using InGaAs-InP Core-Shell Nanowire/Si Heterojunction”, 2015 International Conference on Solid State Devices and Materials (SSDM2015), K-2-4, Sapporo, Japan, September 27-30, 2015.
- [15] K. Tomioka, F. Ishizaka, J. Motohisa, and T. Fukui, “Steep turn-on property of vertical tunnel FET using InGaAs/InP core-shell nanowire/Si heterojunction”, 2015 Materials Research Society (MRS) Fall Meeting, Boston, USA, November 28 - December 4, 2015.
- [16] T. Fukui, F. Ishizaka, and K. Tomioka, “Semiconductor nanowire array grown by selective area epitaxy and their applications”, The International Chemical Congress of Pacific Basin Societies 2015 (Pacifichem 2015), Honolulu, USA, December 15–20, 2015. (Invited)
- [17] K. Chiba, K. Tomioka, F. Ishizaka, A. Yoshida, J. Motohisa, and T. Fukui, “Selective-Area MOVPE Growth of InGaAs Nanowires for Optical Communication Band”, 35th Electronic Materials Symposium (EMS35), Shiga, Japan, July 6-8, 2016.
- [18] K. Tomioka, F. Ishizaka, J. Motohisa, and T. Fukui, “Selective-area growth of InGaAs/InP/InAlAs/InP core-multishell nanowires on Si and tunneling transistor application”, 43th International Symposium on Compound Semiconductors, MoD4-3, Toyama, Japan, June 26-30, 2016.
- [19] K. Tomioka, F. Ishizaka, J. Motohisa, and T. Fukui, “Heterogeneous Integration of InGaAs-Related Nanowires on Si and Their Device Applications”, 18th International Conference on Metalorganic Vapor Phase Epitaxy (IC-MOVPE18), 4B-1.1, San Diego, USA, July 10-15, 2016. (Invited)
- [20] A. Yoshida, K. Tomioka, F. Ishizaka, K. Chiba, J. Motohisa, and T. Fukui, “Growth of InGaAs Nanowires on Ge(111) by Selective-Area Metal-Organic Vapor-Phase Epitaxy”, 18th International Conference on Metalorganic Vapor Phase Epitaxy (IC-MOVPE18),

PS-2.21, San Diego, USA, July 10-15, 2016.

- [21] K. Tomioka, F. Ishizaka, J. Motohisa, and T. Fukui, “Selective-area growth of InGaAs-based core-multishell nanowires on Si(111) with modulation-doped layer toward tunnel FETs”, The 18th International Conference on Crystal Growth and Epitaxy (ICCGE-18), Nagoya, Japan, August 7-12, 2016.
- [22] K. Chiba, K. Tomioka, J. Motohisa, F. Ishizaka, A. Yoshida, and T. Fukui, “Study on Selective-Area Growth of InGaAs Nanowires for Optical Communication Band”, The 18th International Conference on Crystal Growth and Epitaxy (ICCGE-18), Nagoya, Japan, August 7-12, 2016.
- [23] K. Tomioka, F. Ishizaka, J. Motohisa, and T. Fukui, “InGaAs/Si heterojunction tunnel FET with modulation-doped channel”, 2016 International Conference on Solid State Devices and Materials (SSDM2016), A-2-05, Tsukuba, Japan, September 26-29, 2016.
- [24] T. Fukui, Y. Hiraya, F. Ishizaka, and K. Tomioka, “Phase Transition from Zinc Blende to Wurtzite and Green Emission of AlInP Grown on (10-10) GaN by Crystal Structure Transfer Epitaxy”, 2016 International Conference on Solid State Devices and Materials (SSDM2016), D-4-03, Tsukuba, Japan, September 26-29, 2016.
- [25] A. Yoshida, K. Tomioka, F. Ishizaka, K. Chiba, and J. Motohisa, “Selective-Area Growth of Vertical InGaAs Nanowires on Ge for Transistor Application”, The Electrochemical Society (ECS) 230th Meeting, Honolulu, USA, October 2-7, 2016.
- [26] K. Chiba, K. Tomioka, F. Ishizaka, A. Yoshida, and J. Motohisa, “Heterogeneous Integration of InGaAs Nanowires on Si(111) for Si Photonics”, The Electrochemical Society (ECS) 230th Meeting, Honolulu, USA, October 2-7, 2016.
- [27] A. Yoshida, F. Ishizaka, K. Tomioka, and J. Motohisa, “Heterogeneous Integration of Vertical  $\text{In}_x\text{Ga}_{1-x}\text{As}$  Nanowires on Ge(111) Substrates by Selective-Area MOVPE”, 29th International Microprocesses and Nanotechnology Conference (MNC 2016), Kyoto, Japan, November 8-11, 2016.
- [28] K. Tomioka, F. Ishizaka, J. Motohisa, and T. Fukui, “High-Performance InGaAs/Si Tunnel FETs Using Core-Multishell Nanowire-Channel”, 2016 Materials Research Society (MRS) Fall Meeting, NM1.17.06, Boston, USA, November 27 - December 2, 2016.

## Domestic conference

- [1] 池尻圭太郎, 石坂文哉, 富岡克広, 福井孝志, 「InP ナノワイヤの双方向成長機構」, 第73回応用物理学学会学術講演会, 12p-PB11-3, 愛媛, 2012年9月11日～9月14日.
- [2] 富岡克広, 吉村正利, 中井栄治, 遠藤隆人, 池尻圭太郎, 石坂文哉, 福井孝志,

- 「MOVPE 選択成長法によるシリコン上の GaAs/InGaP コア・マルチシェルナノワイヤ成長」, 第 73 回応用物理学会学術講演会, 12a-J-2, 愛媛, 2012 年 9 月 11 日～9 月 14 日.
- [3] 池尻圭太郎, 石坂文哉, 富岡克広, 福井孝志, 「MOVPE 選択成長法によるポリシリコン薄膜上の GaAs ナノワイヤの作製と評価(II)」, 第 74 回応用物理学会秋季学術講演会, 18p-C11-7, 京都, 2013 年 9 月 16 日～9 月 20 日.
- [4] 富岡克広, 石坂文哉, 中井栄治, 福井孝志, 「Si/InAs ヘテロ接合縦型トンネル FET のチャネル層ドーピング効果」, 第 61 回応用物理学会春季学術講演会, 19a-F12-13, 神奈川, 2014 年 3 月 17 日～3 月 20 日.
- [5] 富岡克広, 石坂文哉, 中井栄治, 福井孝志, 「Ge(111)基板上の垂直 InAs ナノワイヤの選択成長」, 第 75 回応用物理学会秋季学術講演会, 18a-A6-7, 札幌, 2014 年 9 月 17 日～9 月 20 日.
- [6] 平谷佳大, 石坂文哉, 富岡克広, 福井孝志, 「MOVPE 法による GaN 基板上のウルツ鉱構造 AlGaP 作製の試み」, 第 75 回応用物理学会秋季学術講演会, 19p-PB5-7, 札幌, 2014 年 9 月 17 日～9 月 20 日.
- [7] 富岡克広, 石坂文哉, 中井栄治, 福井孝志, 「III-V 族化合物半導体ナノワイヤ選択成長と電子素子応用」, 2014 年電気化学会秋季大会, 札幌, 2014 年 9 月 27 日～9 月 28 日. (招待講演)
- [8] 富岡克広, 石坂文哉, 中井栄治, 本久順一, 福井孝志, 「MOVPE 選択成長法による Si(001), SOI 基板上の InAs ナノワイヤ成長」, 第 62 回応用物理学会春季学術講演会, 12a-A20-3, 神奈川, 2015 年 3 月 11 日～3 月 14 日.
- [9] 富岡克広, 石坂文哉, 中井栄治, 本久順一, 福井孝志, 「Si/InGaAs ヘテロ接合界面縦型トンネル FET のシェル層歪」, 第 62 回応用物理学会春季学術講演会, 11a-A23-11, 神奈川, 2015 年 3 月 11 日～3 月 14 日.
- [10] 平谷佳大, 石坂文哉, 富岡克広, 福井孝志, 「MOVPE 法による GaN 基板上のウルツ鉱構造 AlInP 成長」, 第 62 回応用物理学会春季学術講演会, 13p-D4-6, 神奈川, 2015 年 3 月 11 日～3 月 14 日.
- [11] 富岡克広, 石坂文哉, 本久順一, 福井孝志, 「InGaAs-InP コアシェルナノワイヤ/Si トンネル FET のスイッチ特性改善」, 第 75 回応用物理学会秋季学術講演会, 14p-2Q-2, 名古屋, 2015 年 9 月 13 日～9 月 16 日.
- [12] 平谷佳大, 石坂文哉, 富岡克広, 福井孝志, 「結晶構造転写による AlInP のウルツ鉱構造への結晶相転移」, 第 75 回応用物理学会秋季学術講演会, 13p-PB2-15, 名古屋, 2015 年 9 月 13 日～9 月 16 日.
- [13] 福井孝志, 石坂文哉, 平谷佳大, 富岡克広, 「結晶構造転写による GaP 系混晶の直接遷移型ウルツ鉱への相転移」, 第 45 回結晶成長国内会議(NCCG-45), 19aA02, 札幌,

2015 年 10 月 19 日～10 月 21 日.(招待講演)

- [14] 富岡克広, 石坂文哉, 本久順一, 福井孝志, 「変調ドープ構造 InGaAs ナノワイヤ/Si トンネル FET の作製」, 第 63 回応用物理学会春季学術講演会, 20p-S422-14, 東京, 2016 年 3 月 19 日～3 月 22 日.
- [15] 平谷佳大, 石坂文哉, 富岡克広, 福井孝志, 「GaN(10-10)上へのウルツ鉱構造 AlInP の成長と緑色発光」, 第 63 回応用物理学会春季学術講演会, 21p-H112-10, 東京, 2016 年 3 月 19 日～3 月 22 日.(注目講演)
- [16] 吉田旭伸, 富岡克広, 石坂文哉, 千葉康平, 本久順一, 福井孝志, 「Ge(111)基板上 InGaAs ナノワイヤ選択成長」, 第 63 回応用物理学会春季学術講演会, 19p-W834-6, 東京, 2016 年 3 月 19 日～3 月 22 日.
- [17] 千葉康平, 富岡克広, 石坂文哉, 吉田旭伸, 本久順一, 「Si 基板上 InGaAs ナノワイヤの組成制御」, 第 77 回応用物理学会秋季学術講演会, 14p-D64-1, 新潟, 2016 年 9 月 13 日～9 月 16 日.
- [18] 吉田旭伸, 富岡克広, 石坂文哉, 本久順一, 「Ge 上 InGaAs ナノワイヤ選択成長と組成変調」, 第 64 回応用物理学会春季学術講演会, 16p-P15-10, 横浜, 2017 年 3 月 14 日～3 月 17 日.

## 5. Awards

- [1] 石坂文哉, 「平成 25 年度電子情報通信学会北海道支部学生員奨励賞」, 2014 年 3 月 25 日.
- [2] 石坂文哉, 「第 38 回 (2015 年春季) 応用物理学会講演奨励賞」, 2015 年 5 月 8 日.  
対象論文: 石坂文哉, 平谷佳大, 富岡克広, 福井孝志, 「InP/AlGaP コアシェルナノワイヤの結晶構造評価」, 第 62 回応用物理学会春季学術講演会.
- [3] K. Ikejiri, F. Ishizaka, K. Tomioka, and T. Fukui, “ICEAN-2012 Best Poster Award”, October 2012.  
対象論文: K. Ikejiri, F. Ishizaka, K. Tomioka, and T. Fukui, “Bi-directional Growth of InP Nanowires by Selective-area MOVPE”, 1st International Conference on Emerging Advanced Nanomaterials (ICEAN-2012).
- [4] K. Tomioka, F. Ishizaka, J. Motohisa, and T. Fukui, “SSDM Paper Award 2016”, September 27, 2016.  
対象論文: K. Tomioka, F. Ishizaka, J. Motohisa, and T. Fukui, “Steep-Slope Tunnel FET using InGaAs-InP Core-Shell Nanowire/Si Heterojunction”, 2015 International Conference on Solid State Devices and Materials (SSDM2015).

## 6. Patents

- [1] 福井孝志, 石坂文哉, 富岡克広, 「発光素子およびその製造方法」, 特願 2013-138894.  
(2013 年 7 月 2 日出願)