Blue LEDs

International Edition: DOI: 10.1002/anie.201501651
German Edition: DOI: 10.1002/ange.201501651

Growth of GaN Layers on Sapphire by Low-Temperature-Deposited Buffer Layers and Realization of p-type GaN by Magesium Doping and Electron Beam Irradiation (Nobel Lecture)**

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blue LEDs · electron beam · gallium nitride · light-emitting diodes · semiconductors

This Review is a personal reflection on the research that led to the development of a method for growing gallium nitride (GaN) on a sapphire substrate. The results paved the way for the development of smart display systems using blue LEDs. The most important work was done in the mid to late 80s. The background to the author's work and the process by which the technology that enables the growth of GaN and the realization of p-type GaN was established are reviewed.

1. Motivation to Research Blue LEDs

To explain blue-light-emitting diodes (LEDs), it is worth showing an example of how they have changed our lives. Handheld game consoles and smart phones are very familiar items, especially to young people. The world's first handheld game console was released in 1979[1] and cellular phones first became commercially available in 1984.[2] But until the end of the 90s, all the displays of handheld game consoles and cellular phones were monochrome. So, it should be emphasized that the younger generation can now enjoy full-color handheld game consoles and cellular/smart phones because of the emergence of blue LEDs. Today, the applications of blue LEDs are not limited to displays. In combination with phosphors, blue LEDs can act as a white-light source[3] and are also used in general lighting.

In this introduction, let me briefly explain why I became interested in the development of blue LEDs. The two giant computer-related companies, Microsoft and Apple, were established by Bill Gates and Paul Allen in 1975[4] and by Steve Jobs and Stephen Wozniak in 1976,[5] respectively. Since then, the market size of computers, especially personal computer (PC) systems has expanded enormously.[6] When these companies were first established, Braun tubes were used in almost all displays as well as in television systems, but they were too big to be used in laptop PCs. Also, the use of Braun tubes in televisions meant that they were too bulky to be comfortably used in small Japanese houses. So, when I found nitride-based blue LEDs listed as an undergraduate dissertation topic in Professor Akasaki's laboratory, Nagoya University, in 1982, I was excited. The reason why I chose his laboratory was that as a naive undergraduate student, I thought that the subject of nitride-based blue LEDs would be easy to understand. I thought that if I could achieve the production of blue LEDs, I would contribute to improving the quality of life of people by helping to realize wall-mounted television systems and elegant PC systems, meaning that I would change the world. Of course, I was not aware at that time of the difficulty of this subject.

2. Difficulties of Developing GaN-Based Blue LEDs

When we try to grow bulk GaN crystals from a solution, we need a very high pressure and high temperature, similar to those needed for diamond growth, or even higher.[7,8] So, we have to use a chemical reaction to reduce the pressure and temperature required for the growth of GaN. Also, we have to use foreign substrates. For the synthesis of GaN, we used ammonia as the nitrogen source[9] because nitrogen molecules are inert and do not actively react with metallic Ga. Ammonia is very active at temperatures of around 1000 °C, at which GaN can be synthesized, therefore the range of materials that could be used as the substrate was limited.

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Sapphire was one of the most promising substrate materials because it is stable at high temperatures and does not react with ammonia so strongly.[10] But the most serious problem with sapphire is its large mismatch with GaN of up to 16% for each (0001) plane. In general, for heteroepitaxial growth, some people think that the lattice mismatch should be less than a few percent,[11] so a mismatch of 16% should make it almost impossible.

In 1971, Professor Pankove developed the first GaN-based blue LEDs, which were metal-insulator-semiconductor (MIS) systems fabricated by hydride vapor-phase epitaxy (HVPE), which involved the chemical reaction of Ga and hydrogen chloride to form GaCl and ammonia.[12] At that time, it was believed to be impossible to grow p-type GaN because of self-compensation.[13] Self-compensation means that if we dope acceptors as an impurity, the same number of intrinsic donors, such as nitrogen vacancies, are generated to compensate for the doped acceptors.

Another reason why bright blue LEDs are so difficult to prepare is related to the sensitivity of the human eye. The responsivity of the human eye to pure blue light is only 3% of that to 555 nm yellow-green light.[14]

3. Funding Situation of Universities in Japan in the Mid 1980s and the Difficulties of Growing GaN on a Sapphire Substrate

Let me go back to the early 80s. Professor Akasaki started his research on nitrides in 1967[15] at Matsushita Research Institute Tokyo (MRIT), now Panasonic, first investigating powdered AlN. Then, his group started to grow GaN by molecular beam epitaxy (MBE) and observed its cathodoluminescence. Then, his group switched to HVPE and succeeded in fabricating MIS-type blue LEDs with a flip-chip configuration in the late 70s.[16] Unfortunately, however, MRIT decided to abandon its project on GaN-based blue LEDs, so Professor Akasaki moved from MRIT to Nagoya University in 1981. I joined his laboratory in 1982 as an undergraduate student.

The problem of fabricating MIS-type blue LEDs using HVPE was that the growth rate was so high that it was difficult to control the thickness of the insulating layer in the MIS-type structure. Therefore, the operating voltage could not be controlled. Also, Professor Akasaki noticed the difficulty of growing GaN by MBE. Therefore, he decided to use metal–organic vapor-phase epitaxy (MOVPE) for the growth of GaN. At that time, funding for research at Japanese universities was insufficient.[17] Also, there was no commercially available MOVPE system especially designed for the growth of GaN. Therefore, it was impossible to buy an MOVPE system. So, in 1982, a Master's student two years older than me developed the first vertical-type MOVPE reactor.[18] At that time, the flow rate was so low that we could not grow GaN using hydrogen as the carrier gas. I tried to visualize the flow pattern by using the reaction between $TiCl_4$ and H_2O to form TiO_2 powder and found that the flow rate would be insufficient if I used hydrogen as the carrier gas.

In 1984, a PhD student, now Dr. Y. Koide, joined Professor Akasaki's laboratory and started research on AlGaN and AlN, while I focused on growing GaN. From experience, I knew that the flow rate would be insufficient if I used the old configuration of gas supply tubes in the reactor, so I merged all the gas lines into one line and increased the flow rate from a few $\mathrm{cm\,s^{-1}}$ to more than $4\,\mathrm{m\,s^{-1}}$.[19] Then, I successfully grew GaN on a sapphire substrate, even though I

Hiroshi Amano was born in Hamamatsu, Shizuoka Prefecture, Japan, on September 11, 1960. Hamamatsu is famous as the birthplace of Professor Kenjiro Takayanagi, a Japanese pioneer in the development of televisions, and also Soichiro Honda, who established Honda Motor Co., Ltd. In addition, several engineering and manufacturing companies, such as motorbike companies, musical instrument companies, and optoelectronics companies, are based in Hamamatsu. A possible reason why he considered a carrier in engineering may have been in the influence of growing up in such an industrial city.

He spent elementary school, junior high school, and senior high school at Hamamatsu, then moved to Nagoya in 1979 to enter Nagoya University as a student of the Department of Electrical Engineering. In 1982, he joined Professor Isamu Akasaki's laboratory, where he started research on nitride-based blue LEDs as his dissertation topic. He then continued to devote himself to the research and development of group III nitride semiconductors and their device applications. In 1983, 1985, and 1989, he received his Bachelor of Engineering, Master of Engineering, and Doctor of Engineering, respectively, from Nagoya University, Japan.

In 1985, he developed the low-temperature-deposited buffer-layer technology, which enabled the development of high-quality group III semiconductor-based LEDs and laser diodes. In 1988, after finishing his Ph.D. program, he became a Research Associate of the School of Engineering, Nagoya University. In 1989, he succeeded in growing p-type GaN and fabricating a p-n junction LED with his colleagues for the first time in the world.

In 1992, he moved to the School of Science and Technology, Meijo University, to work with Professor Akasaki, where he became an Assistant Professor. In 1998 and 2002, he became an Associate Professor and Professor, respectively. In 2010, he moved to the Engineering Department, Nagoya University, where he continued work as a Professor. He has been Director of Akasaki Research Center, Nagoya University, since 2011.

He has been awarded several honors, such as the IEEE/LEOS Engineering Achievement Award, IEEE, in 1996, the Rank Prize, Rank Prize Foundation, UK, in 1998, the Marubun Academic Award, Marubun Research Promotion Foundation, Japan, in 2002, the Takeda Award, Takeda Foundation, Japan, in 2002, the Japanese Association for Crystal Growth Award, JACG, Japan, in 2008, the NISTEP Award, National Institute of Science and Technology Policy, Japan, in 2009, the Order of Culture from the Japanese Emperor, in 2014, and the Nobel Prize in Physics, Nobel Foundation, Sweden in 2014.

He has been a fellow of the Japan Society of Applied Physics, JSAP, Japan, since 2009 and a fellow of the IOP, Institute of Physics, UK, since 2011. He is also a member of several academic organizations. Selected activities include Sub Chair of the Program Committee of the International Symposium on Compound Semiconductors in 2007, Program Committee Chair of the Second International Symposium on Growth of Nitride Semiconductors in 2010, Program Committee Chair of the 3rd International Symposium on Growth of Nitride Semiconductors in 2012, and Organizing Committee Chair of the International Workshop on Nitride Semiconductors in 2012.

used hydrogen as the carrier gas. Unfortunately, the surface was quite rough and the quality was very poor.

I tried to grow GaN many times while varying the growth temperature, the flow rate of the source and carrier gases, the configuration of the linear tubes, the susceptor shape, and other parameters. But I could not grow high-quality GaN with a smooth surface. The problem of the large lattice mismatch of 16% was too great for a Master's student to overcome. So, almost two years passed without any success.

4. Low-Temperature-Deposited Buffer Layers

In February 1985, I was almost at the end of my Master's course. A foreign student and I had decided to start a PhD program from April. While all the other Japanese students went on a graduation trip, I carried out lonely experiments. At that time, Dr. Koide was growing Al-containing nitrides, such as AlN and AlGaN, and I was growing GaN. When we compared his Al-containing crystals and my GaN, the surface of his crystals seemed to be smoother. Therefore, I thought that AlN could be used to effectively grow GaN with a better surface morphology. So, I tried to grow a thin AlN layer on a sapphire substrate just before the growth of GaN. At that time, I knew that the epitaxial temperature of AlN should be higher than 1200 °C. Because the old oscillator did not work well, I could not get the temperature to reach 1200 °C. However, I suddenly remembered a discussion in the laboratory. Dr. Sawaki, an associate professor at that time, explained the growth process of boron phosphide (BP) on Si,[20] for which the lattice mismatch is as large as 16%. He explained the effectiveness of a preflow of phosphorus as a source gas just before the growth of BP and mentioned that the phosphorus atoms appear to act as nucleation centers. So, I imagined that if I supplied a small amount of AlN at a low temperature, it should provide nucleation centers. The temperature sequence in the growth process is shown in Figure 1. Usually, I looked inside the reactor during growth to see whether there was an interference pattern on the substrate, by which I could check that the source gas had been properly supplied. But at that time, I was tired and forgot to check the interference pattern. When I took the sample out from the reactor and saw that it had a perfectly smooth surface and was perfectly transparent, I thought, "Oh, I've made a mistake! I forgot to supply trimethylgallium!".

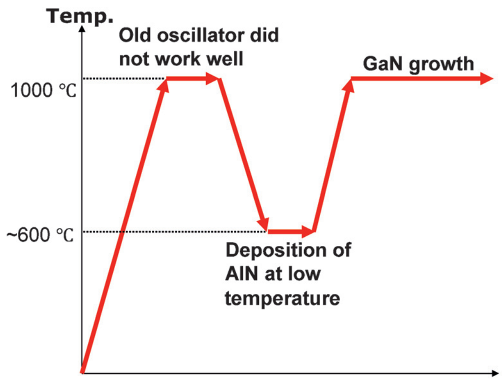

Figure 1. Susceptor temperature sequence in the growth of GaN on a sapphire substrate using a low-temperature-deposited AlN buffer layer.

But after rethinking, I recognized that I had not made a mistake.

So, I checked the surface using a Nomarski-type microscope and found that I had succeeded in growing atomically flat GaN as shown in Figure 2. Following the suggestion of Professor Akasaki, I evaluated other qualities, such as the crystalline, optical, and electrical qualities, all of which were superior to those in previous reports. This process is known as "low-temperature-deposited buffer layer technology" and has been used by many researchers worldwide.[21–37]

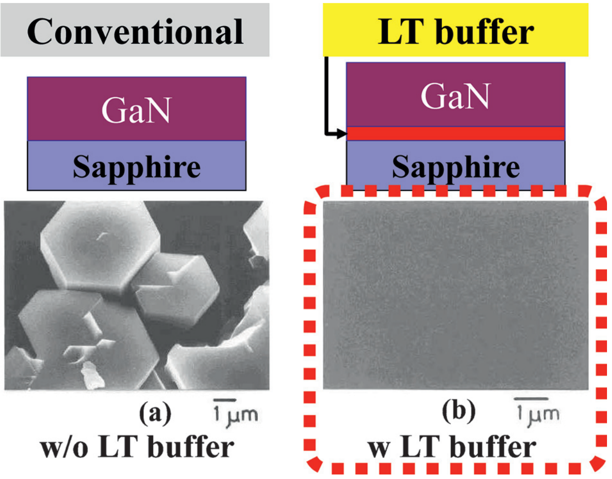

Figure 2. Scanning electron microscopic images of GaN on a sapphire (0001) substrate a) without and b) with a low-temperature-deposited AlN buffer layer.[19]

5. Realization of p-Type GaN

The next task for us was to realize p-type GaN. I grew Zn-doped GaN many times, but all the samples were highly resistive or n-type. In 1987, during my PhD program, I observed very sharp exciton emission from Zn-doped GaN grown on *c*-plane and *a*-plane sapphire at a cryogenic temperature.[22] I also measured the deformation potential of the GaN. I was excited by these results and tried to present them at the Japan Society for Applied Physics annual fall meeting held at Nagoya University. However, I was surprised to see that there were only four people in the room for my presentation, the chairman, Prof. Akasaki, one other guy and me. At that time, other researchers were interested in other compound semiconductors, such as GaAs and ZnSe, and GaN researchers were in the minority. Also in 1988, during my internship as part of my PhD program, I found that Zn-related blue emission was enhanced irreversibly during cathodoluminescence measurement, as shown in Figure 3.[38] So, I called this process low-energy electron beam irradiation (LEEBI) treatment. But even after the LEEBI treatment, Zn-doped GaN did not show p-type conductivity.

In 1989, I became a research associate in Professor Akasaki's group at Nagoya University. When I read the

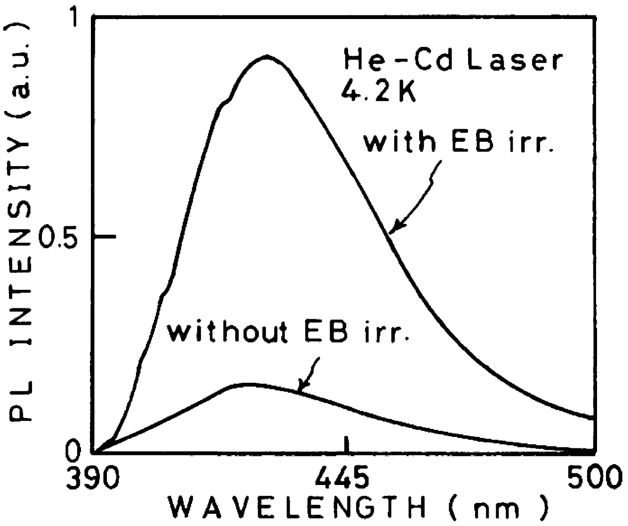

Figure 3. Change in blue PL intensity upon electron beam (EB) irradiation of Zn-doped GaN.[38]

textbook “Bonds and Bands in Semiconductors”, written by Dr. Phillips,[39] I found one graph particularly interesting. It shows that Mg is better than Zn for the activation of acceptors. However, the Mg source, Cp_2Mg, was too expensive. So, I begged Professor Akasaki to let me buy some. He kindly gave permission, and after waiting several months for it to arrive, I was able to grow many Mg-doped samples with my laboratory partner Mr. Kito, at that time a Master’s student.

Here, I would like to mention the pioneering work of Dr. Maruska in 1972,[40] who at that time was a student at Stanford University. He succeeded in fabricating the world’s first MIS-type violet LED using Mg-doped GaN.

All our Mg-doped GaN samples were initially highly resistive after their growth. But after LEEBI treatment, some samples showed p-type behavior when subjected to hot probe measurement. I knew that hot probes are not so reliable and that no one would believe that p-type conduction had been achieved. So, Mr. Kito subjected the samples to Hall effect measurement and we finally recognized that we had obtained p-type GaN for the first time in the world. We also fabricated p-n junction ultraviolet LEDs as shown in Figure 4.[41–44] Soon after this achievement, Dr. Nakamura’s group also used LEEBI treatment.[45,46] In 1992, Dr. Nakamura claimed that p-type GaN could be obtained by simple thermal annealing.[47] Today, almost all LED companies use this method.

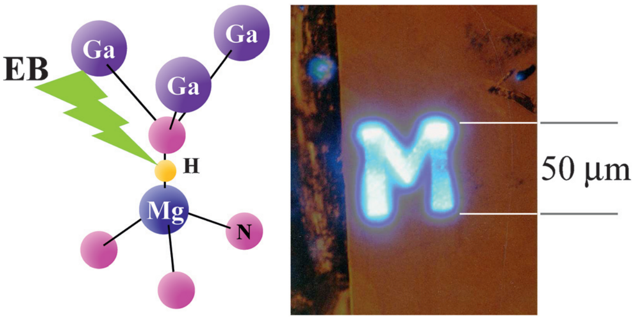

Figure 4. Activation of hydrogen-passivated Mg in GaN[48] and electroluminescence pattern of a GaN LED in which only the area of the “M” was irradiated with an electron beam.[41]

The mechanism of p-type conduction involves the desorption of hydrogen near Mg acceptors, as shown in Figure 4. This mechanism was first pointed out by Professor Van Vechten[48] and later confirmed experimentally by Dr. Nakamura.[47]

6. Attempts to Grow InGaN

For us, another important task was to realize true blue emission using a band-to-band transition. So, we tried to grow InGaN. However, this was also very difficult and we only succeeded in growing InGaN with an In content of less than 1.7 %.[49]

In 1989, Dr. Matsuoka’s group at NTT reported the successful growth of InGaN under an extremely high ammonia supply, while also using nitrogen as a carrier gas.[50] They also reported blue-violet photoluminescence (PL) at 77 K, indicating the incorporation of In. At room temperature, deep-level-related yellow emission could be observed. The mechanism of In incorporation in InGaN has been clarified by thermodynamic analysis by Professor Koukitu et al.[52,53]

Finally, by combining high-quality-crystal growth technology using a low-temperature-deposited buffer layer with p-type growth technology and InGaN growth technology, Nichia Corporation succeeded in commercializing double-heterostructure-type InGaN blue LEDs for the first time in the world in 1993.[54] They also fabricated single-quantum-well LEDs in 1995,[55] which are also a very important technology for enhancing the efficiency of nitride LEDs because a very narrow quantum well suppresses the quantum-confined Stark effect,[56] thus increasing the transition probability.[57]

7. Contribution of InGaN-Based Blue LEDs to Energy Saving

To conclude, let me explain how InGaN LEDs can contribute to improving the electricity situation, especially in Japan. Many people remember the great earthquake of east Japan and the meltdown of the nuclear power plants in 2011. Currently, none of the 48 nuclear electricity generators in Japan are in operation.[58] Before 2011, about 30 % of Japan’s electricity was generated by nuclear reactors. So, we have to find a way of adapting to the loss of 30 % of Japan’s generating capacity. The US Department of Energy predicted that more than 70 % of lighting will have been replaced with LED lighting systems by the year 2030 in the United States, resulting in a 7 % reduction in electricity use.[59] In the case of Japan, the penetration of LED lighting systems into the market is expected to be much faster. A research company in Japan has predicted that by 2020 more than 70 % of general lighting systems will have been replaced with LED lighting.[60]

More importantly, we can develop and supply compact lighting systems to the younger generation, especially chil-

Figure 5. Image of the Earth at night (provided by NASA).[61]

dren in remote areas without access to electricity. Figure 5 shows an image of the Earth at night provided by NASA.[61] Using an LED lighting system with a solar cell panel and a battery, children can read books and study at night as shown in the inset images of Figure 5.

Finally, I would like to address younger researchers. When we obtained the LT buffer, I was a 24-year-old Master's student, and when we first realized p-type GaN, I was 28 years old. Of course I was very lucky to have carried out research under the excellent supervision of Prof. Akasaki and many distinguished colleagues. These days, facilities and funding are much better than in the 80s. So, I would like to see the younger generation attempting to tackle subjects that will greatly contribute to improving the quality of human lives. By doing so, the younger generation can develop a much better world for themselves.

Acknowledgements

I would like to thank the following people: Isamu Akasaki, Nobuhiko Sawaki, Kazumasa Hiramatsu, Shigeru Tamura, Atsushi Shimizu, Yasuo Koide, Kenji Itoh, Takahiro Kozawa, Masahiro Kito, Kouichi Naniwae; the previous students of Professor Akasaki's group at Nagoya University, Satoshi Kamiyama, Tetsuya Takeuchi, and Motoaki Iwaya; the previous students of the group of Akasaki and Amano at Meijo University, Masahito Yamaguchi, Yoshio Honda, Guangju Ju, Kaddour Lekhal, and Siyoung Bae; the students of Amano, Yamaguchi, and Honda Laboratory at Nagoya University, Aki Eguchi, Masako Yasui, Yoko Tatsumi, Tomoko Hosoe, Michinari Hamaguchi, Hideyo Kunieda, Yoshihito Watanabe, Yasuo Suzuoki, and Seiichi Matsuo; the staff of Nagoya University, Koichi Ota, Naoki Shibata, Nobuo Okazaki, Katsuhide Manabe, Michinari Sassa, Hisaki Kato, Masahiro Kotaki, and Tadashi Arashima; the staff of Toyoda Gosei, Masafumi Hashimoto, Akira Hirano, Masamichi Ipponmatsu, Cyril Pernot, Hidemasa Tomosawa, and Toshihiko Kai; and the staff of UVCR and Nikkiso. Finally, I would like to express my sincere gratitude to my parents Yoshiko and Tatsuji Amano, my brother Takashi Amano, and my family Kasumi, Aya, and Mitsuru Amano.

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 7764–7769
Angew. Chem. **2015**, *127*, 7874–7879

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Received: February 19, 2015