The Japan Research and Development Center of Metals' National Project on

Light for the 21st Century:

The Development of Compound Semiconductors for High Efficiency Optoelectronic Conversion

Year 2000 Report of Results[1]

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Background

According to the international agreement, COP, energy efficiency is becoming an important consideration for consumer products. The electric power consumed for lighting is about 20% of the total electric power consumed in Japan. Appropriate effort is therefore required to develop energy-efficient lighting equipment.

The Japan Research and Development Center of Metals (JRCM) has organized a 5-year R&D project (1998-2002) to develop energy-efficient lighting equipment using light-emitting diodes (LEDs), with the participation of thirteen member companies and universities, as required by the New Energy and Industrial Technology Development Organization (NEDO).

The current project targets an energy efficiency twice that of traditional fluorescent lamps, through the use of long-life, thin, lightweight, GaN-based high-efficiency blue and ultraviolet LEDs.

This lighting equipment would have the following advantages:

1. Less electricity consumption due to high optoelectronic conversion efficiency.
2. Ease of miniaturization due to the small size of the light source -- the lighting equipment would be smaller, thinner and lighter.
3. Long life.
4. Simple structure -- no special devices would be needed to control the lighting equipment, and the number of components in the equipment would be reduced.
5. High reliability due to the use of all-solid-state devices without any gases or filaments -- very reliable against mechanical shock.

Table of Contents

0 Executive Summary

This is the summary of the "Light for the 21st Century" National Project, based on white light-emitting diodes (LEDs), which has been carried out through a cooperation between universities and industry in the fiscal year 2000. The following results in four research areas have been obtained.

0.1 Fundamental Studies on Light Emission Mechanisms

In order to clarify the light emission mechanism in InGaN-based semiconductors, time-resolved photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopy measurements have been carried out. PLE spectroscopy enabled us to observe clear structures associated with the absorption of InGaN ternary alloys up to room temperature for the first time. It was found that the Stokes shift was independent of temperature, and that the two observed emission components derived from states populated by carrier relaxation from the same excited state. The experimental value of the Stokes shift was in good agreement with a theoretical value based on the electron-phonon interaction. It has therefore been proposed that coupled electron/phonon polaron states contribute to the highly efficient radiative recombination processes in this material system. The obtained results seem to be important for understanding high-efficiency recombination mechanisms in ultraviolet (UV) LEDs.

We have studied carrier recombination processes in InGaN/GaN multiple quantum wells (MQWs) through systematic measurements of the luminescence of LED samples under various conditions. From carrier lifetime measurements over a wide range (7-540K) of temperatures, carrier localization and delocalization characteristics were consistently observed for LED samples with varying In composition. Through a comparison with simulations, we found that the localization energy depth increases with increasing In composition, which prevents the transfer of carriers to non-radiative recombination centers. Non-radiative recombination centers, which are probably dominated by point defects in InGaN, also increase with increasing In composition.

Characteristics associated with more deeply localized states were observed for an LED with higher quantum efficiency based on the temperature dependence of the carrier decay time. By using a near-field PL mapping system with high spatial resolution, the luminescence intensity and wavelength distribution in the plane of the QW (quantum well) of a typical blue LED were observed. The spatial scale of this distribution was estimated to be 0.3-0.5 μm.

The piezoelectric field strength in a 2 nm InGaN QW was studied using PL measurements under reverse bias, taking into account the measured depletion length of the diode, and was estimated to be E_{piezo} = 1.48 MV/cm for x=0.23, close to the published values. Bias-dependent measurements on LEDs suggest that Si doping is important both for modifying the overall band structure of the device and for free-carrier screening of the internal electric field in the QWs.

0.2 Improvements of Epitaxial Growth Processes for Blue and UV LEDs

A MQW structure consisting of AlGaN barrier and InGaN well layers for UV LEDs has been studied. By increasing the growth temperature of the AlGaN barrier layers, the surface morphology of the MQW layers clearly showed steps formed by a step-flow growth mode, and the interface between well and barrier layers was sharp. An AlGaN/InGaN MQW LED was then fabricated on a sapphire substrate. The peak wavelength of the emission spectrum was 390 nm at room temperature. At a forward current of 20 mA, the forward bias voltage and the output power were 3.7 V and about 1 mW, respectively.

We have observed that low-level doping of Si in barrier layers in a MQW increased the output power of the UV LED.

A new GaN growth process called LEPS (Lateral Epitaxy on a Patterned Substrate) was developed. It has been found that the LEPS process is effective in decreasing the dislocation density and for improving the output power of UV LEDs. When the LEPS UV LED die was operated at a forward bias current of 20 mA at room temperature, the emission wavelength, the output power and the external quantum efficiency were measured to be 382 nm, 2.5 mW and 3.7%, respectively.

We have developed a new technique for GaNP growth. A laser-assisted MOCVD method was applied to GaNP growth. It is anticipated that, through ArF laser irradiation, source gases will be decomposed at lower temperatures, resulting in GaNP with a high P composition. Using this method, we obtained GaNP with 10% P composition. This composition is the highest reported value for MOCVD-grown GaNP. A $GaN_{0.9}P_{0.1}$/GaN single quantum well (SQW) LED was fabricated and bright blue emission at 425 nm was observed for the first time.

0.3 Substrates for Homoepitaxy and their Characterization

We have investigated the effect of nitrogen pressure ramp rate on the size and morphology of GaN bulk single crystals grown by the pressure-controlled solution growth (PC-SG) method. A GaN single crystal with a surface area of 334 mm^2, which is the largest GaN single crystal ever grown by the solution growth method, was obtained by natural nucleation without any seeds. To characterize the GaN bulk crystals, improvements were first made to the lapping and polishing techniques. Next, the GaN crystals were lapped and polished to achieve flat surfaces. Finally, these high quality flat surfaces were characterized by XRD, AFM, TEM and PL. The resulting data indicated that the crystals with good morphology also had good crystallinity. It was found that reductions in nitrogen pressure ramp rate and temperature fluctuations are necessary to grow larger GaN bulk single crystals with good morphology and good crystallinity. We have also studied the crystal growth of GaN on a hetero seed by the PC-SG method. A GaN crystal with a diameter of 47 mm with a normal axis in the (0001) direction, could be grown on a 2-inch sapphire substrate.

Homoepitaxial growth of GaN thin films on GaN bulk single crystals prepared by pressure-controlled solution growth (PC-SG) method has been carried out using molecular beam epitaxy. A correlation between the lattice-polarity of bulk GaN substrates, the lattice-polarity of homoepitaxial GaN layers, and their optical properties, was determined. The luminescence intensity of homoepitaxial layers has been greatly improved as compared to that of heteroepitaxial layers on sapphire substrates. Relatively lower minimum yields (χ_{min}) of polarity-controlled GaN epilayers as measured by Rutherford backscattering have indicated a high crystalline quality.

We have succeeded in growing GaN crystals using a new vapor phase growth technology which allows high-yield low-cost substrates for GaN based LEDs. We have constructed an innovative semi-closed system where metal gallium is in a quartz ampoule and nitrogen gas activated by microwaves is introduced to synthesize GaN on a substrate. A high growth rate of 100 μm/h was achieved by adjusting the growth conditions. We have indications of the possibility of maximum growth rates up to 1 mm/h by using high-frequency-discharge nitrogen plasma. By optimizing the growth conditions (microwave power, nitrogen pressure and growth temperature), we have obtained a thick GaN crystalline film on a sapphire substrate of 10x4 mm^2 area. The surface showed good uniformity. However, our best results were obtained using a GaN substrate. The grown surface showed 6-fold symmetric grain boundaries and the full width at half maximum (FWHM) of the x-ray rocking curve was about 360 arcsec.

By the newly developed FACELO (Facet Controlled ELOG) method, we successfully lowered the etch pit density (EPD) to as low as 10^4-10^6 cm^2, the lowest level in the world as far as we know. On a GaN template with low EPD grown by optimizing the nuclei density, we carried out FACELO growth using a two-step process: ELOG growth of inclined {1122} facets for the first step, followed by growth of vertical {1120} facets for the second step. A trial of growth on 2 inch sapphire was carried out; however, the overgrowth over the masks remained incomplete and only a rough surface morphology was obtained. The effective reduction of the dislocation density was attributed to the following phenomena: (1) bending of the a+c type threading dislocations (TDs) toward the <1120> direction due to the inclined facet and termination of the laterally propagating dislocations due to the void surface, (2) bending of the a type TDs parallel to the mask stripe, (3) generation of new dislocations above the coalescence line at the top of voids, and (4) the blocking of the penetration towards the surface due to a SiO_2 mask layer by the second FACELO (vertical facet) process. From μ-PL spectroscopic observations, it was suggested that the degree of impurity inclusions into regrown GaN layers in the FACELO process depends on the type of facet, in the order {1120} > {1122} > {0001}.

From time-resolved PL spectroscopy measurements it was confirmed that in comparison to ELOG GaN films grown with an SiO_2 mask, ELOG-GaN films grown with a W mask exhibit a longer free exciton lifetime.

0.4 Technologies for Phosphor-Based White LEDs and Basic Properties of LED Lighting Sources

We have pointed out that it is important to measure precisely the absorption, internal and external quantum efficiency of red, green and blue phosphor materials. It is expected using the best candidate phosphors that the emission efficiency of the red phosphor will be higher than that of the usual one.

In the area of electrode formation technology, 70% reflectivity and $2x10^{-5}$ ohm-cm^2 contact resisitivity in the n-type electrode were obtained by optimizing the conditions for Ti/Al contact formation. For the formation of the p-type electrode, Rh and Pt, which are electrode materials with lower contact resistance compared to Ni/Ag, were explored.

Chip shaping was studied in order to improve light extraction efficiency. It was proposed that etching the end face to produce inclined facets was effective in directing the light, which would otherwise be absorbed internally, through the substrate for extraction. Inclined facets were formed by the dry etching method.

For white LED device development, application technologies for phosphors have been examined. Both basic evaluation of typical RGB phosphors and simulation of mixed RGB white phosphors have been carried out. Transmission of ultraviolet radiation through the phosphor layer can be controlled by the phosphor layer fabrication method. Luminescence and color rendering properties of the white LED lamp have been investigated. The ultraviolet radiation was reflected over a phosphor layer mounted on the UV LED chip, and an optical thin film filter, into which the visible light can penetrate, was formed. It was confirmed that the transmission intensity of ultraviolet radiation was decreased from 31% to 13% and that the luminous flux of all white LED lamps can be improved up to 30% by coating the side edge of the UV LED chip with the phosphor.

We have examined the luminescence properties of reflection type light sources which are composed of blue LEDs and YAG phosphor by using optical computer simulation. It was found that the computer simulation results agree well with the properties of the actual light source. This fact suggests that light sources can in principle be designed by using this simulation method.

Furthermore, we have examined the changes of correlated color temperatures of white LEDs formed from combining red and green LEDs, and evaluated color rendering properties for each condition. We examined light source properties for five correlated color temperatures by controlling the intensities of the three LEDs. In particular, a high color rendering index (Ra=95) was obtained under daylight conditions. We psychophysically measured the effects of visual stress induced by the light sources composed of LEDs using the method of magnitude estimation. The results indicate that the glare ("mabushisa") and discomfort ("fukaikan") sensations are closely correlated to one another and that magnitude estimates exponentially increase as a function of illuminance.

The light efficiency was evaluated in order to design light guides for mass-production. The parameters (the deformation of the pattern, the LED location, etc.) were chosen, and the relationship between each parameter and light efficiency was simulated to evaluate the allowed variability of these parameters. Moreover, in order to reduce the influence of fabrication errors, new methods (the trapezoidal pattern shape, the corner LED setting, etc.) were proposed.

The effect of the directivity conversion method utilizing a prism sheet was evaluated for high-directivity application, for example, a footlight and a spotlight. High directivity was realized by utilizing a prism sheet on a 4 inch light guide. The uniformity of the light intensity was also evaluated. It is confirmed that the uniformity is not affected by using a prism sheet.

We fabricated lighting fixtures using white LEDs which have the highest-level luminous efficacy (15 lm/W) in commercially available devices. We also studied the utility of chip-type LEDs and tried to clarify potential benefits of downsizing while still providing reasonable lighting characteristics. Through the prototyping of LED table lamps and LED down-ceiling lights, it is suggested that a drastic energy saving can be achieved by downsizing. In addition, it is necessary to investigate the flexibility in designing LED light sources and the benefits of utilizing LEDs were discussed from the point of view of installation.

1 Summary, Plan, and Research

1.1 Details of Research and Development

At the 3rd Session of the Conference of the Parties to the United Nations Framework Convention on Climate Change (COP3) held in 1997 Japan was called upon to reduce emissions of greenhouse effect gases by 6% (compared to 1990 levels). To combat global warming, Japan's promotion of energy-saving measures in commercial, civilian, and transportation sectors has become an urgent task [1]. Development of energy-saving technologies for lighting is especially important since it represents over 20% of the energy consumed by the public. In 1998, the Ministry of International Trade and Industry (presently the Ministry of Economy, Trade and Industry) launched a national project entitled "Development of Compound Semiconductors for High Efficiency Lighting" (commonly referred to as "Light for the 21st Century") for the purpose of developing practical applications of white LED light sources that exceed the energy efficiency of conventional incandescent and fluorescent lamps [2, 3].

Over the years since the project started, the term LED (light-emitting diode) "semiconductor lighting" has become firmly established [4]. Most notably, with the practical application of blue LEDs using InGaN nitride semiconductors, white LEDs having a luminous efficiency of better than 20 lm/W have been developed by combining yellow phosphors (YAG:Ce) and high luminance blue LEDs capable of over 10 candela. As such, white LEDs are receiving worldwide attention as a next-generation energy-saving light source [5]. What's more, innovative semiconductor structures have been developed for UV LEDs that emit light via the short-wavelength ultraviolet region, raising expectations for practical uses of white LEDs as an illumination source [6].

This report discusses primary research achievements over the three years of the project. This Chapter outlines objectives and plans of the research, characteristics of white LED light sources, and the project's cooperative arrangement and policies. Chapters 2 through 15 present fourteen research themes, and Chapter 16 sums up the achievements of 2000 and future policy.

1.2 Plans and Actions Surrounding Each Research Challenge

1.2.1 Research & Development Plans and Objectives; Overseas Trends

By making highly efficient white LEDs practical, the national project "Light for the 21st Century" aims to promote energy savings, to aid in the prevention of global warming, and to create new lighting applications and culture. As a result, the effect of energy savings achieved in 2010 through the use of white LED illumination is estimated at a market penetration of 13% with an equivalence of 83,000 kl of crude oil.

At present, the following four R&D programs are underway to make white LEDs practical.

(1) Discovery of light emitting mechanisms of mixed crystal semiconductors and chemical compounds based on AlN, GaN, InN for UV LEDs.

(2) Development of substrates for homoepitaxy.

(3) Improvement of epitaxial growth technologies for blue and UV LEDs and development of UV LEDs of high luminosity.

(4) Development of highly efficient RGB phosphors and discovery of practical uses of white LEDs as an illumination system.

As shown in figure 1.2.1-(1), a number of high performance products using UV LEDs already exist in 2001, based on growth of high quality semiconductor crystals and development of highly efficient LEDs and evaluation of materials. We hope to achieve white LEDs with an efficiency of 80 – 100 lm/W by about 2003 and then 120 lm/W by 2010, thus paving the way for lighting fixtures that eventually exceed the efficiency of fluorescent lamps.

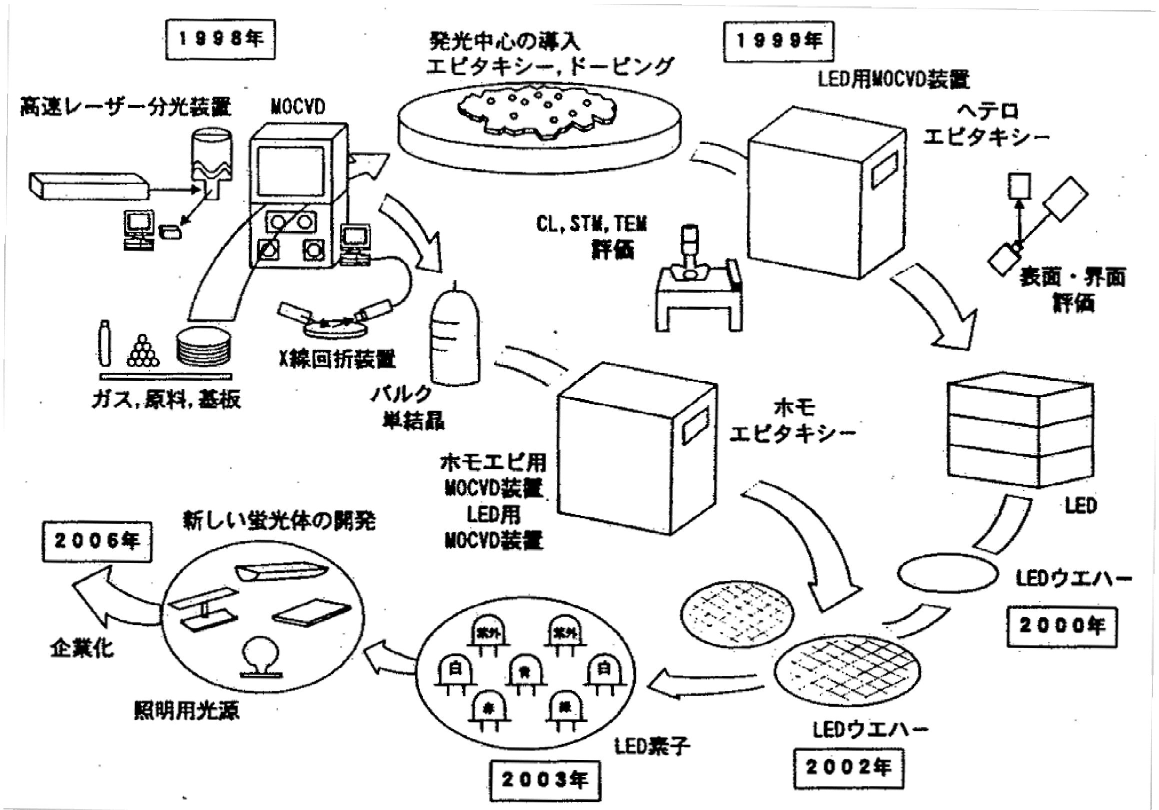

Figure 1.2.1-(1): Research on Semiconductor Lighting under the "Light for the 21st Century" Project.

1998: 1) high-speed laser spectrometer; 2) chemical agent (gas), raw materials, substrates; 3) X-ray analysis device; 4) bulk single crystals; 5) introduction of luminescence center - epitaxy, doping; 6) CL, STM, TEM evaluation

1999: 1) MOCVD for LEDs; 2) heteroepitaxy; 3) evaluation of surface and boundary face

2000: 1) LED wafers; 2) MOCVD for homoepitaxy, MOCVD for LEDs; 3) homoepitaxy

2002: 1) LED wafers

2003: (1) LED elements; (2) white, red, blue, green, white, UV, UV

2006: (1) development of new phosphors; (2) lighting sources for illumination; (3) industrialization

At present, semiconductor manufacturers and primary light fixture manufacturers in America and Germany are establishing joint ventures (GELcore, LumiLeds, Osram Opto, Cree Lighting) and aggressively pursuing research and development of white LED lighting technologies and applications. Japan's national project is influencing the overseas lighting industry, starting with the U.S. and its Solid State Lighting Initiative of 2001, followed by Taiwan which is likewise establishing projects to find practical uses for white LEDs.

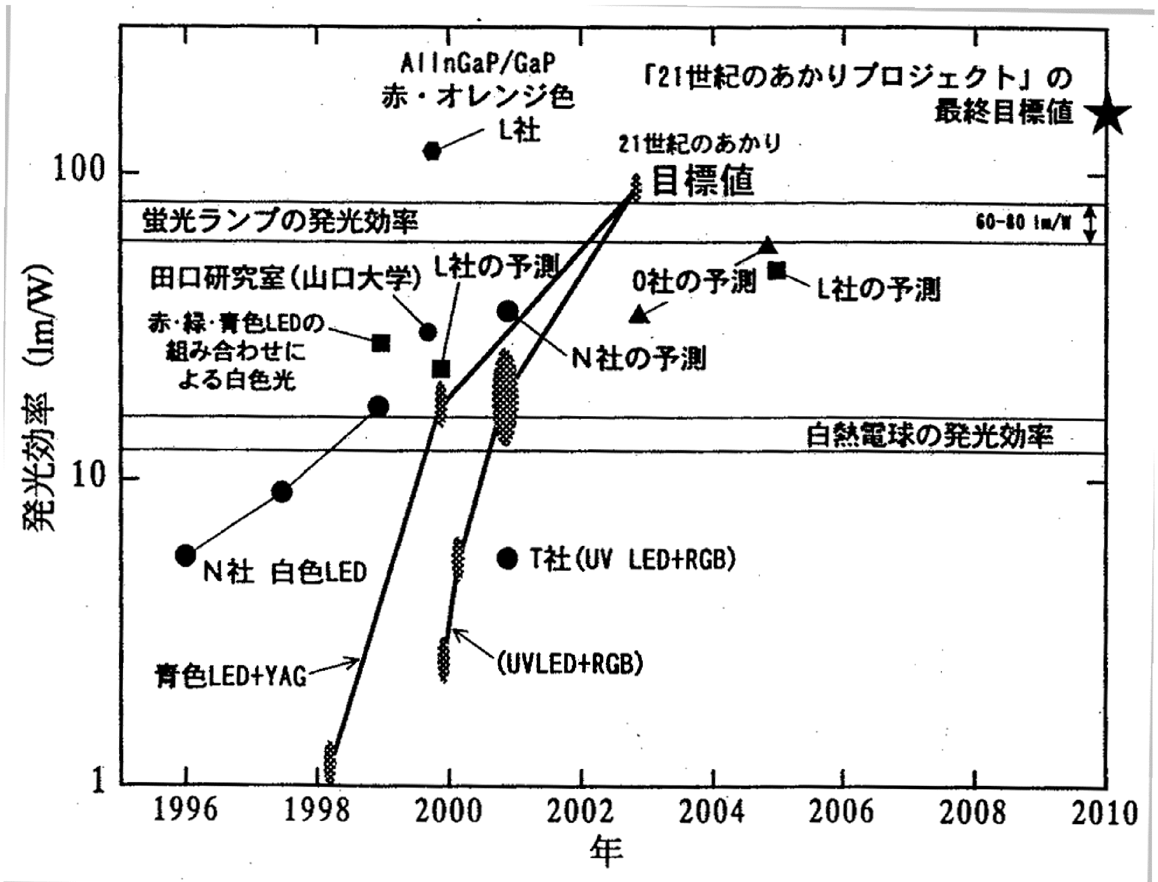

Figure 1.2.1-(2): Evolution by Year of White LED Luminous Efficiency and Future Predictions (bold line(s) represents this project).

Axes: Year; Luminous Efficiency (lm/W).

*Labels: Blue LED + YAG; Company N - white LED; Company T (Toyoda Gosei)- UV LED + RGB; luminous efficiency of an incandescent lamp; white illumination by combining red, green, and blue LEDs; Taguchi research lab (Yamaguchi University); Company L (LumiLeds) estimate; Company N estimate; Company O (Osram Opto) estimate; Company L estimate; luminous efficiency of a fluorescent lamp; Goal of Light for 21st Century project; Company L - red, orange; * Ultimate goal of Light for 21st Century project.*

1.2.2 White Diodes and Luminescence Characteristics

A light emitting diode emits light when a current is applied in the forward direction to the p-n junction of a semiconductor, injecting a negative electron and a positive hole into the active layer and causing a radiation recombination process. Usually a double heterojunction or a quantum well structure is used for light and charge confinement.

In general, the luminous efficiency (wallplug efficiency) of an LED is found through the following equation and is based on three independent efficiency factors.

(1) $$\eta_{wp} = \eta_v \cdot \eta_i \cdot \eta_{ext}$$

In this equation, η_{wp} is the input to output wallplug efficiency, η_v is the potential efficiency, η_i is the internal quantum efficiency, and η_{ext} is the light extraction efficiency.

As shown in Figure 1.2.2-(1), using a wavelength λ_0 (UV) of a UV LED, the luminous efficiency that can be gained from a white LED by exciting the three primary color phosphors is given in the following equation [3].

$$\eta_{white} = \frac{\int [\lambda_0(UV)/\lambda] \cdot F_{ph}(\lambda) \cdot \kappa(\lambda) d\lambda}{I \cdot V \cdot \int F_{ph}(\lambda) d\lambda} \cdot P \cdot \eta_{uvph} \cdot \eta_{ph}$$

(2)

Here, P is the output from the UV LED, η_{ph} the efficiency of the phosphor, η_{uvph} the conversion efficiency, $F_{ph}(\lambda)$ the phosphor's emission spectrum, and $\kappa(\lambda)$ the visibility coeffecient. Assuming η_{uvph} equals 95% and η_{ph} equals 90%, a 30 mW LED will achieve about 100 lm/W.

Within the Light for the 21st Century project, output light of 15.6 mW (at 20 mA) and 38 mW (at 50 mA) has been achieved at 382 nm with an external quantum efficiency of 24% (at 20 mA) [6].

To obtain a whiteness with high color rendering index (Ra >= 85) using an LED, there are basically two methods (single chip and multi-chip), as shown in Table 1.2.2. The first (single-chip) method involves exciting phosphors using LEDs radiating blue or UV light as the excitation source. The second (multi-chip) method is to simultaneously use two or three different colors of LEDs, such as red, green and blue, or blue and yellow. The second method presents challenges for practical use, such as differences in drive voltage, luminous output, element life and thermal characteristics among LEDs. In contrast, the first method employs only one type of element and the drive circuit design is quite simple.

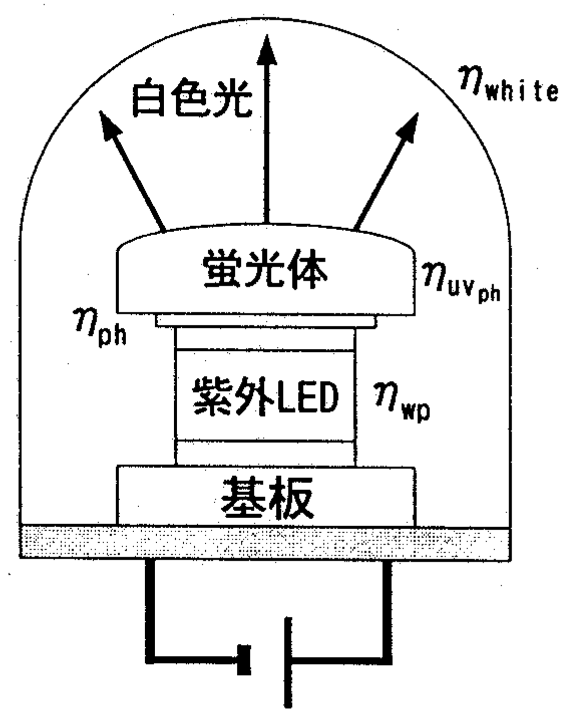

Figure 1.2.2-(1): Conceptual Diagram of White LED by Combining UV LED and Phosphors and the Relationship of Efficiency.

Labels: White light; Phosphor; UV LED; Substrate.

Within the first (single-chip) method, there are two approaches [8]. The first approach excites a yellow phosphor using a blue LED. The second approach uses a UV LED to excite RGB phosphors. The second approach was proposed for the first time under the Light for the 21st Century project and was developed as a new white LED light source for illumination.

Method	Excitation Source	Light Emitting Material and Fluorescent Characteristics	Principles of Light Emission
Single Chip	Blue LED	InGaN/YAG, ZnS-based	Blue light excites yellow phosphor
	UV LED	InGaN/RGB phosphors	RGB phosphors excited by UV light in same manner as in fluorescent lamps
Multi-Chip	Blue LED Yellow LED	InGaN, GaP, AlInGaP	Two complementary colors placed in a single package.
	Blue LED Green LED Red LED	InGaN, AlInGaP, AlGaAs	Three primary color LEDs placed in a single package.

Table 1.2.2: Methods for producing white light with LEDs and phospohors.

Figure 1.2.2-(2) shows the dependence of the injection current of the emission spectrum of a white phosphor made by combining red (Y_2O_2S: Eu^{3+}), green (ZnS: Cu, Al), and blue $(Sr, Ca, Ba, Mg)_{10}(PO_4)_6Cl_2$:$Eu^{2+}$ phosphors using a UV LED (light wavelength of 371 nm, output of 5 mW (at 20 mA), and external quantum efficiency of 5%) as an excitation source.

The peaks are at 626, 528, and 447 nm respectively [9]. Even if the current is increased, no significant change is seen in the emission spectrum. The luminosity of each tends to increase linearly with an increase in current. The average color rendering index is Ra = 83.

The white LED light source used to excite the RGB phosphors can emit various colors of light according to the particular combination of phosphors, making their range of application for illumination purposes broad. Nonetheless, the luminous flux of each LED is weak (1 lm), making it necessary to arrange multiple LEDs to serve as a source of illumination.

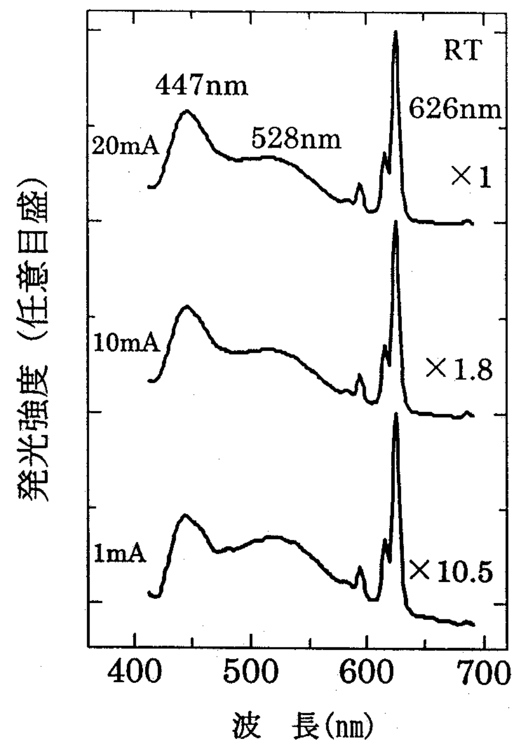

Figure 1.2.2-(2): Changes in the emission spectrum with a rise in injection current of RGB white phosphors.

Axes: Luminosity (free scale); Wavelength (nm)

To develop LED-based illumination, optimized design of a device system including light distribution from multiple LED integrated elements is necessary. As such, models to calculate the ideal luminous intensity and illumination distribution of multi-point LED light sources are being studied [10].

1.3 Cooperative Project

This project is promoted by a joint research body established by 13 companies and 4 universities (Yamaguchi University, Mie University, Tokyo University, and Chiba University) under the purview of the Japan Research Center for Metal-based Materials (JRCM). In 2001, prototype UV LEDs were developed whose characteristics surpass those exhibited by LEDs of leading manufacturers. In the coming year, it is expected that further research will yield additional improvements in lighting efficiencies.

1.4 Participation in "21st Century Dream Technology Exhibition"

Nihon Keizai Shimbun hosted "The Exhibition of Dream Technologies for the 21st Century" at the Tokyo International Exhibition Center for 17 days from July 21 through August 6, 2001. This project was introduced as part of the NEDO exhibit to show the promise of LED lighting. The exhibit showed the principles of LEDs, the potential of LEDs as illumination sources, and displayed prototype LEDs and LED-based lighting fixtures.

Figure 1.4: Exhibition Booth at the Exhibition of Dream Technologies for the 21st Century

1.5 Report on Technology Trends from MRS 2000 Fall Meeting

We attended the Material Research Society (MRS) 2000 Fall meeting held in Boston from November 25 through December 1, 2000 to research market trends, primarily from the GaN symposium.

The MRS is a non-profit organization established in 1973 among governmental, academic, and industry participants to share knowledge on new materials and to promote exchange of information through the publication of related books. The Fall meeting was the second major meeting for GaN materials.

1.5.1 Overview of 2000 Fall Meeting

Forty-one symposia - some large, some small - were held at 3 sites: the Hynes Convention Center, the Sheraton Hotel, and the Marriott Hotel. Among these, the symposia on GaN-based and SiC-based materials were of primary interest while other symposiums were of tangential relevance. There were 2,703 talks, 1,556 poster exhibits, and 3,639 research announcements.

Other than a few symposia like that on GaN-based materials, most of the names of the symposia were different than the previous year, making it quite difficult to identify relevance. Based on the limited number of symposia viewed, it appeared that the number of attendees of each lecture was proportional to the number of research announcements. The great success of the symposium on organic optoelectronic materials was especially impressive.

1.5.1.1 GaN-based Materials Symposium

Similar to last year, the symposium on GaN-based materials was the largest, with a total of 271 announcements, including lectures and poster exhibits. Announcements on GaN-based materials could also be seen here and there at other symposiums.

Announcements involved research bodies from 25 countries comprised of 331 universities, 109 commercial firms, 45 governmental research labs and 10 military research labs, for a total of 495 organizations. The U.S., Japan, Germany, France, and South Korea were at the top.

Announcements on GaN-based materials worthy of attention are listed below.

1.5.1.2 Nanomaterials

Among the 7 symposiums obviously covering nanomaterials, there were 841 announcements. Still, there were a large number of announcements at other symposiums that could be categorized under nanomaterials. Among the numerous applications of nanomaterials expected to be in semiconductor devices and displays, 9 announcements on hydrogen occlusion via a nanotube gained much attention.

1.5.1.3 Interesting Announcements from Symposium on GaN and Related Alloys

Among the announcements made on GaN-based compounds and semiconductors, those relevant to this project are listed below, categorized as: substrates, UV light emission, elemental structures and processes, and LEDs.

Substrates

"Structure and Optical Properties of GaN Bulk Crystals Grown from the Liquid Phase", M. Albrecht, Erlangen-Nuernberg University (with Ioffe Inst. and TDI)

- While melting GaN, LPE growth at 1000°C, less than 2 barometric pressure on a 50 mm GaN crystal substrate.
- At present, achieved oriented polycrystals. Maximum length 15 mm, diameter 20 mm, dimension of crystal grain <= 3 mm x 1.5 mm.

"Growth of Self-Seeded Aluminum Nitride by Sublimation-Recondensation and Substrate Preparation", C. Rojo, Crystal IS (with Rensselaer Polytechnic Inst.)

- AlN single crystals a promising substrate for growth of GaN mixed crystals, especially Al-rich ones.

- Sublimation. Transport by a temperature gradient in Al + N_2 state. 2000°C Growth rate of 0.9 mm/h.
- Diameter of 15 mm, grain size of 10 mm x 6 mm, poly portion also present.
- Yellow or colorless. With CL, strong emission from a deep level which is about 0.8 times the band edge energy.
- AlN film formed on substrate. Various tests and HEMT prototype performed.

"Characteristics of FIELO-GaN Grown by Hydride Vapor Phase Epitaxy", A. Usui, NEC

- FIELO-GaN grown film by HVPE exhibits a dislocation density of 10^6 cm^{-2}, PL decay time of 1.3 ns at its longest, which is significantly longer than that by conventional MOVPE.
- Achieved ϕ35 mm GaN substrate by depositing 60 to 400 μm GaN film on a ϕ2˝ sapphire substrate and then cooling it to allow thermal expansion to naturally cause separation between substrate and film.
- Created InGaN MQW blue LD on FIELO-GaN.

Several additional announcements (Air Force Research Lab. + University Massachussetts + Samsung + Wright State Univeristy + University of Dayton; Tech. University of Munich; and others.) covered formation of independent GaN film by HVPE, GaN film growth thereon and its characteristics.

UV Light Emission

"UV Emitter Based on High-Efficiency GaN/AlxGa1-xN Multi-Quantum Wells", M. Iwaya, Meijo University (Meijodai)

- Luminosity distribution is observed at the light emission surface of an LED where the region of high luminosity is found to be at the region of low dislocation density.
- PL luminescence characteristics close to GaN obtained at room temperature via low dislocation density and Si doping.

"Current Injection UV-Emission from InAlGaN Multi-Quantum Well Light Emitting Diodes", A. Kinoshita, Riken (with Waseda University)

- 230 nm PL observed on InAlGaN at room temperature.
- Substrate is CREE (0001) SiC.
- MQW, thick luminous layer, add SL layer on top (above and below) the active layer.
- Peak wavelength during current injection found to be 360 nm with MQW and 340 nm with thick light emitting layer.

"Improved Optical Quality of BAlGaN/AlN MQW Structure Grown on 6H-SiC Substrate by Controlling Residual Strain Using Multi-Buffer Layer", Hideo Kawanishi, Kogakuin.

- B 5-13% possible with BAlGaN on 6H-SiC.
- Light emission wavelength of 248.1 nm with $B_{0.07}Al_{0.52}Ga_{0.41}N$/AlN MQW
- Growth temperature of 1460 / 1200ºC

- Conductivity still unobtainable

Elemental Structures and Processes

"Transfer of Nitride Device Heterostructures from Sapphire Growth Substrates to Silicon by Metal Bonding and Laser Lift-Off", T. Sands, UC Berkeley

- GaN element separated from sapphire substrate by irradiating with an excimer laser
- The substrate/nitride boundary area reaches 1000ºC, but most of the nitride portion remains at 400ºC.
- Grow In film on the electrodes to make a In/Pd/GaN/sapphire substrate, then attach it to a Pd/Si substrate by heating to 200ºC, causing it to bond via a Pd-In reaction. Then separate the sapphire substrate via laser irradiation. This leaves a GaN/electrode/inner layer/Si structure.
- No changes in LED characteristics before and after separation (lift off).

"Integration of $In_xGa_{1-x}N$ Laser Diodes with Dissimilar Substrates by Laser Lift-Off", W.S. Wong, Xerox

- Apply Si or Cu atop an LD structure (GaN/sapphire substrate), then separate the sapphire substrate using laser lift off. Heat dissipation when using Cu is good.
- Even if the Al_20_3-GaN boundary area reaches 900ºC, the GaN beyond 2μm from the boundary area reaches only 200ºC.
- By removing the Si or Cu temporarily applied, it is possible to create an "LD film". It is also good to attach this atop a diamond base.

"Group-III Nitride Quantum Heterostructures Emitting in the Whole Visible Range", N. Grandjean, CNRS

- Creation of quantum dots by employing island structures produced naturally during MBE.
- Island height (3 nm to 5.5 nm) supported by PL light emission wavelength (2.6 eV to 1.9 eV).
- Unclear whether the wavelength change mechanism is due to quantum size or Stark effects.
- It is possible to achieve white LEDs.

"Drastic Reduction of Threading Dislocation Density of AlGaN on SiC by Using Highly-Si-Incorporated AlGaN Superlattice", M. Ainoya, Riken (with Waseda University)

- AlGaN containing $1.2 \times 10^{20}/cm^3$ Si
- The thermal dislocation density (TDD) changes from $10^{10}/cm^2$ to $10^8/cm^2$ with (AlGaN 80 nm + AlGaN:Si 20 nm) x 6.
- Dislocations bend within the Si doping layer.
- Same effects observed with both SiC substrates and sapphire substrates.

"Growth and Characterization of the GaN Underlying Layer Used in Blue-Violet GaN-Based Laser Diodes on Sapphire", Kenji Funato, Sony

- Dislocation reduced by improving underlayer, life extended (1000 h or more).
- Relaxation of crystals increases dislocation and threshold current rises.
- Growth pressure was 0.9 to 1.6 atm. Raising the pressure tends to restrain relaxation.
- PL strength was reduced remarkably to better than EPD 1.2 x $10^7 cm^{-2}$.
- With lines of 2 μm and spaces of 10 μm, the dislocation density of the wing equaled mix < $10^5 cm^{-2}$ and edge < $10^6 cm^{-2}$.
- LD life: the life of ELO is twice that of sapphire at low output, but the difference grows smaller at higher output.
- The output with ELO is 1.21 W/mA (74mA). With sapphire it is 0.92 W/mA (90mA).
- The minimum dislocation density on sapphire is 4 x $10^8 cm^{-2}$. With ELO it is below 1 x $10^6 cm^{-2}$.

"Gallium Nitride Films on Liquid Precursors", M. Puchinger, Max-Planck-Inst. (with UCSB)

- GaN crystals obtained by spin coating liquid precursors onto the substrate and then heating within N_2.
- At present, only multi crystals are obtained with thick film, but single crystals of GaN film (<= 20 nm) can be obtained on sapphire even if facet exists.

LEDs

"Development of High Power Nitride LEDs for Semiconductor Lighting", S. A. Stockman, Lumileds

- The present maximum levels are 100 lm/W (600 nm yellow) for AlInGaP and 80 lm/W (540 nm yellow green) for InGaN.
- Due to the heat resistance of epoxy resins, an artillery shell shape is thought to limit light output to <= 0.1 W. (currently 5 to 10 mW). On the other hand, 1 W per element is desired immediately.
- Direct bonding to a copper block holds promise. Concept of 18 LEDs mounted to a square substrate that is 2 to 2.5". Some thinking of enlargening the chip size and then forming into a flipchip or multi-chip module.
- With an increase in chip size, comb-shaped electrodes will be needed. A prototype is being worked on.
- However, there is data suggesting that the efficiency quickly degrades as the chip size grows larger. Therefore, LumiLeds is aiming for a segregated chip plus a multi-chip approach.
- <While demonstrating a blue LED> Compared to a conventional LED, it outputs 20 times the light at 15 times the current. There are also white LEDs. These use red and green phosphors but the efficiency is still low.
- <Application> LCD backlight, indoor lighting, road and tunnel lighting, etc. 10W device is hoped for.

- The most important problem to solve is that of heat.

1.6 Patent Search

Registrations and open applications for patents and new uses dealing with GaN-based LEDs from the years 1998 and 1999 have been entered into a database, categorized according to their importance, and then studied. New applications for the year 2000 will be entered into the database. The content of those in dispute has been researched.

1.6.1 New Open Applications and Registrations

1.6.1.1 New Data Supplement

A patent search was performed to locate patents covering important technological problems pertinent to this project. The contents of these patents have been read from a CD-ROM published by the patent office and added to a database. During the period spanning from December 5, 1999 to November 13, 2000, there were 477 new filings and patent awards relating to this project. This is broken down further as follows:

New patent filings: 402

New patent awards: 79

Among these, as shown in Table 1.6.1-(1), four had already been awarded when filed. While these were new filings, they also constituted new patent awards. Care must be taken because it cannot be determined by checking public disclosure (patent filings) only that they were already awarded.

Public Disclosure Number	Date of Disclosre	Award Number	Date of Award
2000-105321	April 11, 2000	2954203	July 16, 1999
2000-114597	April 21, 2000	3019085	January 7, 2000
2000-114664	April 21, 2000	3031415	February 10, 2000
2000-196196	July 14, 2000	2995187	October 22, 1999

Table 1.6.1-(1): Patents Already Awarded upon Public Disclosure

1.6.1.2 Grant Classifications

Table 1.6.1-(2) shows the number of registered patents and open filings according to grant classification of the 477 registered patents and open applications.

The number of patents relating to MOCVD-based crystal growth and buffer layers exceeded all others, followed by element isolation and cleavage, substrate materials, active layers, current constriction layers to create lasers and stripes, etching, and dopant-related patents. This study found patents relating to phosphors and combined white light emission, but none had reached the award stage.

Classification Number	Classification Description	New Applica-tions	New Registra-tions
A01	Substrate Material: Sapphire	11	1
A02	Substrate Material: GaN	8	
A03	Substrate Material: Other	16	4
B01	Layer Structure: Dopant	10	1
B02	Layer Structure: Buffer layer	51	7
B03	Layer Structure: Contact layer	11	
B04	Layer Structure: Clad layer	7	
B05	Layer Structure: Active layer	12	5
B06	Layer Structure: Current constriction layer	10	6
B07	Layer Structure: Barrier layer	3	
B08	Layer Structure: Heterostructure	2	1
B09	Layer Structure: Quantum well structure	9	2
B10	Layer Structure: MIS structure	2	
B11	Layer Structure: Ridge structure	6	
B12	Layer Structure: Carrier concentration	7	1
B13	Layer Structure: Stripe	10	
B14	Layer Structure: Other		
C01	Electrode: Ohmic	9	2
C02	Electrode: P-structure	4	1
C03	Electrode: N-structure	1	2
C04	Electrode: Shape	3	4
C05	Electrode: Material		2
C06	Electrode: Wire bonding		
C07	Electrode: Other	1	
D01	Manufacturing Technology: MOCVD, MOVPE	45	15
D02	Manufacturing Technology: MBE, PVD	4	4
D03	Manufacturing Technology: Heat processing	7	1
D04	Manufacturing Technology: Etching	12	2
D05	Manufacturing Technology: Isolation, Cleavage	25	1
D06	Manufacturing Technology: Sealant	2	
D07	Manufacturing Technology: Bonding	3	2
D08	Manufacturing Technology: Other	4	1
E01	Element Structure: Single		

E02	Element Structure: Multiple	4	1
E03	Element Structure: Direction of light extraction	7	1
E04	Element Structure: Combination with phosphors	12	1
E05	Element Structure: Phosphor material		
E06	Element Structure: Other	1	
F01	Element Morphology: LED	6	
F02	Element Morphology: LD	5	
F03	Element Morphology: Other	6	3
G01	Mount Structure: Package	9	1
G02	Mount Structure: Lead frame	1	
G03	Mount Structure: Flipchip	3	
G04	Mount Structure: Face down	3	
G05	Mount Structure: Other	4	
H01	Characteristics: High		
H02	Characteristics: Blue light, UV light		
H03	Characteristics: White light, multi-colored light	10	
H04	Characteristics: Surface luminescence	2	
H05	Characteristics: Crystallization		
H06	Characteristics: Other (heat resistance, etc.)	6	

Table 1.6.1-(2) Number of Patents based on Grant Classification.

1.6.1.3 Examples of Important New Patent Registrations and Applications

Tables 1.6.1-(3) through 1.6.1-(6) below show examples of patent registrations and applications pertaining to buffer layer structures.

Number	Claimant	Description
302687	Toyoda Gosei	Low temperature growth (400 – 900 degrees) AlN Wursted-structure buffer layer (film thickness of 10 – 15 nm).
3091593	Nichia Chemical	MOCVD using a GaAlN buffer layer on sapphire + GaN formed substrate.
3036495	Toyoda Gosei	Stripe or lattice AlGaN buffer layer (on Si substrate).
3028809	Sanken Electric	TiN buffer layer.

Table 1.6.1-(3): New Patent Registrations on Buffer Layer Structure

Number	Claimant	Description
2000-261037	Sharp	Super lattice formation on n-type clad layer.
2000-068594	Nichia Chemical	Super lattice buffer layer.
2000-040842	Toyoda Gosei	Multi-crystal buffer layer.
2000-040843	Toyoda Gosei	Two GaN buffer layers on sapphire substrate.

Table 1.6.1-(4): Open Applications (those relating to growth methods for layer structures).

Number	Claimant	Description
2000-077336	Sony	Ion implantation stripe mask usage
2000-164929	Sony	Specific crystal facet growth
2000-021789	Toshiba	SiO_2 stripe mask usage
2000-101194	Sanyo	SiO_2 stripe mask + surface polishing
2000-124500	Toshiba	Growth of crystals on a cyclically irregular surface
2000-058918	Murata Manfacturing	Striping of an N-type electrode
2000-068609	Ricoh	Two stage stripe masking
2000-156348	Nichia Chemical	Growth on substrates with height differences
2000-106348	Matsushita Electric	Growth on porous substrates
2000-174343	Sharp	Cross layer stripe mask usage

Table 1.6.1-(5): Open Applications Founded on Same Concept as Patent 3036495 (lateral growth by stripe and substrate surface irregularities).

Number	Claimant	Description
2000-036617	Murata Manufacturing	ZnO buffer layer (on Si substrate)
2000-058451	Showa Denko	Phosphorus boron (BP) buffer layer
2000-133843	Fuji Electric	Fluoride thin film buffer layer
2000-188260	Samsung Electric	Boron nitride (BN) buffer layer
2000-031537	Matsushita Electric	GaN buffer layer containing arsenic
2000-031539	Hewlett-Packard	MgZnCd-doped boundary layer

Table 1.6.1-(6): Buffer Layers Based on Non-Conventional Materials.

1.6.1.4 Distribution of Applicants by Technology Classification

Table 1.6.1-(7) shows the distribution of patent applicants and assignees of new published unexamined patent applications (Kokai) and registered patents by technical field.

Classification Number	Classification Description	Number of Applicants	Number of Assignees
A01	Substrate Material: Sapphire	10	1
A02	Substrate Material: GaN	5	
A03	Substrate Material: Other	10	4
B01	Layer Structure: Dopant	6	1
B02	Layer Structure: Buffer layer	25	10
B03	Layer Structure: Contact layer	8	
B04	Layer Structure: Clad layer	4	
B05	Layer Structure: Active layer	11	5
B06	Layer Structure: Current constriction layer	8	5
B07	Layer Structure: Barrier layer	3	
B08	Layer Structure: Heterostructure	2	1
B09	Layer Structure: Quantum well structure	8	2
B10	Layer Structure: MIS structure	4	
B11	Layer Structure: Ridge structure	5	
B12	Layer Structure: Carrier concentration	11	1
B13	Layer Structure: Stripe	8	
B14	Layer Structure: Other		
C01	Electrode: Ohmic	10	2
C02	Electrode: P-structure	4	1
C03	Electrode: N-structure	1	1
C04	Electrode: Shape	3	4
C05	Electrode: Material		2
C06	Electrode: Wire bonding		
C07	Electrode: Other	1	
D01	Manufacturing Technology: MOCVD, MOVPE	20	14
D02	Manufacturing Technology: MBE, PVD	4	4
D03	Manufacturing Technology: Heat processing	5	1
D04	Manufacturing Technology: Etching	13	2
D05	Manufacturing Technology: Isolation, Cleavage	12	1

D06	Manufacturing Technology: Sealant	2	
D07	Manufacturing Technology: Bonding	3	2
D08	Manufacturing Technology: Other		
E01	Element Structure: Single		
E02	Element Structure: Multiple		
E03	Element Structure: Direction of light extraction		
E04	Element Structure: Combination with phosphors		
E05	Element Structure: Phosphor material		
E06	Element Structure: Other		
F01	Element Morphology: LED		
F02	Element Morphology: LD		
F03	Element Morphology: Other		
G01	Mount Structure: Package		
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G05	Mount Structure: Other		
H01	Characteristics: High		
H02	Characteristics: Blue light, UV light		
H03	Characteristics: White light, multi-colored light		
H04	Characteristics: Surface luminescence		
H05	Characteristics: Crystallization		
H06	Characteristics: Other (heat resistance, etc.)		

Patent Disputes

Blue highlighting indicates missing pages.

Table 1.6.1-(7): Number of Participants by Technology Classification.

1.7 Conclusions

The 21st Century is certainly the era of technology innovation with semiconductor lighting and this project is playing a leadership role. Differing from conventional visible light LEDs, white LEDs have strong needs as a general lighting source. Nonetheless, since such applications need a high volume of light (several tens to several thousands lm) in future new and innovative technologies by researchers and engineers of semiconductor technology, light emission element technology, and illumination engineering in collaboration with lighting and interior designers is critical to the realization of white LED lighting systems. It is hoped that further technology innovation in white

LEDs for illumination will not only create a new lighting culture through LED applications, but will also build a safe societal foundation which produces less environmental waste.

1.8 Future Course

Research is progressing as planned according to the flow shown in Figure 1.2.1-(1). The light emission mechanism of the UV LED developed this year has been uncovered and defect densities have been reduced, contributing to improvements in external quantum efficiency. From here, we plan to pursue improvements in the precision of the epitaxial growth process and to strengthen the cooperation among project participants so that the evaluation of film quality in growth layers and end characteristics can lead to improvements in LED structures. Additionally, with regard to white LED lighting, we plan to lead the world in proposing concrete applications and standardization of LED lighting fixtures through lighting system section meetings.

1.9 References

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