Research on Nitride Semiconductors

Target of Initial Stage in Research: Realization of Blue-Light Emitting-Devices

- Device Structure: Double heterostructure (DH structure) as shown in Fig. 1
- Materials constructing device structure: Control of conduction type and materials enabling to DH structure



Fig. 1 Operation principle and device structure for emitting device with high efficiency.

1987-1. Proposal of Quaternary Material InGaAIN

- Starting research on nitride semiconductors for realizing blue emission
- Proposal of quaternary material InGaAIN for constructing DH structure as shown in Fig. 2.

This figure has been widely used all over the world since I showed it.





- [1] T. Matsuoka, H. Tanaka, T. Sasaki, and A. Katsui, "Wide-Gap Semiconductor (In, Ga)N", International Symposium on GaAs and Related Compounds (Karuizawa, Japan, Sept. 25-29, 1989); in Inst. Phys. Conf. Ser., 106, pp. 141-146 (1990).
- [2] H. Tanaka, T. Matsuoka, and K. Oe, "Semiconductor Light-Emitting Devices", Application in 1987.7.13, Japanese Patent 1985649 in 1995.10.25.
- [3] T. Sasaki and T. Matsuoka, "Fabrication Method of Semiconductor Light-Emitting Devices", Application in 1991.8.5, Japanese Patent *3147316* in 2001.1.12.



Fig. 3 Lattice constants and band-gap energies of semiconductors

1987-2. InGaN growth

Undertaking epitaxial growth of blue-light-emitting material InGaN

Before my work, no body mentioned the equilibrium vapor pressures of nitrogen P_N on the terminal material AlN, GaN and InN although the growth was performed with the gas phase. I searched these pressures from literature and picked up as shown in Fig. 4. This has been also used all over the world. P_N of GaN grown at higher than 1000 °C is extremely higher than P_{As} of GaAs and P_P of InP grown at 600 °C. For InN, P_N is much higher. I considered this high P_N became a large obstacle.



Fig. 4 Equilibrium vapor pressure of nitrogen over AlN, GaN, and InN compared with conventional semiconductor materials of GaAs and InP

1988 First Success in Growth of Single Crystalline InGaN

- Single crystalline InGaN was grown by changing hydrogen usually used as a carrier gas in all the growth of materials to nitrogen in Metalorganic Vapor Phase Epitaxy (MOVPE).
- The band-gap energy of InGaN with indium content of 42 % equal to the reported value of 2 eV polycrystalline InN

I predicted the band-gap energy of InN was much smaller than the reported value.

- [4] T. Matsuoka, H. Tanaka, T. Sasaki, and A. Katsui, "Wide-Gap Semiconductor (In, Ga)N", International Symposium on GaAs and Related Compounds (Karuizawa, Japan, Sept. 25-29, 1989).
- [5] T. Matsuoka, T. Sasaki, and A. Katsui, "Composition control of In_{1-X}Ga_XN (0≤X≤1) by MOVPE growth", in Abstract of Fall Meeting of The Japan Society of Applied Physics, p.249 (28p-Y-14) (1989).
- [6] T. Matsuoka, H. Tanaka, T. Sasaki, and A. Katsui, "Wide-Gap Semiconductor (In, Ga)N", in Proc. of Inst. Phys. Conf. Ser., 106, pp. 141-146 (1990).

Key point overcoming high equilibrium vapor pressure of nitrogen



Fig. 5 Chang of carried gas for group-III source from hydrogen conventionally used to nitrogen

• MOVPE growth of GaN on 6H-SiC with lattice-mismatch of 3.4 % to GaN much smaller than 13.8 % of sapphire

I got bulk SiC with 5 mm cubic, cut and polished by myself because a SiC substrate was not commercially available. From this study, I noticed the crystallographic polarity as shown in Fig. 6. I confirmed this polarity thorough GaN growth on a Si-face SiC substrate.



Fig. 6 Crystallographic polarity in wurtzite structure

[7] T. Sasaki and T. Matsuoka, "Substrate-Polarity Dependence of Metal-Organic Vapor-Phase-Epitaxy-Grown GaN on SiC", J. Appl. Phys., 64, pp. 4531-4535 (1988).

<u>1990 ~ 1992 InGaN</u>

• Composition control of InGaN As shown in Fig. 7



Fig. 7 Composition control [6]

- First observation of blue emission from InGaN
- [8] T. Matsuoka, N. Yoshimoto, T. Sasaki, and A. Katsui, "Wide-Gap Semiconductor InGaN and InGaAlN Grown by MOVPE", J. Electronic Mat., 21, 2, pp. 157-163 (1992).
- The miscibility gap in the composition control of InGaN

I predicted the miscibility gap from the calculation and experiments as shown in Fig. 8.

- [9] T. Matsuoka, "Calculation of Unstable Mixing Region in Wurtzite In_{1-X-Y}Ga_XAl_YN", Appl. Phys. Lett. 71, pp. 105-106 (1997).
- [10] T. Matsuoka, "Phase Separation in Wurtzite In_{1-X-Y}Ga_XAl_YN", MRS Internet J. Nitride Semicond. Res. 3, 54 (1998).



Fig. 8 Phase separation of InGaAlN

Oct. 1991 ~ Mar. 1994: Interrupted Research

Reason

The photonics materials laboratory in NTT optoelectronics laboratories which I joined decided to focus on the research on ZnSe system by the success of ZnCdSe/ZnSe blue-laser-diode by 3M in USA on Jun. 1991. On this occasion, I was also changed from the nitride research to ZnSe-system one.

1995 ~ 2006 Growth of N-polar GaN

• Analysis of Growth Mechanism in Two-Step Growth: Relation between the reactor pressure and the shape of growth islands as shown in Fig. 9



Fig. 9 Initial stage of direct growth of GaN on sapphire substrate

[11] T. Sasaki and T. Matsuoka, "Analysis of 2-Step Growth Conditions for GaN on an AlN Buffer Layer ", J. Appl. Phys. 77, 192 (1995).

• Success in N-polar GaN growth on sapphire substrate as shown in Fig. 10

The crystalline quality is not inferior to Ga-polar GaN.





(a) Differential interference microscope image of N-polar GaN surface



(b) Atomic-force-microscope image of Npolar GaN surface



(c) X-ray Rocking curve of GaN 0002 diffraction



Fig. 10 Crystallographic properties of N-polar GaN

- [12] T. Matsuoka, T. Mitate, H. Takahata, S. Mizuno, Y. Uchiyama, A. Sasaki, M. Yoshimoto, T. Ohnishi, and M. Sumiya, "N-Polarity GaN on Sapphire Substrate Grown by MOVPE", *Phys. Stat. Sol. (b)* 243, 1446 (2006).
- Comparison between both polarities in MOVPE growth of GaN on sapphire substrate as shown in Fig. 11





• Notice that the crystalline polarity is effective for the device design because the polarization in a crystal depends on the crystalline polarity as shown in Fig. 12

The success of N-polar GaN means the possibility of high quality InN, which is the most difficult material in nitride semiconductor because of extremely high equilibrium vapor pressure of nitrogen. In the growth of N-polarity, a nitrogen atom is caught with three gallium atoms. For III group-polarity, the situation is opposite. Therefore, by N-polar growth, the characteristics of InN can be expected to be improved. In near future, the properties of InN, which is not clear at present, will be precisely measured. Moreover, the device design becomes flexible because we can control the direction of spontaneous polarization.

- Fig. 12 Conclusion of the paper pointing out the importance of the crystalline polarity in the device design
- [13] T. Matsuoka, T. Mitate, H. Takahata, S. Mizuno, Y. Uchiyama, A. Sasaki, M. Yoshimoto, T. Ohnishi, and M. Sumiya, "N-Polarity GaN on Sapphire Substrate Grown by MOVPE", *Phys. Stat. Sol.* (b) 243, 1446 (2006).

2002 Growth of InN Single Crystal and its Correction of Band-Gap Energy

- The band-gap energy of InN was experimentally shown to be 0.7~0.8eV as shown in Fig. 13.
 - It was shown that nitride semiconductors could be covered from infrared to ultraviolet.



Fig. 13 Corrected band- gap energy of InN

[14] T. Matsuoka, H. Okamoto, M. Nakao, H. Harima, and E. Kurimoto, "Optical Band-Gap Energy of Wurtzite InN", Appl. Phys. Lett. 81, 1246 (2002).

2009 Development of Pressurized-Reactor MOVPE System and its Effect

- Development of the pressurized-reactor MOVPE system up to 5 atmospheres based on understanding the process of two-step growth as shown in Fig. 9
- Observation of the initial stage in InN, which was not grown yet, growth by using the pressurized-reactor MOVPE system as shown in Fig. 14

In this observation, the N-polar growth was used for promoting nitrogen incorporation. This reason why N-polar growth can promote the nitrogen incorporation is that one nitrogen atom is captured with only one Ga atom and three Ga atoms in Ga-and N-polar growth, respectively. As a result, the N-polar growth can increase the efficiency of nitrogen incorporation. Therefore the N-polar growth is advantageous for the growth of materials with high equilibrium pressure of nitrogen.



Fig. 14 Effect of pressurized reactor in N-polar InN MOVPE-growth

- [15] Y. H. Liu, Y. T. Zhang, T. Kimura, M. Hirata, Y. Ohta, S. Y. Ji, T. Matsuoka, "Effect on Reactor Pressure in MOVPE Growth for InN Growth", in *Abstract of Spring Meeting of The Japan Society* of *Applied Physics*, 31a-ZJ-1 (Tsukuba, Mar. 20-Apr. 2 2009).
- [16] T. Matsuoka, Y. H. Liu, T. Kimura, Y. T. Zhang, K. Prasertsuk, and R. Katayama, "Paving the Way to High-Quality Indium Nitride -The Effects of Pressurized Reactor -", Proc. SPIE, 7945, 794519 (2011).
- Realization of InN growth with extremely higher quality than grown one as shown in Fig. 15

The interface between an InN film and a sapphire substrate is smooth, and InN is dense. On the

other hand, for In-polarity InN near the interface becomes porous and its surface rough.



Fig. 15 SEM-observed Cross-sectional view of InN grown by MOVPE with the reactor pressure of 2400 Torr

2014 Application of N-Polar Growth for Solar Cells

• Influence of polarity in solar cell





- [17] S. Inoue M. Katoh, A. Kobayashi, J. Ohta, and H. Fujioka, "Investigation on the Conversion Efficiency of InGaN Solar Cells Fabricated on GaN and ZnO Substrates", *Phys. Stat. Sol.* RRL4, 88 (2010).
- Fabrication of N-polar solar cell



Fig. 16 Layer structure and surface pattern of fabricated N-polar solar cell

• Experimental confirmation that the extraction current of N-polar solar cell is 8 times larger than that of Ga-polar one





[18] T. Tanikawa, J. H. Choi, K. Shojiki, R. Katayama, and T. Matsuoka, "Demonstration of N-Polar InGaN/GaN MQW Solar Cells", 6th World Conference on Photovoltaic Energy Conversion (WCPEC-6), 1TuPo.2.16 (Kyoto, Japan, Nov.24-27, 2014).

2015 Full-Color Display Consisted of All Nitride Semiconductors

• Fabrication of blue to red LEDs by using N-polar growth with high efficiency of nitrogen incorporation

| Table 3 N-polar LEDs | | | | | | | |
|----------------------------|------|-------|------|--|--|--|--|
| | Blue | Green | Red | | | | |
| Photograph | | | | | | | |
| λ (nm) | 450 | 530 | 630 | | | | |
| In-content of InGaN (%) | 16.6 | 28.7 | 40.0 | | | | |

- [19] K. Shojiki, T. Tanikawa, J. H. Choi, S. Kuboya, T. Hanada, R. Katayama, and T. Matsuoka, "Red to Blue Wavelength Emission of N-Polar (000 1) InGaN Light-Emitting Diodes Grown by Metalorganic Vapor Phase Epitaxy", Phys. Express 8, 061005 (2015).
- Promotion of long-wavelength emission in N-polar LEDs due to high nitrogen-incorporation



Fig. 17 Comparison with polarity of relation between the wavelength of electroluminescence and the growth temperature in InGaN/GaN quantum well

2017 Application of Nitride Semiconductors for Transistors ~Inverted HEMT~

Comparison between materials of applications for transistors

4H-SiC GaN β-Ga2O3* Diamond Property Band-Gap Energy 3.3 3.4 4.8 5.47 [eV] Breakdown Field [MV/cm] 3.3 4.0 2.5 8 Electron Mobility [cm²/Vs] 1,000 1,200 300 1.800 Thermal conductivity [W/cmK] 9.7 9.0 10 20.9 Baliga's Index* 340 870 3,444 49,000 Large Wafer * M. Higashiwaki et al., APL 100, 013504 (2012). Mobility in 2DEG:2000 10 S 10³ Average Output Power SiC 10² GaN 10¹ Si 10⁰ GaAs InGaAs 10 100 mm wave UHF µm wave Frequency (GHz)

Table 4 Comparison of wide band-gap semiconductors with respect to properties and performance of transistors

- Fig. 18 Average output power versus switching frequency of Si, GaAs and InGaAs devices with the expected specification of SiC and GaN high-frequency power devices
- [20] S. Yoshida, "Improvement of High Power Device Characteristics by Using Wide Bandgap Semiconductors", *Bulletin of the Electrotechnical Laboratory* 62, 493 (1999).

• HEMT structure ~Difference in operation principle between GaAlAs/GaAs and GaAlN/GaN~



 Table 5 Comparison between GaAs and GaN in generation of two-dimensional electron gas

Courtesy: Prof. Tetsuya Suemitsu of Tohoku

• Relation between crystallographic polarity and both spontaneous and piezoelectric polarizations



Fig. 19 Spontaneous and piezoelectric polarization in crystal with wurtzite structure

• Comparison of polarity in band structure of HEMT structure



Fig. 20 Comparison of band structure in HEMT between crystallographic polarities Courtesy: Prof. Tetsuya Suemitsu of Tohoku University

• Advantage expected in N-polar HEMT (so-called Inverted HEMT)

Table 6 Characteristic comparison between Ga- and N-polar HEMTs

| Polarity | Ga-Polarity | N-Polarity | | | |
|-------------------------|-------------------------|----------------------------|--|--|--|
| | HEMT | Inverted HEMT | | | |
| HEMT Structure | S G D High GaAIN Gro | Temp. S G D wth z InGaN | | | |
| | GaN 2-D | EG GaAIN | | | |
| | GaN Low T | GaN GaN | | | |
| Fabrication Process | Difficult | Easy | | | |
| Quality of Interface | Low | High | | | |
| On- Resistance | High | Low | | | |
| Operation | Low | High | | | |

• Issue of crystal quality in devices of N-polar GaN system



- Fig. 21 Relation between step bunching at the crystal surface and off-angle of sapphire substrate from c-plane Here, for large off-angle, Ga-polar cases are shown because there is no data about large off- angle substrate for N-polar growth_o
- [21] K. Hiramatsu, H. Amano, I. Akasaki, H. Kato, N. Koide, and K. Manabe, "MOVPE Growth of GaN on a Misoriented Sapphire Substrate", J. Cryst. Growth 107, 509 (1991).
- [22] T. Matsuoka T. Mitate, H. Takahata, S. Mizuno, Y. Uchiyama, A. Sasaki, M. Yoshimoto, T. Ohnishi, and M. Sumiya, "N-Polarity GaN on Sapphire Substrate Grown by MOVPE", *Phys. Stat. Sol. (b)* 243, 1446 (2006).
- Structure and characteristics of recess MIS-gate N-polar HEMT



[23] K. Prasertsuk, T. Tanikawa, T. Kimura, S. Kuboya, T. Suemitsu, and T. Matsuoka, " N-polar GaN/AlGaN/GaN Metal-Insulator-Semiconductor High-Electron-Mobility Transistor Formed on Sapphire Substrate with Minimal Step Bunching ", *Phys. Express* 11, 015503 (2018).

<u>1988 ~ 2019</u> Substrate for Realizing High-Voltage and High-Power Transistors

In 1986 at the initial development of nitride semiconductor, there was no GaN substrate, differently from Si, GaAs, and InP. I progressed the research on nitride semiconductors including development of substrates. Now, GaN substrates are gradually becoming to be commercially available. Its price is about a half million yen for 2-inchi-diameter.

| | Mismatching to GaN (%) | | | |
|----------------|------------------------|----------------------------------|--|--|
| Substrate | Lattice constant | Thermal expansion coefficient | | |
| (0001) Al2O3 | 13.8 | -25.5 | | |
| (0110) Al2O3 | -1.9, 2.6 | 9, 62 | | |
| (0001) 6H-SiC | 3.4 | 25 | | |
| (101) NdGaO3 | 1.2 | 20.6 | | |
| (111) MgAl2O4 | 9.5 | • • • | | |
| (001) LiGaO2 | +0.2, 2.2 | +19.5, 73.5 | | |
| (201) Ga2O3 | 10.1 | | | |
| (0001) LaBGeO5 | -9.7 | | | |
| (0001) ZnO | -1.9 | 48 | | |
| (001) ScAIMgO4 | -1.9 | -37.4, -10.9 | | |
| | | | | |

Table 7 Researched crystals for GaN substrate

 $Mismatch = \frac{GaN - Substrate}{GaN}$

- [24] T. Matsuoka, "Lattice-Matching Growth of InGaAlN Systems", in *Proc. Fall Meeting of Material Research Symposium* 395, 39 (1996).
- GaN epitaxial growth on 6H-SiC with lattice-mismatch of 3.4 % to GaN (1988)

SiC substrates were fabricated from SiC boules by ourselves

- Lattice-matching growth of InGaN on ZnO substrate fabricated by ourselves (1992)
- New substrate ScAlMgO₄ (SCAM) was reported from Dr. C. D. Brandle of Bell lab. in Fall Meeting of Materials Research Society (Boston, Nov. 1995)



Fig. 23 Crystal structure of SCAM and its lattice-mismatch to GaN



Fig. 24 2-inch-diameter SCAM boule grown with Czochralski method and epi-ready wafer fabricated with cleavage from its boule.

Courtesy: Fukuda Crystal Laboratory

- Starting the collaboration for enlarging SCAM boule between Dr. C. D. Brandle and Fukuda Crystal Laboratory (2013)
- LED fabrication on SCAM substrate (2017)



Fig. 25 LED fabricated on SCAM substrate

• Trail for fabricating free-standing GaN wafer by using the cleavability of SCAM





(a) GaN spontaneously separated from SCAM substrate during cooling after growth

(b) SCAM substrate after self-separation

Fig. 26 GaN grown on SCAM substrate with HVPE SCAM substrate self-separated can be reused.

- [25] K. Ohnishi, M. Kanoh, T. Tanikawa, S. Kuboya, T. Mukai, and T. Matsuoka, "Halide Vapor Phase Epitaxy of Thick GaN Films on ScAlMgO₄ Substrates and their Self-Separation for Fabricating Free-Standing Wafers", Appl. Phys. Express 10, 101001 (2017).
- [26] K. Ohnishi, S. Kuboya, T. Tanikawa, T. Iwabuchi, K. Yamamura, N. Hasuike, H. Harima, T. Fukuda, and T. Matsuoka, "Reuse of ScAlMgO₄ Substrates Utilized for Halide Vapor Phase Epitaxy of GaN", *Jpn. J. Appl. Phys.* 58, SC1023 (2019).

2016 ~ 2018 Development of Evaluation for Substrate ~Visualization of Dislocations~

• Focusing on Principle of Multiphoton-excitation microscope used for observing dislocations in SiC Feature

The light with energy smaller than band-gap energy of SiC is used for excitation. This light can invade over the deep region of specimen. In the observation of the photoluminescence emitted from the specimen, light with energy of a little smaller than band-gap energy of a specimen. The photoluminescence from the deep region of a specimen can be observed in its surface. By scanning excitation light on the surface of a specimen, the two-dimensional information can be obtained. For obtaining the profile along the deep direction, the focusing position of the excitation light is controlled with a lens. Finally, the three-dimensional information can be obtained. As a result, the form and the position of dislocations can be observed because the dislocations can emit any light.



Fig. 27 Observation principle of dislocations with two-photon excitation

- [27] R. Tanuma, M. Nagano, I. Kamata, and H. Tsuchida, "Three-Dimensional Imaging and Tilt-Angle Analysis of Dislocations in 4H-SiC by Two-Photon-Excited Band-Edge Photoluminescence", Appl. Phys. Express 7, 121303 (2014).
- Preparation of two-photon excitation photoluminescence microscope



Fig. 28 Two-photon excitation photoluminescence microscope Ti: Sapphire laser as an excitation light is shown in the back side. https://www.nikoninstruments.com/Products/Multiphoton/A1RMP-Multiphoton • Observation of dislocations in GaN epitaxially grown on sapphire substrate



Fig. 29 Dislocations in GaN by two-photon excitation microscope. For easily discrimination, the black and white is inverted.

[28] T. Tanikawa, K. Ohnishi, M. Kanoh, T. Mukai, and T. Matsuoka, "Three-Dimensional Imaging of Threading Dislocations in GaN Crystals by Two-Photon-excitation Photoluminescence", Appl. Phys. Express 11, 031004 (2018).

Summary of Nitride Semiconductors in Device Applications



Fig. 30 Application field of nitride semiconductors

The already introduced field in society and the expected one is shown with blue and green color, respectively

Contribution to Energy Saving in Lighting of White LEDs Based on Blue LEDs

- Transition of lighting devices and progress of luminosity as shown in Fig. 31
- Contribution to energy saving by enhancing the efficiency of lighting as shown in Table 8



Fig. 31 Development process of lighting devices

 Table 8. Contribution to energy saving by enhancing the efficiency of lighting devices

 Courtesy: Nichia Chemicals

| | year | 2005 | 2010 | 2015 | 2020 | 2025 |
|-----------------------|--------|------|-------|--------|--------|---------|
| LED Penetration | % | 0.05 | 2 | 12 | 30 | 55 |
| Energy Saving | TWh/yr | 2 | 67 | 330 | 720 | 1,100 |
| Energy Cost Saving | M\$/yr | 200 | 6,700 | 33,000 | 72,000 | 110,000 |

[29] R. Haitz, F. Kish, J. Tsao, and J. Nelson, "The Case for a National Research Program on Semiconductor Lighting", SANDIA REPORT, SAND2000-1612. (2000).

<u>Published Book for Understanding the Mechanism of Epitaxial Growth for Nitride</u> <u>Semiconductors ed. by T. Matsuoka and Y. Kangawa</u>



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