Increasing the external quantum efficiency of yellow-green LEDs.

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Abstract:

LEDs, long finding their application only as indicator lights, finally find a place in more common use as high-tech automobile lights. Not only do these excellent devices have extremely long life, but the lack of moving parts or a vacuum (such as that in an incandescent bulb) means that they could be used in many ways that fluorescent and incandescent lights never could. This paper briefly explains these possibilities and then explores a potential solution to one of the many obstacles facing widespread acceptance of LEDs as a general source of lighting. The blue-tint thought to be characteristic of white LEDs gives them a cold feeling that the public would not accept for use in their homes; this problem can be overcome by more completely developing LEDs that emit light in the yellow-green part of the spectrum.

Introduction:

Light: symbol of clarity and knowledge, victor over fear and hate. Festivals are built around it, deities clothe themselves in it, and a certain university's spiritual center was designed for it. Humans see nothing but light. Yet the development of convenient artificial lighting sources is relatively new for humans. For thousands of years, the only source of light was some sort of flame. Not until Thomas Edison invented the incandescent light bulb in 1879 did mankind start using artificial lights commonly. Now, in cities, the night looks nearly like the day.

Still, many problems exist with these lighting sources. Incandescent bulbs, especially, are known to be energy hogs. They, like their flame predecessors, are based on the idea of heating something up so that it emits light as the excited electrons cool back down. Most of the energy used in this process is dissipated simply as heat, instead of being turned into light.

Enter the Light Emitting Diode. Revolutionary lighting devices that work off of injection electroluminescence rather than heat, transferring electrical energy directly to electron potential energy. Whereas with the best current lighting sources, fluorescent lights, the maximum efficiency achievable is 28% by the simple physics of how the devices work, the maximum achievable efficiency of LEDs could reach 100%. Currently they struggle to compete with fluorescent lights for efficiency, but they are in the early stages of development, whereas fluorescent lights have all but reached their limit.

Most essential to LEDs making their way into the general illumination market is the quality of the light. Efficiency and cost of LEDs has continued to sink, but there remain concerns with the quality of the light produced.

Two methods exist for creating white light with LEDs: the use of a phosphor in conjunction with the LED, the same sort of phosphor that is used in a fluorescent light; and a

combination of differently colored LEDs. The first method limits not only the efficiency of the device, requiring that additional conversions between energy types happen rather than one simple electricity-to-light conversion taking place, but lacks also the extreme functionality of the second approach. With the polychromatic technique, wherein two to five monochromatic LEDs are mixed to give white, there exist possibilities never dreamed of with prior lighting techniques. Lights can be mixed differently to give multiple colors of lights, lighting can be adjusted for the environment or person, light-color-quality can be traded off for efficiency, and so on. As LEDs are solid-state devices, no precautions must be taken with them such as those taken with their bulb-laden ancestors. LEDs could eventually find their way into previously unthought-of places, such as clothing and furniture.

The two most efficient LEDs are made with AlInGaN and AlInGaP. The nitride-based LEDs are the heavy-hitters of the blue region, the phosphates dominate the reds. Both of them slack off a bit in the yellow and green area. This is especially problematic because humans are most perceptive of this yellow-green region and it is the region most prevalent in sunlight. For a lighting source to be accepted for general use, it needs to be a good producer of yellow light.

Efficiency in LEDs can mean a lot of things. In this case, it is both the external quantum efficiency and the luminous efficiencies that these two particular LEDs excel in. In general, the two go together. This paper will concern itself with the external quantum efficiency, which is the product of the number of photons created in the LED (internal quantum efficiency) and the number of photons that make it out of the material (light extraction efficiency).

This paper looks at experimentation aimed at improving the material quality of AlInGaN. Whereas AlInGaP fails at producing yellow light due to inherent features of its composition,

AlInGaN becomes a poor-producer of yellow due to poorer quality of the material. This paper looks at two methods of improving the quality of this substance.

First, the possibility of matching the AlInGaN with a better substrate is looked at. The goal of this approach is to increase the light-extraction efficiency and therefore the external quantum efficiency. Three different substrates are tested; a test-diode is constructed using each of the three and they are compared to a commercially available AlInGaN yellow LED.

Second, the possibility of doping AlInGaN with another element is looked into. Computer simulations are set up using four different doping materials. After finding the most appropriate substance, methods of producing this improved AlInGaP are discussed.

With the proposed modifications to AlInGaN, a 50% increase in the external quantum efficiency of yellow-green LEDs should be achievable. This improvement makes polychromatic LED white-light sources cheaper to make and more efficient. Whereas with the previous substances and techniques the only acceptable quality of white light was achievable with four or five monochromatic LED sources, a usable quality of light seems achievable with only three. These numbers are discussed in the closing of the document.

Literature Review

When Henry Joseph Round stumbled upon LEDs in 1907—about twenty years before quantum mechanics was able to attempt to explain them—he understandably had no idea what caused the light. In his letter to the editors of Electric World in February of that year, he stated that about half of silicon carbide crystals would emit yellow light when a potential of ten volts was applied across them. He also noted that when a voltage of one hundred ten was applied, a large percentage of the samples would glow, though not only yellow this time, but also orange, green, or blue. His letter was sent to ask if anyone else knew what might cause the light; his best guess was that the current heated the silicon dioxide, producing light by the only known process at the time: thermoluminescence (Shur 2005). In 1907, the world still exclaimed at the wonder of Thomas Edison's incandescent light bulb, no one cared at all about the inefficiencies of the process. Round's newly discovered light was far too dim for any practical use, and the physics of the time could not explain what happened. Round's inquiry to other scientists seems to have gone unanswered for at least fifteen years, and the discovery of a brand new process, electro-luminescence, was not noticed by most of the world (Steigerwald 2002).

Electroluminescence was not understood not only because of a lack of quantum mechanics but also because theories on material properties were lacking as well. Doping, the process by which a material has small amounts of impurities added to it in order to alter its properties, was not yet understood or consciously done. For this reason, Round would have found it difficult to control the properties of his silicon carbide enough to make a large number of samples that emitted light when only a ten-volt potential was applied.

What Round had unknowingly created was a diode, or a p-n junction. Diodes are formed by joining a p-doped semiconductor and an n-doped semiconductor, hence the term p-n junction.

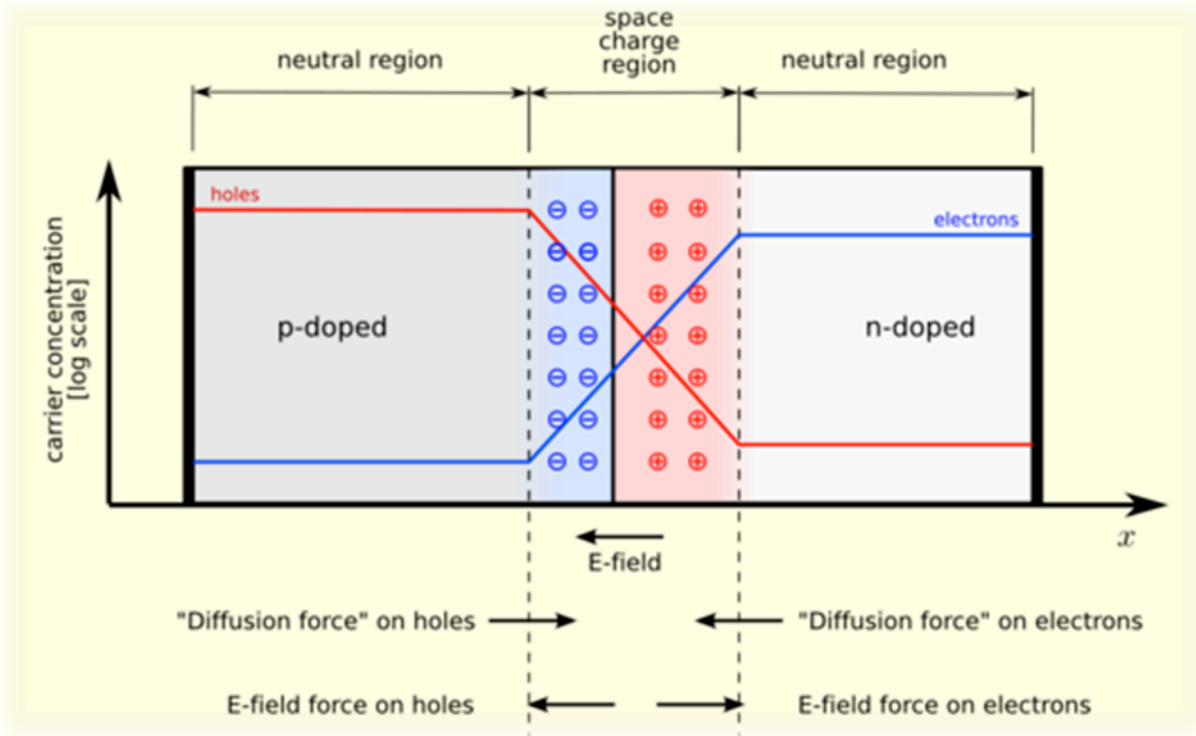

Figure 1: A Schematic of the internal workings of an LED – a p-doped semiconductor and an n-doped semiconductor are put together in a junction, in which holes from the p-doped combine with electrons from the n-doped, releasing energy as a photon. From Wikipedia.

A schematic of this can be seen in Figure 1. P-doped semiconductors have a slight "lack" of electrons, which means that "holes", or atoms that are missing an electron, carry the current. N-doped semiconductors have a slight "excess" of electrons, so that electrons carry current. If the two are joined, current can only flow from the positive to the negative (p-type to n-type), and the holes of the p-type semiconductor will join with the electrons of the n-type semiconductor, releasing energy. This energy is typically released as a photon. With careful tuning of the impurities (that is, with careful doping), the energy, and therefore color, of the photon can be specified precisely (Bergh 2001).

In 1907, no one had much reason to get excited about electroluminescence or the light-emitting diode. Incandescent bulbs were not yet thirty years old, and LEDs had a long way to go

to catch up to them. But one hundred years later, incandescent bulbs seem cumbersome and inefficient. Most of the current running through the filament is converted to heat rather than light, as the generation of heat is actually what causes the light (Bergh 2001). The tungsten filament must be heated to extremely high temperatures (about 2500°C) in order to emit light, and if oxygen is present the filament will burn: thus, a bulb is necessary to shield the filament from oxygen (Mehmet 2002). LEDs have no such restrictions. Since electroluminescence causes direct conversion of current into light without heat acting as a middleman, it is possible (though not yet feasible) to have an LED in which one hundred percent of the energy put into the device is transferred to usable light (Gessman 2001).

Not only do these improvements on their predecessors make LEDs attractive economically, but also broaden the possible uses of light. An example of how LEDs can be utilized where ordinary lights never could can be seen at http://graffitiresearchlab.com/?page_id=6, a screen-shot of which can be seen in Figure 2. In this video, LED "throwies" are made with multiple-colored LEDs, a battery, and a magnet. Many of these devices are then taken and thrown against a metal wall. Eventually, the wall is decorated

Figure 2: LED Throwies (taken from http://www.instructables.com/id/LED-Throwies/)

with an eye-pleasing assortment of colored spots. This simple endeavor would not have been possible with previous lighting technologies for three reasons: 1) old lighting technologies are heavy, 2) they require more power than LEDs (adding even more weight, due to larger batteries), and 3) they have bulbs, which break when thrown against walls. With time, many more applications of shock-resistant lighting technologies will be developed, presumably with benefits not only in style but in technical advancement (Tsao 2004).

Despite the purposeful creation of an LED in the 1920's by the Russian scientist Oleg Vladimirovich Losev, these benefits did not become apparent to scientists until the 1950's when a researcher at Radio Corporation of America discussed the infrared-light-emitting capabilities of gallium arsenide. In 1962, Nick Holonyak Jr. developed a red-colored LED, earning him the distinction of the "father of the light-emitting diode". One of his graduate students, ten years later, developed the first usable yellow LED and then red and orange LEDs that were ten times brighter than his old professor's. Decades later, a blue LED was finally developed by Shuji Nakamura, leading to white-appearing LED lamps which finally went into production in 1993 (Shur 2005). Prior to this time, LEDs were mainly used as indicator lights in all manner of applications, such as guitar pedals and the Nintendo Gameboy (Mehmet 2002).

Nakamura was able to develop the high-brightness blue LED only after advances in materials science. Indium gallium nitride (InGaN) was the substance used, and techniques for controlling the amount of impurities were necessary so that the same color was generated from each sample. The advance, in this case, involved the growing of GaN on a sapphire substrate (Shur 2005). Thanks to this advancement and others like it, LEDs are finally finding uses in general lighting applications.

Breakthroughs such as Nakamura's come with new complications, however. The larger LEDs used in such devices require greater currents to drive them, causing the p-n junction to heat up. Whereas incandescent bulbs operate at extremely high temperatures already, LEDs operate most efficiently at temperatures below 120°C. Not only is life-span is significantly shortened when this temperature is exceeded, the efficiency is lowered and the color shifts more toward longer wavelengths. New methods of cooling and new materials for LED substrates will need to be developed to combat this problem (Mehmet 2004).

Nakamura utilized the technology on which fluorescent lamps operate for his white LED lamp, using the blue light from his LEDs to excite yellow phosphors (Shur 2005). This is not the only method by which white light can be generated with LEDs. Organic light-emitting diodes can be utilized: these have the ability to emit white light intrinsically. Or, third, a cluster of multi-colored LEDs can be utilized, wherein the light from all of them combine to give white (Bergh 2001).

LED-phosphor combinations were a convenient way of making white light for Nakamura because the technology had already been in use for years in fluorescent lights. The yellow-emitting phosphor in this case was cerium-doped yttrium-aluminum garnet (YAG:Ce), which is still typically used in LED lamps utilizing this technology.

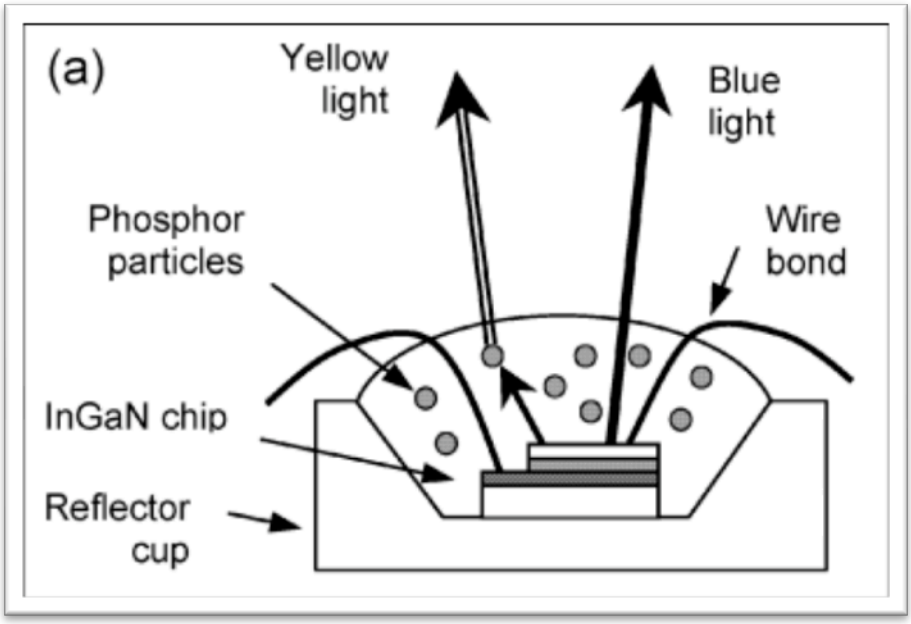

Figure 3: How an LED-phosphor-combination lighting system works (courtesy of Shur, Michael S., A. Z. (2005). Solid-State Lighting: Toward Superior Illumination. *The IEEE , 93* (10).)

Operation proceeds fairly simply: the LED emits blue light into a resin filled with the YAG:Ce phosphors. Some of this light simply travels through the resin without any interaction with the phosphors, the rest will collide with the phosphors, as seen in Figure 3. When the blue photons collide with the phosphors, the phosphors will emit yellow photons. Some energy is lost in this conversion as heat, limiting the maximum efficiency of devices with this architecture, though this is not a very large concern right now. More distressingly, though blue light and yellow light will combine to appear white to the human eye, red is notably absent. Consequently, a red object, when observed in the light given off by one of these devices, will appear to be nearly black (Shur 2005). For certain applications this is acceptable, but it is obviously undesirable to use such light for general purposes.

Organic light emitting diodes can be split into two categories, those with lighter, smaller organic molecules, typically denoted as OLEDs, and those with larger, more polymeric materials, called light-emitting polymers, or LEPs. These technologies function essentially the same way as their inorganic cousins, but the materials making up the p-type and n-type junctions are organic. These technologies share all of the benefits of inorganic LEDs, but have some added advantages and some serious disadvantages (Bernius 2000).

LEPs have the magnificent advantage of being able to be printed onto substrates, so that the manufacturing of devices using LEPs could be done in little time for minimal cost. Light emitting-polymers are also flexible, meaning that devices made with them could also be flexible, allowing for applications of lighting in previously impossible situations, such as t-shirts with changeable graphics and roll-up screens. Unfortunately, LEPs are short lived, compared not only with inorganic LEDs but also with other lighting technologies used in screens. Whereas liquid crystal displays, plasma displays, and LEDs will last about 60,000 hours, light-emitting polymers

have a life of about 5,000 hours. However, there is no current theoretical model that really explains organic LEDs, which means that improvements on their longevity have no predictable ceiling. With time, LEPs could be made that have a comparable lifespan to other such technologies (Bernius 2000).

Lower-weight OLEDs avoid this major downside of decreased life-expectancy but are not as easy to manufacture. Unlike inorganic LEDs which emit basically monochromatic light (that is, light mainly of one wavelength), OLEDs emit light over a spectrum. However, no OLED has yet been found that emits light over the entire visible spectrum. Due to the fact that no competent theory explaining them exists, it is difficult to know what sort of material improvements must be made to tailor an OLED that emits light over this spectrum. Typical OLEDs currently emit light over about one third of the visible spectrum, so that white OLED lamps must employ the use of three different OLEDs which emit over the red, green, and blue spectrums (D'Andrade 2004).

To create white light with regular inorganic LEDs, the concept is much simpler. All that needs to be done is to combine at least three monochromatic light sources so that the combination appears white and will illuminates objects accurately. Theoretically, a much greater control of the light is obtained, with light color being determined by simply flicking different switches (Bergh 2001). No prior lighting technology was this flexible.

Of course, actually executing this concept is quite complicated. First of all, making acceptable-quality white light using only three LEDs is difficult for now, largely due to a lack of high-brightness yellow-green LEDs. Therefore, for acceptable light quality, four or five LEDs are typically needed. Though the additional need for energy and the weight that come with the added LEDs is undesirable, it also allows for additional control. Not only can the color be

controlled with such a system, but the quality of the light can be traded off for efficiency (Shur 2005). If one is merely cleaning or working at a computer, three LEDs would suffice to illuminate the room; energy would be saved. On the other hand, if painting or a surgery are to be performed, all five LEDs could be switched on, giving a much more accurate representation of the environment.

Another concern with this color-mixing technique is the variable intensity of colors. Some LEDs last longer than others, which obviously causes problems if, say, a green LED dies, leaving only blue and red behind. In addition to this problem, which is not that alarming considering the longevity of LEDs, during an LEDs life the intensity of the light given off will vary, meaning that the white light given off by a lamp will sometimes be tinted (Bergh 2001). If the blue LED happens to be more intense at a certain time while the red and green are of equal intensity, the light will have a blue tint. Even more problematic, the intensity and hue of LEDs can vary with temperature also, causing the white light to have different tints at different temperatures. This can be overcome with a stabilizing microcontroller, but this uses extra energy. This will take a great deal of cleverness to be overcome (Shur 2005).

Light quality is of utmost concern when designing a white-light source. Of most interest in this field is how the light will render various colors. A painting will look different under fluorescent lights than under the sun. Different colors of light are more prevalent in each of these sources, yellow being more prevalent in sunlight and blue being more prevalent in fluorescent lights. Commonly, the Color Rendering Index (CRI) is used to rate the quality of a light source, but the accuracy of this method is disputable. Though everyone agrees that the painting looks *different* under different sources, not everyone agrees on which light is *best* for the painting. Light quality and color-rendering are largely subjective measurements. However, the human eye

is most sensitive to yellow light, and everyone agrees that the best light source is the sun (Color Kinetics Incorporated). Artificial light sources must emulate the sun's attributes for the most pleasing response from people. This makes yellow a key player.

Interesting that yellow should be the color most needed in LEDs when the first discovery of electroluminescence was in a yellow SiC LED. As has been the case for the entire history of this technology, the solution will come in the form of an improvement in materials science. Better explanations of the processes behind organic light-emitting diodes could be conceived, allowing for better material manipulation and better white light. Or improvements in non-organic materials could be made, leading to better yellow-green LEDs and therefore better color-mixing for use in a white light device. Energy savings alone make the arrival of these breakthroughs internationally anticipated, and the latter improvement will allow for the greatest customizability and control of light sources the world has ever known.

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An article providing an excellent introduction to the idea of solid-state lighting, it's benefits and the challenges that must be overcome for it to be feasible. Included is a brief history of SSL, the economic incentives for SSL, making white light with SSL, LED performance details, and an overview of OLED technology.

Bernius, Mark T., M. I. (2000). Progress with Light-Emitting Polymers. *Advanced Materials , 12* (23), 1737-1750.

This paper examines research endeavors aimed at landing light-emitting polymers used in LEDs into commercial applications. The materials science and engineering related to this field is discussed as well as the reasons that so many researchers are interested in LEDs.

D'Andrade, Brian, S. F. (2004). White Organic Light-Emitting Devices for Solid-State Lighting. *Advanced Materials , 16* (18), 1585-1595.

D'Andrade and Forrest discuss white organic LEDs (WOLEDs) and the initial reasons for researching them and where they stand now. After outlining how many improvements in the technology were made, the authors explore advantages and disadvantages of the technology and note why exactly the technology is not yet in wide-spread use.

Gessman, Th. , E. F. (2004). High-efficiency AlGaInP light-emitting diodes for solid-state lighting applications. *Journal of Applied Physics , 95* (5), 2203-2216.

Gessman and Schubert discuss the particular LED material AlGaInP and the major categories of structures made from it. They discuss why this material will be important in the exciting future of LED lighting. They go through a sort of history of LED-making with this material and explain more recent developments such as TS-LEDs and TF-LEDs and what makes them superior to older structures. Finally, recently-developed ODRs are explained and the authors show how they significantly outperform older methods of using AlGaInP, such as Bragg reflectors.

Mehmet, Arik, C. B. (2004). Thermal Management of LEDs: Package to System. *Third International Conference on Solid State Lighting* (pp. 64-75). Bellingham, WA: General Electric Company.

Arik explains how the move toward general-illumination LEDs have led to the need to investigate the thermal properties of LEDs and how this is a key design parameter for them. Two types of chips are looked at specifically: SiC and Sapphire chips, and the SiC chips are found to have much better thermal performance. Passive air-cooling for conceptual LED lighting systems is then examined for effectiveness.

Mehmet, Arik, J. P. (2002). Thermal Challanges in the Future Generation Solid State Lighting Applications: Light Emitting Diodes. *Inter Society Conference on Thermal Phenomena* (pp. 113-120). Niskayuna, NY 12309: General Electric Company.

This article discusses the transition of LEDs from indicator and special-situation lights to general-purpose illumination and how this has moved them from producing low amounts of heat that don't need to be specifically dealt with to a compelling design concern. The authors explain level-1 packaging and developments in LED power packaging due to the increased current used to drive LEDs.

Narendran, N., Y. G. (2004). Solid-state lighting: failure analysis of white LEDs. *Journal of Crystal Growth* , 449-456.

The authors examine why white LEDs might have significantly less life than their non-white counterparts. It first examines the common 5mm epoxy-encapsulated phosphor-converted white LED and what past studies have hypothesized causes its shortened life, namely, junction heat and amount of short-wavelength emission. After testing two groups of white LEDs for each of these conditions, it was found that both of these factors affected the life-span, but that the temperature effect was much greater than the short-wavelength effect. A second method of degradation is proposed, that being that the phosphor medium surrounding the die causes some light to circulate between the phosphor layer and the reflector cup. A second experiment was performed and it was found that LEDs with the phosphor layer further from the die wore out more slowly.

Shur, Michael S., A. Z. (2005). Solid-State Lighting: Toward Superior Illumination. *The IEEE , 93* (10).

Shur goes over the history of lighting and the move to LEDs and the benefits and challenges therein and then focuses on comparing two ways of producing solid-state white light: phosphor LEDs and multichip LEDs. Benefits/uses of each are considered.

Steigerwald, Daniel A., J. C. (2002). Illumination with Solid State Lighting Technology. *IEEE Journal on Selected Topics in Quantum Electronics , 8* (2), 310-320.

After going over incentives for making solid-state lamps in the first place and potential future markets for them, Steigerwald discusses current illumination-capable LEDs, 100+ lumens of white light, and challenges that remain to be overcome.

Tsao, J. Y. (2004). Solid-state lighting: lamps, chips, and materials for tomorrow. *Circuits and Devices Magazine, IEEE , 20* (3), 28-37.

This article gives an overview of lighting technology and where it could go in the future with a focus on inorganic LEDs rather than OLEDs, reasoning that regular LED technology is closer to use in general illumination. A description of some very simple yet very important lamp, chip, and material design choices that will need to be made as the race to general illumination continues.