Improving the Efficiency of Solid State Light Sources

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OBJECTIVE OF THE PROPOSAL

This proposal addresses the national need to develop a high efficiency light source for general illumination applications. The goal is to perform research that would lead to the fabrication of a unique solid state, white-emitting light source. This source is based on an InGaN/GaN UV-emitting chip that activates a luminescent material (phosphor) to produce white light.

White-light LEDs are commercially available which use UV from a GaN chip to excite a phosphor suspended in epoxy around the chip. Currently, these devices are relatively inefficient. This research will target one technical barrier that presently limits the efficiency of GaN based devices. Improvements in efficiencies will be achieved by improving the internal conversion efficiency of the LED die, by improving the coupling between the die and phosphor(s) to reduce losses at the surfaces, and by selecting phosphors to maximize the emissions from the LEDs in conversion to white light. The UCSD research team proposes for this project to develop new phosphors that have high quantum efficiencies that can be activated by the UV-blue (360-410 nm) light emitted by the GaN device.

SCIENTIFIC ACHIEVEMENTS: DEVELOPMENT OF NEW PHOSPHORS

***Objective*:** The main goal for the UCSD team was to develop new phosphor materials with a very specific property: *phosphors that could be excited at long UV-wavelengths (λ=350-410 nm).* The photoluminescence of these new phosphors must be activated with photons emitted from GaN based dies. The GaN diodes can be designed to emit UV-light in the same range (λ=350-410 nm). A second objective, which is also very important, is to search for alternate methods to fabricate these phosphors with special emphasis in saving energy and time and reduce pollution.

Achievements: The UCSD group has pioneered a method, combustion synthesis, to rapidly produce multicomponent oxides. The combustion synthesis method is based in the use of metal nitrates (oxidizers) and a fuel (urea, carbohydrazide or hydrazine) that initiates a highly exothermic reaction, as described in more detail in [1,2]. As an example of this process, $EuAlO_3:Eu^{3+}$ is synthesized by reacting two precursors, $Eu(NO_3)_3$ and

$Al(NO_3)_3$ using hydrazine as a fuel in a controlled atmosphere which is heated below <200°C to produce the combustion reaction. The powder obtained is red-emitting (λ=610 nm) with strong absorption in the UV (λ= 365 nm). The product is then exposed to a heated ammonia flow which yields $EuAlO_3$:Eu^{2+} green luminescent powders. Thus, a new phosphor material that absorbs efficiently photons in the range λ=250-400 nm and with a broad emission peak centered at λ=525 nm is synthesized.

In this work we also found that combustion synthesis is a powerful technique to develop novel materials. Under pressurized conditions a new monoclinic structure (not reported in the literature) of europium-aluminum oxide has been developed. The luminescent properties of the new monoclinic material $EuAl_2O_4$ are similar to the $AlEuO_3$:Eu^{2+}. This material can be efficiently activated by long UV (350-420 nm) photons which makes it a promising phosphor for applications in solid state white-emitting lamps. A patent disclosure has been submitted to UCSD Technology Transfer & Intellectual Property Services (June 2003).

With the same method is possible to produce Y_2SiO_5:Ce^{3+} a blue-emitting oxide phosphor that is efficiently excited at λ=365 nm. Figure 1 shows these three phosphors excited by UV at a wavelength of 365 nm and the corresponding luminescence spectrum of the blend of these three colors producing a white-emitting phosphor.

Another white emitting phosphor developed in this research project is single host Y_2SiO_5:Ce^{3+},Tb^{3+}. This new composition was made by combustion synthesis of nitrates that reacted with carbohydrazide (fuel) in air. Tb^{3+} emission in Y_2SiO_5 is excited by long wavelengths via an energy transfer from Ce^{3+} to Tb^{3+}. The non-radiative cerium to terbium transfer allows for an increased efficiency and has been found to occur via the inductive-resonant mechanism proceeding from the 5d levels of Ce^{3+} to the $^5D_3$-level of Tb^{3+}, as illustrated in Figure 2 [3]. Tb^{3+}, which is normally excited at 250nm (short UV), can be excited at long UV wavelengths due to this energy transfer. The optimum doping level of cerium has been found to be [Ce]=0.75 at.%. High levels of terbium, [Tb]>3 at.%, show a dominance of Tb^{3+} emission ($^5D_3 \rightarrow {}^7F_6$) with a strong peak at 550nm and a rather brilliant green emission. This allows for $(Y_{0.9625}Ce_{0.0075}Tb_{0.03})_2SiO_5$ to serve as an efficient single host for white emission. Compositions $(Y_{0.9625}Ce_{0.0075}Tb_{0.03})_2SiO_5$ and $(Y_{0.95}Ce_{0.02}Tb_{0.03})_2SiO_5$ were found to have chromaticity close to D_{65}.
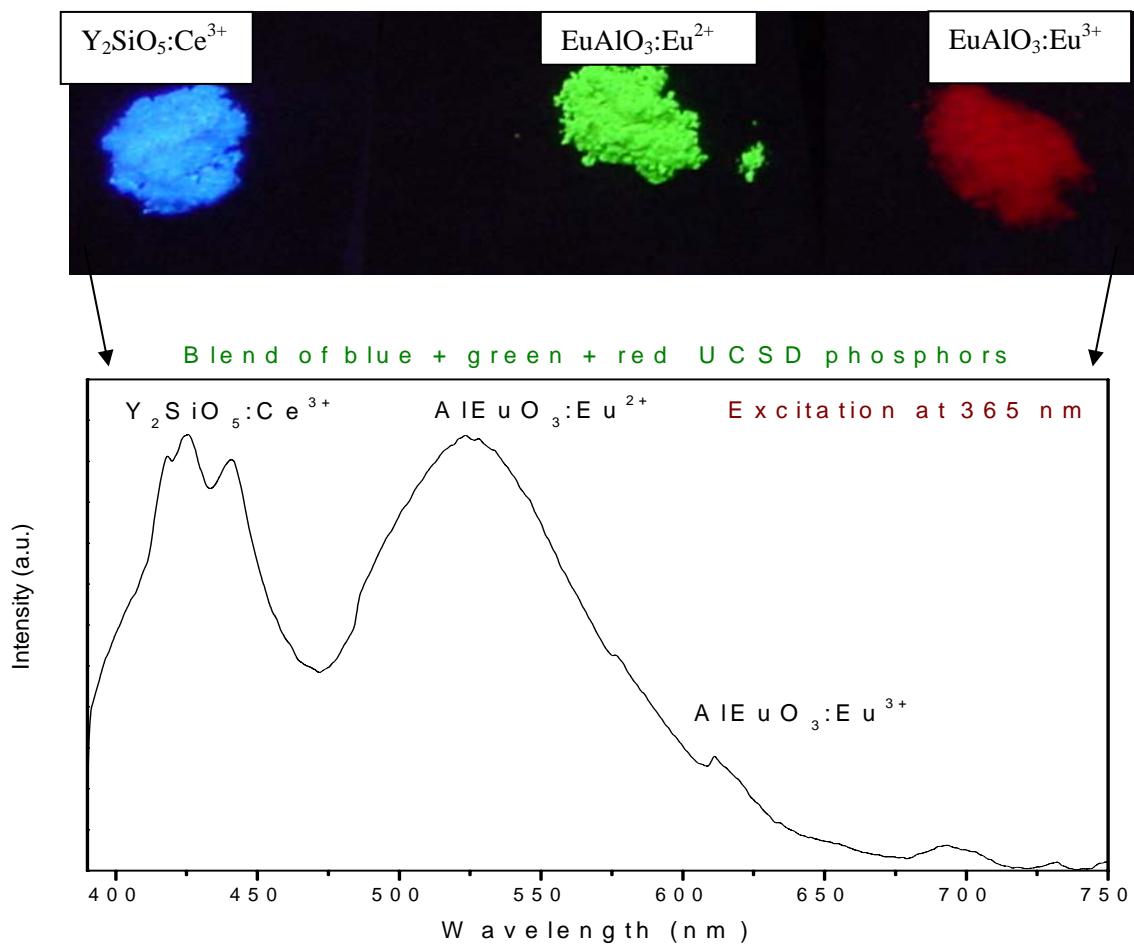
Figure 1. $Y_2SiO_5:Ce^{3+}$ (blue), $AlEuO_3:Eu^{2+}$ (green) and $AlEuO_3:Eu^{3+}$ (red) phosphors produced by combustion synthesis. The luminescence spectrum of the blend of these phosphors produced a white color excited at λ=365 nm.
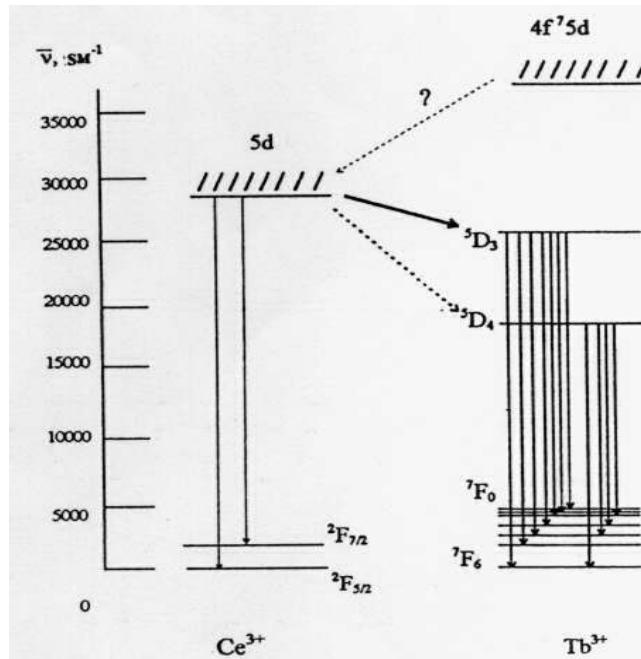
Figure 2.   The energy level diagram for the transfer between Ce^{3+} and Tb^{3+} and emission of the pumped terbium via the ^5D-$^5D_3$-$^7F_6$ pathway.

Figure 3 shows the white emission from $Y_2SiO_5:Ce^{3+},Tb^{3+}$ with long UV wavelength (λ=365 nm). This new material ($Y_2SiO_5:Ce^{3+},Tb^{3+}$) produced by combustion synthesis is clearly more efficient (for white-emission) than other commercial lamp phosphor when exposed to long wavelength UV photons.
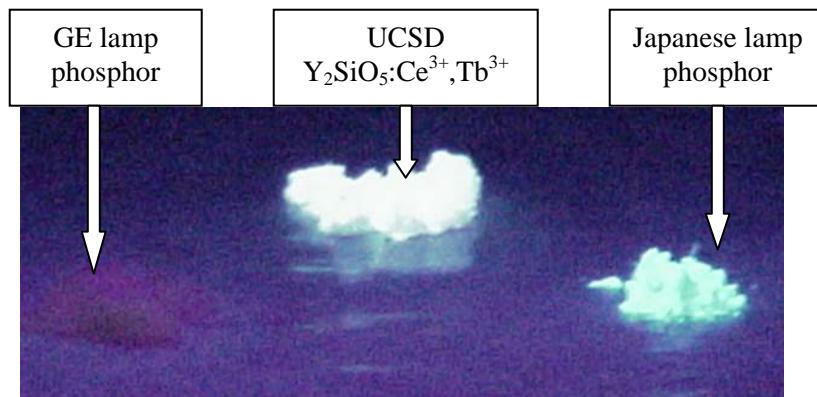
Figure 3. $Y_2SiO_5:Ce^{3+},Tb^{3+}$ white emitting phosphor excited at UV-long wavelength (λ=365 nm) compared with two commercial lamp phosphors.

Another new efficient phosphor (red-emitting) with extended excitation range to long UV wavelengths (max. at 365 nm) was developed. The composition is Y_2O_3:Eu,Bi has an excellent excitation spectrum in the long-UV (320-380 nm) has shown in Figure 4.

Excitation Spectra: Y2O3:Eu=.04,Bi=.005 (220-420nm)
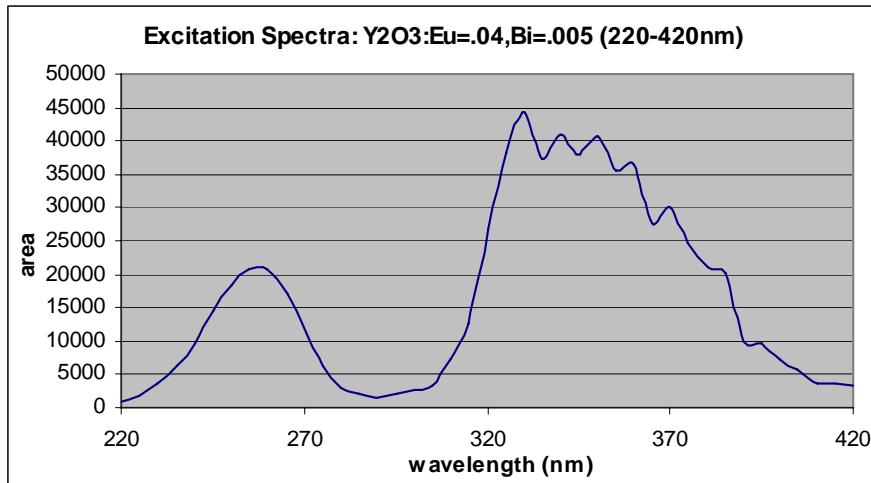
Figure 4.   Excitation spectrum of the new Y_2O_3:Eu,Bi powder phosphor produced by combustion synthesis

Figure 5 show the emissions of the optimum concentration of bismuth at 0.5% (Y_2O_3:Eu,Bi) and Y_2O_3:Eu excited at short UV wavelengths (Fig. 5(a)) and long UV wavelength (Fig. 5(b)). As can be observed, when excited at short-wavelengths (=254 nm) the emission intensity in Y_2O_3:Eu is higher than Y_2O_3:Eu,Bi, while at an excitation of =330 nm, the emission in the new phosphorY_2O_3:Eu,Bi is very high as compared to the Y_2O_3:Eu.

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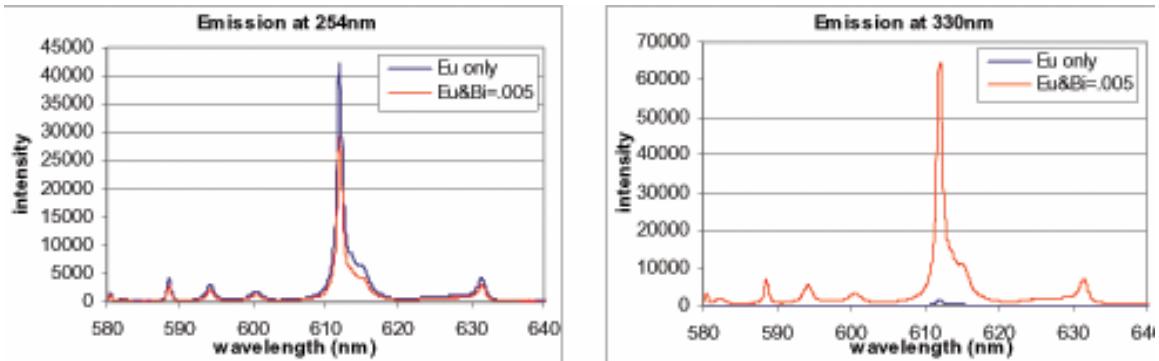
Figure 5.   Emission spectra of Y_2O_3:Eu (Eu=4%) versus Y_2O_3:Eu,Bi (at Eu=4%,Bi=0.5%) at two different excitations. (a) At the characterisitic maximal excitation of 254 nm from Y_2O_3:Eu, and at (b) the characteristic maximal excitation of 330 nm from Y_2O_3:Eu,Bi.

Electrophoretic deposition of white-emitting powders on of GaN-based diodes has been explored. Figure 6 shows the first successful example of direct electrophoretic coating on LED's. Deposition times of < 2 min. provide complete coverage. This appears to be the best method of coupling the phosphor with the diode, in contrast to physical deposition techniques, where high temperature annealing would be necessary after the deposition.
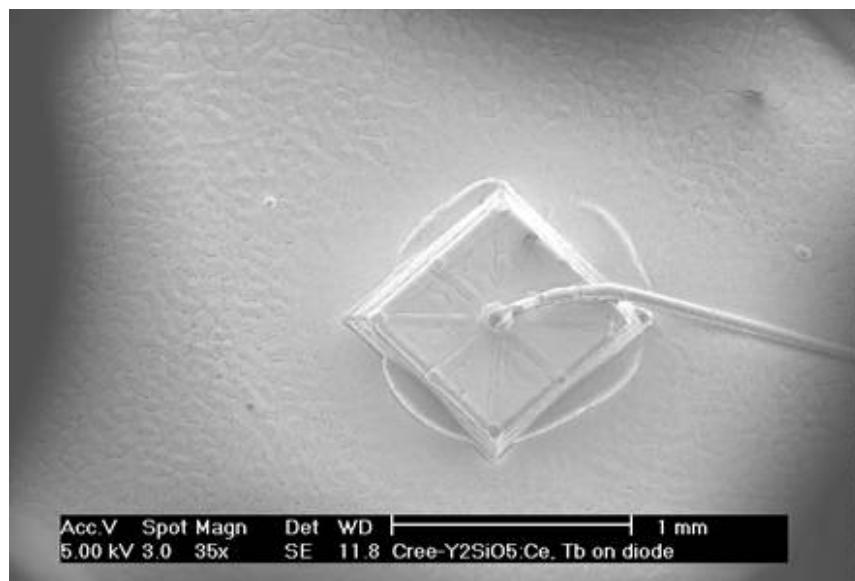
Figure 6.   SEM picture showing the uniform coating distribution by electrophoretic deposition of luminescent phosphors on top of a GaN diode.

MILESTONES

We have met and exceeded all of our milestones.

Month 1-3: White-emitting phosphor composition identification
* Purchase or synthesize compositions, samples to UCB for n measurement

     We have synthesized new compositions of a white-emitting phosphor
* Evaluate and compare PL properties

     `Figures 1, 3 and 5 demonstrate that we have developed high intensity, white

     light   emitting phosphors
* Fabricate targets for thin film deposition

     UCB changed direction

Month 4-6: Optimization of deposition
* Deposition of phosphors onto LEDs provided by UC Berkeley

     Figure 6 shows a phosphor coated LED
* Identify problems associated with small size device

     Using our phosphors, we were able to electrophoretically deposit our phosphors

     on a GaN chip successfully. Size is not a problem for electrophoretic deposition.
* Provide LBNL with phosphor coated LEDs

     UCB changed direction

Month 7-12:   Evaluate reproducibility
* Identify post-processing conditions that may improve properties

     We have discovered that mixing a red-emitter such as Y_2O_3:Eu improves the

     spectral characteristics.
* Epitaxial growth of thin-film phosphors

     UCB changed direction
* Phosphor samples sent to LBNL

     Samples were sent

Conclusions

We have fulfilled our objectives and milestones for this grant. By means a low-cost combustion synthesis we have synthesized new phosphor materials with excellent luminescent properties for possible applications in GaN-based solid-state white-light emitting devices. We have discovered five new phosphors: two green emitting, two red emitting and a white emitting that are efficiently excited by long UV radiation, We have submitted three invention disclosures to the UCSD Technology Transfer Office A new monoclinic structure of green luminescent $EuAl_2O_4$ has been discovered. We found that is possible to produce blue, green and red efficient phosphors than can be excited at long UV wavelengths. Other possible materials for white-light devices were examined and a detailed compositional study were performed and the luminescent properties were evaluated. The electrophoretic deposition of luminescent powders directly on top of GaN LED was also investigated. It was found that electrophoretic deposition is an excellent low temperature method for deposition of phosphor powders, and can be achieved in times < 2 min.

Publications and Conference Presentations Resulting from this Grant

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2) F.E. Ramos, R.Garcia, G.A. Hirata, E.J. Bosze and J. McKittrick "A New Combustion Synthesis Technique for Rare Earth-doped III-Nitride Luminescent Powders*,"* **Modern Phys. Lett. B 15** (2001) 655.

3) O. Ozuna, N. Rakov, F.E. Ramos, G.A. Hirata and J. McKittrick, "Synthesis and Luminescence Properties of Eu^{3+} activated Al_2O_3 and $EuAlO_3$," (submitted to *Advanced Materials*).

4) O. Ozuna, N. Rakov, G.A. Hirata and J. McKittrick, "Luminesence Properties of $(Eu_xAl_{1-x})_2$ Prepared by Low Temperature Combustion Synthesis Technique*,"* Proceedings of 2002 International Conference on the Science and Technology of Emissive Displays and Lighting, **Vol 1**, 2002, pp. 93-96.

5) E.J. Bosze, G.A. Hirata and J. McKittrick, "Combustion Synthesis Effects on the Powder Properties of Cerium Activated Yttrium Silicate Phosphor," Proceedings

of 2002 International Conference on the Science and Technology of Emissive Displays and Lighting, **Vol 1**, 2002, pp. 117-120.

6) G.A. Hirata, F.E. Ramos, E.J. Bosze and J. McKittrick, "Unusual Luminescence Behavior in Eu-activated Europium Aluminum Oxide," Proceedings of 2002 International Conference on the Science and Technology of Emissive Displays and Lighting, **Vol 1**, 2002, pp. 259-262

7) E.J. Bosze, G.A. Hirata and J. McKittrick, "Luminescent Thin Films as Temperature Sensors," Proceedings of 2002 International Conference on the Science and Technology of Emissive Displays and Lighting, **Vol 1**, 2002, pp. 395-398

8) O. Ozuna, N. Rakov, G.A. Hirata, J. McKittrick, "Pressure Influenced Combustion Synthesis of α and γ-Al$_2$O$_3$ Nanocrystalline Powders," (submitted to *Journal of Materials Research*)

9) F.E. Ramos, J. Carver, E.J. Bosze, G.A. Hirata and J. McKittrick, "Long UV-Excited White Emitting Phosphors," SPIE Conf. Proc., **Vol. 4776**, 2002. (in Press) SPIE Conference Proceedings, Optical Science and Technology: Solid State Lighting II, **Vol. 4776**, 2002, pp. 325-330

10) E.J. Bosze, J. Carver, G.A. Hirata and J. McKittrick, "White Light Emission in Rare Earth Activated Yttrium-Oxyorthosilicates," (in preparation)

11) G.A. Hirata, O. Ozuna, N. Perea, J. McKittrick, F. Spada, S. Horiuchi, O. Contreas and E.J. Bosze, "Development of New Luminescent Materials with Strong UV Excitation for Applications in Solid State White Lamps," (Submitted to Nature Materials)

Patent Disclosures

1. E.J. Bosze, G.A. Hirata, and J. McKittrick, "A White-emitting Phosphor Based on a Silicate Host Lattice," Invention Disclosure Application No. SD2003-15. Submitted to UCSD Technology Transfer & Intellectual Property Services (July 2002).

2. G.A. Hirata, E.J. Bosze, F. Ramos, and J. McKittrick, "Long-UV Excited Europium Aluminum Oxide Activated with Eu^{2+} (EuAlO$_3$:Eu^{2+}) Luminescent Powders," Invention Disclosure Application No. SD2003-30. Submitted to UCSD Technology Transfer & Intellectual Property Services (August 2002).

3. G.A. Hirata, E.J. Bosze and J. McKittrick, "Development of a New Europium Aluminum Oxide Monoclinic Structure," Invention Disclosure Application. Submitted to UCSD Technology Transfer & Intellectual Property Services (June 2003).

Industrial Interactions

Industrial contact with **Cree Corp.** and **Durel, Inc.** have been established. In the near future we will discuss the possibility to provide them with our rare earth-doped phosphor materials for applications in electroluminescent solid-state light devices.

References

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2) R. Garcia, G.A. Hirata and J. McKittrick, *J. Mater. Res.*, **16** (2001) 1059.
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UC Berkeley Contribution

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Introduction

The research effort at UC Berkeley was a multi-part approach aimed at tackling three key problems presently limiting the efficiency of GaN-based LEDs for Solid-State Lighting applications. These key problems are: 1) low electrical conductivity of p-type GaN; 2) limited light extraction efficiency from the LED structure; 3) limited internal quantum efficiency due to built-in electric fields in polar InGaN/GaN and AlGaN/GaN quantum wells.

1. Improving electrical conductivity of p-type GaN

The low electrical conductivity of p-type GaN results from the inherently low hole mobility and inherently high acceptor ionization energy in GaN [1]. Furthermore the maximum acceptor solubility is limited due to auto-compensating defects that are introduced at high doping levels in wide-gap semiconductors [2]. Consequences of the low conductivity are reduced wall plug efficiency due to electrical power wastefully dissipated in the resistive p-GaN film and p-electrode, and reduced internal quantum efficiency due to significant heating of the LED when operated at high current. Self-heating effects due to the high p-GaN resistivity also reduces the device lifetime and reliability [3]. The following approaches were investigated in an attempt to improve the conductivity of p-GaN, to be explained in the Results and Discussion section.

1(a). Carbon doping of GaN grown by molecular-beam epitaxy (MBE)
1(b). Carbon and magnesium co-doping of GaN grown by MBE
1(c). Ultraviolet-assisted magnesium doping of GaN grown by MBE

2. Improving light extraction efficiency from GaN-based LED structures

Maximizing the fraction of photons generated within the semiconductor quantum wells that actually escapes out of the device structure is a major challenge for any LED design [4]. Even supposing 100% internal quantum efficiency is achieved, the overall wall plug efficiency of the LED will still be poor if the light extraction efficiency is low. Limitations to light extraction result mainly from total internal reflection at the GaN/air and/or GaN/sapphire interfaces, and absorption of these reflected rays within the device layers. Two approaches were investigated to understand and reduce the effects of these phenomena on GaN LED efficiency:

2(a). Measurement of absorption coefficients of magnesium-doped GaN
2(b). Processing of p-GaN surface to minimize wave-guide effects

3. Improving internal quantum efficiency of LEDs by growing non-polar GaN without detrimental internal electric fields

Heterostructures utilizing GaN-based materials exhibit strong internal electric fields when grown in the C-axis direction, the growth axis used for all LED structures to date. The built-in fields result from the piezoelectric effect due to lattice strain along the polar C-axis of the semiconductor heterostructure [5]. These electric fields have detrimental effects on device performance, the most serious of which is an increase in the radiative carrier lifetime (reducing internal quantum efficiency).

Although the C-axis is polar and so suffers from piezoelectric effects, other crystal planes of GaN, such as the M-plane, are non-polar and do not experience built-in electric fields at heterostructures. Thus GaN-based LEDs grown in non-polar crystal orientations should in principle have substantially higher internal quantum efficiencies. The C-plane is the energetically preferred crystal facet of GaN so it is easier to grow films in the C-axis orientation. But researchers have recently reported growth of non-polar M-plane GaN on unconventional substrates such as R-axis sapphire (rather than C-axis sapphire) [6]. Results achieved at UC Berkeley on growth and p-type doping of non-polar M-plane GaN on R-plane sapphire substrates will be presented in part 3 of the Results and Discussion section.

Results and Discussion

1(a). Carbon doping of GaN grown by molecular-beam epitaxy (MBE)

Carbon is known to have a somewhat lower acceptor ionization energy than magnesium, and recently very high p-type conductivity was reported for zincblende-structure GaN films grown with carbon doping [7]. Besides the potential for higher p-type conductivity, carbon has other advantages over magnesium such as much lower volatility and diffusivity. Zincblende-structure GaN is a metastable phase difficult to synthesize on a production scale, and thus is not considered a viable material for solid-state lighting applications. Research is needed to determine whether the superior performance of carbon as an acceptor for zincblende-structure GaN is also applicable for the normal wurtzite-structure material.

The Berkeley team extensively investigated carbon doping of wurtzite-structure GaN as a function of carbon concentration using different MBE growth conditions and two types

of carbon vapor dopant sources (CCl$_4$ and CS$_2$) [8,9]. However, significant p-type conductivity for wurtzite GaN could not be obtained using carbon as the acceptor dopant. The explanation for the lack of p-type conduction is that carbon dopants form pair defects on the growing wurtzite GaN surface, and the pairing behavior results in a very low fraction of net carbon acceptors compared to the total concentration of carbon in the crystal. This carbon pairing phenomenon apparently does not occur for the zincblende-structure GaN crystal surface [7].

Although no improvement in p-type conductivity was made, an interesting side effect of carbon doping was observed which could be useful in solid-state lighting applications. Figure 1 (following page) shows the photoluminescence spectrum of a representative carbon-doped GaN film. Strong yellow (~560 nm) and blue (~430 nm) luminescence bands are observed, which are related to defects introduced by carbon doping. The relative intensities of the yellow and blue bands can be controlled by adjusting the carbon concentration and/or by adding additional dopants. Films with intense yellow emission and low resistivity (0.1 ohm-cm, n-type) can be grown with C and Si co-doping.
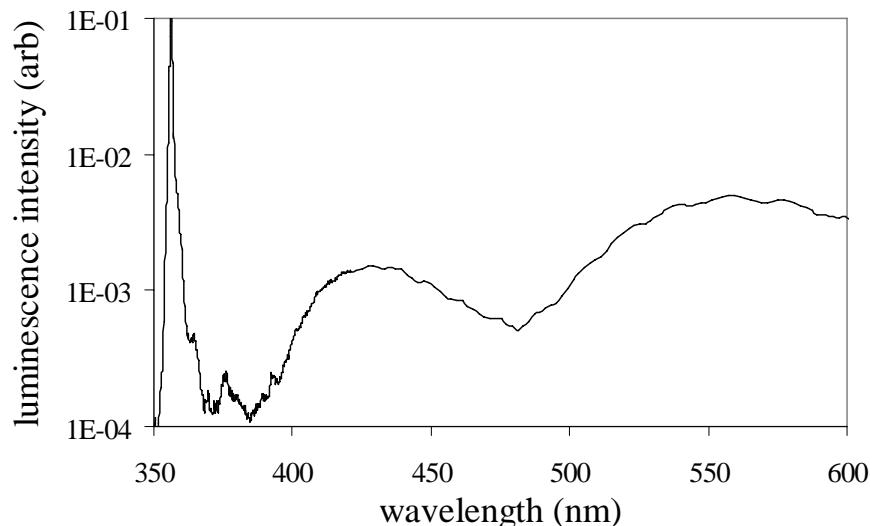

Figure 1.   Photoluminescence spectrum of a GaN:C film measured at 11 K.

This material might be applied as a top n-contact layer in an LED structure, which would absorb some of the blue photons emitted from the InGaN quantum wells and convert them into yellow light. Thus white LEDs could be possible *without* using a phosphor

coating; the phosphors could be replaced by a carbon-doped GaN film to produce yellow emission. Such a design would simplify white LED fabrication and hence reduce cost. Further research is needed on the absorption and emission efficiencies of yellow-emitting GaN:C to evaluate the technological feasibility of this approach.

1(b). Carbon and magnesium co-doping of GaN grown by MBE

The reason for the lack of p-type conductivity in wurtzite carbon-doped GaN was understood to be pairing of carbon defects on the growth surface [9]. These pairs consist of one carbon acceptor (on a nitrogen site) sitting adjacent to a carbon donor defect occupying a gallium or interstitial site. Since the pair consists of one acceptor and one donor, on the whole it contributes no holes for conduction.

It was thought that a flux of magnesium supplied simultaneously with carbon would occupy gallium surface sites with magnesium acceptors and prevent formation of the undesirable carbon pair defects. This carbon and magnesium co-doping approach should then lead to higher p-type conductivity than magnesium doping alone.

Preliminary experiments were made to test this hypothesis. Two GaN:Mg films were grown with all conditions maintained the same except for carbon doping. One sample was doped with a carbon concentration in the range 10^{18} cm^{-3} range, while the other was doped only with magnesium. The magnesium flux was controlled at a fairly low value (effusion cell temperature 335 C) so that the influence of the carbon doping could be seen clearly. The magnesium on its own is not expected to have a high enough concentration to cause significant p-type conductivity.

Photoluminescence spectra for the two samples are shown in Figures 2 and 3 (following page). The spectra are clearly different. The carbon co-doped sample shows a dominant acceptor- bound exciton (A_0X) peak, but the sample with only magnesium doping shows a dominant donor-bound exciton (D_0X) peak as well as deep-level defect luminescence (2.3-2.4 eV). This indicates that the carbon co-doped sample contains a higher concentration of acceptors and is p-type conducting, while the sample with light magnesium doping only is n-type conducting. Unfortunately, due to problems with the experimental apparatus, the electrical properties of the films could not be evaluated, but

in this case the luminescence results are a valid proof of the benefit of carbon and magnesium co-doping. These preliminary results indicate that Mg co-doping could be the key to obtain p-type conduction with carbon.
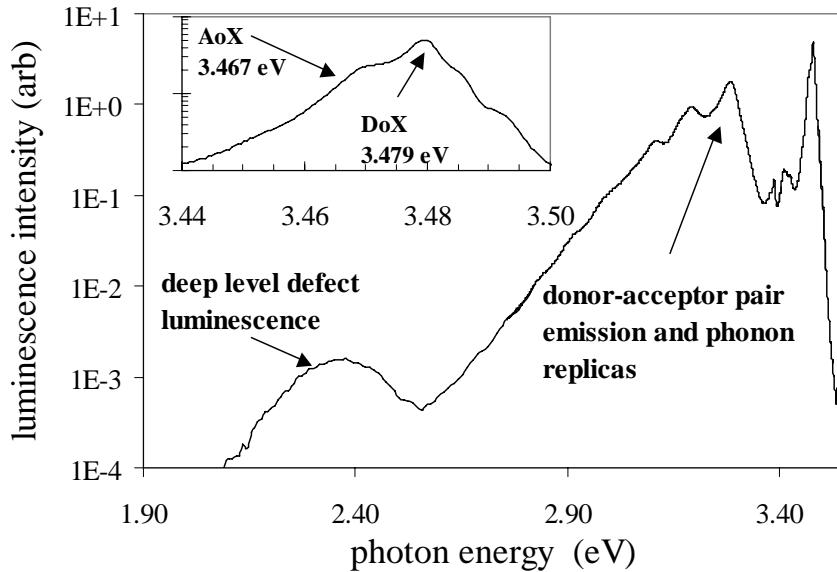

Figure 2.   Photoluminescence spectrum measured at 13 K for lightly-doped GaN:Mg (magnesium cell temperature = 335⌗C)
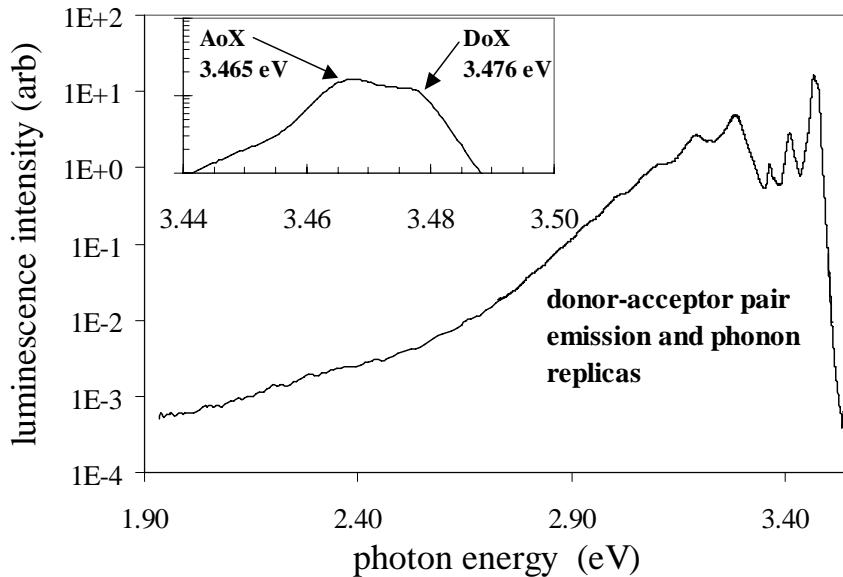
Figure 3.   Photoluminescence spectrum measured at 13 K for Mg and C co-doped GaN, with Mg concentration similar to the sample of Fig. 2

1(c). Ultraviolet-assisted magnesium doping of GaN grown by MBE

For magnesium doping above a critical limit, it is well known that the p-type conductivity actually decreases rather than increases [2]. This phenomenon results from exceeding the solubility of magnesium acceptors; additional magnesium atoms are incorporated as electrically inactive defects when the Fermi level moves close enough to the valence band. Intense ultraviolet irradiation during film growth could in theory circumvent the magnesium acceptor solubility problem by creating a photo-induced electron-hole plasma (EHP). Presence of such an EHP while the GaN crystal is growing would eliminate the auto-compensation phenomena that limit the maximum acceptor solubility under ordinary growth conditions. To assess the feasibility of this idea, heavily Mg-doped GaN films were prepared with the beam from a 200 W mercury arc lamp focused on the 1 x 1 cm substrate during growth. The "illuminated" film was compared to a normal film grown without the Hg lamp. Aside from the UV illumination, all other growth conditions were reproduced as closely as possible.

The near band-edge photoluminescence spectra suggest UV illumination during growth is indeed beneficial, as shown in Figure 4. The illuminated sample is dominated by acceptor-bound exciton emission, as would be expected for a conducting p-type film of high electrically active acceptor concentration. On the other hand, the reference sample shows only a weak acceptor-bound peak and is characterized mainly by free exciton emission. This suggests the majority of magnesium in the reference sample is incorporated as electrically inactive defects, which may also be responsible for its dramatically reduced overall luminescence intensity. Unfortunately, again due to equipment problems, electrical measurements could not be carried out on these samples.
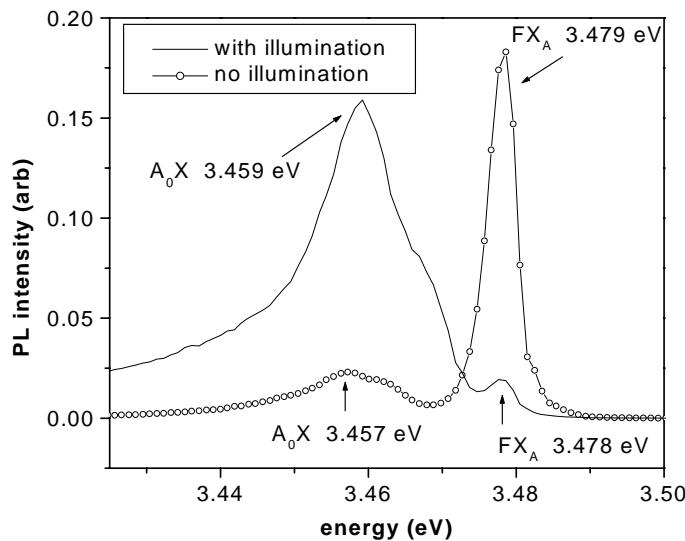
Figure 4.   Near band-edge photoluminescence spectra for GaN:Mg (T_{Mg} = 425⊕C) samples with and without ultraviolet illumination during crystal growth.

It should be pointed out that the effects of UV illumination on GaN:Mg could be quite complicated. For example, photo-induced desorption of the volatile magnesium from the film surface could occur. So while these preliminary experiments are encouraging, additional work is needed to reproduce and better understand the results.

2(a). Measurement of absorption coefficients of magnesium-doped GaN

Heavily magnesium-doped GaN is known to absorb blue and near-ultraviolet light based on the results of photocurrent and photoluminescence measurements [10,11]. However, these types of measurements cannot obtain quantitative values for the absorption coefficient, the parameter that ultimately determines the light extraction efficiency, and hence the most important parameter for optical modeling of the LED. Despite this, there are hardly any reports of optical transmission data for p-type GaN films in the literature.

The optical transmission spectra for p-type GaN:Mg and n-type GaN:Si films were measured using a standard spectrophotometer and compared with the spectra for nominally undoped films. The backs of the sapphire substrates (ordinarily rough) were
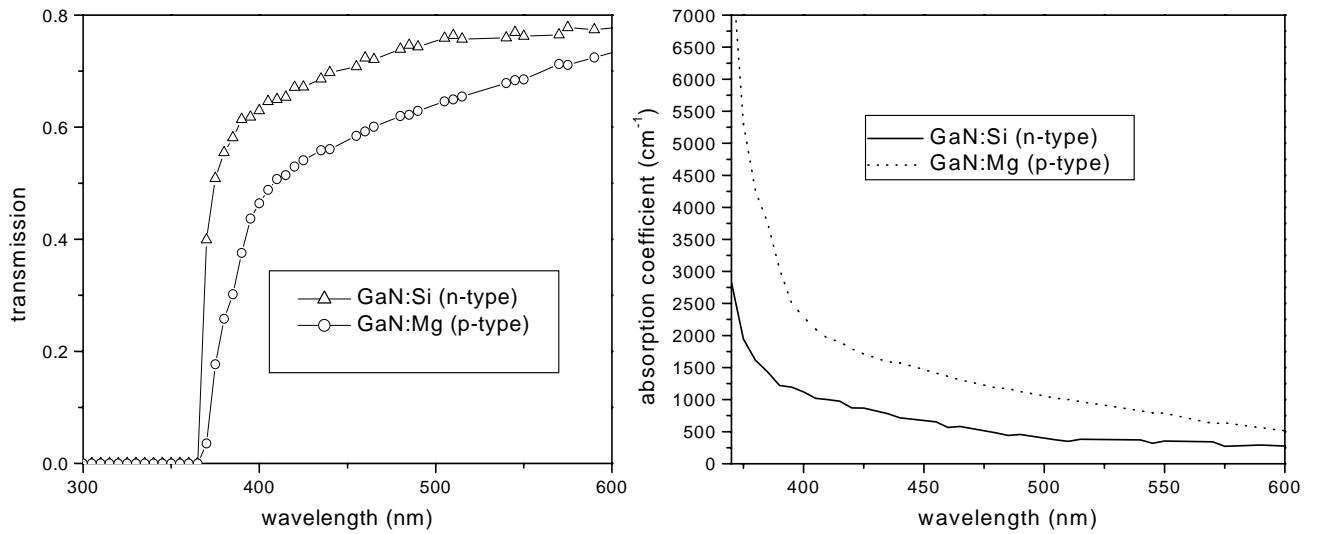
Figure 5.　　**a)** Transmission spectra for n-type and p-type GaN films, 2 µm thick grown on sapphire by MBE; **b)** Absorption coefficients extracted from a)

polished prior to the transmission measurements. The transmission spectra are shown in Figure 5 a) and the absorption coefficients extracted from this data are shown in Figure 5 b). A constant reflectance of 17% was assumed, which may introduce minor errors in the absorption coefficients since the reflectance actually varies slightly with wavelength.

The optical transmission of p-type GaN:Mg films is dramatically different from that of n-type GaN:Si films. The absorption coefficient of GaN:Mg is substantially higher for all wavelengths in the range 350-600 nm. The increase in absorption associated with Mg doping is about a factor of 2 for wavelengths in the 400-450 nm range typically used for LEDs in solid-state lighting applications. Also the steep rise in absorption normally associated with the GaN energy band gap (365 nm) occurs at a lower energy (~400 nm) for p-type films. Thus both the magnitude and spectral dependence of the GaN absorption coefficient are significantly changed by Mg doping.

These results confirm our expectation that significant sub band-gap absorption occurs in p-type GaN layers. In terms of device design, the conclusion is that the p-type layer thickness should be made as thin as possible without compromising the electrical characteristics of the LED. At a minimum, the p-type layer has to be at least thick enough that it is not fully depleted of carriers by the p-n junction, i.e. more than 200 nm.

2(b). Processing of p-GaN surface to minimize wave-guide effects

A major limitation to the external light extraction efficiency of GaN-based LEDs is total internal reflection of emitted light at the various optical interfaces within the device. The internally reflected light is essentially wave-guided through the GaN film, allowing multiple passes for internal absorption. This detrimental effect could be eliminated by roughening one or both surfaces of the "waveguide" so that they become diffuse rather than specular reflectors.

Using plasma etching to roughen the top p-GaN surface has been considered as method to eliminate the waveguide effect and increase external light extraction efficiency. However, it was found that plasma processing of p-type GaN surfaces tends to introduce defects which destroy the p-type conductivity [12]. Therefore this idea was not pursued further.

3. MBE growth and doping of non-polar M-plane GaN

The higher photoluminescence efficiency of AlGaN/GaN quantum wells grown in the M-plane orientation has very recently been confirmed by two different groups [6,13]. However, no electroluminescent devices (e.g. LEDs) have been demonstrated with M-plane GaN yet. The first obstacle toward this goal is proving that p-type doping of M-plane GaN is in fact possible, which has not been reported so far in the literature.

To overcome this problem, the UC Berkeley team has grown GaN films by MBE on R-plane sapphire substrates and characterized the films by *in-situ* reflection high-energy electron diffraction (RHEED), x-ray diffraction, Hall effect, and photoluminescence measurements.

Usually MBE is initiated on C-plane sapphire by exposing the substrate to nitrogen plasma at ~700°C, which creates a thin AlN layer on the surface that acts as a good crystalline template for subsequent GaN growth [14]. However, for the R-plane sapphire substrates this nitridation procedure resulted in a spotty RHEED pattern, indicating roughening of the substrate surface. Such a rough surface is not desirable for subsequent GaN epitaxy. The roughening during nitridation of R-plane sapphire is probably due to the fact that the R crystal plane is terminated by both Al and O atoms, while the C-plane is terminated only by O atoms. On the basis of the *in-situ* RHEED observations, a modified MBE process was developed for growth on R-plane sapphire. The nucleation process consisted only of deposition and annealing of a gallium-rich low-temperature GaN buffer layer [15] *without* nitriding the sapphire substrate. Both silicon-doped films and magnesium-doped films were grown.

X-ray diffraction scans (Figure 6) confirmed the non-polar crystal growth axis for the GaN films. For the films grown on R-sapphire, the (002) reflection for the polar GaN C-axis is completely absent. Only the (110) reflection is observed; this result together with x-ray rocking curves confirms the film is epitaxial non-polar M-plane oriented GaN. Although the desired GaN crystal orientation was achieved, the x-ray results indicate the film structural quality on R-sapphire is poor compared to that of polar GaN on C-plane sapphire. This finding agrees with the results of other groups [6,16] and shows there is still much work to be done before a-plane GaN is optimized for use in LEDs.
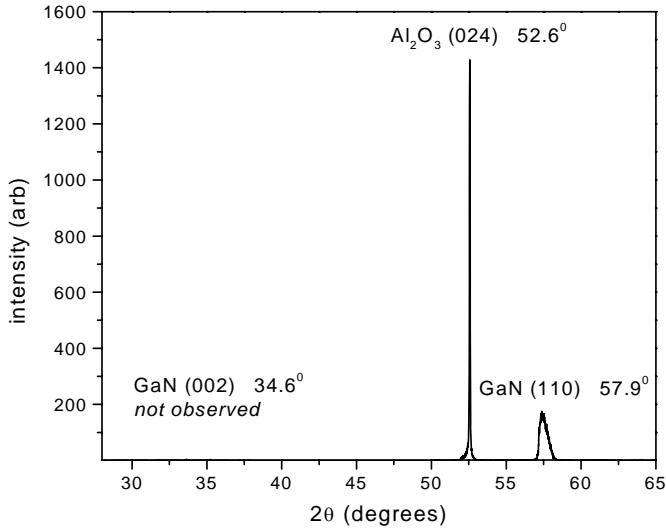
Figure 6.   X-ray normal scan for M-plane non-polar GaN:Mg film grown on R-plane sapphire substrate.

Electrical properties of the films as determined by the Hall effect are shown in Table I. Si-doped and nominally undoped films show n-type conductivity, as is also typical of polar GaN grown on C-sapphire. However, the electron mobility of M-plane GaN is about a factor of 10 lower than for C-plane GaN layers grown by MBE [15]. This is not surprising given the poorer structural quality found by x-ray measurements. On the other hand, the magnesium-doped M-plane GaN films show encouraging electrical properties, with p-type conductivity actually higher than is found for C-plane GaN:Mg grown under similar conditions. This the first report of p-type conductivity in M-plane GaN. The improvement for M-plane GaN most likely reflects a higher sticking coefficient for Mg dopant atoms [17] on the M-plane versus the nitrogen-polar C-plane, leading to a higher acceptor and hence hole concentration. The hole mobility in GaN is inherently low and hence not significantly reduced by the crystal defects in the M-plane layer versus C-plane layers of better structural quality.

Table I. Hall effect results for non-polar M-plane GaN films

Doping	Carrier concentration	Mobility
T_{Si} = 850°C	1×10^{18} cm^{-3} (n-type)	18 cm^2/Vs
T_{Mg} = 350°C	3×10^{17} cm^{-3} (p-type)	5 cm^2/Vs
T_{Mg} = 400°C	6×10^{17} cm^{-3} (p-type)	2 cm^2/Vs

As an independent check for the Hall effect results indicating p-type conductivity, the samples were also characterized by photoluminescence (Figure 7). Due to the rather poor structural quality of the M-plane GaN layers, some key luminescence features such as the exciton peaks cannot be resolved. However, the broad emission band centered around 2.8 eV is similar to luminescence usually observed in p-type GaN:Mg grown on C-plane sapphire. The absence of any yellow luminescence (~2.2 eV) in Figure 7 also supports the fact that the sample is p-type conducting.
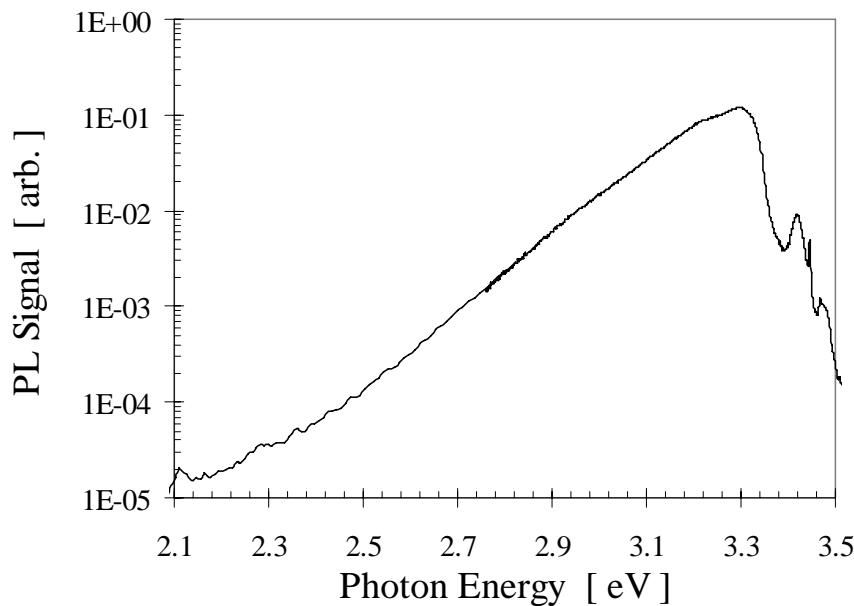

Figure 7.   Photoluminescence spectrum for an M-plane non-polar GaN:Mg film.

Conclusions

A number of approaches have been investigated for improving the efficiency of GaN-based LEDs for solid-state lighting applications. The areas targeted for improvement were the electrical conductivity of p-type GaN layers, light extraction efficiency through

studying and modifying LED optical properties, and internal quantum efficiency through elimination of built-in internal electric fields by changing the crystal growth axis.

Unlike the case for zincblende-structure GaN, in the normal wurtzite polytype of GaN carbon doping on its own was not found to yield significant p-type conductivity. However, carbon doping introduces yellow and blue luminescence bands into GaN which might potentially be useful in solid-state lighting applications. Carbon and magnesium co-doping was found to produce p-GaN films and could perhaps lead to higher p-type conductivity than magnesium doping alone. Exposing the film to intense ultraviolet light during growth appears to be a promising approach to increase the maximum electrically active magnesium acceptor concentration in GaN, and hence increase the p-type conductivity.

The absorption coefficient in p-type GaN in the range 400-450 nm was found to be about twice as large as that of n-type GaN grown under similar conditions. This has important implications for modeling the LED light extraction efficiency and emphasizes the importance of optimizing the p-type GaN layer thickness.

Non-polar M-plane oriented GaN films have been grown on R-plane sapphire substrates. For the first time, p-type conductivity was demonstrated in this non-polar crystal orientation, and the hole concentrations achieved are sufficient for fabrication of efficient LEDs. However, further work on growth optimization is needed to bring the crystalline quality of M-plane GaN on par with that of C-plane GaN. The absence of internal electric fields in quantum wells based on M-plane GaN should ultimately lead to a substantial increase in the internal quantum efficiency of LEDs.

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