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Wide Bandgap Semiconductors

Fundamental Properties and Modern Photonic and Electronic Devices

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With 394 Figures and 36 Tables

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Preface

The p–n junction was invented in the first half of the twentieth century and the latter half saw the birth of light emitting diodes: red and yellow/green in the 1960s and yellow in the 1970s. However, theoretical predictions of the improbability of synthesizing p-type wide bandgap semiconductors cast a long shadow over hopes for devices emitting in the elusive blue part of the electromagnetic spectrum, which would complete, with red and green, the quest for the primary colors making up white light. At a time when many researchers abandoned their efforts on nitrides, Professor Isamu Akasaki of Nagoya University at this time remained committed to his belief that "synthesis of high quality GaN crystals would eventually enable p-type doping" and in 1989 he succeeded in fabricating the world's first GaN p–n junction light emitting diode.

Professor Isamu Akasaki kindly accepted our invitation to contribute to this book and describes his journey 'from the nitride wilderness' to the first experimental results of blue emission from GaN p–n junctions: Japan's major contribution to the development of wide bandgap semiconductor devices.

The discovery of blue emission from GaN p–n junctions in 1989 was the major technological turning point during the development of wide bandgap emission devices with wide reaching scientific, industrial and social implications. In Japan, I assembled a group of academics and industrialists to discuss the feasibility of setting up a research committee under the Japanese Society for the Promotion of Science (JSPS) to study nitride semiconductor optical devices. Together, we submitted a proposal to the JSPS on establishing an 'academic/industrial/government' committee to assess nitride optical devices. The JSPS accepted our proposal, and a JSPS committee on "Wide Band Gap Semiconductors and Optoelectronic Devices", the *162 Committee*, was formally set up in 1996. The Committee consists of internationally recognized leaders who were instrumental in triggering the 'blue-tsunami' that led to the renaissance of blue-light semiconductor research and the birth of a viable technology as exemplified by the ubiquitous GaN LEDs.

In 2001, the Committee's areas of interest were widened to include wide bandgap electronic devices in addition to optical structures. In April 2006, Professor Akihiko Yoshikawa of Chiba University was appointed Chairman of the 162 Committee and under his guidance new topics such as nanostructures, biotechnology and high temperature devices, will also be covered.

The invention of the blue LED and laser in the 1990s led to the establishment of new industries based on blue technology including solid state traffic signals, UV nitride lasers in high density DVD recorders, solid state white light illumination, biotechnology, nano-structures and high temperature devices.

The six chapters of this unique book were written by innovators from Japanese academia and industry recognized as having laid the foundations of the modern wide bandgap semiconductor industry. Apart from the in-depth description of recent developments in the growth and applications of nitride semiconductors, this book also contains chapters on the properties and device applications of SiC, diamond thin films, doping of ZnO, II–IVs and the novel BeZnSeTe /BAlGaAs material systems. Practical issues and problems such as the effect of defects on device performance are highlighted and potential solutions given based on recent research.

I expect that this book will be a valuable source of up to date information on the physical properties, current trends and future prospects of wide bandgap semiconductors for professional engineers, graduate students, industrial planners responsible for charting projects and think-tank managers monitoring developments in the semiconductor electronics industry.

The contents of this book are based on the Japanese language, *Wide Gap Semiconductors, Optical and Electron Devices*, published in March 2006 by Morikita Shuppan Co. Ltd.

I would like to express my sincere thanks to the Industry Club of Japan for their financial contribution to a part of the cost of preparation of this book by "Special Fund for the Promotion of Sciences" which was made available by the Japan Society for the Promotion of Sciences (JSPS).

Finally, I would like to thank the members of the 162 Committee, JSPS, Morikita Shuppan Co. Ltd and Springer Publishing, for their support, time and energy spent in the production and publication of this book.

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Lifetime of Research on Nitrides – Alone in the Wilderness

I. Akasaki

Blue light emitting devices fabricated using nitride semiconductors are ubiquitous. They are used in mobile phones, traffic signals and outdoor screens in soccer stadiums. The situation 30 years ago was a lot different when many groups withdrew from this subject of research due to unfavorable results. In spite of the lack of progress in this field at the time, I made a conscious decision to make research on nitride semiconductors my life work. This is a recollection of my thoughts and memories about my contribution to the blue renaissance [1–3]. I hope that the mistakes and moments of jubilation will inspire young scientists and engineers to have confidence in your own beliefs, not be swayed by trends and fashions, and move forward with passion and commitment.

First Meeting with Light Emission and Compound Semiconductors

In 1952, I graduated from the Faculty of Science of Kyoto University and joined Kobe Kogyo Corp. (now Fujitsu Ltd). At the time, the company employed many talented researchers and was committed to a wide range of research activities. Two years after my arrival, the company was one of the first to begin manufacturing cathode ray tubes for televisions; I was put in charge of the fluorescent screens. Polycrystalline, powder Zn(Cd)S-based phosphors were applied to the interior of the CRT face plate and electron irradiation enabled production of images. Now, Zn(Cd)S is a group II–VI compound semiconductor and this was my first 'meeting' with these materials and luminescence. Looking back, this work had a great effect on my research career implicitly and explicitly, publicly and privately, in every possible way.

In the early 1950s, industrial researchers were pre-occupied with the implications of the invention of the transistor and Kobe Kogyo already had a team working on the development of transistors using single crystal Ge. The term 'single crystal' resonated with me because of the problems I was having with the poor reproducibility of experimental data due to polycrystalline Zn(Cd)S powder for the CRT screens. I seriously considered, and dreamt, about the possibility of using single crystal Zn(Cd)S and transparent Zn(Cd)S thin films for the CRT screens. Perhaps this unconscious interest in single crystal semiconductors was part of the reason I worked on single crystal GaAs, GaP and GaN, which emit light, during my days at Matsushita Research Institute Tokyo, Inc. (MRIT).

In 1959, I accepted an invitation to move to the Department of Electronics at Nagoya University where I worked with Professor Tetsuya Arizumi on setting up a series of technologies ranging from production of Ge ingots by reduction of germanium oxide and subsequent purification by zone refining, growth of single crystals, impurity doping, and device fabrication. At the time, p–n junctions were produced by diffusing arsenic (or antimony) into slices of p-type Ge. However, I was anxious about this method: the n-region in p–n junctions formed by 'diffusion' was compensated with p-type impurities which were introduced beforehand, and the impurity distribution is limited to the complementary error function. In order to overcome these drawbacks, I thought a new method about which was later known as 'epitaxial growth' of thin film semiconductors by which single crystalline Ge films could be grown through gas phase reactions of Ge compounds on Ge substrates. In collaboration with Professor Nishinaga (a prospective graduate student at that time and current president of Toyohashi University of Technology), we studied vapor phase epitaxial growth (VPE) of Ge from its very inception. I think that this research laid the foundations for my work at MRIT on epitaxial compound semiconductors including metalorganic vapor phase epitaxial growth (MOVPE) of nitride semiconductors. In fact my work on Ge epitaxy was the reason for an invitation by MRIT to join their new institute in 1964.

The Nitride Challenge

At Matsushita, I was put in charge of a laboratory with freedom to decide my research activities. My basic policy for semiconductor research was "make our own crystals, characterize their physical properties, use the results to optimize growth conditions, produce extremely high quality crystals and develop novel device applications". At the time, I first focused on the growth of so-called 'magic crystal', namely GaAs and related III–V compounds such as GaP, GaAsP, GaInP and their development for red and green/yellow light emitting diodes. In spite of the fact that I managed to produce the best results for such materials at the time, for a variety of reasons, these semiconductors were not used for fabrication of commercial devices. However, I was determined to develop blue light emitting devices using p–n junctions; something that no one had yet succeeded in producing.

Realization of blue light emitting devices requires growth of high quality single crystals of semiconductors with bandgaps (E_g) larger than 2.6 eV and control of their electrical conductivity, in particular realization of p-type material. At the time, however, theoretical studies indicated the improbability of achieving p-type ZnSe and other such wide bandgap semiconductors due to self compensation; almost all the major groups were pessimistic about realization of ZnSe and in particular GaN p–n junctions. The only example of success was SiC p–n junctions used to produce green/yellow emitting devices. However, I had absolutely no interest in this material for photonic device applications because of its indirect bandstructure did not enable the possibility of achieving high emission efficiency and hence laser oscillation would be impossible. Soon after my move to Matsushita, my belief in the potential of nitrides led me to start research on the VPE growth of AlN (1966) [4] in parallel to the GaAs-based work. I confirmed blue emission from AlN using CL and PL and was enjoying working with light emitting materials, but EL was not possible due to the excessively large bandgap.

Thus, in 1973 I decided to focus first on GaN growth.

In fact, in 1969, Maruska et al. [5] had reported on the growth of single crystals of GaN by hydride vapor phase epitaxy (HVPE) and used optical absorption to determine its bandstructure to be direct with Eg of $\sim$3.39 eV. Then in 1971, Pankove et al. fabricated MIS-type blue LEDs [6]. These reports triggered a sudden increase in research on blue light emitting devices [Fig. 1, period (A)]. However, the surfaces of GaN crystals were very rough with cracks and pits, and p-type GaN was impossible to produce. Thus many groups retired from GaN research and some moved on to other materials such as ZnSe and activities on nitrides declined [Fig. 1, period (B)]. From my experience of VPE growth of high quality GaAs [7], I was confident that drastic improvements in the crystal quality of GaN would eventually enable p-type conduction of this material as well. My view was, "It is too early to discuss self-compensation in poor quality GaN. High quality GaN crystals (residual donor density of at least less than $10^{15}\,\mathrm{cm}^{-3}$) must first be produced before discussing such physical properties."

Then in 1973, I decided to make "realization of blue light emitting devices by GaN p–n junctions", an idea abandoned by many, my life's work.

A slight digression, but at the time, apart from groups working on SiC, almost all researchers were studying ZnSe which has a direct bandgap of $\sim$2.7 eV and shows bright CL and PL emission. In addition, its lattice constant is similar to GaAs thus enabling epitaxial growth on GaAs substrates. Thus many researchers were reasonable in thinking of ZnSe as being the first choice as a material for blue or green light emitting devices. (Later, in 1986, very few people showed interest in GaN even after we reported on the successful growth of high quality GaN crystals.) However, apart from ZnSe being 'softer' than GaN, I was also anxious about the crystallinity and stability of ZnSe because of its low growth temperature. On the other hand, the melting point and vapor pressure of GaN are both much higher than ZnSe making its crystal growth extremely difficult. In addition, the E_g of GaN is very large compared with ZnSe, which makes it much more difficult to produce p-type GaN compared

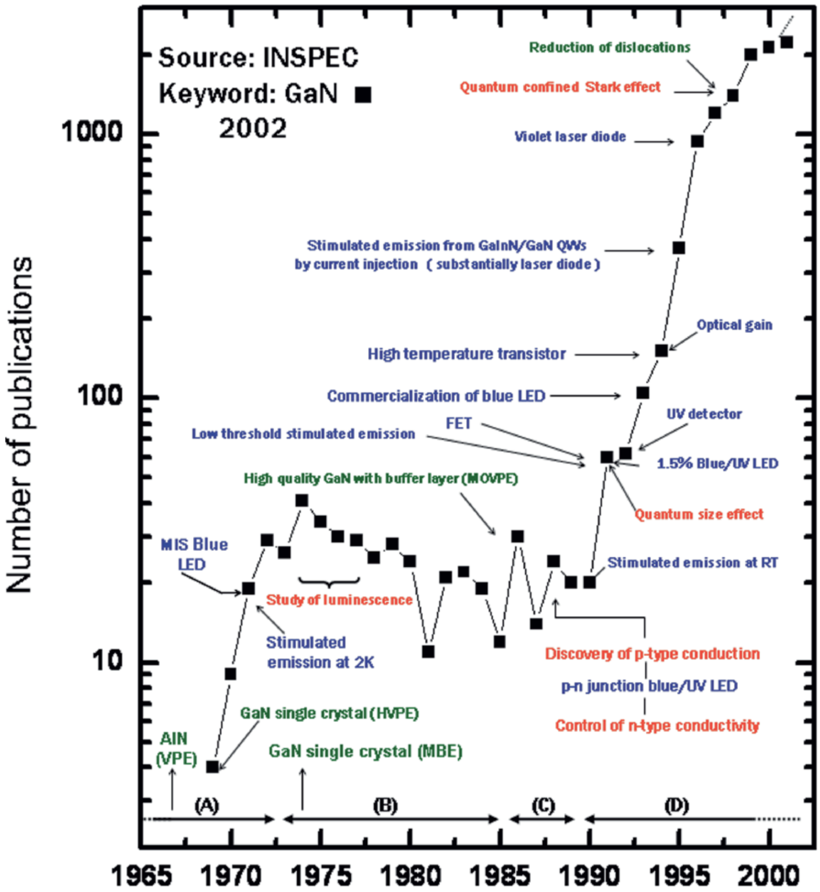

Fig. 1. Number of Publications (INSPEC) and activities related to nitrides between 1965 and 2000. All events are marked in the years, when they were first achieved. Most of important results were achieved by MOVPE using LT-buffer layer after 1986. It is clear that the start of the steep increase of numbers of publications and accomplishments is due to the key inventions (high quality GaN, conductivity control and p–n junction blue LED etc.) in the late 1980s. Green: Crystal Growth, Blue: Devices, Red: Conductivity Control and Physics

with ZnSe crystals. However, I was not discouraged by the problems with GaN because I still believed in the potential of GaN and once the problems were resolved, then compared with ZnSe, nitrides would enable production of more robust and shorter wavelength p–n junction light emitting devices.

Choice of MOVPE as the Preferred Growth Method

Until 1973, GaN was mostly grown by HVPE and no one used molecular beam epitaxy (MBE). However, I decided to use MBE for the first time. Using Ga and NH_3 as sources, I was able to produce single crystal GaN, albeit material with non-uniformities. I sent a proposal for a project entitled, 'Development of blue light emitting devices by ion implantation into single crystal GaN' to the Ministry of International Trade and Industry (MITI) at the time and in 1975, was awarded a three-year research grant to conduct the project [8].

Following many difficulties, and with the assistance of my team of researchers at MRIT, we were able to produce blue GaN LEDs with much better emission characteristics than ever reported, and succeeded in achieving the aims of the project. Approximately 10,000 GaN blue light emitting test devices with the newly developed as-grown cathode electrodes were manufactured (an example is shown in Fig. 2). But due to poor surface uniformity and low yield of MIS structures, the devices were not sold commercially. My goal was p–n junction devices, so I was not discouraged by the lack of success of these MIS LEDs. Two years later, we reported our results at an international conference [9] (where we were the only group to report on GaN related work) but without much of a reaction since most researchers had lost interest in GaN work.

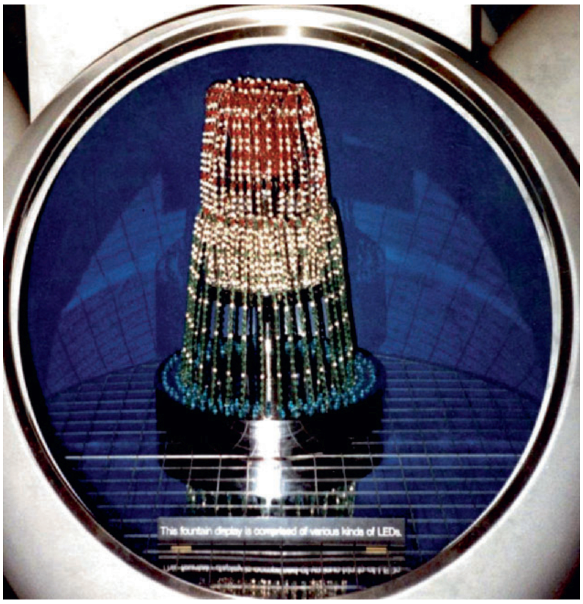

Fig. 2. Fountain display using tricolor LEDs, which was later in 1981 demonstrated in Chicago by Matsushita Electric Industrial Co. Ltd

However, as a result of my increasing experience with handling GaN crystals, fluorescence microscopy showed the existence of high quality microcrystals in parts of larger crystals containing cracks and pits. Also, we found that clusters of needle-like crystals ('GaN-fungus!') left inside the growth reactors exhibited highly efficient light emission. From these experiences, I reconfirmed the great potential of GaN and believed that p-type GaN could indeed be produced if a whole wafer could be made of the same quality as the GaN microcrystals left in the growth reactor.

I then decided to go back to basics and reconfirm the fundamentals of crystal growth: I had experience of growing at least ten kinds of semiconductors and intuitively I knew that crystal quality depended greatly on growth conditions and hence the choice of growth method would be the critical factor in determining the future of the research.

Epitaxial GaN can be grown by MBE, HVPE and MOVPE. MBE was prone to nitrogen desorption and also the growth rate was slow at the time. In HVPE, the growth rate was too fast and crystal quality was affected by reversible reactions. So I thought that this method was not suitable for producing high quality crystals.

On the other hand, the MOVPE method, which at the time was hardly used for GaN growth, uses thermal dissociation reactions at a single temperature and has negligible reversible reactions. Also, the growth rate was intermediate between the other two methods thus enabling growth of nitrides on substrates with a large lattice mismatch. Thus in 1979, I decided to adopt MOVPE as the most suitable method for the growth of GaN. Another advantage of this method was that alloy composition and impurity doping could be readily controlled by varying the source flow rate. Looking back, this decision had a tremendous effect on the development of nitride semiconductors (Fig. 1, caption).

The next problem was the choice of substrate. I experimented with growth on Si, GaAs and sapphire substrates. Eventually, in 1979 I decided on using sapphire because it was stable at temperatures above 1,000^{o}C as well as being able to withstand NH_3 during growth. This choice, at the time, was also appropriate and afterwards led to the first demonstration of p–n junction blue LEDs.

Two Important Breakthroughs

In 1981, I returned to my old nest at Nagoya University. One of the most important research themes of my group was 'research and development of blue light emitting devices using GaN based p–n junctions'. Prospective graduate students who showed interest in this theme included Hiroshi Amano (now professor at Meijo University) and Yasuo Koide (now group leader (Optical Sensor Group) of National Institute for Materials Science)). With the support of my colleague, associate professor Nobuhiko Sawaki (now professor and dean of Graduate School of Engineering, Nagoya University) and Koide and Amano, I set up a clean room and MOVPE growth facilities. In spite of our efforts, however, MOVPE growth did not yield favorable results.

I thought that the main reason was because of the extremely large interfacial energy between GaN and sapphire due to the large mismatches between these materials. Then I had an idea: the insertion of a soft, 'low temperature (LT) buffer layer' to relax the strain. For the buffer layers, I thought about using AlN, GaN, ZnO and SiC because these materials had similar physical properties to those of GaN and sapphire. In a discussion with Amano, I said that the buffer layers should be less than 50 nm and deposited at less than 500^{o}C. Amano, in spite of the poor results up until that time, worked intensely on the use of MOVPE for growth of GaN. Quite accidentally, when the growth reactor was not functioning properly, he deposited a thin AlN layer at low temperature (according to my suggestion) followed by the growth of GaN on top. He showed me the sample he had just grown: the GaN surface was flat and optically transparent [Fig. 3 (right)] [10]. I can still remember the excitement at seeing the reality of the dreams of my Matsushita days: mirror-like, crack and pit free, transparent GaN crystals.

The residual donor density of the GaN crystals grown with LT-buffer layer was also drastically reduced [10,11] but in spite of repeated efforts on acceptor-doping, it was not possible to produce conducting p-type materials using Zn as a dopant. In 1987, when Amano was carrying out CL measurements on high quality Zn-doped GaN crystals grown with the LT-buffer layer, he said that "the emission intensity continues to increase the longer we irradiate the Zn-doped GaN sample with the electron beam during the CL measurements". I thought that this was an important observation, which might be related to the p-type conduction, and asked for more detailed measurements. The results did not show p-type conduction, but the discovery was that: Zn-related

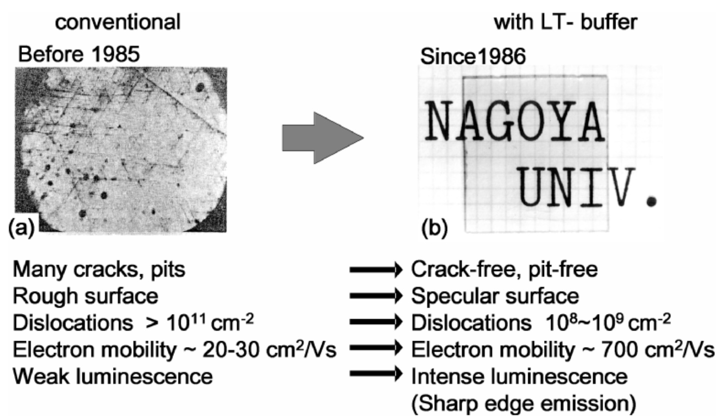

Fig. 3. Optical images of GaN grown on sapphire by MOVPE without (**a**) and with (**b**) LT-AlN buffer layer. The latter is transparent and crack and pit free