Phosphor-free white: the prospects for green direct emitters

Christian Wetzel and Theeradetch Detchprohm
Future Chips Constellation, Rensselaer Polytechnic Institute, Troy NY 12180 U.S.A.
Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy NY 12180 U.S.A.

ABSTRACT

Energy efficiency has been the primary driving force for solid state lighting to replace wasteful incandescent lamps by light emitting diodes (LEDs). Recently, rising cost for rare earth metals has redoubled the push to also replace fluorescent and compact fluorescent lighting. Phosphors in fluorescent lamps heavily rely on rare earth metals and even first generation LEDs use such phosphors, albeit at much lower quantities. The role of phosphors to expand a narrow wavelength source into a wider spectrum is a very lossy process in itself and can be circumvented altogether by second generation LEDs, where the full visible solar spectrum is directly replicated by direct emitting LEDs. We here report progress of our work towards this goal, in particular by the development of high brightness direct emitting green group-III nitride LEDs.

Keywords: solid state lighting, energy efficiency, rare earth element, direct emitting LED, green LED, yellow LED, GaInN-GaN, MOVPE

1. ENERGY EFFICIENCY BY SOLID STATE LIGHTING

Running water and electrical lighting are some of the most basic indicators of rural human development. Beyond the ability to socialize after night fall, artificial domestic lighting provides the opportunity of reading during non-work hours and therefore the basis for education. As an opportunity, a status symbol, and ultimately a necessity, electric lighting is still only in its infancy to reach a majority of the global population in vast rural areas of Central Asia and sub-Saharan Africa.[1] More than a hundred years since Edison's development of the incandescent light bulb, solid state lighting finally addresses its wasteful inefficiency in the generation of visible light.[2] Unlike semiconductor electronics, where function is attained by a design layout of mostly elemental materials, solid state lighting requires semiconductors where the function of light emission is a property of material inherent design. In particular, the group-III nitride semiconductors have proven suitable for high efficiency light emitting diodes (LEDs),[3] yet a tremendous amount of know-how lies in the proper formulation and epitaxial growth approaches to achieve lamps of reliable efficiency, color stability, and reproducibility. In other words, there is no computer code at any level that could reliably predict LED performance. High efficiency LEDs therefore are far from becoming an easily transferrable commodity.

40 years of GaN materials' system development have lead to a highly stable, highly efficient pn-junction for high flux electro-optical energy conversion, when properly executed.[4] Metallurgical alloying of GaN with InN into $Ga_{1-x}In_xN$ allows the variation of the emission wavelength all across the visible spectrum, yet highest efficiency is limited to a region near 450 nm. Therefore, solid state lighting's approach mostly relies on narrow band blue LEDs in combination with complementary phosphors optically excited by the same. The concept is very similar to fluorescent lighting including compact fluorescence lighting where narrow band UV light is down-converted in a phosphor to a rather broad emission spectrum of visible light (Fig. 1b) The detailed composition of the phosphor determines spectrum and efficiency.

For example, 450 nm blue light is commonly achieved by $BaMgAl_{10}O_{19}:Eu^{2+}$ (BAM), making use of Europium; 545 nm green by $LaPO_4:Ce^{3+},Tb^{3+}$ (LAP) using Lanthanum, Cerium, and Terbium; and 610 nm red $Y_2O_3:Eu^{3+}$ (YEO) utilizing Yttrium and Europium.

Rare earth elements in general and their global supply lines have recently become of concern for high technology industry worldwide. The majority of rare earth oxides 29% (by volume) go towards metal alloys such as permanent magnets as used in wind power generators and electric vehicles motors. Electronics in general uses 18%, chemical catalysis 14%, while as much as 12% go into the comparatively narrow aspect of phosphors.[5] By the same account, 67% of all Gallium consumed goes towards integrated circuits and 31% towards optoelectronic devices such as

Eleventh International Conference on Solid State Lighting, edited by Matthew H. Kane, Christian Wetzel, Jian-Jang Huang,
Proc. of SPIE Vol. 8123, 812308 · © 2011 SPIE · CCC code: 0277-786X/11/$18 · doi: 10.1117/12.899259

LEDs. Indium in turn, whose limited supply has repeatedly been voiced in the public, goes to a very fraction of 80% into coatings, such as transparent conductors in highly popular LCD screens.[5]

Significant natural resources of rare earth elements are known in the Southwest of the USA, China, and Vietnam.[5] The mining and production, however, is a cost intensive and potentially environment polluting industry. As it currently stands, 95% of the worldwide production capacity is located in China.[5] Any dependency on such a highly concentrated key source constitutes a major supply line risk. Consequently, recent international trade disruptions of rare earth elements alerted high technology industry in major industrialized nations and drew political attention on the stage of global trade policies.[6]

By transitioning from fluorescent to solid state lighting, it has already been possible to reduce the amount of phosphor materials needed per lumen of generated light. However, in order to realize the desired global energy savings potential of solid state lighting, further drastic reductions in the use of rare earth phosphor elements is dearly needed. Specifically for the use in lighting, the supply of Europium, Terbium, and Yttrium is deemed critically limited.[5] A recent assessment by the U.S. Department of Energy classifies various rare earth elements plus the here considered alternatives of Gallium and Indium along their "supply risk" and "important to clean energy".[5] In reference to the here considered elements, Terbium, Yttrium, Europium, Indium, Cerium, Lanthanum, Tellurium and Gallium are deemed in the third of a possible four levels of importance. Their distribution in terms of supply risk is given with Terbium and Yttrium: 4; Europium and Indium: 3: Cerium, Lanthanum, and Tellurium: 2; and Gallium: 1; where 4 is the highest risk.[5] Considering a period further into the future, namely 5 to 15 years, the supply risk of Yttrium is reduced to 3 and Indium reduced to 2, while the importance of Lanthanum and Cerium is reduced to 2.[5]

Apparently, clean energy technology is to a critical extend depending on the highly risky supply of a few very distinct chemical elements. This situation bears the risk, that the United States could be face severe hurdles in the transformation of its high technology industry into a clean energy technology. Any remedies seem warranted that reduce this risk.

The individual aspects of those transition metals are so specific that a simple replacement with any other or similar chemical element is always accompanied by cuts, if not major cuts in performance. Reduction of the quantities used per measure of performance are therefore more likely paths to reducing the dependency. The conversion from phosphors for fluorescence lighting to phosphors for solid state lighting falls into this category. By dramatically increasing the photon flux density in the phosphor of LEDs, a significant usage reduction of rare earth elements per quantity of light has been achieved. This anticipated shift is reflected in the forecast reduction of importance and supply primarily Yttrium from a supply risk of 3 to 2 over a 5 to 15 year period. This transition, however, also is heavily cost driven, since cost of phosphors likely represent a significant portion of the cost of fluorescent lighting.[5] In fact, Osram and Philips, both world leading producers of conventional and solid state light sources have announced drastic pricing increases for fluorescent and compact fluorescent lamps in September 2011 and justified them by prizing explosion in rare earth elements.[7]

A critical aspect of lighting in general is the quality of the white light and consumers' satisfaction with colors rendered when illuminated by the respective white light source. The spectral sensitivity of the human eye reveals three more or less distinct wavelength channels (Fig. 1a), so that to a first order, stimulation of each of the colors sensations blue, green and red could most efficiently be performed with narrow band light sources operating at 450 nm, 550 nm and 600 nm respectively. In fact, this concept is utilized in the well-known RGB encoding of color television, digital cameras, and computer displays. Yet, those spectral eye response functions also show a certain linewidth and characteristic amount of overlap. These aspects to a very fine detail determine how narrow band optical spectra are being perceived by the human brain. For example, consider optical interference fringes of mother of pearl or water on oil.

Whenever the linewidth of the light source comes close to the spectral linewidth of the optical scattering event, the chromatic equivalent of Moiree fringes must be expected. The shortcomings can be summed up by the experience that a certain spectral feature of an object observed cannot be observed if the light source does not contain the respective wavelength. While humans might favor such an artificial distortion of their vision as evidenced in the preferred purchase of television sets with oversaturated colors,[8] scientific remote sensing of optical events requires a full spectrum light source. In contrast to such novelty seeking preferences, the proper rendering of human skin complexion is a most basic aspect of human social interaction. The myriad variety of makeup color products offered by the cosmetics industry is evidence of the high sociological relevance placed on detailed nuances of the full sun spectrum for the identification of friend or foe.

Therefore, the golden illumination standard without doubt is the spectrum of the sun as it is perceived in human's natural environment, the surface of the earth. We also know that this spectrum varies with time of day and time of year and while the periodic variation itself is being considered a vital necessity for human wellbeing, the recreation of the suns spectrum is not an easy task. Incandescent light bulbs are nearly ideal in providing a continuous spectrum due to their thermal emission properties. The obvious disadvantage is the huge radiation power generated in spectral portions that are not visible to the human eye leading to the low energy efficiency of such light sources.

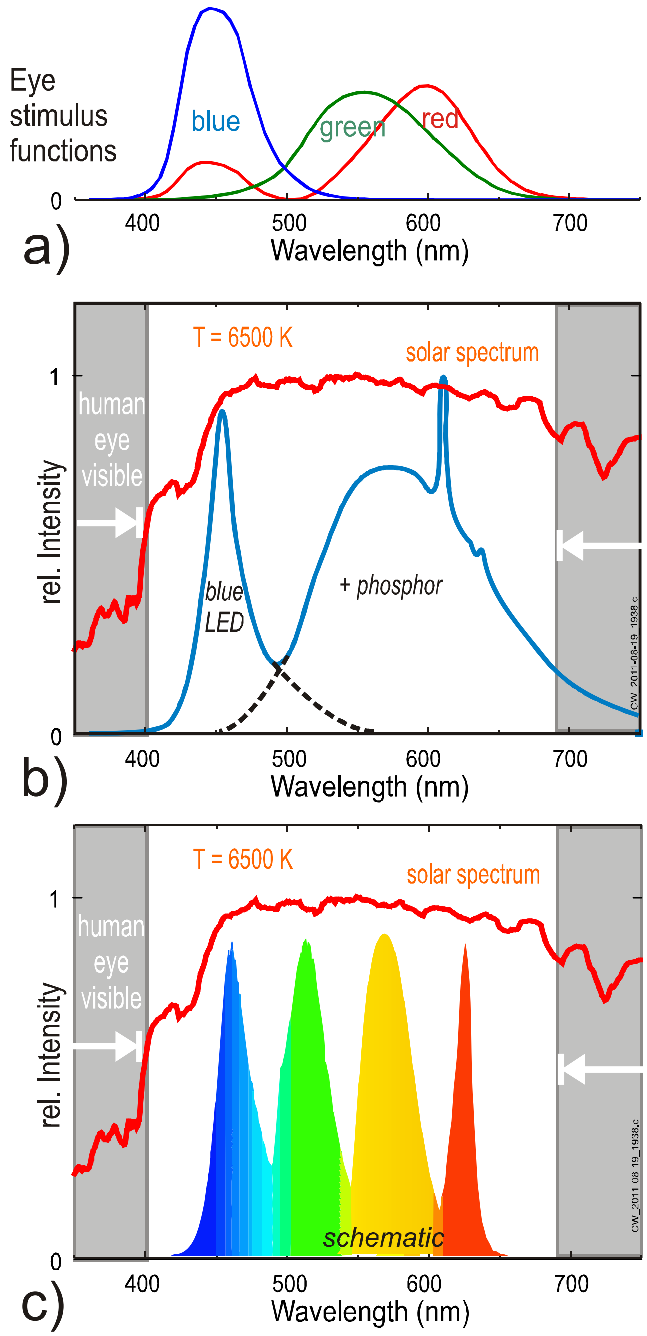

Figure 1 a) Human eye response curves revealing three rather distinct channels of sensitivity. b) The midday solar spectrum on earth and current white light LEDs utilizing a narrowband blue source and broadband yellow phosphors. In advanced designs a narrow band red phosphor is added. c) A schematic of combining blue, green, yellow and red LEDs to provide a more even approximation of the solar spectrum for enhanced color fidelity.

The energy saving aspect of LEDs comes from the rather narrow-band emission in contrast in combination with the opportunity to reach unity quantum efficiency of electron to photon conversion. Furthermore, in ideal cases, the applied bias voltage must lie only marginally higher than the equivalent photon energy. The latter aspect is not possible in phosphor converted emitters due to the built-in large Stokes shift converting primary excitation light into target portions of the emission spectrum. For example, utilizing 450 nm radiation to generate 550 nm is equivalent to 22% of such Stokes losses. Those Stokes losses are the prime obstacle for power efficiencies to reach the potentially high values of the quantum efficiency. In a fully developed direct emitting LED solution in turn a variety of efficient drivers could supply current at the individually necessary voltage to maximize achieve overall system wall plug efficiency.

2. SOLID STATE LIGHTING WITHOUT RARE EARTH ELEMENTS

Therefore, in the next iteration step, the goal must be to bypass the usage of rare earth element phosphors. In fact, bypass the use of phosphors altogether and so avoid the inherently lossy mechanism of photon Stokes shifting between optical excitation and emission wavelengths. The goal must be to drive any wavelength of the visible spectrum with only a minimum of overvoltage, a feat typical for well-developed LEDs. The opportunity to tune the $Ga_{1-x}In_xN$ alloys' emission across the entire visible spectrum is a most natural choice to literally expand the market reach of the widely deployed workhorse of all solid state lighting, the existing $Ga_{1-x}In_xN$/GaN blue LED.[9]

Full spectrum white LEDs could now be achieved by a combination of LEDs of different emission wavelength to compose a spectrum that could approximate the solar spectrum to an arbitrary fine detail. Naturally, the winning solution will be a competitive compromise of spectral portions delivered by individual LEDs with their respective bias voltage. A chosen spectral composition could be impinged by individual power controls or built-in varying chip sizes and wiring serial wiring schemes. One example could be the combination of four LEDs, namely blue, green, yellow, and red LEDs (Fig. 1 c, schematic). A case for such an approach, but utilizing very narrow band emitters has previously been made by the Sandia group.[10] However, thanks to the availability of the $Ga_{1-x}In_xN$/GaN LED technology, in principle, a high number of individual LEDs or a more limited number of broad emission LEDs could be implemented.

The challenges of full spectrum LEDs are well defined and their solution lies square in the intersection of materials science, electrical engineering, and semiconductor physics. The currently achieved highest performance for $Ga_{1-x}In_xN$/GaN LEDs lies at 450 nm, but so far no scientific reason has been compellingly identified, that would exclude other LED emission wavelengths to reach a similar level of performance.

In narrow band blue emitters, external wall plug efficiencies as high as of 44% at 35 A/cm^2 have been achieved, while green values hover in the 20% range.[11] Typically the highest efficiencies are obtained under low injection current density (<10 A/cm^2), while, in order to improve the lumen cost of ownership, current densities of 35 A/ cm^2 and above are required. Under such conditions, efficiency may have reduced to half of the top values, a phenomenon called "droop" of uncertain but heavily studied origin. Nevertheless, such blue LEDs are currently the most widely deployed active element of solid state lighting.

Using highly developed metal organic vapor phase epitaxy in polar c-axis growth on basal plane sapphire and non-polar a- and m-plane growth on bulk GaN we have worked to push LED emission from blue over green to even longer wavelengths while at the same time improving light output powers and efficiency.[9] Our approach has been to avoid the generation of defects, e.g. as seen in cross sectional transmission electron microscopy, and the optimization of layer smoothness and composition uniformity to the highest level possible. Under such approaches, up to 10 quantum wells (QWs) of nominally 3 nm $Ga_{1-x}In_xN$ embedded in nominally undoped GaN barriers have been capped by an $Al_yGa_{1-y}N$ electron blocking layer and embedded in vertical GaN pn-junctions. Typical dopants of Mg and Si are used for the p- and n-layers respectively. Utmost attention was played to the proper formation of the QWs, in particular its uniform and high incorporation of In into the GaInN alloy.

Particular effort further more was paid to avoid the disturbance of the active quantum well layers by any kind of structural defects such as threading dislocations permeating from the substrate interface or misfit dislocations or V-defects generated within the quantum wells.[12-14] The results are progressively increasing light output powers at ever longer emission wavelengths.

The light output power achieved in electroluminescence as a function of dominant wavelength is summarized in Figure 2. For better comparison, measurements have been performed in an easily implemented standard configuration as follows: Full LED wafers were characterized by applying 1 mm diameter In contacts and light output was measured through the sapphire substrate side in the 1 cm diameter orifice of an integration sphere. The fact of this limited collection angle is reflected in the attribute "partial" to light output power. No efforts have been made to enhance the light extraction from the wafer, i.e. by surface roughening or index matching encapsulation. DC current of 100 mA is applied, leading to a geometric current density of some 12.7 A/cm^2. Each symbol represents the center portion of a wafer produced in an individually designed epitaxial growth run. Open red triangles represent results achieved before the critical improvement step, while full blue circles show results with the benefit of these improvements. The crucial distinction of both regimes was the identification of growth schemes that avoid the formation of V-defects within the active QW region. Dashed lines furthermore guide the eye to different development stages with the latest indicating a power at 580 nm yellow that reaches 1/6 of that achieved at 500 nm.

The achievement of such high powers in the very long wavelength range of yellow to orange indicates a substantial progress along the goal to develop full LEDs of any color and wavelength within a single semiconductor system.

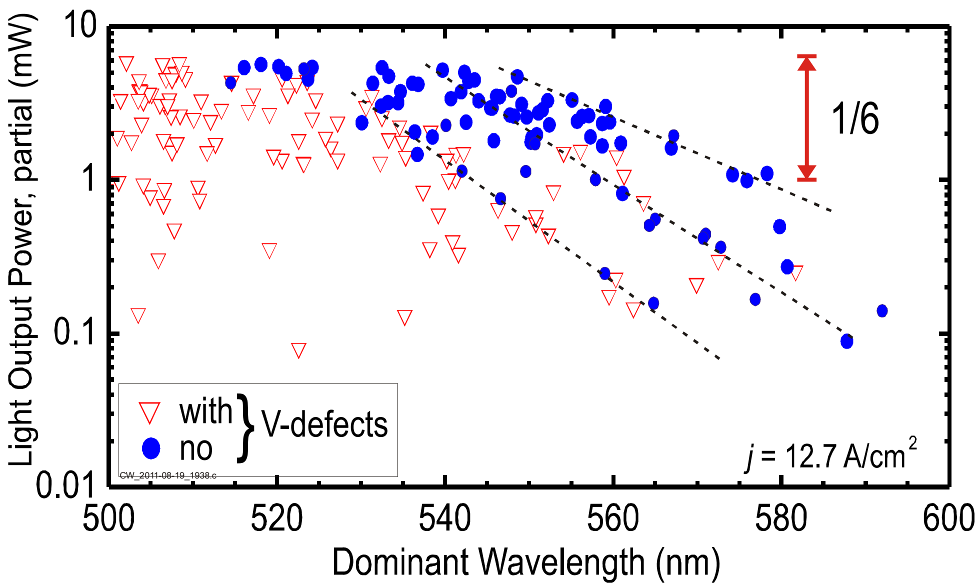

Figure 2 Bare wafer light output performance as measured through the substrate sides versus dominant wavelength. Open triangles show wafer-typical values for epitaxy approaches resulting in V-defect generation. Full circular dots represent epitaxy approaches avoiding V-defects. Orange full circles refer to wafers specifically discussed here. The progressive increase of light output power at the longer wavelengths with further reduction of defects becomes apparent. Parity with blue efficiency becomes a possibility.

3. CONCLUSIONS

As predicted, the global race towards energy efficiency has caught up with lighting. Fluorescence and compact fluorescence lamps, once considered the efficient alternative to incandescent lamps have run into a pricing crisis due to their expansive use of increasingly costly rare earth elements. Solid state lighting by means of energy efficiency LEDs currently uses a hybrid solution, a direct-emitting blue LED and spectrum broadening rare earth phosphors. The real solution to both, energy efficiency and rare earth element avoidance lies in direct-emitting all color or full spectrum LEDs. We here demonstrated that progress has lead to green and yellow LEDs within close reach of the performance levels of blue LEDs.

ACKNOWLEDGEMENTS

This work was supported by a DOE/NETL Solid-State Lighting Contract of Directed Research under DE-EE0000627. This work was supported in part by the Engineering Research Centers Program of the National Science Foundation under NSF Cooperative Agreement No. EEC-0812056 and in part by New York State under NYSTAR contract C090145.

REFERENCES

[1] Meisen, P. and Cavino, N., "Rural Electrification, Human Development and the Renewable Energy Potential of China," Global Energy Network Institute, October 2007 http://www.geni.org/globalenergy/research/china-development/china-development.pdf.

[2] U.S. Department of Energy Solid State Lighting, http://www1.eere.energy.gov/buildings/ssl.

[3] Akasaki, I. and Wetzel, C., "Future Challenges and Directions for Nitride Materials and Light Emitters," Proc. IEEE **85**(11), 1750 (1997), DOI:10.1109/5.649652

[4] Akasaki, I. and Amano, H. "Breakthroughs in Improving Crystal Quality of GaN and Invention of the p–n Junction Blue-Light-Emitting Diode," Jpn. J. Appl. Phys. **45**, 9001 (2006), DOI:10.1143/JJAP.45.9001.

[5] Critical Materials Strategy, U.S. Department of Energy, December 2010, http://www.energy.gov mirror at cr.aiag.org/files/criticalmaterialsstrategy.pdf.

[6] Bradsher, K., "Amid Tension, China Blocks Vital Exports to Japan," New York Times, New York, September 22, 2010 http://www.nytimes.com.

[7] Maier, A., "Seltene Erden verteuern Energiesparlampen," Financial Times Deutschland, Hamburg, August 30, 2011, http://www.ftd.de.

[8] Narendran, N. and Deng, L., "Color Rendering Properties of LED Light Sources," Solid State Lighting II, Proc. SPIE, **4776**, 61, (2002).

[9] Wetzel, C. and Detchprohm, T., "Wavelength-Stable Rare Earth-Free Green Light-Emitting Diodes for Energy Efficiency," Optics Express **19**(S4), A962-A971 (2011), DOI:10.1364/OE.19.00A962

[10] Neumann, S., Wierer, J., Davis, W., Ohno, Y., Brueck, S., and Tsao, J., "Four-color laser white illuminant demonstrating high color-rendering quality," Optics Express **19**, A982-990 (2011).

[11] Solid-State Lighting Research and Development: Multi Year Program Plan March 2011 (Updated May 2011) U.S. Department of Energy, http://apps1.eere.energy.gov/buildings/publications/pdfs/ssl/ssl_mypp2011_web.pdf

[12] Zhu, M., You, S., Detchprohm, T., Paskova, T., Preble, E., A., Hanser, D., and Wetzel, C., "Inclined Dislocation Pair Relaxation Mechanism in Homoepitaxial Green GaInN/GaN Light Emitting Diodes," Phys. Rev. B **81**, 125325 (2010), DOI:10.1103/PhysRevB.81.125325.

[13] Li., T., Fischer, A., M., Wei, Q., Y., Ponce, F., A., Detchprohm, T., and Wetzel, C., "Carrier localization and non-radiative recombination in yellow emitting InGaN quantum wells," Appl. Phys. Lett. **96**, 031906 (2010), DOI:10.1063/1.3293298.

[14] Zhu, M., You, S., Detchprohm, T., Paskova, T., Preble, E., A., and Wetzel, C., "Various Misfit Dislocations in Green and Yellow GaInN GaN Light Emitting Diodes," Phys. Stat. Sol. A **207**, 1305 (2010). DOI:10.1002/pssa.200983645.