Journal of the Korean Crystal Growth and Crystal Technology
Vol. 12, No. 1 (2002) 11-20

Wide bandgap III-nitride semiconductors: opportunities for future optoelectronics

Yoon-Soo Park†

Office of Naval Research, 800 N. Quincy Street, Arlington, VA 22217, USA

(Received April 27, 2001)

Abstract The world at the end of the 20th Century has become "blue". Indeed, this past decade has witnessed a "blue rush" towards the development of violet-blue-green light emitting diodes (LEDs) and laser diodes (LDs) based on wide bandgap III-Nitride semiconductors. And the hard work has culminated with, first, the demonstration of commercial high brightness blue and green LEDs and of commercial violet LDs, at the very end of this decade. Thanks to their extraordinary properties, these semiconductor materials have generated a plethora of activity in semiconductor science and technology. Novel approaches are explored daily to improve the current optoelectronics state-of-the-art. Such improvements will extend the usage and the efficiency of new light sources (e.g. white LEDs), support the rising information technology age (e.g. high density optical data storage), and enhance the environmental awareness capabilities of humans (ultraviolet and visible photon detectors and sensors). Such opportunities and many others will be reviewed in this presentation.

Key words III-Nitride, Optoelectronics, Blue, Green, White LED, Laser diode, Ultraviolet, Photodetector

1. Introduction

The nitrides of group III elements (or III-Nitrides), such as AlN, GaN, InN and their alloys, have all the desired physical properties for a number of tomorrow's optoelectronic devices. Indeed, they are wide bandgap semiconductors, with a bandgap energy from 6.2 to 1.9 eV, which makes them ideal for optical devices operating in the visible-to-ultraviolet spectral region, such as blue, green, ultraviolet lasers and photodetectors. Their exceptional physical properties also bring device applications beyond imaging and data storage. These materials are physically and chemically strong, making them ideal for operation in harsh environments (radiation, heat) such as those typical of space applications and high temperature electronics. To date, III-Nitrides have kept their promises. Ultraviolet photodetectors based on III-Nitrides have shown promising results. Super bright green and blue light emitting diodes made using III-Nitrides are commercialized, as well as very recently blue-violet laser diodes.

In the future, the challenges faced by the semiconductor community will be to develop a reliable III-Nitride material technology to fulfill the full potential of this material system for optoelectronic devices. The current lack of a native III-Nitride substrate has made the use of foreign substrates inevitable. High quality, large area native III-Nitride substrates will have to be developed even though this may take a long time. In the meantime, novel approaches to avoid defects due to lattice and thermal mismatch between III-Nitride films and foreign substrates will have to be developed. An example of such growth technology is lateral epitaxial overgrowth (or LEO). Current device structures will have to be optimized and novel structures developed for new applications. Thanks to improvements in the substrate and growth technology, III-Nitride physical properties are expected to be better understood and device modeling more accurate.

This paper will first aim at describing III-Nitride materials and their use for optoelectronic devices. The current state-of-the-art and future prospects for III-Nitride thin films, heterostructures, and optical devices will then be discussed.

2. Properties of Wide Bandgap III-Nitride Semiconductors

III-Nitride crystals are wurtzite in their stable form with a hexagonal symmetry. They are also polar crystals and thus possess many potentially useful properties such as piezoelectricity, pyroelectricity [1] and second harmonic generation [1, 2]. The large difference in electronegativity between the group III and group V elements results in very strong chemical bonds, which are

---

†Corresponding author
Tel: +1-703-696-5755
Fax: +1-703-696-2611
E-mail: parky@onr.navy.mil

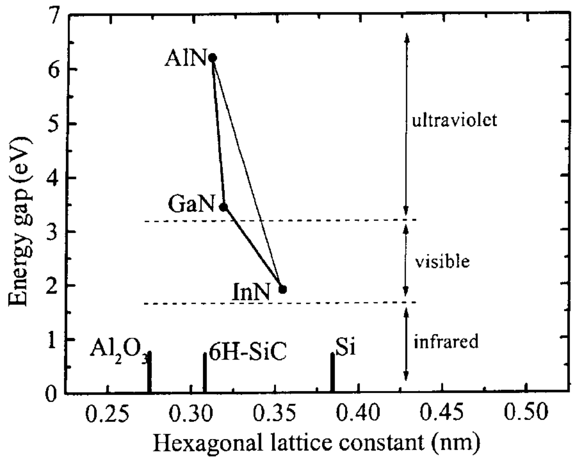

Fig. 1. Energy gap versus lattice constant of III-Nitride semiconductors.

at the origin of most of the interesting III-Nitride physical properties. A direct result of the strong binding is the wide bandgap, ranging from 6.2 to 1.9 eV, corresponding to a wavelength from 200 to 650 nm. This spectral range covers the visible spectrum (blue, green, yellow and red) as well as the near ultraviolet region in which the atmosphere transmits, as shown in Fig. 1. The bandgap is direct which is most appropriate for optical devices. Because the in- trinsic carrier concentration is an exponential function of the energy gap and the temperature, a wider bandgap semiconductor has a much lower intrinsic carrier concentrations over a large temperature range, resulting in lower leakage and dark currents. Reduced leakage and dark currents are especially important in photodetectors. Another consequence of the strong chemical bonding is the physical (high melting points, mechanical strength) and chemical stability of these materials. These also enjoy high thermal conductivity. Their effective masses are higher than conventional semiconductors, thus leading to lower carrier mobilities, but this drawback is made up for by the high saturated electron drift velocities predicted for this material system. The refractive indices of III-Nitrides are lower compared to narrower gap semiconductors, resulting in a lower reflectivity at the interface an advantage for photodetector efficiency, but a disadvantage when trying to achieve lasers with low threshold currents.

Although III-Nitride based devices are being rapidly demonstrated and commercialized, there are many barriers that must be overcome before the full potential of these materials can be realized as reliable devices. First, the high melting point of III-Nitrides and the extremely high nitrogen partial pressures near the melting point make their bulk growth very difficult. Therefore, high quality III-Nitride substrates do not exist. The synthesis of nitride crystals thus has to be carried out in the form of thin films on a non-native substrate. The dissimilarity between the substrate material and the III-Nitrides generally leads to poor structural quality as a result of the lattice and thermal mismatch. Moreover, nitride alloys with different compositions are also lattice-mismatched, which leads to dislocations in III-Nitride heterostructures. Finally, high free electron and hole concentrations are often difficult to achieve because most dopant elements form deep levels in wide bandgap nitride semiconductors. The addition of more dopant source during the growth process frequently results in degradation of the structural and optical properties [4, 5, 6].

3. Applications of Wide Bandgap III-Nitrides for Optoelectronics

One of the driving force behind the exceptional interest in III-Nitride materials has been their potential for optoelectronic device applications, both civilian and military. Two types of devices are the focus of the research work in this area: ultraviolet (UV) photodetectors and violet-blue-green light emitters.

UV photodetectors using III-Nitride materials are sensitive to UV radiation while being insensitive to longer wavelength radiation. Such devices have applications where there is a need to detect or control the source of UV radiation in an existing background of visible or infrared radiation [7]. Examples of such applications include flame detection, furnace and engine monitoring for the automotive, aerospace and petroleum industry, undersea communications, UV astronomy [8], space-to-space communications secure from Earth, early missile threat warning and airborne UV countermeasures, and portable battlefield reagent/chemical analysis system. Because of their theoretical intrinsic solar blindness and low dark currents, III-Nitride based devices are expected to work without optical filters and complex electronics, thus significantly reducing the launch weight for space and airborne applications.

III-Nitrides have been successfully used in commercial bright blue and green light emitting diodes (LEDs). When used with the already available red AlGaAs based LEDs, these new LEDs complete the primary colors (red, green, blue) for large, high brightness, outdoor full-color displays. Traffic lights are starting to use green LEDs because of their superior efficiency and reliability in comparison to incandescent light sources. Solid state white light sources using a combination of red, green, and blue LEDs or using phosphors excited by blue or ultraviolet (UV) LEDs may soon replace conventional light bulbs with better efficiency and reliability. UV LEDs could also replace the inefficient and hot "black" lights that are used in fun houses, tanning salons, and in more mundane applications such as killing bacteria in water.

The main thrust in recent III-Nitride research has been the fabrication of a reliable, short-wavelength (ul- traviolet to green spectral region) laser diode. The primary advantage of shorter wavelengths is the ability to focus the beam to smaller spot sizes which scale as λ^2, thus quadrupling the storage density of optical media by reducing the laser wavelength in half. The objective will be to achieve a digital video disk (DVD) system capable of storing 15 gigabytes by the year 2000. A DVD-RAM system would require a laser diode operating in continuous wave (CW) at 60°C with an output power of 30~40 mW and an operating voltage of 3 V at 100 mA. The requirements for a DVD-ROM system would only be a 4~5 mW CW laser. In both cases, the laser should have a wavelength of 400~430 nm. It must not be too short, in order to avoid transmission losses in air. Visible laser diodes are also expected to be used in projective displays, optical communications, and chemical analysis because the wavelength could be tuned to correspond to ab- sorption lines of specific airborne chemicals to be de- tected. For example, a 55-inch display needs a luminosity of 500 cd/m^2, which requires at least a 6.6 W red, 1.8 W green, and 1.2 W blue laser. Finally, laser printing is also an important application for short wavelength laser diodes. These would need to emit at a wavelength higher than 430 nm to avoid the decomposition of the toner components, with a single mode CW output power higher than 6 mW for fast printing.

4. III-Nitride Semiconductor Materials

4.1. Substrates for wide bandgap III-nitride thin films

Because of their extreme physical properties, bulk III-Nitride single crystals are available with great difficulty. This remains the major issue in the development of wide bandgap III-Nitride semiconductors and optoelectronic devices based on these materials. High-pressure growth was once regarded as a promising technique to achieve bulk GaN crystals but, to date, it remains limited to a few research groups and the crystal size remains small compared to alternative techniques. By using sublimation transport, the growth of bulk AlN yielded up to 13 mm diameter boules, but so far the material was polycrystalline. Bulk growth from solution with a slight overpressure is a method which has gathered interest for GaN over the past few years and yielded GaN boule sizes of 20 mm in length. In spite of intense research work in this area, the quality of these bulk III-Nitrides is not good enough to be used as substrates in the near future. In addition, techniques for the polishing of the epi-ready surface is not yet developed.

Many non-native substrates have therefore been investigated over the years, and the use of thin film deposition techniques such as metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) has been widespread. To date, three substrates stand out as the most promising: silicon, silicon carbide (SiC) and sapphire (Al_2O_3). Silicon is the most widely available substrate in the semiconductor industry and can come in sizes up to 10 inch diameter. It is also the cheapest one and the highest quality. However, it suffers from a poor chemical compatibility with III-Nitride crystals, meaning a crystal structure (bulk and surface arrangement of atoms) that does not lend itself to the proper initial nucleation of oriented III-Nitride crystals. Also, it has a very narrow bandgap in comparison to nitrides, which makes it ill-suited for optical devices. At the other extreme, SiC offers the closest match with III-Nitrides in terms of crystal symmetry, lattice and thermal mismatch. It is a wide bandgap semiconductor being developed for applications in high power electronics. Its drawbacks are its limited availability, small wafer size, quality still not as good as other Si or Al_2O_3 substrates, and its prohibitively high price. Sapphire offers a compromise between Si and SiC, and has become the most often used substrate for III-Nitride epitaxial growth. The appealing features include the high thermal and chemical stability, the large high quality wafers available, and the reasonable cost. However, there are large lattice and thermal mismatches. The dissimilarity between the substrate and nitride materials has been alleviated through the successful development of the growth technology, and more precisely the use of buffer layers [9].

Recently, vapor phase epitaxy (VPE) has gained momentum in achieving free standing III-Nitride films which may serve as quasi-substrates. This is done by first using the high quality films obtained in MOCVD growth on a substrate such as sapphire, then conducting the VPE growth of very thick (150 mm) GaN films, and subsequently removing or etching off the substrate [10].

4.2. Wide bandgap III-nitride materials

AlN thin films are generally grown on basal plane Al_2O_3 or SiC substrates, without a buffer layer, due to the fact sapphire and AlN share a common element: aluminum, which makes the bonding at the interface much easier. Epitaxial films are rarely thicker than 1~1.5 μm. High crystalline quality films have been achieved on Al_2O_3 and SiC substrates with open detector symmetric x-ray rocking curve linewidths as low as 90 and 60 arc-seconds respectively [11, 12]. As grown AlN films are almost always insulating. The optical properties of AlN are generally assessed through optical absorption and cathodoluminescence.

GaN is by far the most studied III-Nitride material. A thin AlN, GaN or AlGaN buffer layer is generally used for the growth. Basal plane Al_2O_3 and SiC substrates are most commonly used. Films as thick as 100 μm have been reported, depending on the growth technique utilized. High crystalline quality GaN thin films have been achieved, with open detector x-ray rocking curve linewidths as low as 30 arc-seconds and asymmetric x-ray rocking curve linewidths as low as 400 arc-seconds [12]. Undoped GaN films are usually either highly resistive or exhibiting *n*-type conduction with a residual carrier concentration $\sim 10^{16}\ cm^{-3}$ at room temperature and an electron mobility as high as 900 $cm^2/V \cdot s$ (theoretical calculations show that the maximum 300 K electron mobility in GaN is 2350 $cm^2/V \cdot s$). The optical properties of GaN are usually assessed through optical transmission and photoluminescence (PL). Free excitons A, B and C have been observed with peak linewidths of ~1~3 meV at 2 K using photoluminescence. The room temperature PL linewidths are typically as low as ~30 meV. Residual acceptor and donor related luminescence transitions are often observed as well. A broad 'yellow' luminescence is sometimes observed and has been attributed to defects in GaN [13].

Ternary $Al_xGa_{1-x}N$ has been grown over the entire compositional range. The resistivity of $Al_xGa_{1-x}N$ was found to increase exponentially with Al concentration [14]. Low Al concentration alloys sometimes show limited *n*-type conduction due to residual donors as in the case of GaN. The optical properties of $Al_xGa_{1-x}N$ have been assessed using cathodoluminescence and optical absorption, in particular to determine the bandgap energy. One of the main advantages of the III-Nitrides over other wide bandgap materials such as SiC is the potential to fabricate heterostructures and achieve bandgap engineering within the same material system. High quality AlGaN/GaN interfaces and heterostructures have been successfully realized, as illustrated by the demonstration of quantum wells and two dimensional electron gas [15].

Ternary $Ga_{1-x}In_xN$ has been grown in the entire composition range. However, the material quality significantly deteriorates as the In concentration increases. It was shown that the $Ga_{1-x}In_xN$ alloy composition and material quality very strongly depended on the growth conditions, in particular the growth temperature, growth pressure, V/III ratio, and growth rate. To grow alloys with higher In concentration, it is generally necessary to lower the growth temperature, raise the growth pressure, increase the V/III ratio and growth rate [16]. Moreover, it has been reported that GaN and InN have a miscibility gap [17]. $Ga_{1-x}In_xN$ films are generally thin (< 0.5 μm) and are grown on thick GaN films (> 1 μm) on basal plane Al_2O_3 or SiC substrates. The x-ray rocking curve linewidths can be as low as 480 arc-seconds (for 14 % In) [18]. As grown $Ga_{1-x}In_xN$ films generally show *n*-type conduction ($n > 10^{17}\ cm^{-3}$ at 300 K). Room temperature photoluminescence measurements showed that $Ga_{1-x}In_xN$ can have a linewidth as low as 70 meV (for 14 % In). Ellipsometry has yielded the refractive index of $Ga_{1-x}In_xN$ to be ~0.05 higher (for $x = 0.06$) than that of GaN. GaInN/GaN heterostructures and quantum wells have been reported, although they have been more often characterized in actual devices [19, 20]. The cathodoluminescence intensity was shown to increase by several orders for GaInN/GaN multi-quantum wells compared to bulk GaInN films [21]. There have been reports of a "composition pulling effect" in thin GaInN films grown on GaN [22]. It was shown that the lattice mismatch between the growing GaInN layer and the underlying GaN prevented the incorporation of indium into the lattice. This effect can be significant in the control of the emission wavelength from GaInN/GaN quantum wells. Finally, the quantum confined Stark effect in GaInN/GaN multiquantum wells due to piezoelectric effects has been recently reported to influence the optical properties of these structures [23]. This effect can be minimized by adequately doping the structures with Si. The strong impetus to fabricate and produce visible optical devices has left much of the fundamental re- search in $Ga_{1-x}In_xN$/GaN heterostructures for the future. Although such study is necessary, it will strongly depend on the improvement of the $Ga_{1-x}In_xN$ material quality.

In spite of all the impressive progress accomplished in synthesizing and understanding III-Nitride materials in the past decade, the science and technology of this material system is still in its infancy. There exists a great opportunity for research and development in this area in the future. The major effort will be the improvement of the material quality through the reduction of defects. A better understanding and control of the structural, electrical and optical properties, especially for ternary and quaternary III-Nitride alloys with various compositions, will also be a challenge. In the next subsection, the doping of III-Nitrides will be discussed.

4.3. *Doping of III-nitrides*

The control of the doping of III-Nitrides is also one of the major issues in the development of optoelectronic devices based on these materials. The *n*-type doping in these materials has generally been much easier than the *p*-type doping, mainly because III-Nitrides have the tendency to exhibit *n*-type conductivity as grown. Like other III-V semiconductors, the *n*-type doping can be achieved using group VI elements, while the *p*-type doping is achieved by incorporating group II elements. Group IV elements, such as Si and Ge, act as donors in III-Nitrides, whereas C seems to act as an acceptor. Si and Ge have an electronegativity closer to Al, Ga and In than N, and thus would be more likely to replace Al, Ga and In than N. The electronegativity of C is closer to N than to the group III elements, and thus would more likely to replace N in the III-Nitride lattice.

The n-type doping of GaN films has been investigated using Si, Ge [24], Se, S [25] and O. The most successful dopants have been Si and Ge. Doping control has been achieved up to a carrier concentration of 10^{20} cm^{-3}. The Si level in the bandgap was estimated to be ~22 ± 4 meV below the bottom of the conduction band [26]. Impurity band conduction is usually observed at low temperatures. Future research work in the *n*-type doping of III-Nitrides includes enhancing the conductivity of *n*-type $Al_xGa_{1-x}N$ for $x > 0.6$. This would allow better optical and electrical confinement in heterostructures, as well as fulfill the potential of III-Nitrides for ultraviolet optoelectronics. In order to achieve this, it may prove necessary to understand the origin of the high resistivity of $Al_xGa_{1-x}N$ for high Al concentrations.

The *p*-type doping of GaN, $Al_xGa_{1-x}N$, and $Ga_{1-x}In_xN$ films have been achieved using Mg. The doping control is not easy at all as it is very sensitive to dopant flow rate. As doped films are generally insulating (except a few reports of as grown p-type GaN by MBE) and require post-growth treatment such as thermal annealing (> 600°C under nitrogen or vacuum) or low energy electron beam irradiation (LEEBI) to activate the p-type dopant [27, 28]. The mechanism by which this happens has been identified as the breaking of Mg-H bond [29]. The concentration of Mg atoms in the lattice is typically $< 10^{19}$ cm^{-3}, but the room temperature free hole concentrations are generally $< 5\times10^{18}$ cm^{-3} for a mobility < 20 cm^2/Vs. The activation energy of Mg has been estimated to be 150~200 meV. Impurity band conduction is also observed at low temperatures in *p*-type GaN films. Much more research work on the *p*-type doping of III-Nitrides is necessary in the future. In particular, a significant increase in the *p*-type conductivity of GaN and $Al_xGa_{1-x}N$ for $x > 0.3$ is strongly desired. This would allow also better optical and electrical confinement in heterostructures, as well as fulfill the potential of III-Nitrides for ultraviolet optoelectronics. Research directions include new doping sources and new doping schemes involving co-doping or short period superlattices [30].

5. III-Nitride Based Optoelectronic Devices

5.1. *Ultraviolet photodetectors*

The development of photodetectors based on III-Nitride material began with the most simple device design, the photoconductor. This device required no *p*-GaN layer to operate, and therefore simplified not only the growth demands, but also the fabrication steps because etching steps were not needed to define the device or contact two electrically different types of GaN layers. The characteristics of current photoconductor devices include $Al_xGa_{1-x}N$ detectors over the entire range $(0 \leq x \leq 1)$ [31, 32] and demonstration of gain mechanism in a metal-semiconductor-metal detector by using interdigitated contact design with a gain over 3000 A/W [33]. GaN detector arrays have also been demonstrated. The kinetics of photoconductivity has also been investigated in GaN photodetectors [34].

Schottky photodiodes are also simple detectors to fabricate and are capable of being extremely fast. Several groups have combined efforts to develop Schottky photodetectors with high responsivity and low noise equivalent power (NEP) [35]. Recently, low dark current, very high speed and high visible blindness GaN Schottky metal-semiconductor-metal photodiodes were demonstrated [36, 37].

Most of the research on UV photodetectors has recently been directed toward the demonstration of

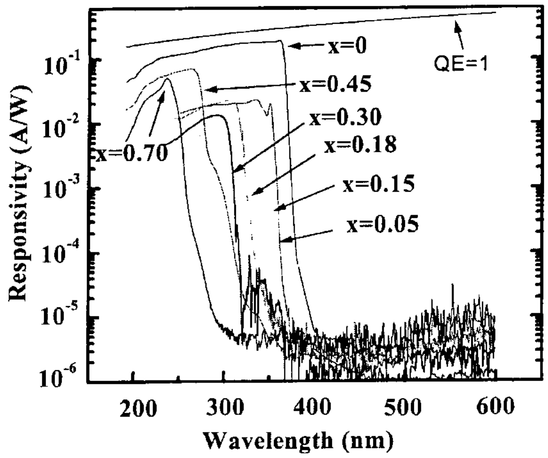

Fig. 2. Responsivity of $Al_xGa_{1-x}N$ *p-i-n* photodiodes showing a cut-off wavelength continuously tunable from 227 to 365 nm, corresponding to an Al concentration in the range 0~70 %.

$Al_xGa_{1-x}N$ based *p-n* and *p-i-n* junction photodiodes, which present the capability of tailoring the cut-off wavelength by controlling the alloy composition and thus the bandgap energy of the active layer. A full range of $Al_xGa_{1-x}N$ *p-i-n* photodiodes has been demonstrated with a cut-off wavelength continuously tunable from 227 to 365 nm, corresponding to an Al concentration in the range 0~70 % [38, 39, 40, 41]. This can be seen in Fig. 2 where the current responsivity of these detectors at room temperature is shown. Their internal quantum efficiencies were up to 86 % when operated in photovoltaic mode (i.e. 0 V bias) and they exhibited a UV-to-visible rejection ratio as high as six orders of magnitude. In addition to these front-side illuminated devices, back-side illuminated AlGaN UV photodiodes have also recently been reported [42].

The progression to a higher wavelength flexibility, faster response, higher rejection of visible light, lower noise interference, and better response are all indicative of not only improved designs, but also a continued increase in the quality of material. III-Nitride based UV photodetectors remain a very promising field for research and development for the future.

5.2. *Visible light emitting diodes*

To generate visible light using III-Nitride materials, one has to use $Ga_{1-x}In_xN$ alloys in the active layer. The first generation of blue and blue/green LEDs were fabricated from GaInN/AlGaN double-heterostructures (DH) [43]. Although these provided high optical output, higher than 1 candela (cd), they had a broad spectrum with linewidths typically ~70 nm, while the emission spectrum ranged from the violet to the yellow-orange spectral range, making the output appear "whitish-blue" to the human eye. Greatly improved LED performance, in terms of both color purity and intensity, have been achieved using single quantum-well (SQW) structures. For example, the emission peak linewidths for blue LEDs (450 nm) have reportedly been reduced to 20 nm with a brightness as high as 2 cd, while green LEDs (520 nm) exhibited a emission peak linewidth of 30 nm and luminous intensity of 12 cd [44, 45, 46]. The latest record has been achieved by using strained single quantum wells of $Ga_{1-x}In_xN$. To date, violet (~405 nm), blue (425~450 nm), green (~520 nm), yellow and even amber LEDs using III-Nitride materials have been demonstrated. Even white LEDs have recently been demonstrated by combining a blue nitride LED with a phosphorescent coating which provides the complementary color to the blue color. They have already shown promise to become a more efficient alternate lighting source to the conventional incandescent bulb. Most of these LEDs are now commercially available [47]. Their typical efficiencies are in the range of 5~10 %, with a typical output power of 4~6 mW and a luminous intensity of 3~10 cd under normal operating conditions, yielding better performance than those made from other materials.

Despite the successful demonstration and commercialization of III-Nitride based LEDs, there remain some important issues. First is the reliability of the devices. These LEDs are still fragile and require careful handling. They can be easily damaged by reverse bias greater than 5 V or forward current higher than 100 mA. This vulnerability is surprising because III-Nitrides are expected to have high breakdown voltages. An improper doping profile or high background carrier concentration in GaInN could be the cause of failure at high reverse bias or large forward current. The second issue is their thermal handling capability. The recommended operation temperature is < 80°C to avoid early degradation of the devices. Ideally, III-Nitride based devices are suitable for much higher temperature operation because of their thermal properties. The unusually low operating temperature could be due to the high defect density in the materials and the thermal instability of the GaInN active layer. The third issue is the price which is still too high for large volume applications. Finally, the white LEDs made from III-Nitrides do not currently emit a pure white light, which makes it uncomfortable for the human eye. In addition, the efficiency of these LEDs needs to be improved to compete with fluorescent light bulbs.

5.3. Violet-blue laser diodes

The realization of III-Nitride based laser diodes eluded the research community for many years. It has been only after thorough research and development on the material, processing and device fabrication technologies that such lasers have been made possible. There has been outstanding success in GaN-based blue laser diodes in the past few years. Several research groups worldwide have demonstrated GaInN based multiple quantum well based violet and blue laser diodes. Violet laser diodes operating at room temperature and in continuous wave mode with a projected lifetime of 20,000 hours have been demonstrated and their commercialization has recently been started by Nichia Corporation in Japan [47]. The typical output power of this laser is 5 mW (and a maximum of 10 mW), peaking at a wavelength typically of 405 nm (range 395~415 nm) at room temperature under continuous wave operation. Its price is currently very high. More recently, an "engineering sample" of a high power laser has been made available and exhibited a maximum output power of 30 mW under continuous wave and 100 mW under pulse operation, and with a peak emission wavelength in the range 395~420 nm, at room temperature.

Most of the current III-Nitride lasers share the following characteristics: the active layer consists of a $Ga_{1-x}In_xN/Ga_{1-y}In_yN$ or GaInN/GaN multi-quantum well (MQW) with an emission peak ranging from 400 to 430 nm, the MQW is not uniform, but has a quantum dot-like structure. These quantum dots are formed most likely because of indium composition fluctuation and segregation, laser performance is enhanced by Si doping of the wells and barriers of the MQW, the general structure of the laser consists of a separate confinement heterostructure, using AlGaN as the cladding layers, the *p*-type contact layer has a hole concentration in the range of 10^{18} cm^{-3}, the dislocation density in the early generation of III-Nitride based lasers was measured to be higher than 10^7 cm^{-2}, which led to very short lifetime and low output power. It has been demonstrated that much higher output power and much longer lifetimes can be achieved by reducing the dislocation density through lateral epitaxial overgrowth (LEO) and even subsequently removing the substrate to leave a thick free standing GaN quasi-substrate. However, there still remain many fundamental issues that need to be addressed, if only to explain to why Nichia Corporation has remained so much ahead of worldwide competition.

First, there is currently no real understanding of the lasing mechanism in III-Nitride lasers. There is experimental evidence that recombination in the MQW active layer is enhanced in these laser diodes by self-formed quantum-dot like structures, or by localization of excitons by potential fluctuation [48, 49, 50, 51, 52]. Theoretical work is necessary to study how these structures are affecting material and modal gain [53], recombination efficiency, emission wavelength (tunable by adjusting the dot or potential feature sizes), and how lasing can be improved by intentionally controlling the formation of such structures. Secondly, the mechanism for the formation of the aforementioned quantum-dot structures or local potentials is also unknown. Is it due to the intrinsic nature of GaInN ternary alloys since compositional modulation due to phase separation would be energetically favored in this material system? [54] Or is it due to compressive strain introduced by lattice mismatch? The understanding of the mechanism would inevitably lead to better devices.

The effect of doping in III-Nitride based lasers is not entirely clear. Generally lasers have intrinsic active layers in order to enhance carrier diffusion and reduce free -carrier absorption in the active layer. However, Si doping in III-Nitride lasers enhances the laser diode performance [55]. It is believed that the doping effectively screens the piezoelectric field in the MQW active region [56]. The *p*-type doping needs to be increased in order to minimize device resistance. Searching for other dopants seems hopeless because of the deep-level nature of acceptor dopants in III-Nitrides, which may be an intrinsic nature of wide bandgap nitride materials, just like ZnSe-based materials. However, new doping schemes such as the piezoelectric effect, which can enhance the ionization of impurities by built-in electrical field, or tunneling-assisted carrier injection should be studied.

Finally, the failure mechanisms in III-Nitride lasers need to be determined and minimized. Potential causes of failure include heat generation due to high series resistance, dislocations and other threading de- fects, as well as optical damage due to reabsorption of stimulated emission at defects which are formed during growth [57]. Reduction of defects is now rapidly being conducted through lateral epitaxy overgrowth [58]. With the progress of bulk GaN growth either by high-pressure technique or hydride VPE or LEO grown, homoepitaxy of III-Nitride devices may be someday be available.

6. Conclusion

In this paper, the technological achievements of the end of the past decade in the area of wide bandgap III-Nitride semiconductors have been presented. The exceptional physical properties of these materials and their use in numerous optoelectronics applications such as ultraviolet photodetectors and violet-blue-green light emitting devices have been reviewed. The current state of the art and technological challenges of III-Nitride materials have been discussed, including substrate and doping issues. The latest developments in ultraviolet photodetectors, blue and green light emitting diodes, and violet-blue laser diodes have been presented, along with some of the remaining issues which need to be addressed in the future in order to realize higher performance devices.

References

[1] A.D. Bykhovski, V.V. Kaminski, M.S. Shur, Q.C. Chen and M.A. Khan, Pyroelectricity in Gallium Nitride Thin Films, Appl. Phys. Lett. 69 (1996) 3254.

[2] J. Miragliotta, D.K. Wickenden, T.J. Kistenmacher and W.A. Bryden, Linear- and Nonlinear- Optical Properties of GaN Thin Films, J. Opt. Soc. Am. B 10 (1993) 1447.

[3] H.Y. Zhang, X.H. He, Y.H. Shih, M. Schurman, Z.C. Feng and R.A. Stall, Study of Nonlinear Optical Effects in GaN : Mg Epitaxial Film, Appl. Phys. Lett. 69 (1996) 2953.

[4] O. Madelung, ed., Semiconductors: group IV elements and III-V compound, Berlin: Springer-Verlag (1991).

[5] O. Madelung, Semiconductors Basic Data, 2nd ed., Berlin: Springer-Verlag (1996).

[6] M. Leszczynski, T. Suski, P. Perlin, H. Teisseyre, I. Grzegory, M. Bockowski, J. Jun, S. Porowski and J. Major, Lattice Constants, Thermal Expansion and Compressibility of Gallium Nitride, J. Phys. D 28 (1995) A149.

[7] M. Razeghi and A. Rogalski, Semiconductor Ultraviolet Detectors, J. Appl. Phys. 79 (1996) 7433.

[8] P. Kung, A. Saxler, X. Zhang, D. Walker and M. Razeghi, GaN, GaAlN and AlN for use in UV Detectors for Astrophysics: an Update, in: Gail J. Brown and Manijeh Razeghi, eds., Photodetectors: Materials and Devices, SPIE Proceedings Series Vol. 2685, Bellingham, WA: SPIE, 126 (1996).

[9] H. Amano, N. Sawaki, I. Akasaki and Y. Toyoda, Metalorganic Vapor Phase Epitaxial Growth of a High Quality GaN Film Using an AlN Buffer Layer, Appl. Phys. Lett. 48 (1986) 353.

[10] L.T. Romano, B.S. Krusor and R.J. Molnar, Structure of GaN Films Grown by Hydride Vapor Phase Epitaxy, Appl. Phys. Lett. 71 (1997) 2283.

[11] A. Saxler, P. Kung, C.J. Sun, E. Bigan and M. Razeghi, High Quality Aluminum Nitride Epitaxial Layers Grown on Sapphire Substrates, Appl. Phys. Lett. 64 (1994) 339.

[12] P. Kung, A. Saxler, X. Zhang, D. Walker, T.C. Wang, I. Ferguson and M. Razeghi, High quality AlN and GaN Epilayers Grown on (001) Sapphire, (100) and (111) Silicon Substrates, Appl. Phys. Lett. 66 (1995) 2958.

[13] X. Zhang, P. Kung, A. Saxler, D. Walker, T. Wang and M. Razeghi, Photoluminescence Study of GaN, Acta Physica Polanica A 88 (1995) 601.

[14] P. Kung, A. Saxler, D. Walker, X. Zhang, R. Lavado, K.S. Kim and M. Razeghi, $Al_xGa_{1-x}N$ Based Materials and Heterostructures, Mater. Res. Soc. Proc. 449 (1997) 79.

[15] C.R. Elsass, I.P. Smorchkova, B. Heying, E. Haus, P. Fini, K. Maranowski, J.P. Ibbetson, S. Keller, P.M. Petroff, S.P. Denbaars, U.K. Mishra and J.S. Speck, High Mobility Two-Dimensional Electron Gas in AlGaN/GaN Heterostructures Grown by Plasma-assisted Molecular Beam Epitaxy, Appl. Phys. Lett. 74 (1999) 3528.

[16] A. Koukitu, N. Takahashi, T. Taki and H. Seki, Thermodynamic Analysis of the MOVPE Growth of $In_xGa_{1-x}N$, J. Cryst. Growth 170 (1997) 306.

[17] I.H. Ho and G.B. Stringfellow, Solid Phase Immiscibility in GaInN, Appl. Phys. Lett. 69 (1996) 2701.

[18] S. Nakamura and T. Mukai, High-Quality InGaN Films Grown on GaN Films, Jpn. J. Appl. Phys. 31 (1992) L1457.

[19] A. Sohmer, J. Off, H. Bolay, V. Härle, V. Syganow, Jin Seo Im, V. Wagner, F. Adler, Andreas Hangleiter, A. Dörnen, F. Scholz, D. Brunner, O. Ambacher and H. Lakner, GaInN/GaN-Heterostructures and Quantum Wells Grown by Metalorganic Vapor-Phase Epitaxy, MRS Internet J. Nitride Semiconductor Res. 2 (1997) 14.

[20] P. Kung, A. Saxler, D. Walker, A. Rybaltowski, X. Zhang, J. Diaz and M. Razeghi, GaInN/GaN Multiquantum Well Laser Diodes Grown by Low-Pressure MOCVD, MRS Internet J. Nitride Semiconductor Res. 3 (1998) 1.

[21] M. Koike, S. Yamasaki, S. Nagai, N. Koide, S. Asami, H. Amano and I. Akasaki, High-Quality GaInN/GaN Multiple Quantum Wells, Appl. Phys. Lett. 68 (1996) 1403.

[22] K. Hiramatsu, Y. Kawaguchi, M. Shimizu, N. Sawaki, T. Zheleva, Robert F. Davis, H. Tsuda, W. Taki, N. Kuwano and K. Oki, The Composition Pulling Effect in MOVPE Grown InGaN on GaN and AlGaN and its TEM Characterization, MRS Internet J. Nitride Semiconductor Res. 2 (1997) 6.

[23] T. Deguchi, A. Shikanai, K. Torii, T. Sota, S. Chichibu and S. Nakamura, Luminescence Spectra from InGaN Multiquantum Wells Heavily Doped with Si., Appl. Phys. Lett. 72 (1998) 3329.

[24] X. Zhang, P. Kung, A. Saxler, D. Walker and M. Razeghi, Observation of Room Temperature Surface-emitting Stimulated Emission from GaN : Ge by Optical Pumping, J. Appl. Phys. 80 (1996) 6544.

[25] A. Saxler, P. Kung, X. Zhang, D. Walker, J. Solomon, M. Ahoujja, W.C. Mitchel, H.R. Vydyanath and M. Razeghi, GaN Doped with Sulfur, in Defects in Semiconductors ICDS-19, ed. Gordon Davies and Maria Helena Nazaré, Materials Science Forum, vols. 258-263 (Switzerland: Trans Tech Publications, 1998) 1161.

[26] W. Gotz, N.M. Johnson, C. Chen, H. Liu, C. Kuo and W. Imler, Activation Energies of Si Donors in GaN, Appl. Phys. Lett. 68 (1996) 3144.

[27] S. Nakamura, T. Mukai, M. Senoh and N. Iwasa, Ther-

mal Annealing Effects on P-Type Mg-Doped GaN Films, Jpn. J. Appl. Phys. 31 (1992) L139.

[28] H. Amano, M. Kito, K. Hiramatsu and I. Akasaki, P-Type Conduction in Mg-Doped GaN Treated with Low-Energy Electron Beam Irradiation (LEEBI), Jpn. J. Appl. Phys. 28 (1989) L2112.

[29] S. Nakamura, N. Iwasa, M. Senoh and T. Mukai, Hole Compensation Mechanism of P-Type GaN Films, Jpn. J. Appl. Phys. 31 (1992) 1258.

[30] A. Saxler, W.C. Mitchel, P. Kung and M. Razeghi, Aluminum Gallium Nitride Short-Period Superlattices Doped with Magnesium, Appl. Phys. Lett. 74 (1999) 2023.

[31] D. Walker, X. Zhang, P. Kung, A. Saxler, S. Javadpour, J. Xu and M. Razeghi, AlGaN Ultraviolet Photoconductors Grown on Sapphire, Appl. Phys. Lett. 68 (1996) 2100.

[32] D. Walker, X. Zhang, A. Saxler, P. Kung, J. Xu and M. Razeghi, $Al_xGa_{1-x}N$ (0WxW1) Ultraviolet Photodetectors Grown on Sapphire by Metal-Organic Chemical-Vapor Deposition, Appl. Phys. Lett. 70 (1997) 949.

[33] Z.C. Huang, D.B. Mott, P.K. Shu, J.C. Chen and D.K. Wickenden, Improvements of Metal-Semiconductor-Metal GaN Photoconductors, J. Electronic Mater. 26 (1997) 330.

[34] P. Kung, X. Zhang, D. Walker, A. Saxler, J. Piotrowski, A. Rogalski and M. Razeghi, Kinetics of Photoconductivity in n-type GaN Photodetector, Appl. Phys. Lett. 67 (1995) 3792.

[35] Q. Chen, J.W. Yang, A. Osinsky, S. Gangopadhyay, B. Lim, M. Lim, A. Anwar, M. Asif Khan, D. Kuksenkov and H. Temkin, Schottky Barrier Detectors on GaN for Visible-Blind Ultraviolet Detection, Appl. Phys. Lett. 70 (1977) 2277.

[36] J.C. Carrano, P.A. Grudowski, C.J. Eiting, R.D. Dupuis and J.C. Campbell, Very Low Dark Current Metal-Semiconductor-Metal Ultraviolet Photodetectors Fabricated on Single-Crystal GaN Epitaxial Layers, Appl. Phys. Lett. 70 (1997) 1992.

[37] D. Walker, E. Monroy, P. Kung, M. Hamilton, F.J. Sanchez, J. Diaz and M. Razeghi, High Speed, Low Noise Metal-Semiconductor-Metal Ultraviolet Photodetectors Based on GaN, Appl. Phys. Lett. 74 (1999) 762.

[38] X. Zhang, P. Kung, D. Walker, J. Piotrowski, A. Rogalski, A. Saxler and M. Razeghi, Photovoltaic Effects in GaN Structures with *p-n* Junction, Appl. Phys. Lett. 67 (1995) 2028.

[39] D. Walker, A. Saxler, P. Kung. X. Zhang, M. Hamilton, J. Diaz and M. Razeghi, Visible Blind GaN *p-i-n* Photodiodes, Appl. Phys. Lett. 72 (1998) 3303.

[40] E. Monroy, M. Hamilton, D. Walker, P. Kung, F.J. Sanchez and M. Razeghi, High Quality Visible-Blind AlGaN *p-i-n* Photodiodes, Appl. Phys. Lett. 74 (1999) 1171.

[41] D. Walker, V. Kumar, K. Mi, P. Sandvik, P. Kung, X.H. Zhang and M. Razeghi, Solar-Blind AlGaN Photodiodes with Very Low Cutoff Wavelength, Appl. Phys. Lett. 76 (2000) 403.

[42] E.J. Tarsa, P. Kozodoy, J. Ibbetson, B.P. Keller, G. Parish and U. Mishra, Solar-Blind AlGaN-Based Inverted Heterostructure Photodiodes, Appl. Phys. Lett. 77 (2000) 316.

[43] A. Saxler, K.S. Kim, D. Walker, P. Kung, X. Zhang, G. Brown, W.C. Mitchel and M. Razeghi, Electroluminescence of III-Nitride Double Heterostructure Light Emitting Diodes with Silicon and Magnesium Doped InGaN, in *Defects in Semiconductors ICDS-19*, ed. Gordon Davies and Maria Helena Nazaré, Materials Science Forum, vols. 258-263 (Switzerland: Trans Tech Publications, 1998) 1229.

[44] S. Nakamura, M. Senoh, N. Iwasa and S. Nagahama, High-Power InGaN Single-Quantum-Well-Structure Blue and Violet Light-Emitting Diodes, Appl. Phys. Lett. 67 (1995) 1868.

[45] S. Nakamura, M. Senoh, N. Iwasa and S. Nagahama, High-Brightness InGaN Blue, Green and Yellow Light-Emitting Diodes with Quantum Well Structures, Jpn. J. Appl. Phys. 34 (1995) L797.

[46] S. Nakamura, M. Senoh, N. Iwasa and S. Nagahama, Superbright Green InGaN Single-Quantum-Well-Structure Light-Emitting Diodes, Jpn. J. Appl. Phys. 34 (1995) L1332.

[47] Nichia Corporation.

[48] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto and H. Kiyoku, Longitudinal Mode Spectra and Ultrashort Pulse Generation of InGaN Multiquantum Well Structure Laser Diodes, Appl. Phys. Lett. 70 (1996) 616.

[49] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku and Y. Sugimoto, Room-Temperature Continuous-Wave Operation of InGaN Multi-Quantum-Well Structure Laser Diodes with a Lifetime of 27 hours, Appl. Phys. Lett. 70 (1996) 1417.

[50] S. Nakamura, M. Senoh, .S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto and H. Kiyoku, Subband Emissions of InGaN Multi-Quantum-Well Laser Diodes Under Room-Temperature Continuous Wave Operation, Appl. Phys. Lett. 70 (1997) 2753.

[51] S. Chichibu, K. Wada and S. Nakamura, Spatially Resolved Cathodoluminescence Spectra of InGaN Quantum Wells, Appl. Phys. Lett. 71 (1997) 2346.

[52] Y. Narukawa, Y. Kawakami, M. Funato, S. Fujita, S. Fujita and S. Nakamura, Role of Self-Formed InGaN Quantum Dots for Exciton Localization in the Purple Laser Diode Emitting at 420 nm, Appl. Phys. Lett. 70 (1997) 981.

[53] Y.-K. Song, M. Kuball, A.V. Nurmikko, G.E. Bulman, K. Doverspike, S.T. Sheppard, T.W. Weeks, M. Leonard, H.S. Kong, H. Dieringer and J. Edmond, Gain Characteristics of InGaN/GaN Quantum Well Diode Lasers, Appl. Phys. Lett. 72 (1998) 1418.

[54] I.H. Ho and G.B. Stringfellow, Solid Phase Immiscibility in GaInN, Appl. Phys. Lett. 69 (1996) 2701.

[55] S. Nakamura, M. Senoh, .S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto and H. Kiyoku, Subband Emissions of InGaN Multi-Quantum-Well Laser Diodes Under Room-Temperature Continuous Wave Operation, Appl. Phys. Lett. 70 (1997) 2753.

[56] T. Deguchi, A. Shikanai, K. Torii, T. Sota, S. Chichibu and S. Nakamura, Luminescence Spectra from InGaN Multiquantum Wells Heavily Doped with Si, Appl. Phys. Lett. 72 (1998) 3329.

[57] D.A. Cohen, T. Margalith, A.C. Abare, M.P. Mack, L.A.

Coldren, S.P. DenBaars and D.R. Clarke, Catastrophic Optical Damage in GaInN Multiple Quantum Wells, Appl. Phys. Lett. 72 (1998) 3267.

[58] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, Y. Sugimoto, T. Kozaki, H. Umemoto, M. Sano and K. Chocho, Continuous-Wave Operation of InGaN/GaN/AlGaN-Based Laser Diodes grown on GaN Substrates, Appl. Phys. Lett. 72 (1998) 2014.