

Enchanted Journeys in Blue Light

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Introduction

It is a great honor and real pleasure for me to receive the Kyoto Prize for my work as a semiconductor scientist, in this year which marks the 25th Anniversary of the Prize.

Today I would like to share with you my long journeys leading up to this day. I will start with a quick look back on from my childhood through graduation from university, and then I will explain how I became drawn to blue light-emitting devices as I worked on various projects. I will also describe how I eventually realized a gallium nitride (GaN) p-n junction blue light-emitting diode (LED) as a result of collaborative work with a large number of my fellow researchers.

I was born in Chiran-cho, in the prefecture of Kagoshima, and grew up in the northeastern part of the city of Kagoshima. Kagoshima is a very scenic place, and back then there was still a great deal of nature in the city. A large number of historic sites were preserved, and historical events were still very much present in memory.

As a young boy, I loved playing in the nearby fields and the Iso-kaigan beach, just like all other children of those times. I would go out running around catching bugs and playing on the rocky shores until the sunset. I was also very interested in crystal habits of minerals and crystals found in mineral specimens, and I still love looking at fieldstones. This may have had something to do with my delving deep into crystals in later years.

I went to the Second Kagoshima Junior High School (a Prefectural Boy's School founded in 1906), which my brother, who was two years ahead of me, had also attended. He was a member of the Keiten-kai association, and I followed suit. This association, as I understood it based on the accounts of senior students, was a part of community educational system that originated in the former Satsuma Domain. Under the system, boys would work hard together and learn from each other, and seniors would mentor juniors. At the Keiten-kai association, each Sunday in the early morning, we would start the day by

cleaning the grounds of the cemetery of Saigo Takamori and his comrades, and the Nanshu Shrine, raising the national flag on a tall Moso bamboo pole and admiring the view of Mt. Sakurajima before us. We would spend the rest of the day feeling serene. Often, we would go camping in the mountains or by the beach, for the purpose of mental and physical training as well as to promote our friendship with each other. The name “Keiten,” by the way, was derived from Saigo Takamori's dying instruction of *Keiten Aijin*, or “Revere Heaven, Love People.”

My years at primary and junior high school fell in the middle of World War II, and thus I received a militaristic education. I went to school from home until May in my ninth grade year, though, and I still took part in Keiten-kai activities and spent time with friends around places like Shiroyama Hill after school (Fig. 1).

My father was a descendant of Satsuma warriors. Being rather taciturn and not exactly an outgoing person, he did not fuss too much over details when it came to what his children would do every day or what course they would take in the future. Instead, he left such matters to my mother. She was a pious Buddhist, always kept a smile on her face, and watched over us with a warm eye. She encouraged us to pursue whatever course we liked, as long as it would not be a nuisance to others.

By the time I was in the ninth grade, however, the war situation was worsening day by day, and mobilization of junior high school students began. In May that year, I left my parents to join other students in making aircraft bunkers, with a straw basket on my back, at the Navy's air fleet base in Kanoya. From April 1945, when I was in my tenth grade year, I worked as a milling machine operator at the Naval shipyard in Sasebo, and I hardly attended any classes at school until the defeat of Japan that ended the war. In September 1945, I returned to school in the second term of my tenth grade year. The city of Kagoshima, however, had been hit by an air raid that had burned down most parts of the city. My parents had been living at an evacuation home deep in the mountains, with no electric light. The house was about ten kilometers away from the city, and it would take a total of three and half hours just to go to school and back. This left me with hardly any time to study. Yet I remember eagerly reading old borrowed books in the dim light of what I think was a fish-oil-fueled lamp. Those were tough times, with severe shortages of food and supplies including textbooks, and I am most grateful to my parents for their understanding of their children's keenness to learn.

In March 1946, I sat for the entrance exam for the Seventh High School under the prewar education system. I was accepted, fortunately; however, the Seventh High School had been burned down, and it was not until the end of November in the year that the school reopened at the former base of the Navy's air fleet in the city of Izumi in northern Kagoshima. The school used former barracks for makeshift buildings. Broken windows remained everywhere, and we would sometimes go to classes wrapped in cloaks to keep ourselves protected from the cold winds. Teachers, who were not able to do so, must have had a hard time. Students and teachers alike were poorly nourished, and this made us suffer even more from the cold. The following summer, we started campaigning to raise funds for the reconstruction of school buildings on the grounds of the ruins of Tsurumaru Castle in the city of Kagoshima. The total time I spent at the Seventh High School was a little more than two years, rather than the three years it should have been. So there is no denying that I did not have enough time to learn the basics during my time at junior and senior high schools. I was fortunate to be blessed with good teachers and friends, however, and I enjoyed my life at a student-governed dormitory at the high school, despite the lack of material comforts.

I had long set my mind on attending Kyoto University. What I had not decided, until half a year before the due date, was my major: physics or chemistry? Because of the strong recommendation from a senior student in my hometown, I eventually chose to major in chemistry in the faculty of science.

During my college years in Kyoto, I would often go out and visit temples and shrines in Kyoto and Nara between lectures or laboratory classes. In the summer, when I did not return home, I would go mountain climbing in Shinshu area (Nagano prefecture), using Kyoto University's Sasagamine Hutte as a base. So the three years at the university felt very short to me.

First encounter with luminescence (Fig. 2)

My first experience with luminescence, or the light emission without the generation of heat, took place in 1954. I was assigned to work on fluorescent screens of Braun tubes (cathode-ray tubes for televisions) at the Akashi Plant of Kobe Kogyo Corporation, which is now known as Fujitsu Limited. Although liquid crystal displays

(LCDs) or plasma display panels (PDPs) have largely replaced them in recent years, Braun tubes were the mainstream for television screens for the first half of a century after television broadcasting started. Zinc cadmium sulfide (ZnCdS)-based powder phosphor is applied to the inner surfaces of the faceplates of Braun tubes. The fluorescent screen of a Braun tube emits light due to excitation by an electron beam accelerated to some ten kilovolts. I have been working on luminescence ever since this first experience with the phenomenon, which left me utterly intrigued. Fluorescent screens are made fairly thick, relative to the depth of electron penetration so as not to allow pinholes to develop. Thus, a considerable amount of the light emitted is absorbed by the powder phosphor layer, resulting in lower brightness. This made me seriously wonder if it would be possible to make images brighter by layering thin transparent crystals, rather than powders, that would emit light via electron beam excitation. This is what we call today the epitaxial growth of light-emitting semiconductor crystals on a glass substrate, but back then it was nothing but a pipe dream. This idea of “light-emitting single crystals,” however, seems to have always been somewhere in my subconscious.

It was during this period that transistors first started to appear, and germanium (Ge) single crystals and transistors were being investigated in the Department of Research and Development at our Kobe headquarters. Being a semiconductor material, germanium doesn't emit light; still, single crystals, rather than powders, appealed to me very much.

Epitaxial growth of semiconductor single crystals

It was in 1958 that division manager Dr. Tetsuya Arizumi, who was my boss at the time, invited me to move to the then-new Department of Electronics at Nagoya University. In the following year, I moved there and started working on growing high-purity single crystals of germanium and studying physical properties of semiconductors. At first, Professor Arizumi and I worked together by ourselves without even a table, but this marked a turning point in my research into crystals and semiconductors. Back then, a p-n junction in germanium was fabricated by diffusing arsenic (As) into a (heated) p-type germanium single-crystal substrate. I started working on what we now call vapor-phase epitaxial growth in 1960. This was a way to create a p-n junction with any impurity distribution without allowing the n-type layer to become

compensated, or soiled, by acceptors in the substrate. I successfully grew germanium single-crystal films, although not with mirror surfaces, in the following year. In 1962, I launched fully into the research of the epitaxial growth of germanium, working together with Tatau Nishinaga, who was then a graduate student. The sense of anticipation and excitement I'd feel when taking the crystals out of the reactor tube led me to commit myself deeply to the world of crystal growth. This work would also land me a position at the newly established Matsushita Research Institute Tokyo, Incorporated, in 1964.

Research on compound semiconductors and light-emitting devices

There I started working on “light-emitting semiconductor single crystals,” which I had long had in my mind; namely, III-V compounds, which include gallium arsenide (GaAs), among others. I focused on the crystal growth of such compounds and their light-emitting devices, such as light-emitting diodes (LEDs) and laser diodes (LDs). III-V compounds are those of elements of Groups III and V in the Periodic Table of the Elements, having eight outer-shell electrons. They are called compound semiconductors, in contrast with elemental semiconductors such as silicon (Si) and germanium.

Red or yellow-green LEDs based on gallium phosphide (GaP) or gallium arsenide phosphide (GaAsP) had already been developed, as had GaAs-based infrared LDs. At the time, the prospect of developing commercial applications for devices emitting blue light, with the largest energy and shortest wavelength in the visible spectrum, had yet to emerge.

The energy of the photons emitted by light-emitting semiconductor devices, such as LEDs, is approximately equal to the energy gap (E_g) of the semiconductor that is being used. The wavelength of blue light is in the range from 455 to 485 nanometers [nm] according to the JIS standards (Fig. 3).

Therefore, there were two requirements for creating blue light-emitting devices. Requirement A: it is essential to use semiconductors with an energy gap of approximately 2.6 electron volts [eV] or larger, equivalent to a wavelength of 485 nm or shorter. Semiconductors that have such a large energy gap are called wide-bandgap semiconductors, while the energy gap of generally used silicon semiconductors is 1.1 eV.

And requirement B: it is definitely advantageous to use direct transition type

semiconductors, because LEDs utilize a process in which conduction band electrons in an excited state are transferred to the valence band, ground state, while emitting light. In direct transition type semiconductors, the momentum of electrons at the bottom of the conduction band is nearly equal to that of holes at the top of the valance band, yielding high radiative recombination probabilities. Silicon and germanium, on the other hand, have a small energy gap, and they are indirect transition type semiconductors, which have lower radiative recombination probabilities.

Furthermore, requirements A and B do not always correspond to sufficient conditions. It is essential to (1) grow high-quality single crystals, and (2) realize p-n junctions successfully for semiconductors that meet both requirements (Fig. 4). It is, however, extremely difficult in general to achieve (1) and (2) in wide-bandgap semiconductors.

While crystals are a solid material with a spatially periodic atom arrangement, single crystals have crystallographic axes in the same directions in any given part of a sample meaning they are not simple aggregates of microcrystals. High-quality single crystals are required, as mentioned earlier in (1), in order to reduce as much as possible the many impurities and lattice defects that may interfere with light emission. It is also essential to enable control of the electrical conductivity of semiconductors to form p-n junctions, as in (2) above.

Some Semiconductors have more holes, or the lack of electrons, than electrons. In other words, they are electrically positive, and thus they are called p-type semiconductors. Others have more electrons than holes, and thus they are electrically negative, or n-type semiconductors. A structure with an atomically continuous junction—we use the word “junction” rather than “contact”—of p- and n-type semiconductors is called a p-n junction. Here, in terms of atom arrangement, the entire thing forms a seamless, single crystal. Such a p-n junction is one of the basic structures of semiconductor functional devices. It gives rise to a number of important functions, including transistor action and highly efficient light emission.

In the 1970s, promising material candidates for blue light-emitting devices included: silicon carbide (6H-SiC) with an energy gap of 3.1 eV; zinc selenide (ZnSe) with an energy gap of 2.7 eV; and gallium nitride (GaN) with an energy gap of 3.4 eV (Fig. 5).

Among these, SiC was the only wide-bandgap semiconductor that could be used

to create p-n junctions in those days, and the development of blue LEDs was attempted using it. It is, however, an indirect transition type semiconductor, and it is not suitable for the development of efficient light-emitting devices.

ZnSe and GaN, meanwhile, were both known as being direct transition type semiconductors, but it is difficult to grow large bulk crystals using them, and no p-type crystals had been realized yet.

When it is difficult to develop large-sized crystals, epitaxial growth methods are used for the growth of single crystal thin films (Fig. 6). Of these, vapor-phase epitaxial growth is a method to provide source materials for a crystal to be grown onto the substrate crystal in a form of gas. Growth then takes place such that the crystallographic axes of the grown crystals agree with those of the substrate crystal. This method is widely used in the growth of high-quality semiconductor nanostructures. We use the term “homoepitaxy” when the grown crystal is the same as the substrate crystal, and “heteroepitaxy” when the two are different. In the latter case, it is necessary for the lattice constants of the grown and substrate crystals to be as similar as possible.

ZnSe can emit a bright light with the excitation of electron beams. It can use GaAs single crystals, which have lattice constants very close to those of ZnSe, as substrate crystals for vapor-phase epitaxial growth to obtain good-quality single crystals. Thus, numerous researchers have worked on ZnSe, aiming to develop blue light-emitting devices.

In the case of GaN, both the melting point and the vapor pressure of nitrogen are very high, making it extremely difficult to produce large-sized bulk crystals. Thus, one must rely on heteroepitaxial growth on dissimilar substrate crystals to produce single crystals of this material.

In 1969, H. P. Maruska and J. J. Tietjen successfully grew single-crystalline films on a sapphire substrate using the hydride vapor phase epitaxy (HVPE) method. Later, J. I. Pankove and his colleagues reported GaN-based metal-insulator-semiconductor-type (MIS-type) blue LEDs in 1971. Stimulated by these successes, the research and development of GaN-based blue LEDs saw a temporary surge. Despite various forms of efforts by researchers around the world, however, the quality of GaN remained fairly poor, and neither p-type crystals nor p-n junctions had been achieved yet. By the late 1970s, many researchers had withdrawn from GaN research or had changed their focus to ZnSe or other materials (Fig. 7).

At that time, it was considered extremely difficult to produce p-type crystals, and hence p-n junctions, in wide-bandgap semiconductors such as ZnSe and GaN due to their self-compensation effects. However, my theory ran as follows: “GaN has a residual donor concentration of as high as 10^{19} -- 10^{20}cm^{-3} . We should first grow high-quality crystals with a residual donor concentration of 10^{15} -- 10^{16}cm^{-3} or lower before discussing this effect. If we make our crystals as clean as possible while doping an appropriate acceptor impurity at about 10^{18}cm^{-3} or higher, it may be possible to produce p-type crystals.”

“Since GaN has a larger energy gap than ZnSe, it should be even more difficult to grow crystals and achieve p-type conductivity with GaN. And yet GaN is superior to ZnSe in a number of points, such as the fact that GaN crystals are far more stable both physically and chemically, and in terms of higher thermal conductivity. So our goal should be to produce high-quality single crystals to realize light-emitting devices that are highly reliable.” I set my mind on this goal.

This was how I embarked on my challenge to develop blue light-emitting devices by means of p-n junction of GaN-based semiconductors, something that no one had ever achieved. The year was 1973.

By that time, the molecular beam epitaxy (MBE) method had already been developed as a way to grow GaAs and other high-quality thin-film crystals, but the method had not been tested on GaN. By the MBE method using metallic gallium and ammonia (NH_3) as the source materials, I successfully grew single crystals for the first time in 1974, although they were inhomogeneous. This was reported in an in-house newsletter only and never published as an article. However, the MBE equipment and method were still in the early development stage at the time, and the growth of good-quality films with them was difficult. In the following year, I started working on the HVPE method, but crystal growth proved to be extremely difficult, and we could not produce the high-quality crystals we were aiming for. Not a one to easily give up, though, I continued working on crystal growth together with Yoshimasa Ohki and other fellow researchers. In 1978, we succeeded in fabricating a blue LED with an external quantum efficiency of 0.12%, which was far brighter than anything we had before that, although it was no comparison to p-n junction type LEDs that came later. This was a flip-chip LED with as-grown n+cathode formed by the first-ever use of selective area growth for GaN, and its application to devices was far easier than with existing MIS-type LEDs, which made it a notable success (Fig. 8). For

certain reasons, however, it was not until two years later in 1981 that we presented the results at the International Symposium on Compound Semiconductors, but it produced no impact. By that time, many GaN researchers around the world had left this field, and there was probably no one who would be interested in GaN at the Symposium. I felt like a solitary soul travelling in the wilderness, but I had no intention to quit my GaN research, even if it meant that I would be the last person remaining in the field.

Recognition of the great potential of GaN

In those days, whenever I had time I would often use a fluorescence microscope to look at GaN crystals grown using the HVPE method, just as I had spent time in my childhood enjoying the crystal habits of mineral ores or later in 1960s examining the surface morphology of epitaxially-grown germanium films. On one such day, I noticed that there were some clean microcrystals, though very few, embedded in a wafer with many cracks and pits. I fixed my eyes on them very intensely for a moment, and I intuitively realized the great potential of GaN as a material that could be used for blue light emitting devices.

From the very beginning of my research on GaN, I had kept telling it to myself, as well as my fellow researchers, that “if you make the crystal quality extremely high, you should definitely be able to realize p-type conductivity, too.” To tell the truth, it was not that I had firm grounds to base this belief on. However, this particular experience led me to become convinced that “if I could make the entire wafer with a quality as high as that of these clean microcrystals, which I imagined would have a mirror surface, then I should be able to gain the control of electrical conductivity, as well as p-type conductivity; the key is crystal growth (Fig. 9).”

With this in mind, I decided to go back to the basics of the research—namely, crystal growth—in 1978. This decision, I think, as a major turning point in not only my own GaN research but GaN research and development throughout the world as well, which had been stagnating at the time.

The quality of crystals is greatly affected by the methods and conditions of their growth. Methods for GaN crystal growth included MBE and HVPE, as well as metalorganic vapor-phase epitaxy (MOVPE), or metalorganic chemical vapor deposition (MOCVD) method (Fig. 10).

There I thought again: “The MBE method is used for growth in high-vacuum conditions, and because GaN has very high vapor pressure of nitrogen, it is prone to nitrogen deficiency; so the method cannot be suitable for growing good-quality GaN. The HVPE method has a growth rate that is too fast to control growth of nanometer-scale structures, and involves reverse reactions (decomposition processes); so this is not good for growing high-quality crystals.” The MOVPE method, on the other hand, was used for the first time by H. M. Manasevit and his colleagues in their attempt to grow GaN in 1971, but the results were unsatisfactory and the method had not been used for GaN growth since then. I had a different opinion, however. “This method uses irreversible thermal decomposition reaction within a single temperature range and does not involve reverse reactions, with an appropriate growth rate and a ease of impurity doping and control of mixed crystal compositions. It should thus be the most suitable method for growing GaN on substrates with a large lattice mismatch, such as sapphire.” Thus, in 1979, I decided to chose to adopt this method as an optimal growth method for GaN.

That my choice was not wrong should be clear from the fact that most of GaN-based crystals and devices are produced using the MOVPE method today.

The next step was to choose an appropriate substrate for GaN growth. This choice needs to take into account similarities in crystal symmetry and in physical properties with GaN, as well as tolerance to the MOVPE growth environment, which involves temperatures of approximately 1,000 degrees Celsius, and the presence of a highly reducing ammonia and so on. Having actually compared different materials such as silicon, GaAs, and sapphire, we decided to keep using sapphire as before, for the time being, at least until more suitable substrate crystals became available.

Development of low-temperature buffer layer technology

After making these two important decisions, I returned to Nagoya University, where I had been invited some time before. Upon returning there in 1981, I immediately started working on GaN growth using the MOVPE method, in collaboration with a team of graduate students including Yasuo Koide and Hiroshi Amano. Even with the MOVPE method, however, it was not easy for us to develop homogeneous GaN crystals. After much trial and error, we made drastic innovations and improvements in the reactor tube and

growth conditions.

The first improvement was that we mixed organometallic compounds—such as trimethylgallium (TMGa), in the case of GaN growth—with ammonia (NH₃) and hydrogen (H₂) gas, as a carrier, right in front of the opening of the reactor tube. This allowed us to suppress the adduct formation inside the tube by the reaction of TMGa with NH₃, thereby enhancing the material use efficiency. At the same time, we blew this mixture of the source material gas and carrier gas through a gas introduction tube onto a substrate inclined at a 45-degree angle, rather than placed horizontally as in previous attempts. We used a flow rate of approximately 110 cm per second, rather than the previous 2 cm per second. We were thus able to suppress convection flows on the substrate and make the gas flows smooth to achieve homogeneous GaN films. The key aspects of this first improvement were the use of a slanted substrate and a high-speed gas flow.

Even though the film thickness was now mostly even for the entire wafer, this does not mean there were no pits or cracks (I mean macroscopic defects). There was no substantial improvement in electrical and optical properties, either, which suggested the presence of many impurities and lattice defects.

This would, for the most part, be due to the large interfacial free energy present between GaN and sapphire, caused by the large lattice mismatch of 16% between the two, I suspected (Fig. 11). In fact, for the epitaxial growth of the semiconductor crystals, it is considered to be gospel to have a lattice match as in GaAs growth on GaAs substrate, and in the case of heteroepitaxial growth, even a mismatch of about 1% would make it difficult to grow good-quality crystals.

In order to overcome this issue, we developed low-temperature buffer layer technology in 1985 (Fig. 12). Specifically, this is a method to deposit materials with physical properties similar to those of GaN and substrate materials to make a thin buffer layer of a thickness of 30--40 nm, which is thin enough not to interfere with the transmission of crystallographic information of the substrate to the epitaxial layer, at a considerably lower temperature—say, 500 degrees Celsius—than the epitaxy temperature for growing GaN single crystals. The temperature would then be increased to the epitaxy temperature, which is approximately 1,000 degrees Celsius, to grow GaN single crystals.

This is based on the idea of having a soft or flexible thin film without a rigid structure like that of single crystals, inserted as a buffer between the epitaxial growth layer

and the substrate, for the purpose of reducing the interfacial free energy between the two and creating conditions as close as possible to those for homoepitaxy, where no interfacial free energy exists in principle. For the buffer layer materials, I considered aluminum nitride (AlN), GaN, zinc oxide (ZnO), and SiC. First, we tried AlN, with which I myself was already familiar. Now, I should note that I had long been interested in nitride semiconductors, and I had been studying the crystal growth and optical properties of AlN since 1967.

In addition to the first improvement I just mentioned, GaN single crystals grown using this buffer layer technology combined with a further accelerated gas flow rate of about 430 cm per second were clear and colorless. They had a mirror surface with dramatically improved crystallographic, electrical, and optical properties compared with those possible with conventional crystals (Fig. 13). It was owing to the tenacity of Hiroshi Amano that we finally identified the optimal conditions after overcoming countless failed attempts.

The thrill I felt when I finally saw GaN crystals with an “Ideal form and content” is simply unforgettable. It was something that I had dreamt of realizing ever since 1973.

Towards realization of p-type conduction

We immediately started experimenting to realize p-type conduction. We repeatedly tried zinc (Zn) doping of high-quality GaN crystals (with a residual donor concentration of 10^{15}cm^{-3} or lower) grown using the buffer layer technology, but no p-type GaN was produced although the crystals became highly resistive.

In 1988, we were applying a low-energy electron beam irradiation (LEEBI) to high-quality Zn-doped GaN to examine the characteristics of Zn-related luminescence. During this time, Hiroshi Amano discovered a marked enhancement of the luminescence intensity while the spectrum shape remained unchanged. The term “LEEBI effects” was later used with reference to this phenomenon (Fig. 14).

We suspected that the Fermi level of the sample must have been changed, potentially to the p-type; yet the sample did not exhibit p-type conduction.

We then re-examined the ionization energy of acceptor impurities. According to the book by J. C. Phillips published in 1973, the difference in the electronegativity between

magnesium (Mg) atoms, which substitute for Ga atoms, and Ga atoms is smaller than that between Zn and Ga atoms. This led us to the assumption that magnesium might be more easily activated. So we imported bis-cyclopentadienyl magnesium (CP_2Mg) and methyl- CP_2Mg (MCP_2Mg) to use as magnesium source materials.

In early 1989, the then-graduate-student Masahiro Kito carried out magnesium doping of high-quality GaN grown by the buffer layer technology using CP_2Mg or MCP_2Mg . We then applied the LEEBI treatment to the samples, and found that the Mg-related luminescence intensity had been markedly enhanced while the spectrum shape remained unchanged—namely, the LEEBI effect—and that the samples had been converted to low-resistive p-type conduction, which was confirmed by the Hall effect measurements.

Obviously, I was most thrilled, just as I had been when I first saw the completely transparent crystals with a mirror surface, which were achieved by the buffer layer technology.

We immediately fabricated some p-n junction LEDs by hand (Fig. 15), and we demonstrated more encouraging current-voltage (I-V) characteristics than we had ever seen with any existing MIS-type LEDs, and we confirmed that p-n junctions were achieved through EBIC and other measurements.

The sight of the piercing blue light emission from the first-ever GaN-based p-n junction LEDs amazed me all over again.

Control of n-type conductivity and other issues

In the meantime, we noticed a new problem with the electrical conductivity of n-type crystals. The introduction of a low-temperature buffer layer resulted in a marked decrease in residual donor concentration, causing the crystals to have a high resistivity. In the real setting of device fabrication, it is necessary to control conductivity over a wide range. In 1989, we succeeded in extensively controlling n-type conductivity by Si-doping using silane (SiH_4) gas, while maintaining high crystal quality by means of buffer layer technology (Fig. 16).

This method of n-type conductivity control is also in widespread use around the world.

This is how we achieved all the basic technologies essential to develop

GaN-based p-n junction light-emitting devices and electronic devices by 1989.

Not long after, in 1990 (Fig. 17), we used high-quality crystals based on the buffer layer technology to successfully achieve stimulated emission from GaN, which is essential for laser oscillation, for the first time at a room temperature, with a light input about an order of magnitude lower than existing figures. This demonstrated the marked improvement in the quality of crystals, and together with the p-n junction LED technology we have just discussed, it also suggested the possibility of realizing GaN-based laser diodes (LDs).

These results triggered an acceleration in the research and development of GaN-based crystals and devices, which in turn led to exponential increases in the number of papers published in this field. High-brightness blue light-emitting diodes became commercialized and other GaN-based devices were developed in succession (Fig. 18).

I moved to Meijo University in 1992, and continued with my research in pursuit of further higher-quality crystals based on aluminum gallium nitride (AlGa_N), GaN, and gallium indium nitride (GaInN). Using nano-level and quantum structures, we verified the piezoelectric effect and the quantum-confined Stark effect in nitride semiconductors in 1997. We had already confirmed the quantum size effect in 1991 while I worked at Nagoya University. In 2000, Tetsuya Takeuchi in my group identified the crystal orientation dependence of the piezoelectric field in nitride crystals, and we also found the presence of nonpolar and semipolar crystal planes. Today, researchers around the world are growing crystals and developing devices on nonpolar or semipolar crystal planes, in order to avoid the adverse effects of the piezoelectric field.

As for the development of new devices, we successfully achieved stimulated emission by current injection using AlGa_N/GaN/GaInN quantum wells in 1995, followed by the oscillation of 376 nm LDs in 1996; in 2004, we developed 350.9 nm LDs—the shortest wavelength in the world at the time. Our other developments included ultrasensitive UV photodetectors in 2000, and a high on/off ratio, low on-resistance, normally-off mode AlGa_N/GaN heterostructure field effect transistor in 2006.

More recently, we have also been working on developing high-quality AlGa_N crystals with high AlN molar fractions, which is essential to create high-power ultraviolet light-emitting devices, as well as high-quality GaInN crystals with high InN molar fractions, with the aim of developing light-emitting devices with wavelengths longer than 500 nm.

Conclusion

As they say, “In the beginning there was light,” light is closely tied to our lives. Light is indispensable for mankind and for many other creatures, and humans have pursued light sources since ancient times. Starting with flame, we developed electric light, and fluorescent lamp, and then semiconductor light-emitting devices in the second half of the 20th century. While these light sources, in general, cover a wide wavelength range, the development of high-energy light sources has largely been lagging behind.

The development of blue LEDs has completed the set of light's three primary colors based on semiconductors. This, then, led to the development of full-color displays and white LEDs using perfect solid-state light-emitting devices, while blue-violet lasers, which have built on the blue LED technology, are being utilized for ultrahigh-density information processing and other applications. In addition to general lighting, their applications are expected to expand into multiple areas, such as medical and agricultural lighting sources.

To conclude my remarks today, I would like to add that I am very much a late starter; ever since I fell under the spell of blue light-emitting devices in my early forties, I have simply performed my work honestly in an attempt to realize actual devices. To a regular researcher like myself, it is more honor than I deserve to be able to give this commemorative lecture today, and this is nothing but the result of tremendous help and support from a number of people (Fig. 19).

I would like to take this opportunity to express my heartfelt gratitude to all the people who have mentored and supported me to this day. Thank you very much.



Fig. 1

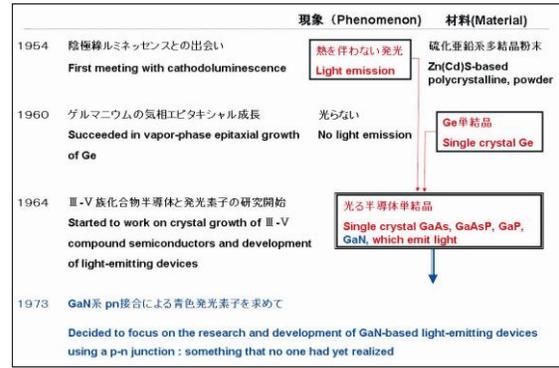


Fig. 2

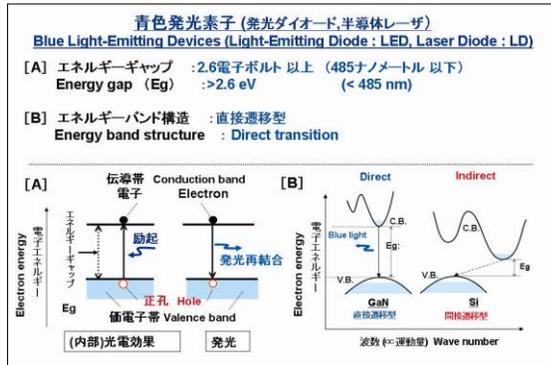


Fig. 3

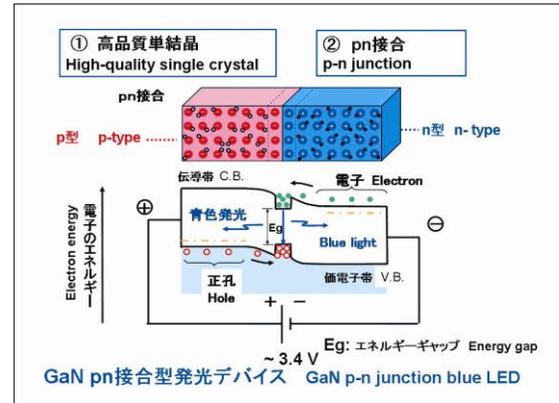


Fig. 4

[1] : 青色LED用材料 Promising materials for blue LEDs (1970s-1980s)

	6H SiC 3.1eV (炭化ケイ素)	ZB ZnSe 2.7eV (セレン化亜鉛)	W GaN 3.4eV (窒化ガリウム)
結晶成長 Crystal growth	△ (×)	△	×
pn 接合 p-n junction	◎	×	×
発光効率 Emission efficiency	間接 Indirect △ (×)	直接 Direct ◎	直接 Direct ◎
機械的性質 Mechanical properties	◎	×	◎
(加工のしやすさ) (Processing)	△	◎	×
化学的安定性 Chemical stability	◎	△	◎
熱伝導 Thermal conductivity	◎	×	○

GaNを選ぶ Chose GaN (1973)

Fig. 5

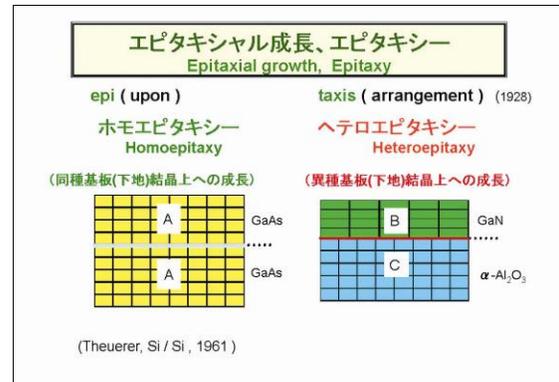


Fig. 6

GaN系青色LEDの研究開発小史 (～1980)	
Brief history of research and development of GaN-based LEDs (～1980)	
1969	GaNの単結晶成長 Single-crystalline GaN by H.P. Maruska and J.J. Tietjen
1971	GaNのMIS型青色LED GaN MIS LED by J.I. Pankove et al.
1971	MOVPE GaN MOVPE growth of GaN by H.M. Manasevit et al.
1970s-	ルミネッセンス、屈折率などの研究
1980s	Study of luminescence and physical properties by B. Monemar, J.I. Pankove and many researchers

1973	GaN研究開始 Akasaki started to work on GaN

Fig. 7

* ハイドライド気相成長 (HVPE) 法による青色LED開発
* 選択成長 (as-grown 陰電極)
GaN blue LED with the first n+ cathode by HVPE in 1978

Y. Ohki, Y. Toyoda, H. Kobayashi and I. Akasaki: Intl. Symp. GaAs and Rel. Comps. (Now. ISCS), (1981)

GaNのポテンシャルを確信
Recognized the great potential of GaN (1978)

Fountain display using tricolor LEDs
1981

Fig. 8

原点: 結晶成長.....に立ち返る 1978
Decided to go back to the starting point: Crystal Growth

p型伝導の実現は、結晶品質の向上から
To realize p-type conduction, it is essential to grow high-quality GaN

(1) 表面の凹凸、クラック、ピットを含む低品質の結晶
Poor-quality with rough and cracked surface

(2) 電気伝導の制御が極めて困難
極めて高密度の残留ドナー
p型伝導は不可能?
Difficulty in conductivity control

鏡面の結晶
クラックフリー
ピットフリー
Specular surface free of cracks and pits

残留ドナー密度の低減
 $10^{13} \sim 10^{15} \text{cm}^{-3}$

高品質の単結晶
 $< 10^{14} \sim 10^{15} \text{cm}^{-3}$
High-quality single crystal

Fig. 9

[2]: GaNの結晶成長法 Crystal growth methods for GaN

MBE 高真空中
 $\text{Ga}(g) + \text{N}(g) = \text{GaN}(s)$ または
 $\text{Ga}(g) + \text{NH}_3(g) = \text{GaN}(s) + \frac{3}{2} \text{H}_2(g)$ (窒素抜け)
Prone to nitrogen deficiency

HVPE 2ゾーン (または 1ゾーン) 50~150 μm
 $\text{GaCl}(g) + \text{NH}_3(g) = \text{GaN}(s) + \text{HCl}(g) + \text{H}_2(g)$ (逆方向反応あり)
Susceptible to reverse reactions
H.P. Maruska and J.J. Tietjen: Appl. Phys. Lett. 15 (1969) 327

MOVPE 1ゾーン 数 μm/h
 $\text{Ga}(\text{CH}_3)_3(g) + \text{NH}_3(g) = \text{GaN}(s) + 3\text{CH}_4(g)$ (逆方向反応なし)
Minimal reverse reactions
H.M. Manasevit et al.: J. Electrochem. Soc. 118 (1971) 1864

MOVPE法を採用 Chose to adopt MOVPE (1979)

Fig. 10

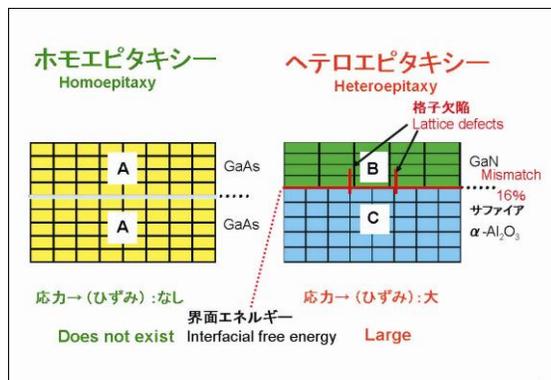


Fig. 11

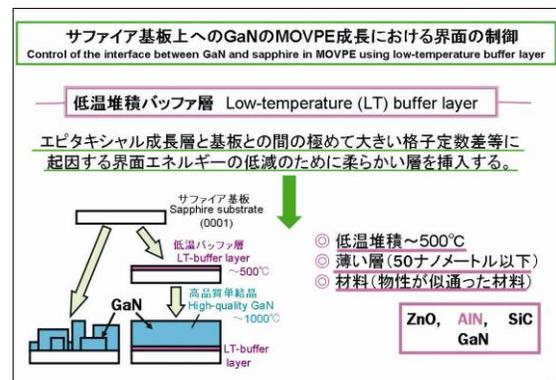


Fig. 12

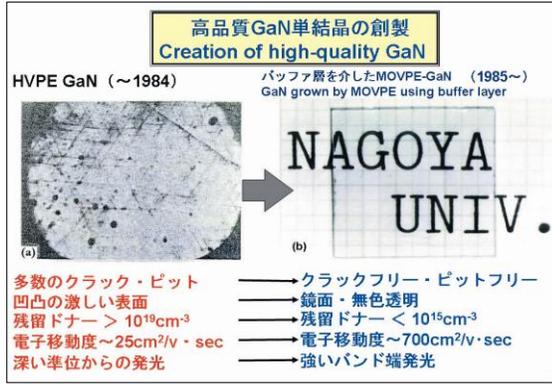


Fig. 13

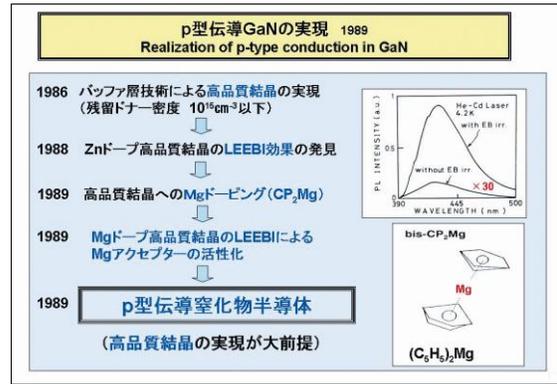


Fig. 14

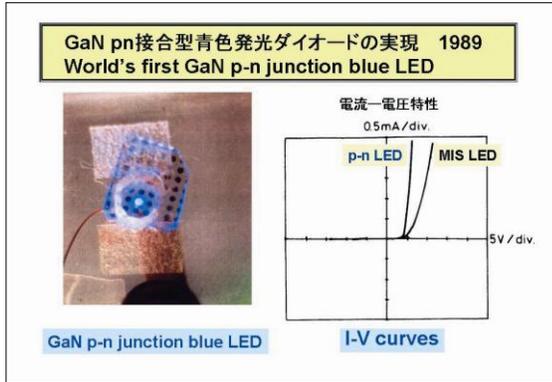


Fig. 15

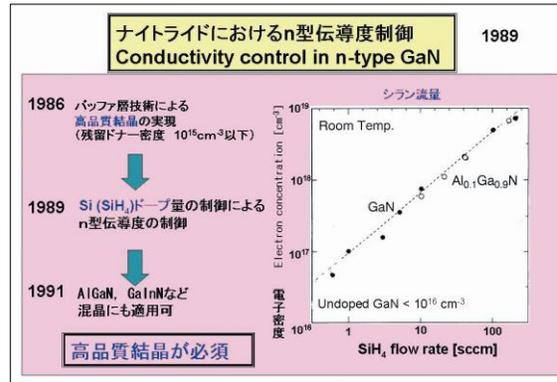


Fig. 16

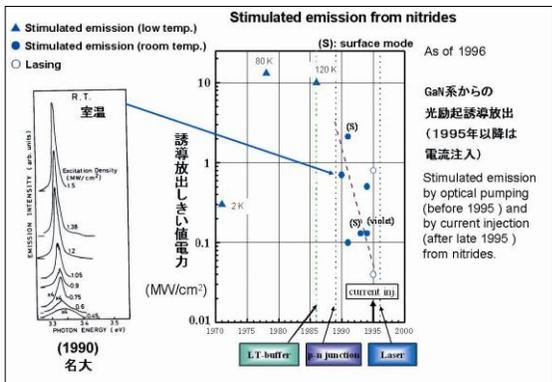


Fig. 17

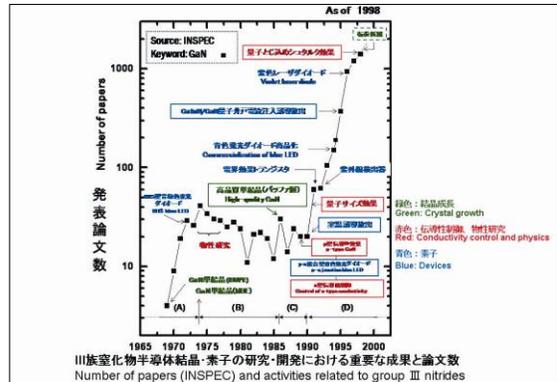


Fig. 18

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- * 名城大学の先生方, 共同研究者, 友人
- * 窒化物半導体研究者仲間
- 他 多くの協力者

Fig. 19