The 2009 Kyoto Prize Workshop in Advanced Technology

“Dramatic Improvement in Gallium Nitride Crystal Quality and Realization of p-n Junction Blue LEDs”

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1. Introduction

I am truly honored to have this opportunity to give the Laureate Lecture here at this symposium on “Nitride Semiconductors and Their Device Applications: Current Status and Future Prospects” in the Kyoto Prize Workshop.

Today, nine guest speakers who are active in the front lines of various research fields related to nitride semiconductors will talk about the current status and future prospects of materials science and device applications of nitride semiconductors. In my presentation, I would like to look back on our journey to realize GaN p-n junction blue light-emitting diodes, which marked the starting point of the research and development of nitride semiconductors being conducted today. (Fig.1)

Nitride semiconductors have been attracting interest as promising materials for realizing blue light-emitting devices since the 1960s. Despite various efforts by researchers around the world, it proved to be very difficult to produce high-quality single crystals. Furthermore, p-type conduction could not be achieved. These problems delayed the development of p-n junction blue light-emitting devices for many years. (Fig.2)

Fig.1

Fig.2

I conducted research on direct bandgap nitride semiconductors. In 1966, I started research on crystal growth focusing on aluminum nitride (AlN), which has largest band gap energy, E_g, of all direct bandgap nitride semiconductors. I then proceeded to conduct studies on lattice vibrations of vapor-grown AlN by infrared reflectivity measurement. *(I.Akasaki and M.Hashimoto: "Infrared Lattice Vibration of Vapour-Grown AlN," Solid State Commun. 5 (1967) 851)* and experiments on blue-light emission by cathodoluminescence (CL) and photoluminescence (PL). However, because the E_g of AlN was too large to realize electroluminescence (EL), I switched my attention to gallium nitride (GaN) in 1973 with the aim of developing a p-n junction blue light-emitting device. In 1974, I grew GaN single crystal, although it was not homogeneous, by molecular beam epitaxy (MBE), which had not previously been used for GaN growth. In those days, MBE was still in an early developmental stage, and hence it was very difficult to grow high-quality crystals by MBE. The following year, I teamed up with Yoshimasa Ohki as well as with my colleagues, then at Matsushita Research Institute Tokyo, to study crystal growth of GaN by hydride vapor-phase epitaxy (HVPE). After numerous failed attempts, we finally succeeded in selectively growing n^+GaN pillars for use as cathodes in n-type films in 1978. This enabled us to develop MIS-type blue LEDs with a flip-chip structure. The process for applying this LED to devices was much easier than previously.
Also the developed LEDs had an external quantum efficiency of 0.12%, which was brighter than earlier blue LEDs, but not comparable to the p-n junction LED that we developed later.

For various reasons, we did not present the results at an international conference until two years later: *Y.Ohki, Y.Toyoda, H.Kobayasi and I.Akasaki: "Fabrication and properties of a practical blue-emitting GaN m-i-s diode," Proc. of the 9th International Symposium on Gallium Arsenide and Related Compounds, 479, (Oiso, 1981)* (Currently, International Symposium on Compound Semiconductors) (Fig.3)

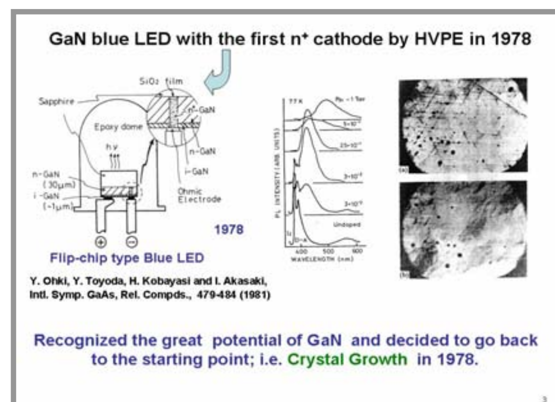

Fig.3

However, there was no response, and I felt like a solitary soul travelling in the wilderness. At that time, many researchers around the world had moved away from GaN research and were switching to zinc selenide (ZnSe). Probably no one at the conference was interested in GaN anymore. As for myself, I was determined to realize a p-n junction and continue my research on GaN, even if I became the last person working in the field.

2. Returning to the starting point of crystal growth

Returning to the early days, in 1978 I performing microscopic observations of the surfaces of GaN single crystals that had many pits and cracks. These crystals had been grown by HVPE (Fig.3). I came across some high-quality microcrystals. This convinced me of the great potential of GaN for blue LEDs.

At that time, wide bandgap semiconductors such as GaN were considered to have self-compensation effects that prevent p-type conduction. On the basis of my experience of growing compound semiconductor crystals, however, I knew that high-quality GaAs grown by vapor-phase epitaxy exhibited excellent physical properties that had not been previously observed. (*I.Akasaki and T.Hara: "Non-Ohmic Properties and Negative Resistance in n-Type GaAs," Proc. of 9th International Conference on the Physics of Semiconductors, II-787, (Moscow, 1968)* and *I.Akasaki: "GaAs---10 to the 14th power barrier," Bussei [in Japanese] (physical properties), Vol. 10, No. 6, 6 (1969)*, etc.)
GaN has lower crystallinity than gallium arsenide (GaAs) and other III-V compounds, and the residual donor concentration in excess of 10^{19} cm^{-3}, which convinced me that p-type crystals could probably be produced by doping with an appropriate acceptor after growing the crystal that did not contain any impurities. But the problem was to find a way to grow high-quality crystals equivalent to such clean microcrystals over an entire wafer. In 1978, I decided to go back to the basics of the research and examine crystal growth. I believe that this decision was a major turning point not only in my own GaN research, but in GaN research and development throughout the world, which had been stagnating at the time.

3. Decision to adopt MOVPE

It is well known that the quality of crystals (especially semiconductor crystals) is greatly affected by growth methods and conditions. Methods for growing GaN include MBE, HVPE, and metalorganic vapor- phase epitaxy (MOVPE). (Fig.4) I thought that because MBE is performed in a high vacuum environment and because GaN has a very high nitrogen vapor pressure, it is prone to nitrogen deficiency. Furthermore, MBE had a very low growth rate in those days. Thus, I considered that MBE was not suitable for growing high-quality GaN. I also considered that HVPE was not suitable for growing high-quality crystals because its growth rate is too fast to control when growing nanometer-scale crystals and

because $GaCl_3$ (g) generation reactions in the reverse direction cannot be completely suppressed. Meanwhile, in 1971, H.M.Manasevit and colleagues had used MOVPE to grow GaN for the first time, but the results were_disappointing and the method had not been used since. I was of a different opinion, however, namely that MOVPE employs irreversible thermal decomposition reactions within a single temperature range and does not involve reverse reactions. It also has an appropriate growth rate for growing GaN on substrates with a large lattice mismatch such as sapphire. Furthermore, it is easy to perform impurity doping and control the compositions of mixed crystals. Thus, in 1979, I decided to adopt this method. That this choice was not wrong should be evident from the fact that most GaN-based crystals and devices are produced by MOVPE today.

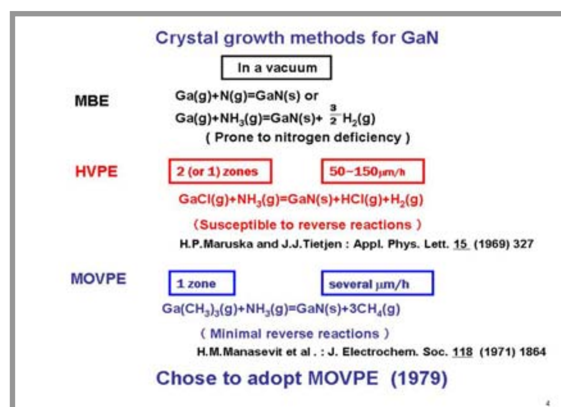

Fig.4

When deciding what substrate to use for MOVPE, the substrate should have a similar symmetry and physical properties to the crystal to be grown, as well being tolerant of the MOVPE conditions (i.e., a temperature of approximately 1,000 °C and a highly reducing atmosphere of hydrogen and ammonia gases). After comparing different substrate materials, including silicon, GaAs, and sapphire, we decided to continue to use sapphire until better substrates became available.

4. Development of low-temperature buffer layer technology

After making this crucial decision, in 1981, I commenced research on GaN growth by MOVPE in collaboration with a team of graduate students (including Yasuo Koide and Hiroshi Amano) at Nagoya University as well as with my co-researchers. However, it was very difficult to grow a GaN film homogeneously over a whole wafer. Through much trial and error, we implemented drastic innovations and improvements to the reactor tube and growth conditions. (Fig.5) First, we mixed organometallic compounds (such as trimethylgallium (TMGa), in the case of GaN growth) with ammonia (NH_3) and hydrogen (H_2) (the carrier gases) immediately before supplying them to the reactor tube. Until this point, we had supplied them separately.

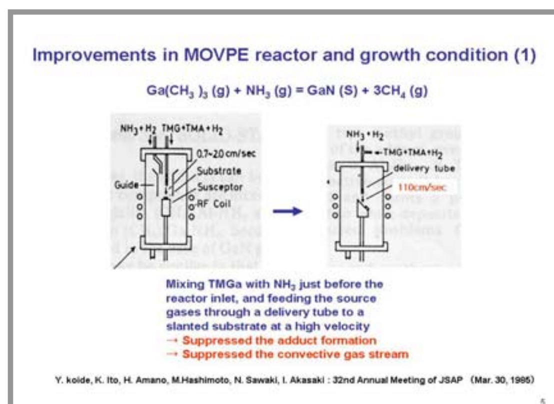

Fig.5

Second, we sprayed this gas mixture through an introduction tube onto a substrate that was inclined at an angle of 45 degrees to the horizontal, rather than horizontal as in previous attempts. The gas was sprayed at a rate of approximately 110 cm per second, in contrast to previous rates of 1 to 2 cm per second. Through these improvements we were able to suppress adduct formation inside the reaction tube, thereby enhancing the material use efficiency and suppressing convection flow on the substrate (which was heated to approximately 1,000 °C). This made the gas flow smooth enabling a homogeneous film to be grown across the entire wafer. The key aspects of this improvement were positioning the substrate at an angle and spraying gas at a high speed. This was the first improvement we made.

However, the surface was not completely a mirror surface and its electrical and optical properties had not improved much. I considered that this was mainly due to the large interfacial free energy caused by the very large lattice mismatch of 16% between GaN and sapphire. To reduce this interfacial free energy, I struck on the idea of employing a low-temperature buffer layer. We subsequently developed low-temperature buffer layer technology. (Fig.6)

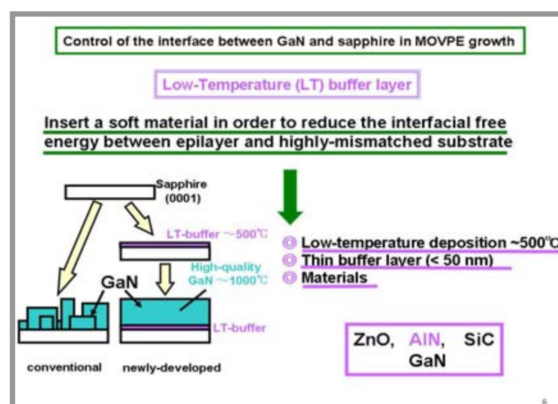

Fig.6

This is a method for depositing materials with physical properties similar to those of GaN or the substrate materials to form a thin buffer layer with a thickness of 50 nm or less. This is sufficiently thin not to interfere with the transmission of crystallographic information from the substrate to the epitaxial layer, at a considerably lower temperature (about 500 °C) than that used for growing GaN single crystals. We then increased the temperature to the epitaxial temperature (approximately 1,000 °C) to grow GaN single crystals.

This is based on the idea of trying to get as close as possible to the growth conditions of homoepitaxy (in which there is no interfacial free energy in principle) by inserting a low-temperature buffer layer, which is a flexible and soft layer that does not have a rigid structure like that of single crystals.

I considered ZnO, AlN, GaN, and SiC as possible buffer layer materials, but as I mentioned earlier, we first tried using AlN, which I had been familiar with since 1966.

In addition to this first improvement, we used buffer layer technology combined with an even higher gas flow rate of 430 cm per second (Fig.7). By doing this, we succeeded in growing very high-quality GaN single crystals with high transparencies and mirror surfaces.

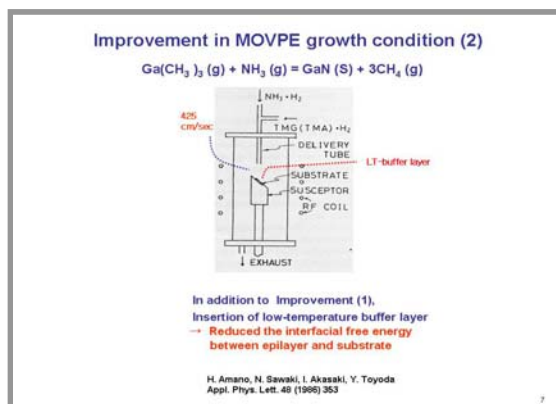

Fig.7

Fig.8 shows SEM images (a) of the surface at each growth stage in the initial GaN growth process on a sapphire surface (c plane) using the buffer layer technology and the corresponding RHEED patterns (b). Fig.8(1) shows the deposition of the AlN buffer layer, which was performed at about 500 °C for 6 minutes. You can see from the enlarged photograph here (Fig.(1)(a)) and from the RHEED patterns (Fig.(1)(b)) that the AlN layer is amorphous and has a high-density of polycrystallites.

This figure (Fig.8(2)) shows the growth of GaN on the AlN layer of (1) at the epitaxial temperature (about 1000 °C) for 5 minutes. You can see that the growth

of a hexagonal pyramidal-mesa GaN with the top surface is truncated at the c plane with the AlN microcrystals in (1) as the nucleus. The RHEED pattern in (2)(b) indicates that they are single crystals.

Likewise, these figures (Fig.8(3), (4), (5)) show the growth of GaN single crystals on the AlN layer (1) after 10, 20, and 60 minutes, respectively. Growth parallel to the substrate surface becomes dominant with increasing growth time (i.e., with increasing GaN layer thickness), so that the GaN islands coalesce. This coalescence progresses and at a growth time of 60 minutes (5), the surface becomes completely flat (GaN c-plane) (Fig.8(5) and Fig.9(a)).

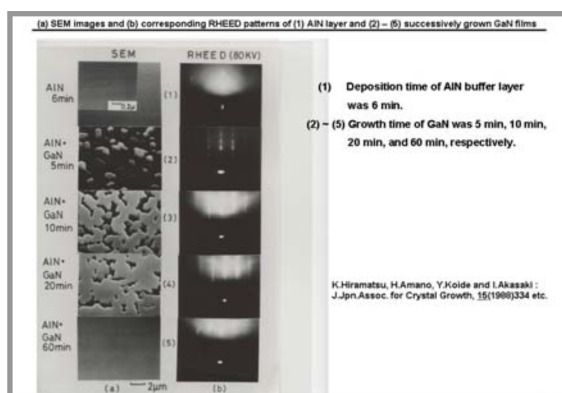

Fig.8

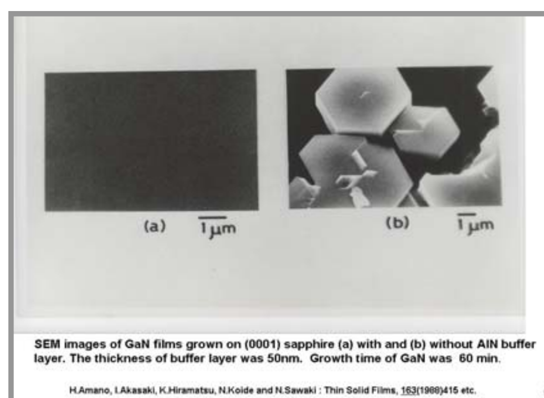

Fig.9

In the case of direct growth without a buffer layer, you can see that random growth of hexagonal columns of GaN with different sizes and heights occurs (Fig.9(b)), and that the polycrystalline GaN surface is very bumpy with many pits. Even after one hour growth, the sapphire substrate surface does not entirely covered with the GaN layer.

Fig.10 shows the growth modes for GaN films (a) with and (b) without a buffer layer. The latter exhibits a typical three-dimensional growth pattern (in the Volmer-Weber mode), whereas the former has a pseudo-two-dimensional growth pattern due to the lower interfacial free energy (in the Stranski-Krastanov mode). After the surface becomes flat, it grows in the Frank-van der Merwe mode. In the same figure, (c) shows the relationship between the heights and the widths of the GaN islands of the hexagonal columns (or pyramids) measured at each growth time (these correspond to the vertical and horizontal growth rates). You can see that the surface becomes flat at a thickness of about 300 nm when a buffer layer is used.

On the basis of the above experimental results, Fig.11 depicts the growth model for GaN films with and without a low-temperature buffer layer on sapphire c plane substrates.

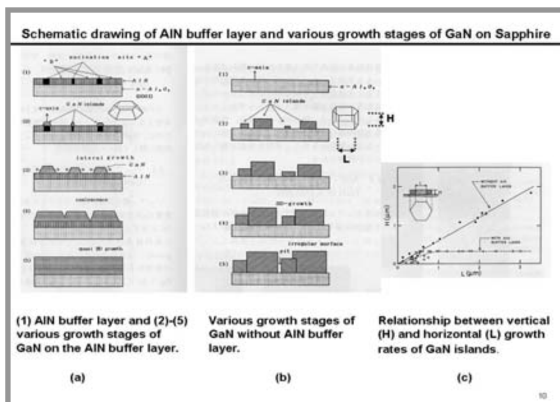

Fig.10

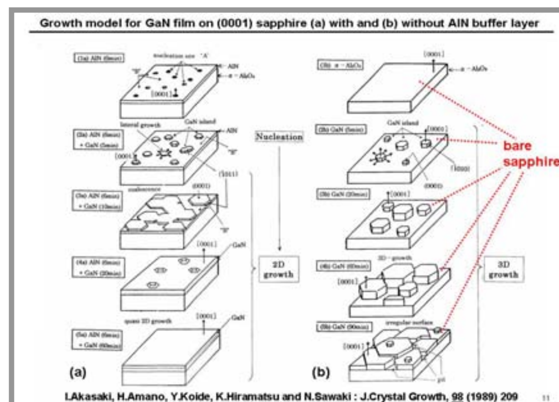

Fig.11

Next, Fig.12 shows cross-sectional transmission electron micrographs (TEM) of GaN grown with a buffer layer. The AlN layer (approximately 50 nm thick) on the sapphire substrate is amorphous during low-temperature deposition, but it becomes polycrystalline as the temperature is increased to the GaN epitaxial temperature. Directly above, you can see a faulted zone with very intense distortion. The strain gradually relaxes and lattice defects decrease at a thickness of 300 nm. You can see a semi-sound zone (or medium-quality zone), and a sound zone (or high-quality zone). As I mentioned earlier, the surface (in Fig.8(5), Fig.9(a), and Fig.10(c)) becomes nearly flat when the thickness of the epitaxial GaN layer is around 300 nm. This qualitatively agrees with the TEM image in Fig.12.

Fig.13 shows a schematic diagram depicting the growth process of a GaN single-crystal film grown with a low-temperature AlN buffer layer on a sapphire c plane. This is based on the results of in-situ TEM observations of the growth process in addition to the results of Fig.12. In the initial growth stage of GaN with a buffer layer, we found that geometric selection of GaN islands occurs after solid-phase epitaxy of an AlN amorphous layer.

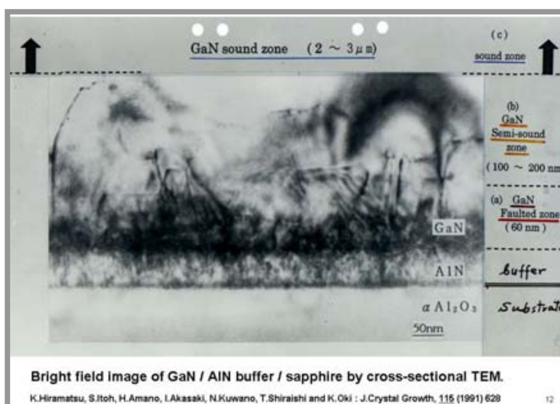

Fig.13

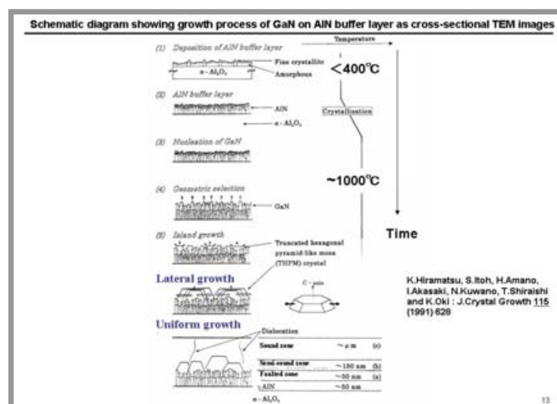

Fig.14

In contrast, in the case of direct growth without a buffer layer, numerous defects were found in the epitaxial layer including on its surface, so the crystal was of poor quality.

These experiments imply that the essential roles of the low-temperature buffer layer are both generating high-density nucleation centers with the same orientation as the substrate and promoting lateral growth of GaN islands and their coalescence due to the reduction in the interfacial free energy between the epitaxial film and the substrates.

It was also found that GaN on the sapphire substrate grows so that its crystallographic axes are orientated at 30 degrees to those of the sapphire substrate, thereby minimizing the energy of the whole system. Figs 14 and 15 show that inserting the low-temperature buffer layer dramatically improves all the critical properties, including the crystallinity(such as the GaN crystal surface morphology and the line width of the X-ray diffraction rocking curve), the electrical properties (such as the residual donor concentration and electron mobility), and the photoluminescence properties.

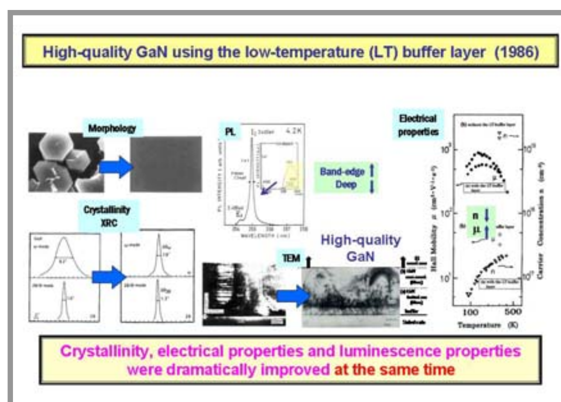

Fig.14

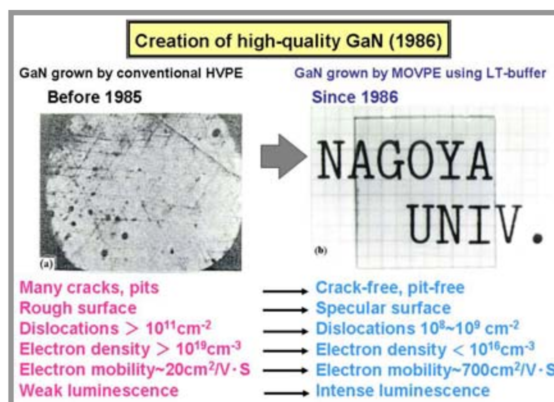

Fig.15

5. Realization of p-type conduction in GaN and GaN p-n junction blue LED

We were unable to achieve p-type conduction despite performing many doping experiments using zinc (Zn) as a promising acceptor and high-quality GaN that had a low lattice defect density and a residual donor concentration of less than 10^{15} cm^{-3}.due to using buffer layer technology. Then, in 1988, Hiroshi Amano discovered that the intensity of Zn-related blue luminescence of this high-quality Zn-doped GaN is_remarkably enhanced by low-energy electron beam irradiation (LEEBI) while its spectral shape remains unchanged (Fig.16). 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 *"Bonds and Bands in Semiconductors" (1973) by J. C. Phillips*, the larger the difference between the electronegativity of an acceptor impurity and that of the Ga atom to be substituted, the larger the acceptor activation energy will be. Because magnesium (Mg) exhibits a lower electronegativity difference (when the effect of valence electron screening is accounted for) than Zn, we assumed that Mg would be more easily activated than Zn. Thus, we used bis-cyclopentadienyl magnesium (CP_2Mg) and methyl-CP_2Mg (MCP_2Mg) as Mg sources. In early 1989, the then-graduate-student Masahiro Kito performed magnesium doping with these dopants on high-quality GaN grown using the buffer layer technology. We then applied the LEEBI treatment to the samples, and found that the intensity of magnesium-associated blue luminescence was markedly enhanced ---namely the LEEBI effect--- and that the samples had been converted to a low-resistivity p-type conduction. This was confirmed by Hall effect measurements.

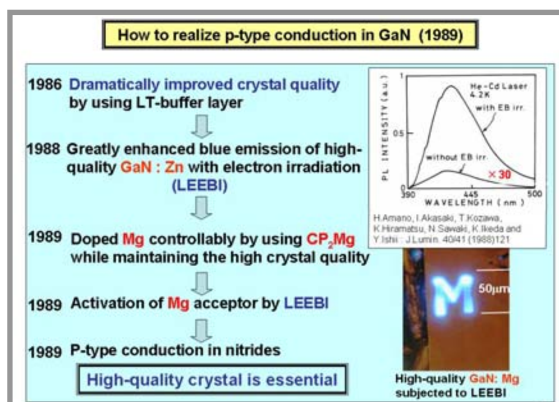

Fig.16

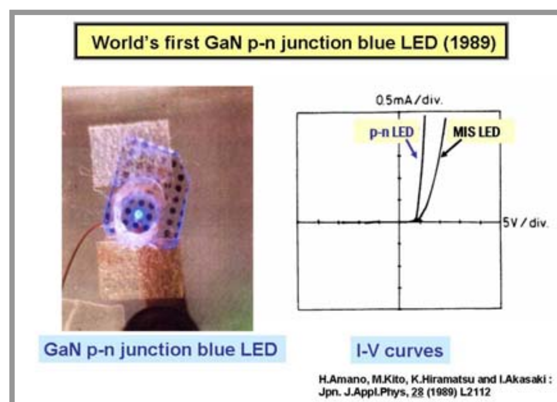

Fig.17

We immediately fabricated the first GaN p-n junction blue/ultraviolet LED that had encouraging current-voltage (*I-V*) characteristics. (Fig. 17)

The LEEBI effect is athermal and occurs even at low temperatures.

It has been demonstrated in many ways that electron-beam irradiation with an acceleration voltage of several kilovolts breaks the magnesium-hydrogen bond and that the hydrogen leaves and magnesium becomes activated.

To realize p-type conduction in nitride semiconductors, we needed to dope Mg and activate it by a method such as electron-beam irradiation or thermal annealing. However, it is essential to use a high-quality crystal.

6. Conductivity control of n-type nitrides and other problems

In the meantime, we noticed a new problem with the electrical conductivity of n-type crystals. The introduction of a low-temperature buffer layer markedly reduced the residual donor concentration (and thus the realization of high-quality crystals), causing the crystals to have a high resistivity. In actual device fabrication, it is necessary to control the conductivity over a wide range from low to high resistivities. In 1989, we succeeded in extensively controlling n-type conductivity by Si-doping using silane (SiH_4) gas while maintaining a high crystal quality by using buffer layer technology. (Fig.18)

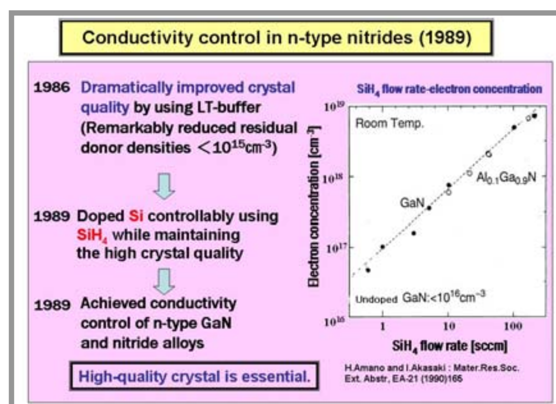

Fig.18

As in the realization of p-type conduction, it is essential to use high-quality crystals here.

Control of n-type conductivity is very important for practical applications as well as for realizing p-type conduction. This method of n-type conductivity control is currently used widely all over the world.

This is how we achieved all of the basic technologies essential for developing GaN-based p-n junction LEDs and electronic devices by 1989.

7. Conclusion

After this, we continued our efforts to further enhance the quality of GaN and mixed crystals such as AlGaN and GaInN using our low-temperature buffer-layer technology. We went on to successfully develop a high-performance short-wavelength laser diode using these high-quality nanoquantum structures, as well as verify the quantum size effect, the quantum-confined Stark effect, and the Piezoelectric effect in nitride semiconductors.

This research thus goes back to the late 1960s when nitride semiconductors were virtually unknown. I would like to express my deepest gratitude to my colleagues at Matsushita Research Institute Tokyo, who cooperated with me in this research,

which I had started all alone, and who shared many joys and sorrows with me, as well as to my co-researchers and students who became increasingly devoted to this study with me at Nagoya University and Meijo University from 1981. (Fig.19)

Fig.19

Finally, I would also like to thank my predecessors and the many researchers who have studied nitride semiconductors.