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コバルトブルーに魅せられて

赤﨑　勇

はじめに

半導体の研究に携わる者の一人として、25周年という節目の年に栄誉ある京都賞をいただき、大変嬉しくかつ光栄に思います。

はじめに、私の少年時代から大学卒業までを振り返り、次に、いろいろな仕事を経験しながら青色発光素子に魅せられていった経緯をお話しした後、多くの方々と力を合わせて窒化ガリウムpn接合型青色発光ダイオードを実現するまでの私の旅路をお話しします。

私は、鹿児島県の知覧町生まれですが、物心ついてからは鹿児島市の北東部で育ちました。鹿児島は風光明媚で、当時はまだ市内も自然が豊かで、史跡も多く、歴史的行事の盛んなところでした。

少年時代は、当時の多くの子どもたち同様、近くの野山や磯海岸あたりで遊ぶのが大好きで、日没まで虫捕りや磯遊びに夢中になっていました。また、鉱物標本の鉱石や結晶の、晶癖や晶相に大変興味があり、今でも大木（巨木）や自然石を見るのが好きです。後年、結晶にのめり込むのは、関係しているのでしょうか。

中学は２歳年上の兄と同じ県立二中に進み、兄も入っていた「敬天会」に入会しました。これは、先輩の話では、旧薩摩藩に伝わる先輩が後輩を育成し、また互いに切磋琢磨する“郷中教育”の一環と思われます。敬天会では、毎日曜日の早朝、西郷墓地や南洲神社の境内を清掃し、国旗を自分たちで建てた孟宗竹の高い柱に掲揚して、桜島と対面し、清々しい気持ちで一日を過ごすのが常でした。また、心身の鍛練と親睦を兼ねて、山や海浜キャンプへよく行きました。因みに、「敬天」は西郷隆盛の遺訓「敬天愛人」に由来します。

小中学校時代は、第二次世界大戦の真っ最中で軍国教育でしたが、中学３年の５月までは自宅通学していましたので、敬天会の活動に参加したり、放課後は相変わらず友達と城山あたりで遊んでいました（Fig. 1）。

父は薩摩士族の末裔で、寡黙で社交性に乏しく、私たち子どもの日頃の行動や進路については細かいことは言わず、一切母任せでした。母は敬虔な仏教徒でいつも微笑を絶やさず、私たちに対しては、他人に迷惑をかけない限り自分の好きな道に進めば良いと、温かく見守ってくれました。

しかし、３年生になった頃から戦況は日増しに悪化し、中学生の学徒動員が始まり、５月から親元を離れて鹿屋の海軍航空隊でもっこを担いで飛行機の掩体壕（えんたいごう）造り、

Enchanted Journeys in Blue Light

Isamu Akasaki

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

城山公園から、鹿児島市と桜島を望む（1940年ごろ）

A view of the city of Kagoshima and Mt. Sakurajima in the early 1940s.

Fig. 1

4年生の（1945年）4月からは佐世保の海軍工廠でフライス盤工として働き、敗戦まで授業はほとんど受けていません。1945年9月、4年生の2学期に復学しましたが、その間、鹿児島市は大空襲を受けて大部分が焼失し、両親は市内から10kmほど離れた山奥の電灯の無い一軒家に疎開していましたので、通学には往復3時間半かかり、時間は大変限られていましたが、薄暗い魚油（？）ランプの灯りで、借り物の古本を貪るように読んだことを覚えています。当時は酷い食糧難、教材などの物資難で大変な時でしたが、私たち子どもの向学心に対する両親の理解をありがたく思っています。

1946年3月、旧制七高を受験し、幸い合格しましたが、七高も全焼しており、県北部の出水市の海軍航空隊跡で開校したのは、同年11月末でした。旧兵舎を利用した教室の窓ガラスはあちらこちら破れたままで、寒風を避けるため、マントを被って授業を受けたこともありました。それができない先生方は大変でした。お互い栄養状態が悪いので、寒さが一層応えるのです。翌年初夏から、鹿児島市の鶴丸城址に校舎建設のための復興資金集めの活動が始まり、本来3年間の七高での授業も正味2年余りだったでしょうか。そんなわけで、中学、高校で基礎を学ぶ時間が少なかったのは否めないことです。幸い、小、中、高校時代は良師・益友に恵まれ、また七高では物質的には不自由ながらも自治寮生活を楽しみました。

大学は、京都に行こうと早くから決めていましたが、物理か化学かは半年前まで決めかねていました。同郷の先輩の強い勧めもあって、理学部の“主として化学専攻”に進みました。

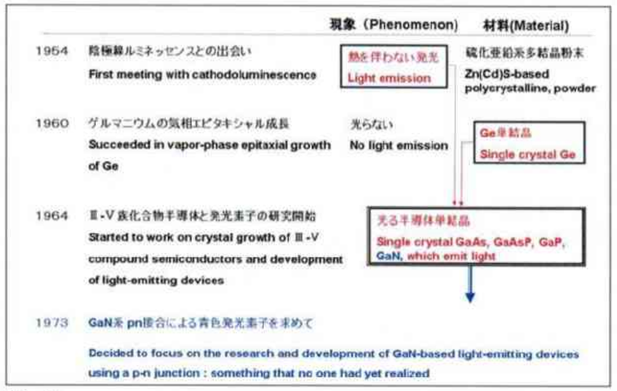
way, was derived from Saigo Takamori's dying instruction of *Keiten Aijin*, or "Revere Heaven, Love People."

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



現象（Phenomenon）　材料(Material)

1954　陰極線ルミネッセンスとの出会い
First meeting with cathodoluminescence
熱を伴わない発光
Light emission
硫化亜鉛系多結晶粉末
Zn(Cd)S-based polycrystalline, powder

1960　ゲルマニウムの気相エピタキシャル成長
Succeeded in vapor-phase epitaxial growth of Ge
光らない
No light emission
Ge単結晶
Single crystal Ge

1964　Ⅲ-V族化合物半導体と発光素子の研究開始
Started to work on crystal growth of Ⅲ-V compound semiconductors and development of light-emitting devices
光る半導体単結晶
Single crystal GaAs, GaAsP, GaP, GaN, which emit light

1973　GaN系 pn接合による青色発光素子を求めて
Decided to focus on the research and development of GaN-based light-emitting devices using a p-n junction : something that no one had yet realized

Fig. 2

京大時代は、講義や実験の合間によく京都や奈良の神社仏閣巡りをしたり、夏休みに帰省しない時は、京大笹ヶ峰ヒュッテを拠点にして、信州の山登りをしていましたので、３年間は大変短く感じました。

ルミネッセンスとの出会い（Fig. 2）

私が熱を伴わない発光であるルミネッセンスに出会ったのは、1954年に神戸工業株式会社（現・富士通株式会社）の明石工場で、テレビ用ブラウン管の蛍光面を担当することになった時です（最近、テレビの画面はほとんど液晶やプラズマ方式に変わりましたが、テレビ放送開始から半世紀の間活躍したのがブラウン管です）。ブラウン管は、フェースプレート内面に硫化亜鉛（カドミウム）(Zn(Cd)S) 系の粉末蛍光体が塗布されており、十数キロボルト［KV］に加速された電子線で励起されて発光する仕組みです。その時初めてルミネッセンスという現象に出会い大変興味を持ち、一生関わることになりました。蛍光面はピンホールができないように（電子の侵入長に比べて）かなり厚く作りますので、発生した光は粉末蛍光体層に吸収されてロスします。そこで、もっと明るい画像を実現しようと、「電子線励起で発光する（粉末ではない）透明な薄い結晶を積み重ねる（今日で言う、ガラス基板上への光半導体結晶のエピタキシャル成長）ことはできないだろうか」――当時は全く夢物語ですが――と、真面目に考えたことがありました。この“光る単結晶”は、ずっと私の潜在意識にあったようです。

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

当時はまた、トランジスタの草創期で、神戸の本社技術部ではゲルマニウム(Ge)の単結晶やトランジスタの研究を行っていました。Ge（半導体）は光りませんが、粉末ではない“単結晶”は私にはとても魅力的に見えました。

半導体単結晶のエピタキシャル成長

1958年、突然上司の有住徹弥部長に誘われて、創設間もない名古屋大学電子工学科に59年に移り、Geの高純度単結晶の作製と半導体物性の研究を開始しました。有住教授と２人だけの、机一つないところからのスタートでしたが、これが、私の結晶や半導体研究への転機でした。当時、Geのpn接合は、（昇温した）p型Ge単結晶基板にヒ素（As）を拡散させて作っていましたが、私は、n型層が基板中のアクセプターによって補償（汚）されることなく、また任意の不純物分布を持つpn接合を作る方法として、1960年、今日で言う“気相エピタキシャル成長”を始め、翌年（鏡面ではありませんが）Geの単結晶膜の作製に成功し、1962年から大学院生の西永頌と本格的に“Geの気相エピタキシャル成長”に取り組みました。結晶を反応管から取り出す時の期待感と興奮から、“結晶成長”にのめりこんで行きました。この仕事が縁で、新設の松下電器東京研究所に1964年に招かれることになりました。

化合物半導体と発光素子の研究

そこで、かねて温めていた“光る半導体単結晶”として、ヒ化ガリウム（GaAs）に代表されるIII-V族化合物の結晶成長と発光素子（発光ダイオード：LED、レーザダイオード：LD）の研究を開始しました。III-V族化合物は、元素の周期表のIII族元素とV族元素の化合物で、８個の外殻電子を持ち、シリコン（Si）やGeなどの元素半導体に対して、化合物半導体と呼ばれています。

当時、リン化ガリウム（GaP）やヒ化リン化ガリウム（GaAsP）などを用いた赤色や黄緑色のLEDやGaAs系の赤外LDは開発されていましたが、可視光の中でエネルギーが最も大きい（波長が最も短い）青色の発光素子の実用化の見通しは全く立たない状況でした。

LEDなど半導体発光素子の発光の（光子）エネルギーは、用いる半導体のエネルギーギャップ（Eg）にほぼ等しく、また青色光の波長は、JISでは455〜485ナノメー

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 excitation 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.

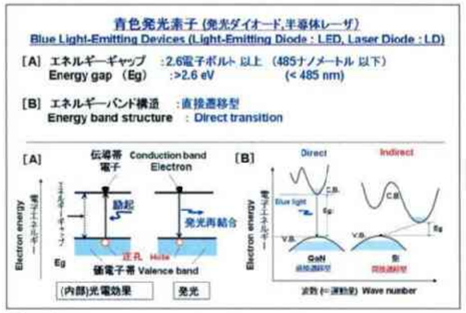


Fig. 3

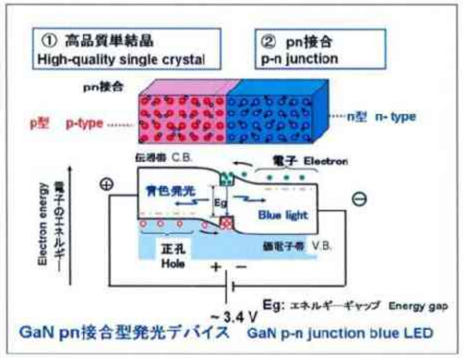


Fig. 4

トル [nm] ですから、青色発光素子を実現するには、[A]：Egが約2.6電子ボルト [eV] 以上（波長換算で485nm以下）の半導体の使用が必須です（Fig. 3）。このように大きいEgを持つ半導体は“ワイドギャップ半導体”と呼ばれています（因みに、広く用いられているSi半導体のEgは、1.1eVです）。

次に [B]：LEDは、半導体内で励起状態にある伝導帯電子が基底状態である価電子帯に光を放出しながら緩和する過程を利用するので、“直接遷移型半導体”を用いるのが断然有利です。直接遷移型半導体では、伝導帯の底にある電子と、価電子帯の頂上にある正孔の運動量がほぼ等しく、高い発光再結合確率が得られるからです。SiやGeなどはEgが小さい上に“間接遷移型半導体”であり、発光再結合確率が低いのです。

さらに、[A]、[B] は必要条件ですが、十分条件ではありません。[A]、[B] を満たす半導体の①：高品質の単結晶の作製と、②：そのpn接合の実現が不可欠です（Fig. 4）。しかし、ワイドギャップ半導体で①や②を実現するのは、一般的に極めて困難です。

結晶は、空間的に周期的な原子配列を持った固体物質ですが、単結晶とは、試料のどの部分においても結晶軸の向きが同じ（微小結晶の集合ではない）結晶を言います。①の高品質単結晶を必要とするのは、発光の妨げになる不純物や格子欠陥をできるだけ少なくして、高効率の発光を得るためです。また、半導体の電気伝導性の制御（②のpn接合の実現）を可能にするためにも必須です。

半導体には、（電子の抜けた）正孔の数が電子の数より多い（電気的にはプラスの）p型半導体と、電子数が正孔数より多い（電気的にはマイナスの）n型半導体が

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 (Eg) 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

あります。p型半導体とn型半導体を完全に原子的に接合（junction：このような場合、接触（contact）ではなく“接合”と言います）させた構造を“pn接合”と呼びます。この場合、原子配列上は全体が一つの単結晶で継ぎ目はありません。このpn接合は、半導体機能素子の基本構造の一つで、これによって、トランジスタ作用や高効率の発光など様々な優れた機能を発現させることができます。

1970年代、青色発光素子用材料の有力候補と目されていたのは、Egが3.1eVの炭化ケイ素（6H-SiC）、II-VI族化合物のEgが2.7eVのセレン化亜鉛（ZnSe）系半導体及びIII-V族化合物のEgが3.4eVの窒化ガリウム（GaN）系の半導体でした（Fig. 5）。

この内、SiCはワイドギャップ半導体の中では唯一、当時からpn接合の作製が可能であり、青色LEDの開発が行われていましたが、間接遷移型であるため高効率の発光素子には不向きです。

ZnSeとGaNは、いずれも直接遷移型半導体であることが知られていましたが、大型バルク結晶の作製は困難で、また、p型結晶は実現されていませんでした。

大型結晶の作製が困難な時、薄膜単結晶作製に用いられるのが、エピタキシャル成長法です（Fig. 6）。

この内、気相エピタキシャル成長とは、成長させるべき結晶の原料物質を、ガス状で下地となる基板結晶の上に供給し、成長結晶の結晶軸を基板結晶の結晶軸に合わせて成長させる手法で、高品質半導体ナノ構造の作製などに広く用いられています。成長結晶と基板結晶が同じ時はホモエピタキシー、異なる時はヘテロエピタキシーと言います。後者では、成長結晶と基板結晶の格子定数ができるだけ近いことが必要です。

ZnSeは電子線励起などで明るく発光し、しかも良質単結晶を得るための気相エピタキシャル成長用基板結晶として、格子定数が極めて近いGaAs単結晶が利用できることなどから、多くの研究者が青色発光素子の実現を目指してZnSeの研究に取り組んできました。

一方、GaNは融点、窒素蒸気圧がともに非常に高く、大型バルク結晶の作製が極めて困難であるため、単結晶作製は異種基板結晶上への“ヘテロエピタキシャル成長”に依らざるを得ません。

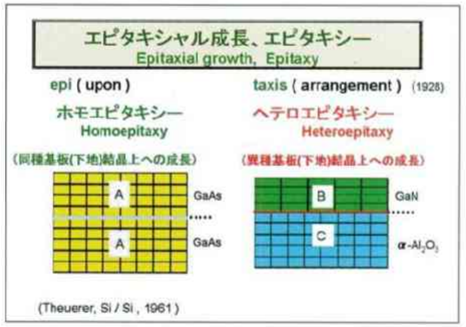
1969年、H. P. MaruskaとJ. J. Tietjenが、ハイドライド気相成長（HVPE）法によりサファイア基板上への単結晶膜の作製に成功し、1971年には金属-絶縁体-半導体（MIS）型GaN青色LEDが、J. I. Pankoveらにより発表され、それらに刺激されてGaN青色LEDの研究・開発は一時急速に立ち上がりました。しかし、世界中の研究者

［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 conducivity	◎	×	○

GaNを選ぶ　Chose GaN (1973)

Fig. 5



エピタキシャル成長、エピタキシー
Epitaxial growth, Epitaxy

epi (upon)　taxis (arrangement) (1928)

ホモエピタキシー
Homoepitaxy
（同種基板(下地)結晶上への成長）

ヘテロエピタキシー
Heteroepitaxy
（異種基板(下地)結晶上への成長）

(Theuerer, Si / Si , 1961)

Fig. 6

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).

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-1980s ルミネッセンス、屈折率などの研究
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

の様々な努力にも拘らず、GaN結晶の品質は相変わらず劣悪で、しかもp型結晶（従ってpn接合）が実現できないため、70年代後半には多くの研究者がGaN研究から撤退したり、あるいはZnSe など他の材料へと転向して行きました（Fig. 7）。

その頃、ZnSeやGaNのようなワイドギャップ半導体では、“自己補償効果”のため、p型結晶（従ってpn接合）の実現は極めて困難とされていましたが、私は「GaNは残留ドナー密度が10^{19}～10^{20}cm^{-3}もある。まず、ドナー密度が10^{15}～10^{16}cm^{-3}以下の高品質結晶を作ってからこのことは議論すべきであり、結晶をとことん綺麗にして、適当なアクセプター不純物を10^{18}cm^{-3}程度（以上）ドープすれば、p型結晶もできないはずはない」と考えていました。

そして「GaNは、ZnSeに比べて結晶成長も、また（Egがより大きいので）p型結晶の実現もより困難と予想されるが、ZnSeに比べて結晶が物理的にも化学的にも遙かに安定で、熱伝導率がZnSeに比べて大きいなど、多くの点で優れており、なんとかして高品質単結晶を作製し、極めて安定で、ZnSeに比べてより短波長の発光素子を実現しよう」——と決心しました。

こうして1973年、この前人未到の“GaN系窒化物半導体のpn接合による青色発光素子の実現”への挑戦を開始しました。

当時、GaAsなどの高品質薄膜結晶の成長法として、分子線エピタキシャル成長（MBE）法がすでに開発されていましたが、GaNに試みられたことはありませんでした。私は1974年、金属Gaとアンモニア（NH_3）を原料とするMBE法で、不均質ながら、初めてGaN単結晶成長に成功しました（所内報のみ、論文としては未発表）が、

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.

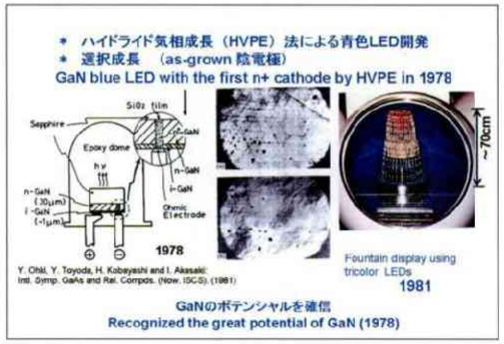
ZnSe and GaN, meanwhile, were both known as being direct transition type semiconductors, but it is difficult to grow large bulk crystals using them, and no p-type crystals had been realized yet.

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 (M IS-type) blue LEDs in 1971. Stimulated by these successes, the research and development of GaN-based blue LEDs saw a temporary serge. 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).



* 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. Compds. (Now, ISCS) (1981)

Fountain display using tricolor LEDs
1981

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

Fig. 8

当時揺籃期にあったMBE装置・方法では、良質膜の作製は困難でした。翌年から、HVPE法に取り組みましたが、結晶成長はやはり困難を極め、望みの高品質結晶はなかなか作製できませんでした。それでも諦めず、大木芳正らと結晶成長を続け、1978年、外部量子効率0.12%という（後のpn接合型とは比較になりませんが）従来に比べて格段に明るい青色LEDを開発しました。これは、GaNに初めて選択成長を適用し、n+陰電極をas-grownで作製したフリップ・チップ型LEDで、従来のMIS型LEDに比べて素子化工程が遙かに容易であるなど、注目すべき成果でした（Fig. 8）。

ある事情から、2年後の1981年に化合物半導体の国際会議に発表しましたが、全く反響はありませんでした。その頃、世界中の多くのGaN研究者がこの分野から撤退しており、会議の参加者も誰一人GaNに関心を持つ人がいなかったのでしょう。私は、その時“我一人荒野を行く”心境でしたが、たとえ一人になっても、GaN研究を止めようとは思いませんでした。

GaNの可能性を直感

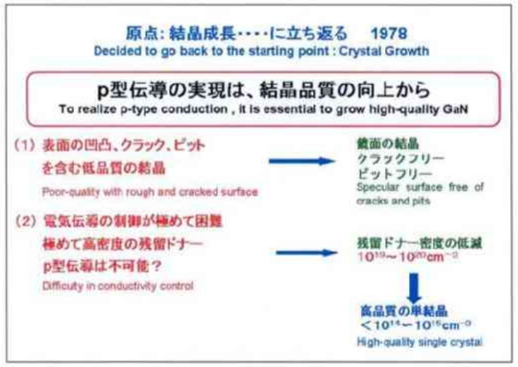
その頃（少年時代に鉱石の晶癖を見たり、名古屋大学でGeのエピタキシャル成長面の観察を楽しんだように）、時間があるとHVPE法で作製したGaN結晶を蛍光顕微鏡で見ていました。ある日、クラックやピットの多いウェハーの中に、ごく稀に綺麗な微小結晶が混じっていることに気づき、一瞬瞳を凝らし、青色発光素子用材料としてのGaNの大きな可能性を直感しました。

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



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
→ 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

（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
→ 残留ドナー密度の低減
10^{19}～10^{20}cm^{-3}
↓
高品質の単結晶
＜10^{14}～10^{16}cm^{-3}
High-quality single crystal

Fig. 9

GaNの研究開始以来、「結晶品質をとことん良くすれば、必ずp型伝導も実現できる」と絶えず自分に言い聞かせ、仲間にも話してきましたが、確たる根拠があった訳ではありません。しかし、この体験から「なんとかして、ウェハー全体を、この綺麗な微結晶と同等の品質に作ることができれば（その時、多分表面は鏡面になると想像しました）、電気伝導制御（p型伝導も）は実現できるだろう——鍵は結晶成長だ」と確信しました（Fig. 9）。

こうして1978年、もう一度この研究の原点である“結晶成長”に立ち返ることにしました。この決断は、私のGaN研究だけでなく、（閉塞状態にあった）世界のGaN研究・開発にとっても大きな岐路だったと思っています。

結晶の品質は、成長法と成長条件に大きく依存します。GaNの結晶成長法としては、MBE法、HVPE法の他、有機金属化合物気相成長（MOVPEまたはMOCVD）法があります（Fig. 10）。

「MBE法は高真空中の成長であり、窒素蒸気圧が極めて高いGaNでは窒素抜けが起こりやすく、良質のGaN成長に適しているとは思いませんでした。HVPE法は、ナノメートルオーダーの結晶の成長を制御するには成長速度が速すぎ、また逆方向の分解反応を伴うので、高品質化には不向き」——と考えました。一方、MOVPE法は1971年、H. M. ManasevitらがGaN成長に初めて試みましたが、良い結果が得られず、その後全く用いられていませんでした。しかし、私は「これは単一温度領域での不可逆熱分解反応を用いる方法で逆方向反応はなく、成長速度も適しており、不純物ドーピングや混晶の組成制御も容易であることから、サファイアのような格子不整合の大

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

MBE　高真空中
$Ga(g)+N(g)=GaN(s)$ または
$Ga(g)+NH_3(g)=GaN(s)+\frac{3}{2}H_2(g)$　（窒素抜け）
Prone to nitrogen deficiency

HVPE　2ゾーン　（または　1ゾーン　）　50~150μm/h
$GaCl(g)+NH_3(g)=GaN(s)+HCl(g)+H_2(g)$（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
$Ga(CH_3)_3(g)+NH_3(g)=GaN(s)+3CH_4(g)$（逆方向反応なし）
Minimal reverse reactions
H.M.Manasevit et al : J.Electrochem.Soc. 118 (1971) 1864

MOVPE法を採る　Chose to adopt MOVPE (1979)

Fig. 10

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 examing 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 conductuctivity, 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

きい基板上へのGaN成長には最適」と判断、採用することにしました（1979年）。

この選択が間違いでなかったことは、今日、GaN系の結晶や素子が、ほとんどMOVPE法で作製されていることからも明らかです。

次は基板の選択です。結晶の対称性、物理的性質の類似性と同時に、MOVPE成長の条件・環境（約1,000℃、強い還元性のアンモニア雰囲気中）に対する耐性などを総合的に検討しなければなりません。Si、GaAs、サファイアなどを実際に比較した結果、やはり当面は（将来、より優れた基板結晶の使用が可能になるまで）、それまでも使用していたサファイアを用いることにしました。

低温堆積バッファー層技術の開発

この二つの重要な決断の後、かねて招かれていた名古屋大学に1981年に戻り、直ちに大学院生の小出康夫や天野浩らとMOVPE法によるGaN成長に取り組みましたが、MOVPE法でも均一なGaN結晶はなかなか得られませんでした。試行錯誤を繰り返し、反応管と成長条件に大きな工夫・改善を行いました。

第一の改善は、原料ガスである有機金属化合物（GaN成長の場合、トリメチルガリウム（TMGa））とアンモニア（NH_3）及びキャリヤの水素（H_2）ガスを反応管入口の直前で混合し、管内での（TMGaとNH_3の反応による）アダクト（adduct）の生成を抑制することにより、原料の利用効率を高めると同時に、これら原料ガスとキャリヤガスの混合ガスを、ガス導入管を通して45度傾けた（それまでは、基板は水平）基板上に、毎秒約110cm（それまでは毎秒2cm）という高速で吹き付けることにより、ガスの基板上での対流を抑制し、ガス流をスムースにすることによって、均質なGaN膜が得られるようになりました。この基板を斜めにして、ガスを高速に吹き付けたことが、第一の改善のポイントです。

しかし、膜厚はウェハー全体ほぼ均等といっても、ピットやクラック（マクロな欠陥）が全く無くなった訳ではありません。また、電気的特性や光学的特性もそれほど向上せず、不純物や格子欠陥が多いことを示唆していました。

これは主に、GaNとサファイアの間の16％という大きな格子定数差のため、両者間に存在する大きな界面エネルギーに起因しているであろう――と考えました（Fig.11）。実際、半導体結晶のエピタキシャル成長では、GaAs上のGaAs成長のような格子整合を金科玉条としており、ヘテロエピタキシャル成長の場合、不整合が1％程度でも

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.

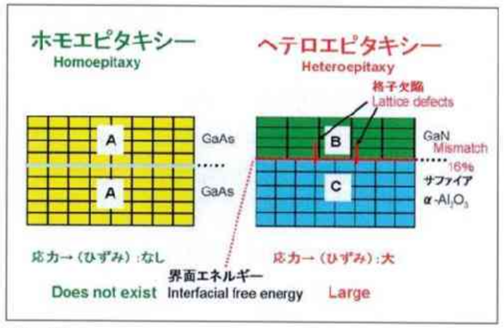
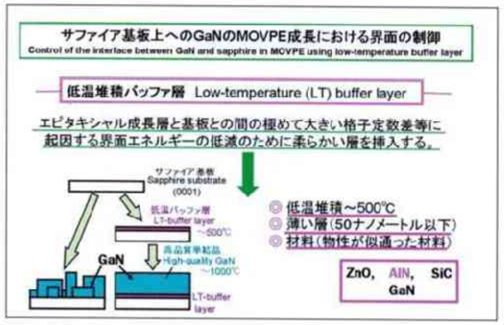


Fig. 11


サファイア基板上へのGaNのMOVPE成長における界面の制御
Control of the interface between GaN and sapphire in MOVPE using low-temperature buffer layer

低温堆積バッファ層 Low-temperature (LT) buffer layer

エピタキシャル成長層と基板との間の極めて大きい格子定数差等に起因する界面エネルギーの低減のために柔らかい層を挿入する。

◎ 低温堆積~500℃
◎ 薄い層（50ナノメートル以下）
◎ 材料（物性が似通った材料）

ZnO, AlN, SiC
GaN

Fig. 12

良質結晶の成長は困難です。

この大きな格子定数差の問題を克服するため、1985年に“低温堆積バッファー層技術”を開発しました（Fig. 12）。具体的には、「GaN単結晶層の成長直前に、GaNの単結晶成長温度（エピタキシー温度）よりかなり低い温度（例えば500℃）で、GaNや基板材料と物理的性質の良く似た材料をバッファー層として、（基板の結晶学的情報のエピタキシャル成長層への伝達を妨げない程度の厚さに）薄く（30~40nm）堆積し、その後エピタキシー温度（約1,000℃）に昇温してGaNの単結晶成長を行う」手法です。

これは、エピタキシャル成長層と基板の間に、単結晶のようにがっしりした構造ではない“ソフトな（融通無碍の）薄い膜をバッファーとして挿入する”ことにより、両者間の大きな界面エネルギーを低減し、可能な限り（原理的には、界面エネルギー

Development of low-temperature buffer layer technology

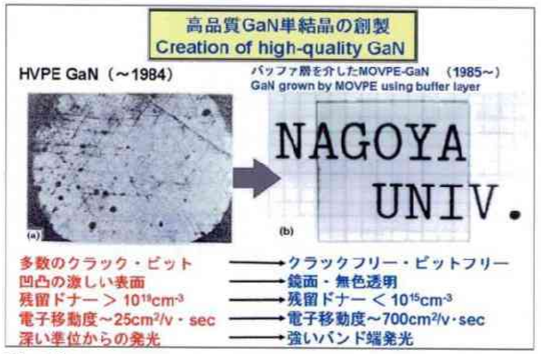
After making these two important decisions, I returned to Nagoya University, where I had been invited some time before. Upon returning there in 1981, I immediately started working on GaN growth using the MOVPE method, in collaboration with a team of graduate students including Yasuo Koide and Hiroshi 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 (NH_3) and hydrogen (H_2) 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 NH_3, 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 an 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



高品質GaN単結晶の創製
Creation of high-quality GaN

HVPE GaN（~1984）	バッファ層を介したMOVPE-GaN （1985~） GaN grown by MOVPE using buffer layer
(a)	(b)
多数のクラック・ピット	クラックフリー・ピットフリー
凹凸の激しい表面	鏡面・無色透明
残留ドナー > 10^{18}cm^{-3}	残留ドナー < 10^{15}cm^{-3}
電子移動度~25cm^2/v・sec	電子移動度~700cm^2/v・sec
深い準位からの発光	強いバンド端発光

Fig. 13

は存在しない）ホモエピタキシーの条件に近づける——というアイディアに基づいています。バッファー層材料としては、窒化アルミニウム（AlN）、GaN、酸化亜鉛（ZnO）やSiCなどを考えましたが、最初に試みたのは以前から馴染みのあるAlNでした（実は、早くから窒化物半導体に関心を持っていた私は、1967年からAlNの結晶成長と光学特性などの研究をしていました）。

上記第一の改善に加え、本バッファー層技術を用いて（同時に、ガス流速を毎秒約430cmとさらに高速にし）作製した結晶は、無色透明・鏡面であり、結晶学的、電気的並びに光学的特性などが、同時に、従来に比べて飛躍的に向上しました（Fig.13）。幾度も失敗を乗り越え、最適条件を見出したのは天野浩の執念でした。

私が1973年以来、その実現を夢見た、すばらしい外観・内容を伴った"文質彬彬"のGaN結晶を見た時の感動は忘れることができません。

p型伝導の実現に向けて

直ちにp型伝導の実現に向けて実験を開始しました。バッファー層技術を用いて作製した（残留ドナー密度が10^{15}cm^{-3}以下の）高品質結晶に亜鉛（Zn）ドーピングを繰り返しましたが、高抵抗化するだけで一向にp型結晶は得られませんでした。

1988年、このZnドープ高品質GaNに低速電子線を照射（Low-energy electron beam irradiation（LEEBI））して、Znの関与する青色発光特性を調べている時、スペクト

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.

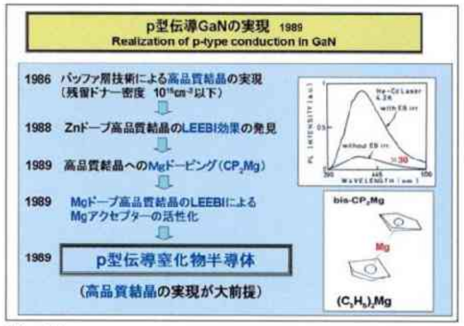
In addition to the first improvement I just mentioned, GaN single crystals grown using this buffer layer technology combined with a further accelerated gas flow rate of about 430 cm per second were clear and colorless. They had a mirror surface with dramatically improved crystallographic, electrical, 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



p型伝導GaNの実現 1989
Realization of p-type conduction in GaN

1986 バッファ層技術による高品質結晶の実現
（残留ドナー密度 10^{15}cm^{-3}以下）

1988 Znドープ高品質結晶のLEEBI効果の発見

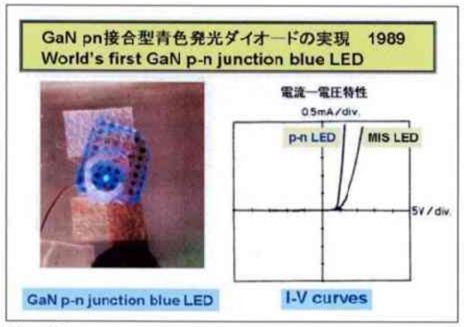
1989 高品質結晶へのMgドーピング（CP$_2$Mg）

1989 Mgドープ高品質結晶のLEEBIによる
Mgアクセプターの活性化

1989 p型伝導窒化物半導体

（高品質結晶の実現が大前提）

Fig. 14



GaN pn接合型青色発光ダイオードの実現 1989
World's first GaN p-n junction blue LED

Fig. 15

ルは不変のままで、強度が著しく増大する現象（LEEBI効果と名付けました）を、天野浩が見つけました（Fig.14）。

これは試料のフェルミ準位が変化しているに違いない（p型に変化している可能性がある）——と思いましたが、試料はp型伝導を示しませんでした。

そこで、アクセプター不純物のイオン化エネルギーを再検討しました。J.C. Phillipsの著書（1973年）によると、Mg原子の電気陰性度と（置換されるべき）Ga原子の電気陰性度の差は、Zn原子のそれより小さいことから、MgがZnに比べてより活性化しやすいのではないかと気づき、Mg原料として、ビスシクロペンタジエニール・マグネシウム（CP$_2$Mg）とメチルCP$_2$Mg（MCP$_2$Mg）を輸入しました。

1989年初めに、大学院生の鬼頭雅弘がCP$_2$MgやMCP$_2$Mgを用いて、バッファー層技術による高品質GaNへのMgドーピングを行いました。その試料をLEEBI処理して、Mgの関与する青色発光強度の著しい増大（LEEBI効果）とともに、試料が低抵抗のp型伝導に変換していることを発見（ホール効果により確認）しました。

バッファー層技術による全く透明な鏡面結晶を見た時と同様に、大変興奮したのは言うまでもありません。

直ちにpn接合型LEDを手作りし（Fig.15）、それまでのMIS型LEDでは見たことのない見事な電流-電圧（I-V）特性を得て、またEBIC観察などでpn接合の実現を再確認しました。

そして、初のGaN pn接合LEDからの眼に沁みるような青色発光を見て、感動を新たにしました。

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$_2$Mg) and methyl-CP$_2$Mg (MCP$_2$Mg) 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$_2$Mg or MCP$_2$Mg. 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

n型伝導度の制御など

一方、n型結晶の電気伝導度について、新たな問題に気づきました。低温バッファー層の導入により、残留ドナー密度が著しく減少したため、結晶が高抵抗化したのです。実際の素子作製では、広い範囲にわたって伝導度を制御する必要があります。そこで、バッファー層技術により結晶を高品質に保ちながら、シラン（SiH_4）ガスを用いてSiをドープすることにより、n型結晶の伝導度を広い範囲に制御することに1989年に成功しました（Fig. 16）。

このn型伝導度の制御法も、現在世界中で広く用いられています。

こうして1989年までに、GaN系pn接合型の発光素子及び電子素子の実現に必須の全ての基礎技術を達成しました。

続いて1990年には、バッファー層技術による高品質結晶を用いて、レーザ発振に必須のGaNからの誘導放出を、室温では初めて、しかも従来より１桁以上少ない光入力で達成し、同結晶の品質が格段に向上していることを裏付けるとともに、先のpn接合LEDの技術と合わせて、GaN系レーザダイオード（LD）実現の可能性を示しました（Fig. 17）。

これらの成果が引き金になり、GaN系結晶・素子の研究・開発が急速に進み、関連論文数が指数関数的に急増するとともに、高輝度青色LEDの商品化を始め、GaN系各種素子も次々に開発されてきました（Fig. 18）。

1992年から名城大学に移り、窒化アルミニウム・ガリウム（AlGaN）、GaN及び窒化ガリウム・インジウム（GaInN）結晶のさらなる高品質化の研究を続け、それらのナノ量子構造を用いて、窒化物半導体における（量子サイズ効果は名大時代の1991年）、ピエゾ効果や量子閉じ込めシュタルク効果を検証しました（1997年）。また2000年には、竹内哲也が窒化物結晶のピエゾ電界の結晶方位依存性を明らかにするとともに、無極性や半極性結晶面の存在を指摘しました。現在、ピエゾ電界の悪影響を避けるためにこれら無/半極性面上への結晶成長と素子開発が世界中で行われています。

新しい素子開発に関しては、1995年、AlGaN/GaN/GaInN量子井戸を用いた電流注入誘導放出に続き、1996年、376nmのLDの発振に成功、2004年には（当時世界最短波長の）350.9nmのLDを実現し、また、超高感度紫外線検出器（2000年）や、高オン/オフ比・低オン抵抗のノーマリオフ型AlGaN/GaNヘテロ電界効果トランジスタ

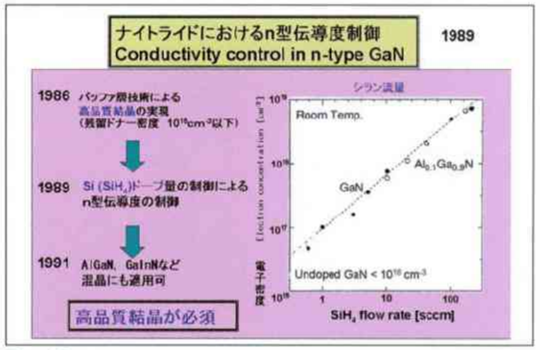


Fig. 16

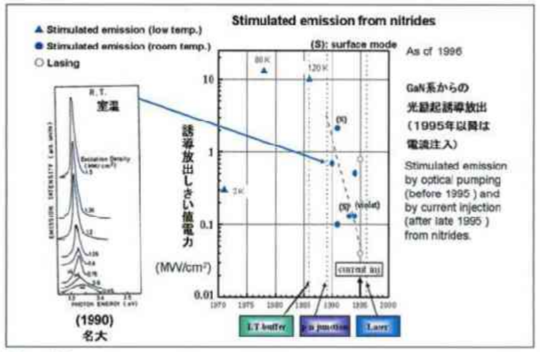


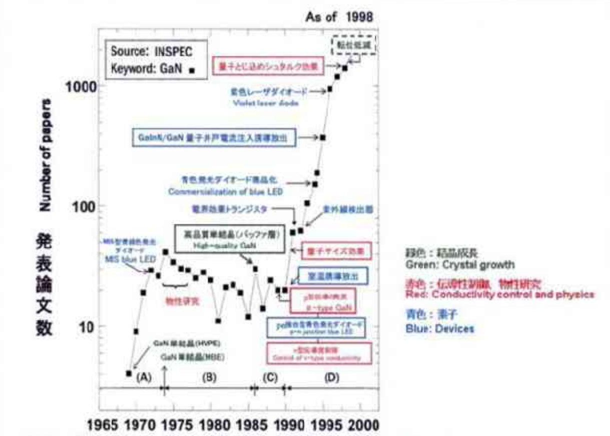
Fig. 17

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



III族窒化物半導体結晶・素子の研究・開発における重要な成果と論文数
Number of papers (INSPEC) and activities related to group Ⅲ nitrides

Fig. 18

(2006年) などを開発しています。

最近は、高出力紫外発光素子実現に必須の高AlNモル分率のAlGaN混晶や500nmより長波長の発光素子の開発に向けた高InNモル分率のGaInN混晶の高品質化にも取り組んでいます。

おわりに

“はじめに光ありき”という言葉が示すように、“光”は私たちの生活に深く関わっています。人類や多くの生物にとって、光はかけがえのない存在であり、古来、人類は、発光体を求め続けてきました。火（灯）の創出に始まり、電灯、蛍光灯に続き、20世紀後半に入り半導体発光素子を実用化しました。これらの光源は全体としては、広い波長範囲をカバーしていますが、概して高エネルギー光の光源の開発が遅れていました。

青色LEDの実現により、半導体による光の三原色が揃い、全固体発光素子によるフルカラーディスプレイや白色LEDが開発され、また青色LED技術を発展させた青

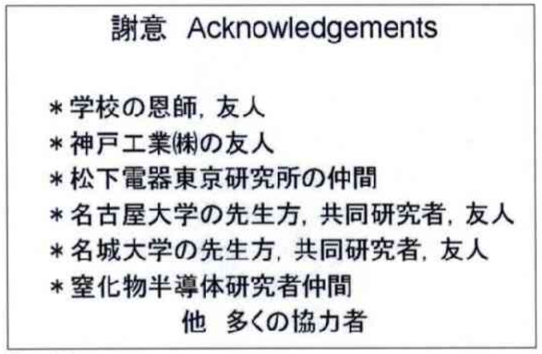
demonstrated the marked improvement in the quality of crystals, and together with the p-n junction LED technology we have just discussed, it also suggested the possibility of realizing GaN-based laser diodes (LDs).

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 (AlGaN), 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 AlGaN/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 AlGaN/GaN heterostructure field effect transistor in 2006.

More recently, we have also been working on developing high-quality AlGaN crystals with high AIN 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.



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他 多くの協力者

Fig. 19

紫色レーザは超高密度情報処理などに活用されています。さらに、一般照明の他、医療や植物栽培用光源などへの応用が広がることを期待しています。

おわりに、私は大変な晩生で、40代の初めに青色発光素子の魅力にとりつかれ、その実現を目指して、ただ愚直に仕事をしてまいりました。ごく平凡な研究者である私が、本日記念講演をさせて頂く機会をいただいたことは、身に余る光栄であり、多くの方々の多大なご協力とご支援の賜物です（Fig.19）。

今日まで、私を導き、支えて下さいました多くの方々に、心から感謝申し上げます。

Conclusion

As they say, "In the biginning 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.

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