Necessity of True Bulk GaN Single Crystal and Trends in Research and Development

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1 Introduction

Today, silicon (Si) semiconductor devices are used in virtually all electronic equipment, spanning a wide range of applications from consumer products, including various types of home electrical appliances such as personal computers (PC), televisions (TV), and cell phones, automobiles, and others, to industry, where examples include electric trains, plant control equipment, etc. Si semiconductors are used mainly in electronic devices such as memories and CPUs (central processing unit) in the form of MOS type transistors, bipolar transistors, and others.

On the other hand, as direct transition-type semiconductors, compound semiconductors, represented by gallium arsenide (GaAs)[NOTE 1] and indium phosphide (InP),NOTE 1) are suited to use in light-emitting devices, and are applied in optical devices such as laser diodes (LD) and light-emitting diodes (LED). LDs are used in optical communications and optical devices such as compact disk (CD) and DVD players, while LEDs are used in a variety of familiar products such as remote controls for home electrical appliances, which operate in the near infrared waveband, and red LEDs in displays. As other features of the compound semiconductors, these devices have high carrier mobility and low leakage current/low capacity, and are widely applied as high frequency transistors in cell phones, satellite broadcast receivers, etc. Silicon carbide (SiC) and other types are also applied in high output devices.

Among the compound semiconductors, GaN-based semiconductor materials,[NOTE 2] centering on gallium nitride (GaN), are wide bandgap semiconductors of the direct transition type, and are therefore semiconductors which are suitable for use in high speed, high power transistors and light-emitting devices in the ultraviolet-blue-green region, which cannot be realized with Si, GaAs, and similar semiconductor materials. Si, GaAs, and similar semiconductors were an object of intense R&D activity from the 1940s into the 1970s, contributing to practical application of this type. In contrast, virtually no practical applications of GaN-based semiconductors have been realized, as R&D requires much time due to the difficulty of growing crystals. A blue LED (pn junction type) was commercialized using a GaN-based semiconductor for the first time in 1993, which was followed by practical application of a white LED, a blue-violet laser diode (BV-LD), and other devices. White LEDs are currently used in practical applications including backlights for various types of liquid crystal displays, beginning with cell phones, and in flashlights and automobile headlights, and efforts are being made to expand this

[NOTE1]

In this paper, GaAs-based semiconductors include AlGaAs, which is a mixed crystal semiconductor of GaAs and AlAs, as well as InGaAs and others. Similarly, InP-based semiconductors include mixed crystal semiconductors containing InP.

[NOTE2]

GaN is a group III nitride semiconductor. In this paper, the group III nitride semiconductors AlN and InN and their mixed crystal semiconductors are referred to as GaN-based semiconductors, and devices using these materials are referred to as GaN-based semiconductor devices.

type into the large market for general lighting in the future. Ultraviolet-blue LEDs are used in deodorizing devices as a light source for the photocatalyst, while blue-green LEDs are used in traffic lights, various types of indicators, and the like. Among LDs, BV-LDs have been applied practically as a light source for the Blu-ray Disc technology, and as such, are used in recording and playback of high definition video images. In electronic devices, active R&D is also underway aiming at practical application of high speed, high output transistors for use in future cell phone ground stations, switching devices for hybrid car inverters, etc. Thus, GaN-based semiconductor devices are becoming a necessary and indispensable part of our daily lives.

According to the "International Comparison of Science and Technology/Research and Development: Electronic Information and Communications – 2008"[1] prepared by the Japan Science and Technology Agency (JST), Japan's GaN-based semiconductor devices were evaluated as either "extremely advanced" or "advanced" in comparison with those in other countries in all of the categories of research, technology, and industry. However, "maintain the status quo" has been a trend in recent years, whereas there is an "upward tendency" in other countries, particularly in China, Korea, and Taiwan. Thus, these countries are closing the gap with Japan.

In substrate materials, Japan holds the top share in Si semiconductors and compound semiconductors such as GaAs/InP, etc., and possesses international competitiveness in this area. The United States holds the lead only in SiC. On the other hand, as will be discussed in detail in this paper, a manufacturing technology for GaN substrate materials has not been established. Therefore, seizing the initiative in crystal growth technology for GaN, which is one of the few remaining materials for which a substrate manufacturing technology has not been established, is considered to be of crucial significance for future GaN-based semiconductor device technology as a whole.

This paper describes the necessity of research and development of a "true bulk single crystal" of GaN in GaN-based semiconductor devices, and the current status and issues for R&D in this area. As used in this paper, "true bulk single crystal" means a bulk crystal which contains minimal crystallographic defects (dislocations) and enables cutting of arbitrary crystal planes, as can already be obtained with Si, GaAs, and InP.

2 Limits of heteroepitaxial technology in GaN-based semiconductors and necessity of bulk crystal

2-1 Range of application of GaN-based semiconductors

Research and development on GaN-based semiconductor materials has a long history. Like GaAs and other compound semiconductors, R&D on crystal growth was carried out using the vapor deposition method beginning in the 1960s. Improvement of crystallinity by using a low temperature buffer layer in 1986[2] and the discovery of p-type conduction in 1989[3], which can be considered two major topics among the scientific breakthroughs in this field, led to the appearance of a commercial blue LED in 1993. Both of these two scientific breakthroughs were achievements of Prof. Isamu Akasaki of Nagoya University (at the time). Subsequently, great progress was made in the development of crystal growth technologies using the vapor deposition method, and practical applications were realized, centering on LEDs and LDs. These devices are now a familiar part of our daily lives. A comparison of the physical properties of GaN-based semiconductors and other semiconductors, and the devices which utilize those properties, is shown in Table 1.

In the area of light-emitting devices, light-emitting devices in the ultraviolet (UV) to visible light region have been realized, taking advantage of the fact that the GaN-based semiconductors are direct transition-type semiconductors and have a wide bandgap. By combining mixed crystals of GaN, AlN, and InN, it may be possible to realize light-emitting devices from the UV to the infrared (IR) region. This is shown concretely in Figure 1. The potential of GaN-based semiconductors as light-emitting devices covers the wavelength region from 200nm, which is the UV region, to near 1500nm, which is used in optical fibers. Of this, at present, LEDs in the wavelength region of 210-550nm and LDs with wavelengths of 342-488nm have been realized as light-emitting devices at the R&D level. Commercial devices include LEDs in the 365-520nm wavelength region and LDs in the

Table 1 : Physical properties of semiconductor materials and features of GaN-based semiconductors

Semiconductor materia	Si	SiC (4H)	Diam-ond	GaAs	Group III nitride (GaN-based) semiconductors			
					GaN	AlN	InN	Devices utilizing features
Transition	Indirect			Direct				
Bandgap (eV)	1.1	3.3	5.5	1.4	3.4	6.2	0.6～0.7	・UV-visible light-infrared light-emitting devices
Electron mobility ($cm^2 V^{-1} s^{-1}$)	1500	1000	1800	8500	1200	–	4000	・Power transistors
Insulation breakdown field ($MV\ cm^{-1}$)	0.3	3.0	4.0	0.4	3.3	–	2.0	・High frequency
Saturation electron velocity ($10^7 cm\ s^{-1}$)	1.0	2.0	2.5	2.0	2.5	2.0	4.2	
Thermal conductivity ($W\ cm^{-1} K^{-1}$)	1.5	4.9	20.9	0.5	2.1	2.9	0.8	

Prepared by the STFC based on Reference [3]

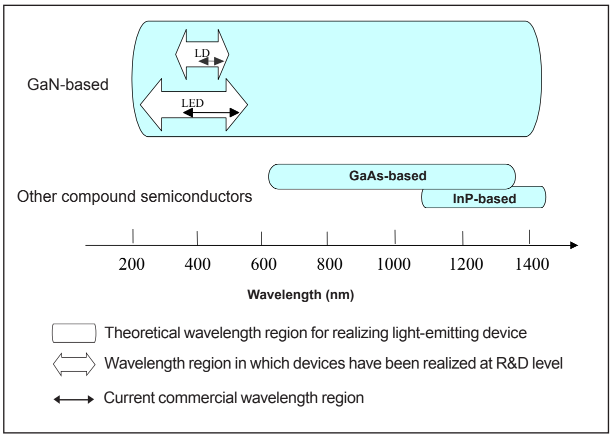

Figure 1 : Suitable wavelengths for light-emitting devices

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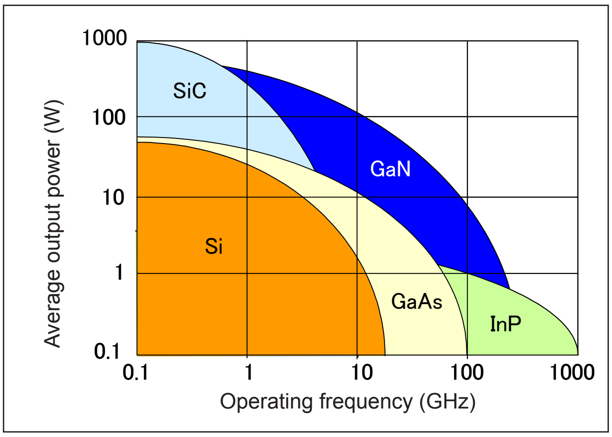

Figure 2 : Applicable regions for high frequency/high output electronic devices

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400-450nm region. However, in spite of the potential of the remaining wavelength region, this region is still unexplored from the practical viewpoint. Future technical innovations will be necessary in order to utilize the remaining wavelength region.

On the other hand, as shown in Table 1, GaN-based semiconductors display excellent electron mobility, dielectric breakdown field, electron saturation velocity, and thermal conductivity properties, and thus have large possibilities as high frequency, high output transistor materials. Figure 2 shows the regions of application of the various types of semiconductors in electronic devices. GaN-based semiconductors have potential in the high frequency, high output region which cannot be realized with other semiconductor materials.

Furthermore, because GaN-based semiconductors do not contain harmful substances like the As in GaAs, they offer high environmental compatibility. Depletion of resources of the elements Ga and N is not a concern, which is also a promising point for future device materials.

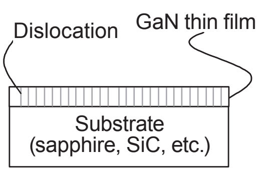
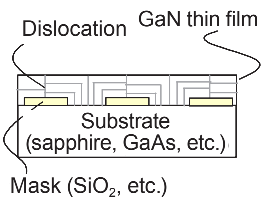
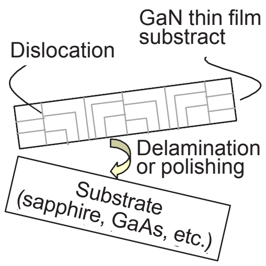
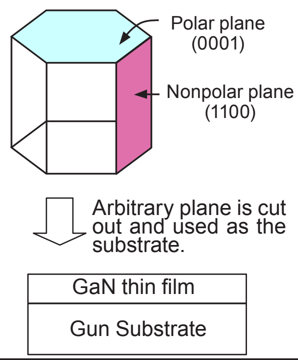
2-2 Applications of heteroepitaxial method and its limits

Because Si, SiC, GaAs, and InP all exist in bulk crystal form, substrates of Si, SiC, GaAs, and InP are used in epitaxial growth[NOTE 3] of their crystals, respectively. This type of crystal growth using a substrate of the same material is termed “homoepitaxial growth.” However, because it is not possible to obtain bulk crystals of GaN, a substrate of a different material must be used with GaN-based semiconductors when growing crystals for device production. This is a major barrier which makes it impossible for GaN-based semiconductors to demonstrate their outstanding potential. At present, GaN-based semiconductor devices are produced by crystal growth of a GaN based semiconductor thin film on a substrate of sapphire (Al2O3) or SiC. This type of crystal growth, in which epitaxial growth is performed on a substrate of a heterogeneous material, is termed "heteroepitaxial growth." Table 2 shows the differences between the various types of heteroepitaxial growth and homoepitaxial growth in the methods of forming GaN-based semiconductor crystals.

In crystals obtained by heteroexpitaxial growth, there are problems related to crystallographic defects (dislocations) and the polar plane. First, because the material being grown and the substrate material are different, numerous dislocations occur due to differences in the thermal expansion coefficient and lattice constant.[4] This has an adverse effect on device performance, particularly output and life.[5,6] Moreover, spontaneous polarization occurs due to the relationship of the orientation of the crystal plane with the heterogeneous substrate, making it difficult to improve light emission efficiency.

In obtaining the GaN crystals used practically in LEDs, a GaN-based thin film with a thickness of several μm is grown on a sapphire or SiC substrate by the Metal Organic Vapor Phase Epitaxy (MOVPE) method at a temperature in excess of 1000°C (Type A in Table 2). However, due to the difference in the lattice constants and thermal expansion coefficients of the substrate and GaN-based material, formation of dislocations with a high density of 10^9cm^{-2} or more is unavoidable. This meant that development of Type A crystals to an expanded wavelength region including UV, higher outputs, LD applications, and the like was not possible. Therefore, research and development were carried out with the aim of reducing the dislocation density by heteroepitaxial growth, and it was possible to reduce the dislocation density to the 10^7cm^{-2} level by growing GaN crystals on a sapphire substrate by Epitaxial Lateral Overgrowth (ELO) using Vapor Phase Epitaxy[7] (Type B in Table 2). Subsequently, as a result of further development of this Type B method, it was possible to obtain a GaN thick film substrate with a dislocation density of around 10^5cm^{-2} by first growing a GaN thick film with

Table 2 : Epitaxial crystal growth of GaN and its applications

	Heteroepitaxial			Homoepitaxial
	Type A	**Type B**	**Type C**	**Type D**
				
Merits/ Demerits	· Large area : To inch class · Crystal defects (dislocations) : To 10^9cm^{-2} · Polarity:Spontaneous polarization by C(0001) plane	· Large area : To inch class · Crystaldefects (dislocations) : To 10^9cm^{-2} · Polarity : Spontaneous polarization by C(0001) plane	· Large area: To inch class ·Crystal defects (dislocations): To 10^9cm^{-2} ·Polarity:Spontaneous polarization by C(0001) plane. · High cost	· High quality · Arbitrary polar plane · Crystal size: mm order
Applica-tions	Near UV to green LED White LED (pseudowhite)	Blue-violet LD (BV-LD; low power)	Blue-violet to blue LD	Not realized

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[NOTE3]
"Epitaxial" refers to crystal growth in an upward direction with the crystallographic axes aligned. The term is derived from the Greek epi ("above") and taxy ("ordered"). Epitaxial is also abbreviated "epi."

a thickness of several 100μm on a GaAs substrate[8] or sapphire substrate, followed by delamination of the GaN crystal substrate.[8,9] (Type C in Table 2). Results in which a dislocation density of less than $10^5 cm^{-2}$ was realized locally have also been achieved with this Type C method.[10] Although the width of this low dislocation region is limited to around 500μm, a practical BV-LD (405nm) for Blu-ray Discs has been realized by using Type C GaN as the substrate. Manufacture of these LDs is possible because the active layer (light-emitting region) of the LD is narrow in this application, having a width of several μm, and this can be aligned with the low dislocation region of the Type C substrate. However, this is inadequate for applications which require a size on the mm order, such as LEDs and transistors. It may be noted that Type B and Type C by the VPE method are technologies which were developed in Japan, and at present, Japanese companies hold the top share in substrates for BV-LDs.

On the other hand, because of the difference in lattice constants with the substrate, orientation of the normal heteroepitaxial growth plane is the (0001) plane (C plane). Because the C plane is a crystal plane which possesses polarity, spontaneous polarization occurs. This is a problem because the carrier injected into the device will not contribute efficiently to light emission or transistor operation if spontaneous polarization occurs. From this viewpoint, there are fundamentally limits to improvement in the performance of crystals grown by heteroepitaxial growth.

Sumitomo Electric Industries, Ltd. and Hitachi Cable, Ltd., which are Japanese makers of compound semiconductor substrates, have mass-produced or shipped samples of Type C thick film GaN substrates.[8,9] Of these, Sumitomo Electric's GaN substrate is applied commercially as a substrate for BV-LDs. This maker succeeded in producing a low dislocation density region with a width of several 100μm by a method in which the dislocations are concentrated while forming pits on a GaAs substrate,[10] and realized a substrate size of 2 inches.

A distinctive feature of the Hitachi Cable method is the substrate delamination method. A GaN thin film is grown on a sapphire substrate by the MOVPE method, a titanium (Ti) film is formed on this film by vapor deposition, and a GaN thick film is then grown to a thickness of several 100μm by vapor phase deposition. This causes voids to form in the vicinity of the Ti film, and it is possible to form a GaN thick film substrate by thermal delamination of these voids during the removal operation. Although the average dislocation density is around $10^6 cm^{-2}$, it is possible to obtain a substrate size of φ3" by this method. However, in both cases, the product displays polarity because the orientation of the principal plane obtained is the C plane (0001), and issues of crystal quality and cost still remain. In particular, the cost of Type C is high, at several \100,000 to 1,000,000 per piece for the φ2" size, because a sacrificial substrate is necessary.

Thus, at present, both of these substrate makers are employing the vapor deposition method, which is a highly realistic method, but this does not mean that a "true bulk single crystal" has been realized. As mentioned previously, because perfect, dislocation-free crystals have been obtained with Si and GaAs and it is possible to cut out and use an arbitrary plane as the substrate, various applications can be realized by homoepitaxial growth on this substrate. Accordingly, for the future, the realization of a dislocation-free "true bulk single crystal"[NOTE 4] (Type D in Table 2) of GaN is awaited.

2-3 Extension of applications by realization of "true bulk single crystal" and its social impact

The improved device properties and expansion of applications shown in Table 3 can be expected by realizing a "true bulk single crystal" with GaN-based semiconductors.

If a "true bulk single crystal" is realized with GaN-based semiconductors, high output, high efficiency, and an expanded wavelength region can be expected in light-emitting devices such as LEDs and LDs by taking advantage of the reduction in defect density

[NOTE4]
In GaN, there are cases in which Type C is called "bulk crystal." In this paper, the expression "true bulk single crystal" is used to refer to bulk crystals which are dislocation-free or have a low dislocation density ($\leqq 10^3 cm^{-2}$) that cannot be realized with heteroepitaxial technology, and also enable cutting of any arbitrary crystal plane.

and the non-polar plane. In lighting using LEDs, in addition to popularization as general lighting devices taking advantage of the high efficiency and high color-rendering property of LEDs, this technology may open the way for new types of technical lighting. Assuming high efficiency and low cost in the white LEDs which are now used in some lighting applications, such as backlights for liquid crystal displays, full-scale replacement of incandescent light bulbs, fluorescent tubes, halogen and other general lighting, and technical lighting by LED lighting will be possible. A trial calculation has shown that an energy saving effect (reduction in annual power consumption) of approximately 20% could be achieved by popularization of LED lighting.[NOTE 5]

As LDs, devices with output power from several 10mW to around 200mW in BV wavelength range (450 nm) are marketed as light sources for Blu-ray Discs. Laser life is secured by alignment of the active layer with the region of a Type C polar substrate having a locally small dislocation density, as discussed previously. In the future, if a Type D substrate can be realized, it will be possible to satisfy both improved performance and reduced cost because a high quality LD structure can be manufactured without considering the distribution or deviations of dislocations. Furthermore, use of the non-polar plane will make it possible to produce longer wavelength devices, contributing to the realization of green (>500nm) LDs. At present, green lasers are generally wavelength conversion devices using Second Harmonic Generation (SHG), but problems related to miniaturization and cost reduction remain. Here, as well, it will be possible to reduce the size and cost of portable projectors, laser TVs, etc. by realizing green LDs with GaN-based devices. With the ongoing trend toward larger screens in liquid crystal TVs and plasma TVs, which are continuing to become the leading television technologies, power consumption is also increasing. If an inexpensive laser TV can be realized, energy consumption can be reduced by 1/2 to 1/3 that of liquid crystal TVs and plasma TVs of the same size, even in larger screen televisions,[13] and it will be possible to satisfy simultaneously large screen size and energy saving. (For details, see the following Column.)

In electronic devices, HFET (Hetero-junction Field Effect Transistor), which are a lateral device,

Table 3 : Expansions of applications by realizing true bulk single crystal (Type D)

Device	Improved features	Expanded applications	Social impact: Energy saving ( ) shows CO_2 reduction
LED	High out put Expanded wavelength region · Shorter wavelengths · Longer wavelengths	· High efficiency and high color-rendering in lighting (post fluorescent, halogen, etc. from general lighting to technical lighting) · Photocatalysts · Medical (sterilization) applications	Reduced power consumption by LED lighting · 2020:12.4billion kWh/yr (6.86 million tons/yr) · 2030:18.7billion kWh/yr (10.39 million tons/yr)
LD	Same as above.	· High speed writing in optical devices (next-generation DVDs) · Laser displays → Portable projectorsLaser television	Reduced power consumption by laser TV · 2012: 14.5 billion kWh/yr (8.02 million tons/yr)
Electronic device	Lateral type transistors (FET) · High output (to 100W) · High frequency Vertical type devices (IGBT, thyristors, etc.) · Low resistance · Normally-off operation	· High speed/high output transistors →High speed and high capacity in mobilecommunications, downsizing of land stations, low power consumption · Power transistors → High efficiency in industrial machinery, hybrid cars, and electric vehicles by high efficiency in inverters	Reduced power consumption by GaN devices[11] Transmitting/receiving amplifiers for cell phone ground stations + general purpose inverters · 2020: 9.8 billion kWh/yr (5.41 million tons/yr) · 2030: 20.2 billion kWh/yr (11.21 million tons/yr)

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[NOTE5]
Assuming penetration of LEDs in indoor lighting is approximately 30% in 2030, as an energy saving effect (reduction of annual power consumption), it is predicted that power consumption can be reduced by 20 billion kWh, corresponding to approximately 20% of that used in lighting in 2005.

are currently manufactured using Type A, and are applied practically in base stations for mobile communications, such as cell phones, as high frequency devices operating at up to the GHz region. In the future, however, high output transistors which operate in the millimeter waveband (30-100GHz) will be necessary in order to achieve higher speed and large capacity in mobile communications. As shown in Figure 2 GaN should be the most suitable material from the viewpoint of material properties,[11] and will contribute to system miniaturization and reduced power consumption. On the other hand, as vertical devices,[NOTE 6] inverters with Si devices are used in industrial applications and hybrid cars. However, here again, higher system efficiency can be achieved by replacing these Si devices with GaN-based devices in the future, and as a result, energy savings and improved fuel economy in automobiles are considered possible. According to a trial calculation, the reduction in power consumption which can be realized by energy saving if GaN-based electronic devices are applied in amplifiers for transmitters in cell phone base stations and industrial inverters is approximately 10 billion kWh/year (2020).[11]

As discussed above, GaN-based semiconductors are materials that can provide the key to contributing to energy saving and reduction of emissions of greenhouse gases (GHG) as light-emitting devices and electronic devices (transistors).

3 Current status and problems of true bulk single crystal growth technology

3-1 Technical trends in true bulk GaN single crystals

The “true bulk GaN single crystal” described here, as mentioned previously, indicates a substrate material of a GaN bulk crystal which is dislocation-free or has a low dislocation density ($\leqq 10^3 cm^{-2}$) that cannot be realized with heteroepitaxial technology, and also makes it possible to cut out any arbitrary crystal plane.

While saying aiming at a “true bulk GaN single crystal,” there are many cases in which the substrate or a seed crystal is used as the seed that forms the basis for crystal growth (excluding cases of self-nucleation growth, as will be discussed later). Methods of crystal growth are broadly classified as the epitaxial bulk (abbreviated “epi-bulk”) method and the bulk method, depending on whether a substrate or a seed crystal is used as the basis of crystal growth. The vapor phase deposition method and liquid phase growth method are used in each of these methods.

To date, research and development has been carried out on both the gas phase and the liquid phase methods as growth methods for bulk GaN single crystals, but a “true bulk GaN single crystal” has not been realized with either method. Difficulties arise in research and development because existence in a melt, as with Si, GaAs, and InP, is difficult due to the high dissociation pressure of nitrogen in GaN.[17] However,

Column: “Satisfying both larger screen size and energy saving by laser TV”

The TVs which are currently available in the market are generally the plasma and liquid crystal types, and larger screen sizes are becoming increasingly popular. In line with this trend, a trial calculation shows that Japanese users will own approximately 12.6 million plasma sets and 20.4 million liquid crystal sets with screens of the 50 inch size or larger in the year 2012.[14] Because the power consumption of plasma and liquid crystal TVs of the 50-55 inch class is around 500W (Panasonic TH50PZ800: 585W, Sony KDL-55XR1: 480W), assuming average TV viewing time is 4 hours per day,[15] the annual power consumption of TVs of 50 inch size and larger is 25.1 billion kWh. If these types of TVs are replaced by TVs with low power consumption of 200W, such as laser TVs, an annual energy saving of 15.4 billion kWh can be realized. Converted by the annual power consumption of a general household in Japan, which is 5,650kWh,[16] this is equivalent to the total power consumption of approximately 2.73 million households. In addition to this energy saving benefit, a high color-rendering property is also a feature of laser TVs.

[NOTE6]

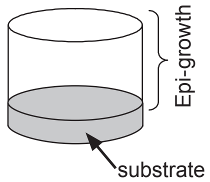
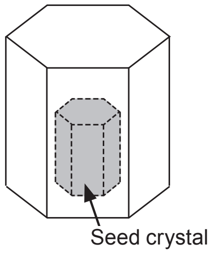
The terms “lateral type” and “vertical type” used when describing transistors mean that the carrier (electron/hole) is transferred and acts laterally or vertically, respectively.

as shown in Table 4, active R&D is being conducted in Japan and other countries with the aim of solving this problem and producing better substrate materials.

In gas phase growth in the epi-bulk method, the VPE method is used. This is a method in which crystal growth of GaN is performed by a vapor phase from gallium chloride gas and ammonia gas on a Type C substrate, and the film thickness is increased to a degree that makes it possible to cut out an arbitrary crystallographic plane in the thickness direction. With this method, uniform growth of high quality crystals is difficult, and although a non-polar plane (m plane) with a size of □10mm in the thickness direction has reportedly been obtained,[18] it was not possible to produce a high quality substrate with a large area. Moreover, because the original substrate was produced by the heteroepitaxial technique, the dislocation density was on the order of 10^5cm^{-2}.

Liquid phase growth techniques in the epi-bulk method include the high pressure solution method, ammonothermal (also called "ammothermal") method, and flux method. The high pressure solution method is a method in which GaN is grown by dissolving nitrogen at an ultra-high pressure (10,000-20,000atm) in a high temperature (1600°C) melt of Ga.[19,20] Growth to a thickness of several 100μm on a substrate has been reported,[21] but a crystal size that can be cut out in the thickness direction was not realized. In the ammonothermal method, a GaN raw material is dissolved and recrystallized in ammonia from supercritical to subcritical (400-500°C, 1000-4000 atm).[22] It has been reported that a crystal with a thickness of several 10μm was grown on a Type C substrate using an acidic mineralizer,[23] and crystals on the order of 5mm was grown using an alkali mineralizer.[24] In the flux method, GaN crystals are grown by dissolving nitrogen at several 10atm in a mixed melt of Ga and an alkali metal such as lithium (Li), potassium (K), or sodium (Na) at around 800°C.[25,26] Because Na is mainly used in this method, it is also called the Na flux method. Using the flux method, R&D has been conducted in an attempt to obtain an epi-bulk crystal on a φ2" substrate,[27] and crystal growth to a thickness of approximately 3mm has been achieved. Figure 3(a) shows an example of a 2" size crystal which was realized by the Na flux method as an epi-bulk method. The number of crystallographic defects is small in comparison to that with other methods, as the dislocation density is on the order of 10^5cm^{-2}. This is considered to be

Table 4 : Development trends in bulk GaN substrates

Method	Growthmethod			Features	Condition
Epi-bulkmethod (growth of thick film using Type C substrate) 	Vapor phas	VPE (Vapor Phase Epitaxy)		Substrate used as basis for growth is Type C (selective growth to thick film by vapor phase on substrate of sapphire, GaAs, etc.; dislocation density is on 10^6cm^{-2} level). GaN substrate on the order of □10mm has been realized by cutting in the thickness direction.	Japanese companies hold the top share of Type C GaN substrates for next-generation DVD;epi-bulk is under development.
	Liquid phase	Liquid phase growth	High pressure solution method	*1 Dissolution of nitrogen in metallic Ga under high temperature, high pressure conditions of 10,000-20,000atm and 1600°C, and epitaxial growth on a substrate. Several 100μm in thickness direction.[18]	*2 Original Polish technology; at present, Poland is still most advanced.
			Ammonoth-ermal method	*3 Dissolution and recrystallization of GaN raw material in supercritical or subcritical NH_3 (temperature and pressure of 400-500°C and several 1000atm). Several 10μm to several mm in thickness direction.	Research in US using an alkali mineralizer and in Japan using an acidic mineralizer.
			Flux method	*4 Dissolution of nitrogen (pressure <100atm) from vapor phase in a metallic melt of Ga and an alkali metal such as N or K, and growth of GaN crystal at a temperature of around 800°C. Several mm in thickness direction.	Original Japanese technology; Japan is most advanced.
Bulk method (use of seed crystal, as shown below; use of self-nucleation growth 	Vapor phase	Vapor phase deposition method		Growth of GaN from vapor of metallic Ga and NH_3 or N_2 under high temperature of 1200°C or higher. Crystal size >1mm	In research phase, but little work in recent years.
		Sublimation method		Sublimation of GaN powder at around 1500°C and crystal growth in seed crystal in low temperature part. Crystal size <1mm.	
	Liquid phase	Solution growth		Growth of GaN crystal on the order of 100μm by slow cooling under high partial pressure of nitrogen and high temperature of 60,000atm and 2200°C or higher.	Research phase; in stage where existence of melt has been confirmed.
		Liquid phase growth	High pressure solution method	Same method as *1. Crystal of mm order is grown by self-nucleation growth without using a substrate.	Same as *2.
			Ammonoth-ermal method	Same method as *3. GaN crystal of 100μm to 1 inch size is grown by self-nucleation growth or seed crystal growth without using a substrate.	Polish company has realized a high quality 1" crystal.
			Flux method	Same method as *4. GaN crystal of several mm size is grown by self-nucleation growth or seed crystal growth without using a substrate.	R&D is being carried out by Japanese universities and companies.

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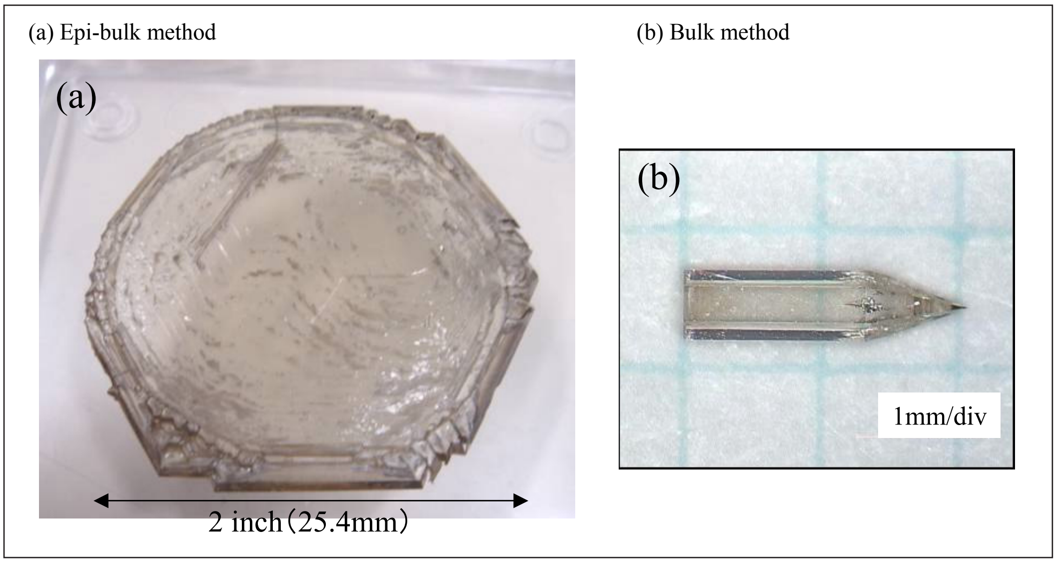

Figure 3 : Photographs of GaN crystals (Na flux method)

Source: (a) Mori Laboratory, Osaka University, (b) Ricoh

because flexure and consolidation of the dislocations in the horizontal direction occurred in the thick film epitaxial growth process.

Vapor phase growth and liquid phase growth are also used in the bulk method. The vapor phase methods are the vapor phase deposition method and the sublimation method. The vapor phase deposition method is a method in which GaN is synthesized directly from Ga vapor and ammonia or nitrogen gas under a high temperature exceeding 1200°C.[28] The sublimation method is a method in which the GaN raw material is sublimated and grown to seed crystals in the low temperature region.[29] However, the size of the crystals obtained is small. Due to the difficulty of crystal growth with the vapor phase deposition and sublimation methods, progress in research has been sluggish in recent years.

Liquid phase growth in the bulk method comprises melt growth and solution growth. Due to the high dissociation pressure of nitrogen in GaN, it has been confirmed that GaN exists as a melt only under high temperature, high nitrogen pressure conditions of 60,000atm and 2200°C or more.[30] Because these are not practical temperature and pressure conditions, R&D is not active. Accordingly, the focus of R&D on liquid phase growth in the bulk method is mainly on solution growth. The above-mentioned high pressure solution method, flux method, and ammonothermal method are also used in solution growth in the bulk method. These three solution growth techniques are basically the same as in the epi-bulk method, but they differ from those used in the epi-bulk method in that crystal growth is performed from self-nucleation growth[NOTE 7]or seed crystal growth. Figure 3(b) shows an example of a crystal obtained by self-nucleation growth. With the high pressure solution method, it has only been possible to obtain platelet-shaped crystals (thickness: approximately 10μm) on the mm order by self-nucleation growth; thus, this method has not reached practical application. With the ammonothermal method, needle-like crystals of several 100μm have been grown by self-nucleation growth using an acidic mineralizer, while wafer-like crystals 1 inch in size have been grown using an alkali mineralizer.[31] With the flux method, high quality columnar crystals of the mm order have been grown by self-nucleation growth and seed crystal growth,[26] and the possibility of increasing the size of the crystal increased by increasing the size of the crucible has been confirmed.

In any case, with the bulk method, it has not been possible to obtain a practical crystal size, namely, several 100μm to several mm. Although quality is extremely high, in that no dislocations can be observed, it is necessary to increase the size of the crystal to a degree which makes it possible to cut out crystals in the radial and axial directions of hexagonal columnar crystals, while maintaining high quality in order to obtain a non-polar plane.

[NOTE7]
Self-nucleation growth means nucleation and crystal growth from a condition in which no seed crystal or substrate exists

4 Efforts by various countries to solve technical problems

4-1 Industry-university-government R&D projects in Japan

(1) High efficiency photoelectric conversion compound semiconductor development project

The High Efficiency Photoelectric Conversion Compound Semiconductor Development Project (commonly known as the 21st Century Lighting Project) was carried out with the support of the New Energy and Industrial Technology Development Organization (NEDO) from fiscal year 1998 to 2003.[32] In this project, research and development on high efficiency near-UV LEDs, phosphors, substrate crystal growth technologies, and other topics were carried out with the aim of realizing LEDs for lighting. As part of the project, R&D on the above-mentioned high pressure solution method was carried out by Yamaguchi University and the Japan Energy Corporation. As a result, high quality platelet crystals with a size of 10mm and a dislocation density of less than 10^3cm^{-2} were obtained by self-nucleation growth. The orientation of the principal plane of the crystal was the C plane (0001), and this was a polar plane.

However, industrial handling was difficult because the thickness of the crystal was several 10μm, and practical application was not achieved due to the large scale of the equipment.

(2) Semiconductor substrate crystal manufacturing technology for next-generation lighting

Using matching funds from the Special Coordination Funds for Promoting Science and Technology, research and development on GaN bulk crystals, centering on the epi-bulk ammonothermal method, was carried out by Tohoku University and the Mitsubishi Chemical Corporation during fiscal years 2004 to 2006.[23] In this project, epitaxial growth of GaN crystals with a film thickness of several 20μm was possible using a φ2” Type C GaN crystal as the substrate. The growth rate was approximately 1μm/h.

However, the orientation of the principal plane of the crystal was the C plane (0001), which is a polar plane. Moreover, because the dislocation density was the same or greater than that of the substrate ($10^{6\text{-}8}cm^{-2}$), practical application was not achieved. Thus, with the ammonothermal method to date, it has not been possible to satisfy both high quality (reduction of dislocations) and a size that makes it possible to cut out an arbitrary crystallographic plane, these being the necessary conditions for a true bulk crystal by the epi-bulk method.

(3) Development of semiconductor for high efficiency UV light-emitting devices

Development of a semiconductor for use in high efficiency UV light-emitting devices was promoted as a NEDO project during the period FY2004-2006. Osaka University, Toyoda Gosei Co., Ltd., and NGK Insulators, Ltd. conducted research and development on the epi-bulk method by the Na flux method.[33] As a result, a φ2” size with a dislocation density of 10^5cm^{-2} was obtained (Figure 3(a)). The substrate used here, as in the above section (2), was a φ2” GaN substrate (Type C) grown by the VPE method. It was possible to grow GaN crystals with film thicknesses up to 3mm on this substrate by the Na flux method. With this method, the dislocation density of the obtained crystal was 10^5cm^{-2}, which is smaller than that of the substrate (10^8cm^{-2}). This reduction is attributed to the fact that flexure and consolidation of dislocations like that in ELO of Type B in Table 2 occurs even without a mask in the crystal growth process by the flux method. The growth rate was also the highest among the liquid phase growth methods, at approximately 30μm/h. The orientation of the principal plane of the crystal was the C plane (0001), which is a polar plane. At present, sample crystals produced using this technology are being supplied by a joint venture called Frontier Alliance, which consists mainly of researchers from Osaka University. For further promotion of practical application, it will be necessary to develop large-scale equipment capable of accelerating the growth rate and maintaining stable long-term growth.

4-2 Other R&D trends in Japan

(4) R&D in private companies

At private companies in Japan, in addition to Japan Energy, Mitsubishi Chemical, Toyoda Gosei, and NGK Insulators, which were mentioned in sections (1) through (3), Ricoh Co., Ltd. is also involved in research and development using the Na flux method.[26] Japan Energy and Ricoh have been able to grow high quality (low dislocation density) crystals by self-nucleation growth, and in particular, it was possible to obtain the m plane (side plane of columnar shape) in a colorless, transparent columnar crystal with Ricoh's Na flux method (Figure 3(b)). However, in all cases, the size of the crystal is still inadequate. In particular, it is not possible to manufacture devices with crystals produced by the high pressure solution method, as the crystal thickness is thin. On the other hand, because the crystals obtained by the Na flux method are of mm order, a further increase in the size of the crystals is desired in order to mass-produce devices.

4-3 R&D trends in other countries

(5) MURI (Multi university Research Initiative) project in United States

This project was carried out during the period 2001-2003 for the purpose of "Growth of Bulk Wide Bandgap Nitrides and Wafering" and centered on the University of North Carolina. In the project, research and development were conducted, respectively, on the vapor phase deposition method, ammonothermal method, and flux method as bulk GaN crystal growth methods. There have been no reports that these efforts have reached practical application.

(6) Research at University of California at Santa Barbara (UCSB) in United States

In the Solid State Lighting and Display Center (SSLDC) at UCSB, 5mm crystals were obtained in 82 days with the ammonothermal method.[24] As in the previous sections (2) and (3), these were obtained by the epi-bulk method using a Type C VPE GaN substrate. The crystals were judged not to be of high quality based on the results of X-ray diffraction and coloration of the crystals. However, the fact that a bulk crystal was obtained for the first time by the ammonothermal method can be considered a significant achievement. In this method, an alkali substance called a mineralizer was used in the material in order to enhance its solubility. When an alkali mineralizer is used, GaN displays negative solubility (i.e., its solubility increases as temperature decreases). On the other hand, in the research in Japan described in (2), an acid mineralizer was used; in this case, GaN displays positive solubility.

(7) R&D in Poland

The high pressure solution method is a method which was originally developed by the High Pressure Research Center (HPRC) in Poland. Although high quality GaN crystals are obtained, the size of the crystal and the equipment required are problems, and practical application has not been achieved.

The company Ammono Sp.zo.o in Poland is involved in R&D on the ammonothermal method, and has announced that it obtained high quality φ1" crystals using alkali mineralizer.[31] However, the growth rate, reproducibility, and industrial potential of this process are all unknown. Although research on the ammonothermal method is underway in Japan, the United States, and other European countries, it can be said that the research in Poland is the most advanced.

5 R&D issues for "true bulk GaN single crystal growth"

As R&D issues for "true bulk GaN single crystal growth," the requirements identified from device needs are summarized in Table 5 by the main crystal growth methods. The principal requirements are a substrate size ≧ φ2 inches, high quality (dislocation density $<10^3 cm^{-2}$), and an arbitrary polar plane (possible to cut out planes either with or without polarity).

Research and development at various institutions is continuing to clarify the technical merits and demerits of each method. The vapor phase epitaxy (VPE) method has a high growth rate (sever 100μm/h), and it is considered probable that improvements in this technology will be made in the future under private-sector initiative. In contrast to this, with liquid phase growth (solution growth), it is expected to be possible to obtain high quality crystals, but the growth rate is slow (several μm/h to several 10μm/h), and both time and breakthroughs are still required for the establishment of device technology and crystal growth conditions.

In the realization of a "true bulk GaN single crystal," the most important requirements are, firstly, the achievement of high quality, meaning a dislocation density $<10^3 cm^{-2}$, and the possibility of cutting out arbitrary crystallographic planes. In achieving these conditions, a key target is to realize a size of 2" or larger. Looking at Table 5, the methods which either satisfy or have the potential to satisfy the essential

Table 5 : Summary of bulk GaN single crystal growth methods

Method		Requirements (needs for practical application from device: Size ≧φ 2	Quality (dislocation density) <10^3cm^{-2}	Arbitrary polar plane
Epi-bulk	VPE	△ (approx.10mm square)	× (low defect density has been achieved locally, but limit of heteroepitaxial method)	○(m plane substrate has been obtained by cutting in the cross sectional direction, but thickness is a problem)
	High pressure solution method	× (thickness to 100μm)	? (same order as substrate)	× (thickness is problem)
	Ammonothermal method	△ (thickness to 5mm)	× (larger than substrate, ≧ 10^3cm^{-2})	△ (thickness is problem)
	Flux method	△ (thickness to 3mm)	△ (to 105cm^{-2}; lower locally)	△ (thickness is problem)
Bulk	High pressure solution method	× (thin platelet shape, thickness of several 10μm)	○	× (polar C plane grows as principal plane)
	Ammonothermal method	△ (φ 1” has been realized using alkali mineralizer)	○	? (thickness is unknown)
	Flux method	△ (to several mm)	○	○

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requirements of quality and an arbitrary polar plane are the flux method in the epi-bulk type and the ammonothermal method and flux method in the bulk type. Among these, the epi-bulk flux method differs from the other epi-bulk methods in that it is possible to produce crystals with a lower dislocation density than the substrate, suggesting the prospect of achieving higher quality. Furthermore, as mentioned in (3), this method was investigated in an industry-university-government project and is already in the stage where samples are being shipped. R&D is currently underway, with the aims of further reducing the dislocation density and achieving a large-scale size for maintaining the arbitrary polar plane. On the other hand, neither the ammonothermal method nor the flux method in bulk approach has been studied in an industry-university-government project up to the present time. With the ammonothermal method, research on high quality and large scale is progressing, particularly in Poland, and foreign countries also hold the lead in intellectual property. In contrast, the flux method is a technology which was discovered by Prof. Hisanori Yamane of Tohoku University in 1997, and active research and development are continuing in Japan even today. Moreover, the patent which is the basis for the flux method is common to the epi-bulk and bulk approaches and is owned by a Japanese company, and peripheral patents have been granted to Japanese companies and universities.

Accordingly, for the time being, it is considered that Japan should aim at realization of a practical “true bulk GaN single crystal” by developing and utilizing crystal growth methods by the flux method in both the epi-bulk method and the bulk method.

The key to practical application of both of these methods is ultimately realizing large scale in the size of the crystal. In starting from high quality crystals and upscaling these to the size of φ2 to 4”, which is necessary for device manufacture, efforts in combination with device development are demanded. As the division of roles in industry-university-government collaboration, it is considered desirable that universities work to elucidate the mechanism of crystal growth, private companies develop the crystal growth process from the design of crystal growth devices, while government serve as a coordinator.

6 Conclusion

Because two of the key scientific breakthroughs in GaN-based semiconductor devices were achieved in Japan in the past, and these have led to the practical applications of today, it is no exaggeration to say that these are Japanese-originated semiconductor devices. The development of crystal growth techniques not only realizes devices with higher functions, but can also make an important contribution to preventing global warming through energy saving.

High quality bulk crystals of Si, GaAs, and InP all exist. Substrates are produced using these bulk crystals, and devices can be manufactured on the respective substrates. However, in the case of GaN, a high quality bulk crystal, that is, a “true bulk single crystal,” does not exist, and for this reason, it is not possible to take full advantage of the intrinsic potential of GaN.

Among GaN crystal growth technologies, the vapor phase epitaxy (VPE) method offers the fastest growth rate, and it is therefore thought that technical improvements will be made in this technology under private-sector initiative. The liquid phase growth method, which should make it possible to obtain an even higher quality “true bulk single crystal,” is currently in the basic research stage, and further breakthroughs and time will be required. Accordingly, in the future, it is desirable to promote research and development of a “true bulk GaN single crystal” by industry-university-government collaboration, based on a division of roles in which universities conduct research to elucidate the mechanism of crystal growth, companies develop the crystal growth process from the design of crystal growth devices, while government coordinates these activities. If Japan realizes a “true bulk GaN single crystal” at an early date, in advance of other countries, it is considered possible to maintain and enhance this country’s international competitiveness in the field of GaN-based semiconductor devices in the future.

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Profile

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