

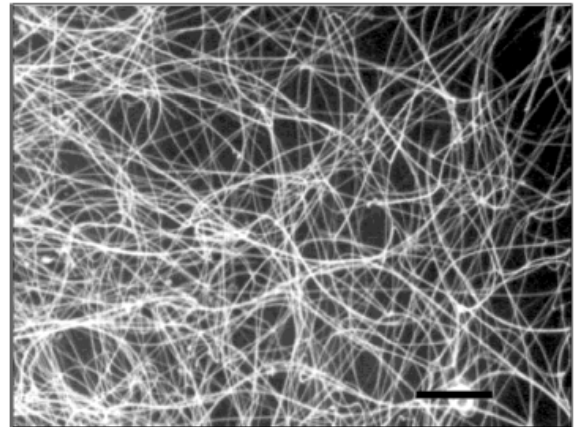
A History of Solid State White Lighting, the Evolution of GaN Nanowires, and New Potentials for White Light Generation Using InGaN Nanowires

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Introduction

This paper will develop the motivations behind my current research at the University of California—Santa Barbara.¹ Doing so in three stages, I will first describe the development of solid state white lighting, particularly white light emitting diodes (LEDs). I will detail their benefits, but perhaps more importantly I will discuss their current shortcomings and where this technology needs to be improved. Next, I will report on the evolution of gallium nitride (GaN) nanowire growth, and the particular aspects of these materials that are potentially useful for lighting applications. Finally, I will demonstrate how these two areas of research can be brought together (hopefully for mutual benefit!), and I will discuss our attempts to adapt current GaN nanowire growth to InGaN nanowires. I will detail the theoretical advantages of using InGaN nanowires in a solid state white lighting context and comment on possible difficulties in implementing InGaN nanowire technology.

A Partial History of Solid State White Lighting: White LEDs

Almost universally crucial to white LEDs are blue/violet GaN/InGaN LED pump sources. This merits a brief review of these LEDs, and the important advances in materials technology that has enabled today's efficient devices.

Chemical Vapor Deposition (CVD) creates thin films of material on a substrate through the use of chemical reactions. Reactive gases are fed into a vacuum chamber and these gases react on a substrate and form a thin film or powder. As grown GaN films grown on a sapphire substrate by metal organic CVD (MOCVD) are n-type. Originally, a thin delivery tube was used to feed a reactant gas to the substrate for the purpose of obtaining high gas velocity. However, this made it very difficult to obtain a high quality film uniformly over the substrate due to convection currents.

A novel MOCVD reactor was developed by S. Nakamura that used two different gas flows: one is the main flow which carries the reactant gas parallel to the substrate with a high velocity.² The other is the sub flow which carries the inactive gas perpendicular to the substrate for the purpose of changing the direction of the main flow to bring the reactant gas into contact with the substrate. This subflow allows the formation of a continuous film as opposed to a few islands on the substrate. Usually a gas mixture of nitrogen or hydrogen is used as the subflow. This system is called a two flow MOCVD (TF-MOCVD).

TF-MOCVD enabled Nakamura to achieve a great deal of success (even bordering on cult-status industrial fame in Japan) in fabricating GaN-based LEDs, particularly green, blue, and violet. For example, the first violet InGaN light emitting diodes (FWHM = 10 nm at peak wavelength = 400 nm) were reported by Nakamura in 1994.³ He continued to develop these LEDs, and reported a high-power InGaN single quantum well (SQW) violet LED that achieved an output power of 5.8 mW.⁴ Using an intrinsic $\text{In}_{0.09}\text{GaN}$ active layer, this device gave an external quantum efficiency of 9.2% with a forward current of 20 mA at room temperature. Blue LEDs with external quantum efficiencies exceeding 9% have enabled hybrid GaN/phosphor white lamp LEDs.⁵

With efficient pump sources thus addressed, we will now turn to the four basic approaches to fabricating white LEDs:

1. InGaN based blue (or UV) sources (~470 nm) are used to pump Yttrium Aluminum Garnet (YAG)-based phosphors to generate yellow down-converted light which mixes with the blue pump to generate white light.

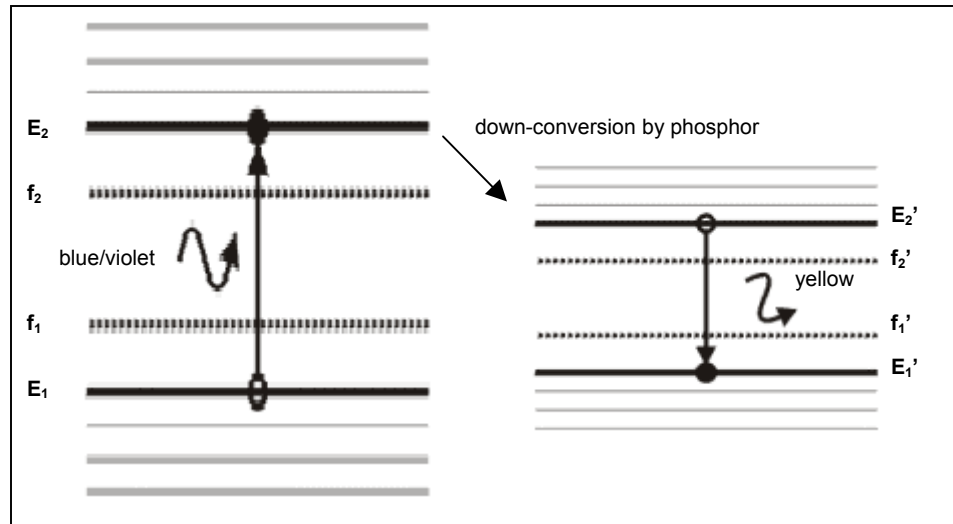


Fig. 1 – band diagram demonstration of the down-conversion mechanism in a blue pumped YAG phosphor white LED.

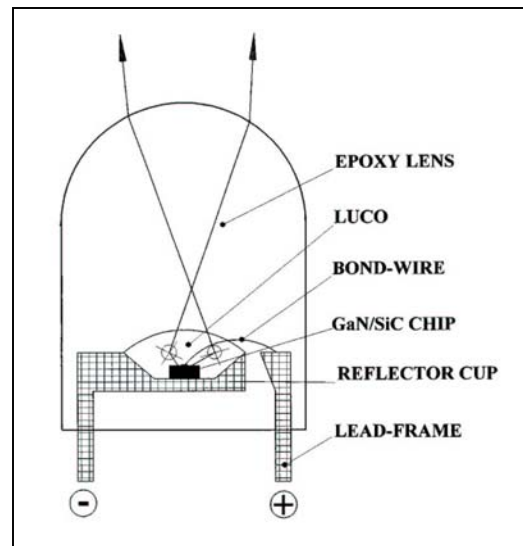


Fig. 2 – Schematic structure of a GaN-based LUCO LED.

2. UV InGaN-based LEDs pump tricolor (RGB) phosphors which subsequently mix to emit white light.
3. Arrays of red, green and blue LEDs are fabricated which combine to emit white light.
4. Blue (or UV) LEDs pump a polymer-based down-conversion medium.

These methods will be detailed in depth below.

The first and most common method to achieve white light emission is to combine a phosphor wavelength down-converter with a blue GaN LED. A blue LED is typically placed in a parabolic mirror and subsequently coated with a phosphor-containing epoxy.⁶ The LED emits blue light which is absorbed by the phosphor and re-emitted as longer-wavelength phosphorescence. This occurs via a process known as down-conversion which is detailed in Figure 1. These two wavelengths (generally blue and yellow) combine to form white light.^{7,8} The most popular phosphor for this application is yttrium aluminum garnet (YAG:Ce³⁺). Contrary to conventional “color wheel wisdom,” blue and yellow light actually can combine to form white light in an emission context. Reflectance is a different scenario: in that case, blue and yellow paint *reflect* blue and yellow light, and mixed together these would form paint which *reflects* green light.

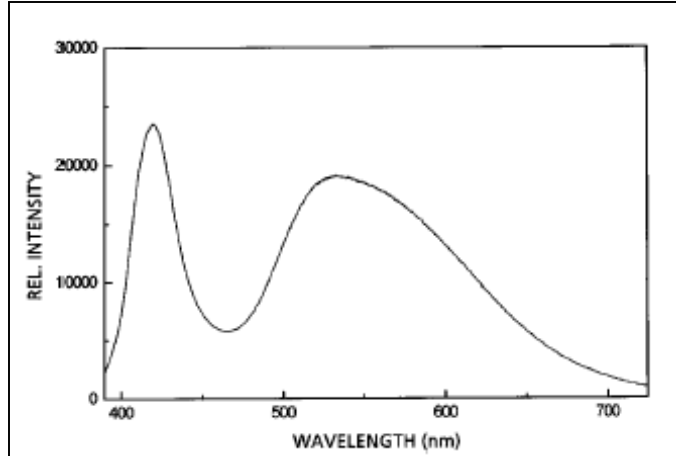


Fig. 3 – Emission spectrum of a white emitting 6H-SiC/GaN//Y₃Al₅O₁₂:Ce³⁺(4f¹) LUCO LED.

White LEDs fabricated in this way were first reported in 1997.^{9,10} Known as LUCO LEDs (luminescence conversion light emitting diodes), these were based on blue LED chips coated with a yellow emitting phosphor (YAG:Ce). Schlotter et al. and Nakamura had concurrently fabricated the first efficient white light emitting LED. Schlotter et al. reported the use of luminescence down-conversion (Stokes shift, see Figure 1) as the primary mechanism for white light emission. They used Y₃Al₅O₁₂:Ce³⁺(4f¹) as the down-converting phosphor medium. At that time, they postulated that the CREE “blue chip” blue LED on silicon carbide (SiC) could be used as an efficient pump to excite organic and inorganic luminescent materials for subsequent photon emission at lower energies. This principle was dubbed luminescence conversion (LUCO), and a schematic portrayal is seen in Figure 2.¹¹ Figure 3 shows the emission spectrum of the GaN/phosphor LED.¹² Note the prominent humps in the blue and yellow wavelengths.

At this time, Nakamura reported the ability to make white LEDs using the same method (blue LED and yellow YAG phosphor).¹³ Extending the data reported by Schlotter et al., Nakamura stated that he could change the peak wavelength of the phosphor emission spectrum between 510 and 570 nm by changing the composition of the YAG phosphor, thus being able to control the color of the white LEDs. A typical emission spectrum of the white LED shows two peaks (Figure 3): one corresponds to the blue LED emission (~465 nm) and the other corresponds to the yellow emission of the YAG phosphor (~555 nm). He reported an output power of 2 mW, a luminous efficiency of 5 lm/W, an average color rendering index (CRI, to be described below) of 85, and a color temperature (to be described below) of 8000 K. (Note: this color temperature implies very “cold” light, a concept to be described below.) V. Härle et al. have achieved a luminous efficiency of 15 lm/W by rigorously adjusting and refining the proportions of devices fabricated according to the method described above.¹⁴

Without significantly altering the device design, white light can also be generated by optically exciting a yellow-emitting phosphor with UV LEDs, similar to a fluorescent light tube. Advantages of this method include a high luminous efficiency (20 lm/W),¹⁵ and ease of fabrication on an industrial level. However, high efficiency UV LEDs have been difficult to achieve due to the low doping efficiency in AlGaIn with high Al content and the poor quantum efficiency of UV LEDs.¹⁶ Additionally, it can be difficult to tune the hue and color rendering of such devices (both UV and blue pumped). Since white light is simply generated by mixing two complimentary colors, hue tuning is restricted to points on the straight line connecting the blue pump and yellow down-converter points on the CIE color diagram (see Figure 4¹⁷).

This addresses one of the most significant drawbacks of this “blue + yellow” approach: dichromaticity. Basically, the color that our eye thinks looks white is, in fact, not white – it is simply a mixture of blue and yellow. True sunlight (i.e., what humans enjoy and call natural light) is actually composed of a full spectrum of colors, rather than discrete values of yellow + blue, or red + green + blue. Therefore, an ideal light source will reproduce this full spectrum spread and blue-pumped phosphor white LEDs do not have this capacity. White light generated by two monochromatic colors has a low color rendering index which results in less “pure” white light.¹⁸ Additionally, dichromatic light generation leads to high color temperatures (usually above 5500 K) which corresponds to “cold” white light.¹⁹ Our eyes can be tricked due to their non-uniform luminous response (see Figure 5²⁰). However, we can detect light characteristics – we can often comment that room light is “cold” or “warm.” These characteristics are easily quantifiable, and will be addressed below. Furthering the dichromaticity dilemma is the fact that the device’s color mixture is not constant throughout the device’s lifetime. Phosphors wear out, so after awhile the emitted light looks bluer and bluer.

As discussed, the perceived warmth of light is given an actual parameter – Color Temperature. This is the temperature to which one would have to heat a “black body” source to produce light of the same spectral characteristics. Low color temperature implies warmer color (reds and oranges – longer wavelength) while high color temperature implies colder colors (blues and violets – shorter wavelength). However, two light sources with the same color temperature can have vastly different color quality – one source may be a continuous spectrum while the other is composed of a few discrete bands of color that mix. These two sources would appear different to the eye, and this difference is quantified by a color rendering index (CRI). The CRI of natural daylight is 100 (being composed of a full emission spectra), and all other light sources are measured against this. Most standard “cool white” fluorescent bulbs range from 60 to 75 CRI.²¹ This is what can give fluorescent lighting (particularly in office buildings) a “harsh,” undesirable tone. Thus, solid state white lighting efforts strive to produce devices with a high CRI, thereby coming as close as possible to replicating natural light.

With these definitions given, we turn back to white LED fabrication. The second method of white light generation uses InGaN-based UV sources (~405 nm) to pump tri-color phosphors and generate white light.²² This method has a primary advantage: it is easy to achieve good color rendering and color stability. Problems exist, however. Tri-color phosphor material tends to degrade more quickly. Nonetheless, in 1998 T. Jüstel et al. stated that this fabrication technique would be an attractive option from a production point of view. Specifically, a rare-earth phosphor mixture (a tricolor phosphor blend) being pumped by an LED emitting at ~370 nm to pump would be able to absorb all of the pumped light, as opposed to the Blue LED/yellow phosphor device which can only partly absorb the incident blue light. Using a UV LED to pump a tri-color phosphor has the additional benefit that it is much easier to consistently produce devices with consistent color coordinates. This is much more difficult for a white LED with only two points on the chromaticity diagram.

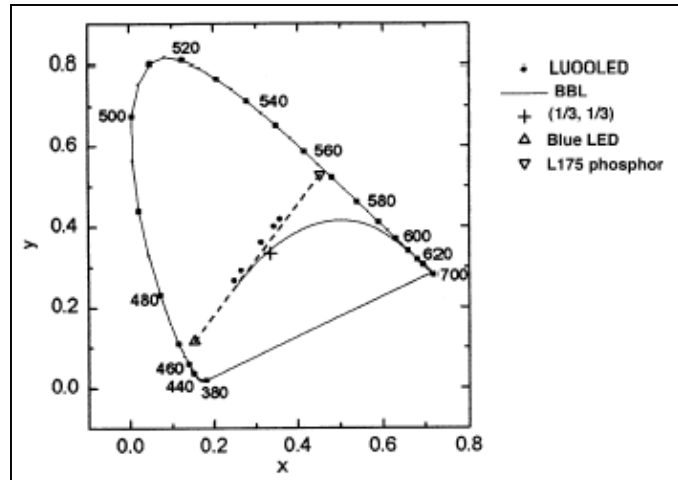


Fig. 4 – CIE chromaticity points of YAG:Ce based LUCOLEDs and of the corresponding GaN LED and YAG:Ce phosphor. The chromaticity points are on the straight line connecting the points of the LED and the phosphor.

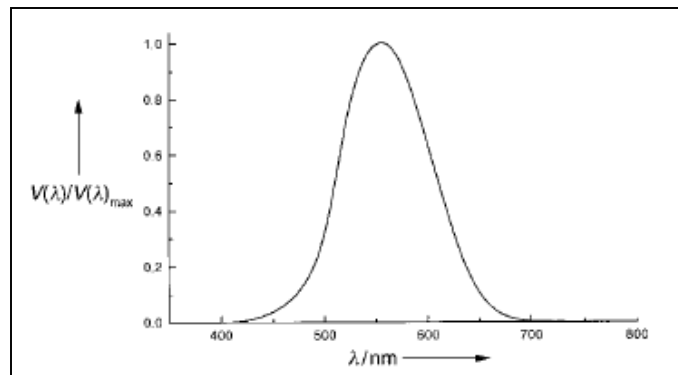


Fig. 5 – Normalized luminous efficiency for the human eye $V(\lambda)/V(\lambda_{\max})$ as a function of wavelength.

U. Kaufmann et al. successfully fabricated an ultraviolet-pumped tricolor phosphor blend white LED.²³ This somewhat overcomes the problem of color rendering – Kaufmann et al. fabricated a RGB phosphor blend pumped by a UV source (LED grown by MOCVD). Radial LEDs (404, 394, 380 nm) were upside down mounted and coated with a white tricolor blend before epoxy encapsulation.

A third method for white light generation involves combining two or three different colors of LEDs of the proper wavelengths and power ratios. The drawback of this method is that the driving circuits of these LED arrays are more complex than their phosphor counterparts. In 1997, Nakamura reported the fabrication of white LEDs by mixing three primary color LEDs (i.e., green and blue InGaN SQW LEDs and a red AlGaAs LED).²⁴ However, he noted one of the primary disadvantages of this scheme: “In this case, we need at least three LEDs, one of each primary color, and must adjust each supply current using a special circuit in order to control the intensity of each color. Therefore, white LEDs [fabricated this way] are much more expensive than single-color LEDs.”

In 1998, T. Jüstel et al. were already predicting much of the course of continuing solid state white lighting research and essentially confirmed the early results reported by Schlotter and Nakamura.²⁵ They correctly cited the two principal methods of generating white light (at that time): arrays of three primary color LEDs, and single white LED made by a blue LED pumping a yellow phosphor. In comparison with the three LED device, they realized that this second option results in an overall decrease in efficiency because of the quantum deficit of the light conversion from blue to yellow. Blue LED/yellow phosphor white LEDs also suffer from CRI light quality. Additionally, they cite the fact that it would take 80 of these LEDs to replace one 10 W light bulb. Therefore, Jüstel et al. proposed a more favorable option: combine a blue LED emitting at ~ 470 nm with a broadband phosphor. Unfortunately, this method still suffers a drawback: one loses device efficiency whenever one decreases the color temperature. But a decrease in color temperature is favorable since the device then produces “warmer” and more appealing light. This is because the YAG:Ce emission (see Figure 3) shows less and less integral overlap with the eye sensitivity curve (Figure 5) when shifted towards longer wavelengths.

F. Hide et al. developed the fourth method of white light generation particularly attractive for display technology. The electroluminescence (EL) from an InGaN LED provides the blue light to excite the photoluminescence (PL) of a π -conjugated polymer film.²⁶ This hybrid InGaN/polymer LED thus produces white light. Polymers are particularly useful for displays since InGaN/polymer hybrids have the potential to be flexible and/or very thin. This work by Hide et al. was followed by the work of C. Zhang, and A. Heeger at UCSB in which they explored a simpler approach to building InGaN/polymer hybrid LEDs with single layers of conjugated polymers or copolymers.²⁷

These are the four most common methods for solid state white light generation. Other novel ways of generating white light have been suggested by J. K. Sheu et al.; by codoping Si and Zn (which form donor and deep acceptor levels) in the active well layer of an InGaN-GaN MQW, white light can be generated due to the combination of donor-acceptor (D-A) pair related broad-band emission and the blue InGaN bandedge emission.²⁸ Additionally, F. Schubert of Boston University is pursuing work in semiconductor converters (PRS-LED) in which photons are recycled to create an efficient device.²⁹ This design involves two active regions which emit two different colors of light. While efficient, this design necessitates a fused interface between a primary source LED and a sapphire substrate which has a secondary source active region; this fusing makes the LED design quite expensive and commercially unattractive. An additional problem arises from the output spectra of a so-called dichromatic PRS-LED; using a current-injected InGaN blue LED as the primary source and a red AlGaInP recycling source, the peaks are fairly narrow and spread apart to the extent that they do not cover the green or orange areas of the spectrum. Consequently, green or orange clothing would appear black under this PRS-LED.

Once the material design of a white light emitted LED has been refined, the physical design of the device must be adjusted to enhance extraction efficiency. Cree Inc., a North Carolina-based pioneer in solid state lighting and LED design, has engineered a series of LED structures that attempt to maximize light extraction efficiency. These involve etched mesa designs, adding reflectors, and even inverting the entire structure and using a bottom-side reflector.

As stated, all of these approaches necessitate a blue/UV LED pump source to generate the white light. This naturally broaches the topic of these LEDs’ efficiency – could we not make more efficient devices by also making more efficient pump LEDs? The answer, of course, is yes. Additional improvements to GaN/InGaN-based LED pumping sources would improve the input efficiency of the devices (and I hope that nanowires will increase the down-conversion and output efficiency as well – that will be detailed below). But there remain several problems impeding the development of extremely efficient blue/UV LEDs.

A perpetual difficulty when dealing with GaN is that there exists no lattice-matched substrate. Sapphire and Silicon Carbide (SiC) are frequently used due to their similar lattice constants (lattice mismatch of Sapphire ~

13%, SiC ~ 3.5%), but defects due to threading dislocations are still a significant problem. Recently, growth of wurtzite GaN on sapphire yielded a 16.1% lattice mismatch.³⁰

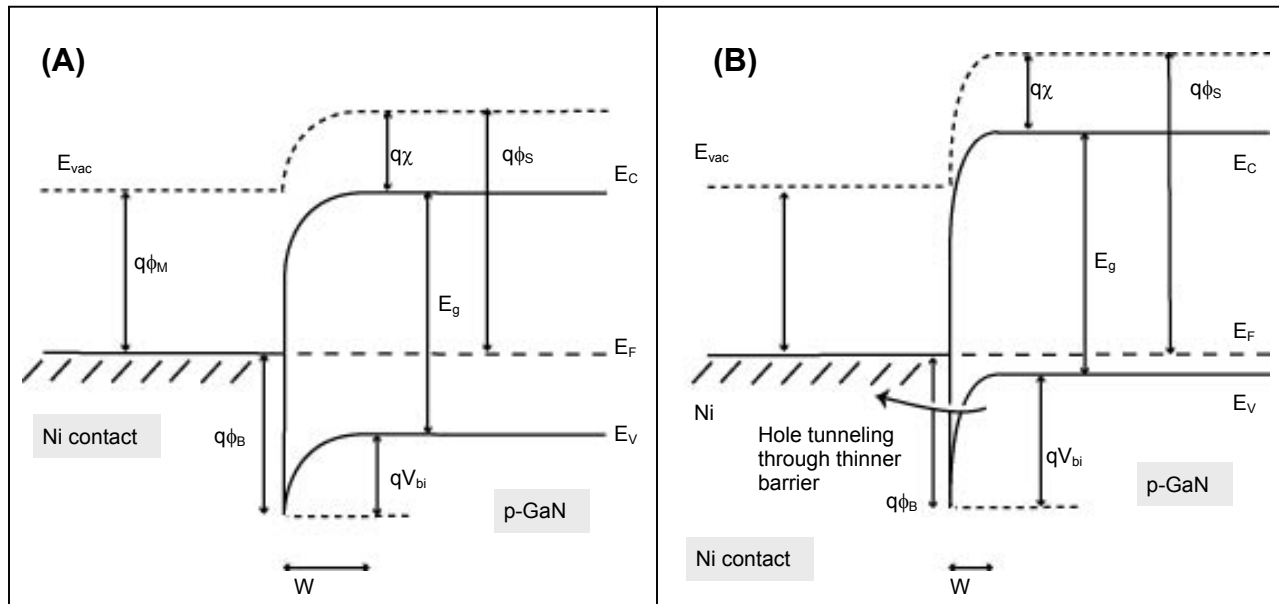


Fig. 6 – A) Nickel contact with p-type GaN. Magnesium dopant has not been activated. There is a significant barrier to hole flow, and thus this is a Schottky barrier. B) With the removal of Hydrogen, the Mg acts as a full acceptor, and thus the effective doping concentration N_A increases. This shifts the band with respect to the Fermi level (as shown). Additionally, the higher doping concentration decreases the depletion width W . This decrease makes the barrier to holes much thinner and permits tunneling; the contact is then more Ohmic.

Thin strained layers of GaN can be grown on Sapphire or SiC, but once the growth surpasses a critical thickness the strain relaxes and defects form at the interface. These dislocations thread throughout the entire growth of the material. An intrinsic GaN buffer layer underneath the n-GaN layer has been shown to reduce the density of threading dislocations in the device structure.³¹ In most blue/UV LED designs, the n-GaN layer is far beyond the critical thickness, so the material generally contains a high concentration of defects that hinder device performance.

Also, high contact resistance of p-GaN contacts is a significant problem. There are traditionally only two ways to decrease this contact resistance: higher p-type doping (which is very difficult to achieve in GaN) or lowering the Schottky barrier until it is effectively ohmic. Since it has, to date, been impossible to find a p-type GaN contact metal with a work function $\phi_M \geq \phi_S$ (the necessary condition for the removal of the Schottky barrier $q\phi_B$), we must resort to barrier manipulation to achieve the most ohmic contact possible. This is achieved through p-type doping which reduces the depletion width and barrier thickness as seen in Figure 6. It was reported that tunneling occurs freely for doping concentrations of $N_A \geq 10^{18}$, where barrier thickness $W \propto N_A^{-1/2}$.³² Additionally, impurity defects at the Ni-GaN:Mg interface create a “leaky” Schottky barrier which enables more holes to transit across the barrier, thus enabling higher current densities and making the contact more ohmic.

There are, unfortunately, additional problems relating to white LEDs. The luminous efficiency of existing white LEDs is still very low, owing to the presence of electrostatic fields within the active layers.³³ These fields are generated by the spontaneous and piezoelectric polarization along the [0001] axis of hexagonal group-III nitrides. Unfortunately, these are the same materials desired for white light generation. However, some work is being done to circumvent this problem, and some of those problems mentioned above. P. Waltereit et al. have demonstrated nitride semiconductors free of electrostatic fields for efficient white LEDs.³⁴ They showed that epitaxial growth of GaN/(Al,Ga)N on tetragonal LiAlO₂ in a non-polar direction allows the fabrication of active layer structures that are free from electrostatic fields, thus improving quantum efficiency.

Furthermore, Nakamura recently received a sizable grant from a Japanese company to produce single crystal bulk GaN.³⁵ Ever since the true emergence of nitride-based electronics and optoelectronics, single crystal GaN has been the veritable “holy grail” of semiconductor research – having such a material available would enable nearly defect-free GaN devices, thus greatly improving their efficiency.

Other solutions to existing white LED problems have been suggested by Damilano et al.³⁶ They have demonstrated monolithic white LEDs based on InGaN/GaN multi quantum wells (MQWs). The emission spectra of these devices can be tuned from blue to orange by adjusting the QW thickness. Then, by combining QWs of differing thicknesses in the same device it is possible to generate white light by combining the different color emissions from each well. This occurs because of the QW eigenvalue's dependence on well thickness, which subsequently alters the change in energy of interband transitions (see Figure 7) governed by,

$$\text{electrons} \rightarrow E_n = \frac{\pi^2 \hbar^2 n^2}{2m_e^* l^2}, E_m = \frac{\pi^2 \hbar^2 m^2}{2m_h^* l^2} \leftarrow \text{holes} \quad (1)$$

Tunable light emission from a single device is an advantage, especially considering that it can be fabricated in a continuous series of growth steps. Current YAG-based white LEDs require an additional step (depositing the down conversion media on the LED chip) which increases fabrication costs.

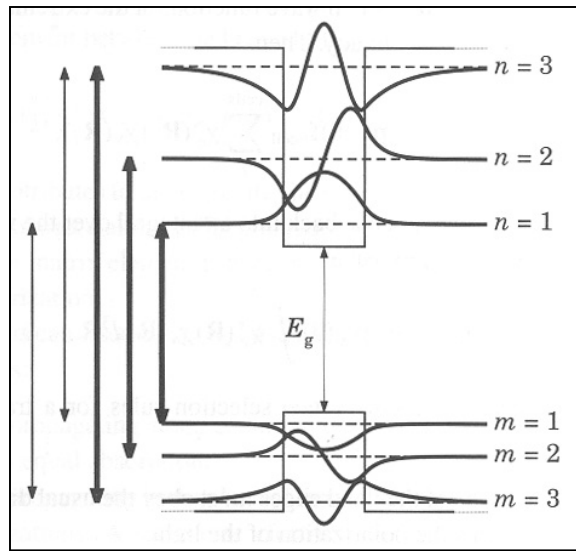


Fig. 7 – Transitions between bound states in the valence and conduction bands of a quantum well. The thick lines indicate the strongest allowable transitions. In the case of a semiconductor MQW laser diode, the primary transition ($n=1$ to $m=1$; E_g) is dominant and becomes the lasing frequency. (Note: only the heavy hole bands are shown.)

Progress in GaN Nanowire Growth

Nanowires are of interest because of their potential use as quantum wires. Quantum wires are a desirable phenomenon that demonstrate a one dimensional density of states, and excellent carrier confinement. Comparing the density of states curves for 3D, 2D, and 1D systems, it is clear that a device that operates in one dimension has the potential to be vastly more efficient than other higher-dimensional devices. This, along with the desire to understand fundamental 1D physics and material processes, has motivated extensive research in nanowire technology. And with the advent of the nitride material system, attention quickly turned to the plausibility of GaN nanowire growth, and their potential applications.

This section will give an account of the evolution of GaN nanowire growth. Several different growth methods have been suggested and successfully employed – two primary methods deserve a brief mention in advance. The first method involves growing carbon nanotubes and reacting In with GaN inside the tubes to form GaN filled carbon nanotubes. Then the carbon is then burned off, leaving GaN nanowires. Essentially, the carbon nanotubes act as a template to confine the GaN reaction, which results in growth of GaN nanorods with a diameter (usually 4 - 50 nm) similar to that of the template nanotubes. The second primary method is known as vapor-liquid-solid (VLS) growth. This can involve a catalyst (particularly In) to initiate the Ga and N reaction. Other attempts have included growth without the In catalyst, altering the VLS recipe, or assisting VLS through laser ablation. The chronology of these results is presented below. But first, a few clarifications are in order.

The scientific literature on this topic casually tosses around a slew of “nanowords” – all types of nouns with the universal “nano” prefix. It can be wearying to distinguish between the various materials and structures. Initially, I encountered a very basic question: Is there any difference between a nanotube, a nanowire, and a nanorod? The answer is, of course, yes. Nanotubes are hollow, whereas nanowires and nanorods are solid. Nanotubes are generally carbon – graphite sheets rolled into tubes. The twisting of the roll determines electrical properties. These were successfully fabricated before anyone had thought of making GaN (or InGaN nanowires). Nanotubes can be other elements or compounds too, but generally they are carbon. On the other hand, Nanowires and nanorods are basically the same thing; they are solid cylindrical structures, not tubes. “Nanowire” and “nanorod” simply connotes a difference in aspect ratio (length/diameter). Nanorods are shorter and stubbier, while nanowires are longer and thinner.

The milestone paper in this field was published in *Science* in 1997. W. Han et al. were the first to report successful fabrication of GaN nanorods.³⁷ This generated significant excitement since several prominent researchers had already been postulating the excellent applications of nitride nanowires in optoelectronic devices.^{38,39,40,41} By reacting Ga₂O with NH₃, they grew GaN nanorods (diameters between 4 and 50 nm) inside carbon nanotubes.

In 1999, Zhu and Fan demonstrated that these nanorods were, in fact, single crystal GaN structures.⁴² The nanorods demonstrated x-ray diffraction patterns identical to those of hexagonal wurtzitic GaN. Next, in a series of papers G. Cheng et al. (with whom I am collaborating here at UCSB) demonstrated that GaN nanowires could be grown on in alumina membranes using In as a catalyst for vapor-liquid solid (VLS) growth.⁴³ This study also confirmed Zhu and Fan’s assertion of GaN nanowire single crystallinity. Cheng et al. fabricated the alumina membrane by means of anodization. Then, the gas reaction of Ga₂O vapor with a constant flowing NH₃ atmosphere was carried out in a horizontal quartz tube at temperatures as high as 1273 K. The alumina membrane was placed on top of mixtures of Ga granules and Ga₂O₃ inside an alumina crucible. They measured GaN nanowires with lengths up to hundreds of μm (and diameters ~ 14 nm) randomly distributed on the membrane surface (seen in Figure 8⁴⁴). They also proposed that the capillary affect of the anodic pores with large aspect ratio (depth/diameter) in the alumina membrane is favorable for the nucleation

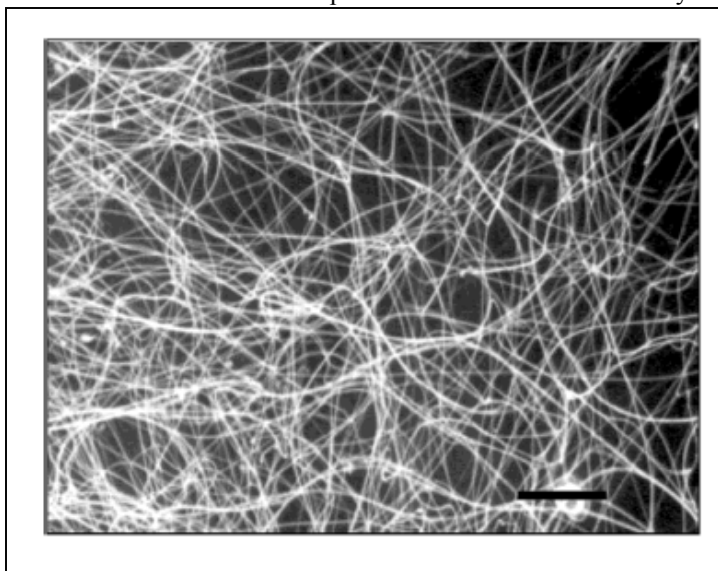


Fig. 8 – Typical SEM image of bulk GaN nanowires. The scale bar corresponds to 500 nm.

and growth of GaN nanowires inside the pores. Continuing their work in 2000, Cheng et al. demonstrated ordered GaN nanowire growth in a honeycomb structure of anodic alumina.⁴⁵ These were synthesized through the gas reaction of Ga₂O vapor with a constant flowing NH₃ atmosphere was carried out in a horizontal quartz tube at temperatures as high as 1273 K in the presence of nano-sized metallic indium catalysis. This involved a two step fabrication method: first, they synthesized the ordered nanostructures substance. Then, the single-crystalline GaN nanowires were assembled into each of the highly ordered honeycomb pores of the anodic alumina through a gas reaction.

Most recently, Cheng et al. have concluded that it is easiest to grow GaN nanowires on porous alumina substrates, where defects are plentiful and it is easier for a wire to find nucleation sites.⁴⁶ The In catalyst is left on the substrate, with the Ga granules and GaO₂ left in the crucible. In the furnace, the In vaporizes, liquid forms in the alumina pores, and Ga₂O₃ and NH₃ vapor flows above the substrate and then condenses in the pores. The In then acts as a catalyst in forming the single crystal hexagonal wurtzite GaN nanowires. Cheng has noted that there is a continuous growth point at the In catalyst particle; essentially, the In catalyst particle rides along on the tip of wire as it grows (as seen in Figure 9⁴⁷).

Concurrently in 2000, C. Chen and C. Yeh reported the large-scale catalytic synthesis of GaN nanowires through a very similar fabrication technique.⁴⁸ Detailing their use of VLS, they state that “the main feature of this mechanism is the presence of intermediates that serve as catalysts between the vapor feed and the solid growth at elevated temperatures under CVD conditions,” adding that “the most important parameter in VLS growth is the catalyst added in the reaction.” Like Cheng et al., Chen and Yeh found that elemental indium was an ideal catalyst in the reaction of gallium and ammonia to form GaN nanowires. In a photoluminescence study of their nanowires (Figure 10⁴⁹), Chen and Yeh observed a band-edge emission at 380 nm.

Significantly, Chen and Yeh also began discussing the actual growth mechanism at work in this VLS nanowire fabrication. While they admitted that the detailed mechanism on ternary phase diagrams of In-Ga-N is still not fully understood, they suggested that very small miscible droplets of In-Ga-N may be generated rapidly during the heating process of the reaction and hence act as nucleation sites in the VLS growth of GaN nanowires.

Chen et al. continued this work in a report published in 2001.⁵⁰ In that paper, they apply a series of catalysts and different reaction parameters to systematically optimize and control the VLS growth of GaN nanowires. Temperature dependence of the nanowires’ PL spectra revealed that the emission mainly comes from wurtzite GaN with little contribution from the cubic phase. They readily admitted that in their first paper⁵¹ the purity and diameters of the nanowires were not well-controlled. They report their newest work as a breakthrough in achieving high purity and high quality GaN nanowires. Like others curious about potential optoelectronic applications, Chen et al. thought “it would be quite interesting to know whether efficient luminescent properties can be achieved in GaN quantum wires.” I wonder the same thing with respect to InGaN nanowires.

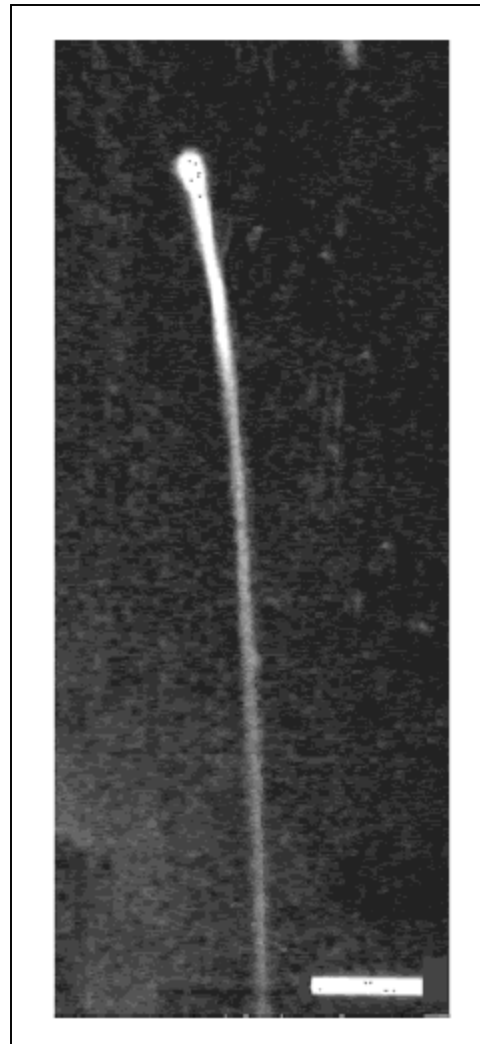


Fig. 9 – SEM image of a GaN nanowire terminated with a nanoparticle at the tip. The white scale bar corresponds to 300 nm.

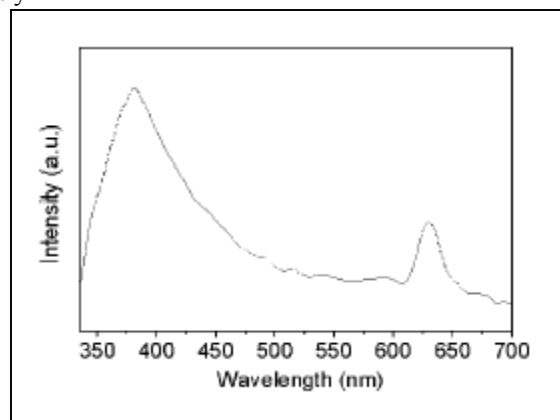


Fig. 10 – Typical photoluminescence spectrum of GaN nanowires. In this case, the PL was taken at 13 K with nanowires excited by a 10 mW He-Cd laser at 325 nm.

In 1998, A. Morales and C. Lieber reported a method for synthesizing Si and Ge nanowires combining laser ablation cluster formation and vapor-liquid-solid (VLS) growth.⁵² Laser ablation was used to prepare nanometer-diameter catalyst clusters that defined the size of the wires produced by VLS growth. Then, in 2000, X. Duan and C. Lieber reported the successful growth of single crystal GaN nanowires using laser-assisted catalytic growth (seen in Figure 11⁵³). Using that technique, laser ablation of a composite target of GaN and a catalytic metal generated liquid nanoclusters that served as reactive sites confining and directing the growth of crystalline nanowires (~10 nm in diameter).⁵⁴ In this method (called LCG – laser-assisted catalytic growth) a pulsed laser is used to vaporize a solid target containing desired material and a catalyst. The resulting liquid nanoclusters formed at elevated temperature direct the growth and define the diameter of crystalline nanowires through VLS. Notable for my purposes, Duan and Lieber believe that their LCG approach, which is based on the predictable choice of catalyst and growth conditions, can be readily extended to the synthesis of InN, InGaN alloys, and related nitride nanowires.

In 2000, He et al. reported a GaN nanowire fabrication approach that did not require any catalyst or laser-assisted growth.⁵⁵ They presented interesting data on the physical characteristics of GaN nanowires, noting that the size of the nanowires is explicitly proportional to the temperature and the NH₃ flow rate. Their wires were fabricated in a direct reaction of metal Ga vapor with flowing NH₃ in a horizontal oven. Further efforts in 2001 confirmed that the diameter of GaN nanowires increases with temperature and NH₃ flow rate.⁵⁶ This work also used a direct reaction of Ga with NH₃ which did not require a catalyst or a template. This relation of nanowire diameter to temperature is valuable to know, but may be somewhat detrimental to efforts to create efficient optoelectronic devices. Cheng has reported that, indeed, higher temperatures yield thicker nanowires, and also a better overall yield of wires.⁵⁷ But lower temperatures yield thinner and fewer wires. This is unfortunate since very thin wires are desired to enhance one dimensional quantum confinement, and thus device efficiency.

An alternate VLS growth recipe was reported by Tang et al. in 2000.⁵⁸ They reacted a mixture of Ga and SiO₂ on a Fe₂O₃ catalyst supported on Al₂O₃ at 950°C. They obtained 10-50 nm thick, single crystal wurtzite GaN nanowires which were observed to grow out of the Fe₂O₃ crystals.

A novel method of GaN nanowire growth was reported by H. Peng et al. in 2000: they grew bulk-quantity highly pure hexagonal wurtzite GaN nanowires using a hot filament chemical vapor deposition (CVD) system.⁵⁹ Notably, no nanometer-sized catalyst was required to grow these wires.

Also, J. Li. et al. grew clumps of 10-50 nm wurtzite GaN nanowires on MgO crystals, reacting Ga metal and ammonia at 920°C.⁶⁰ Additionally, in 2001 this group successfully synthesized GaN nanowires by a simple direct gas reaction without confined space, and fabricated GaN nanotubes using the same method.

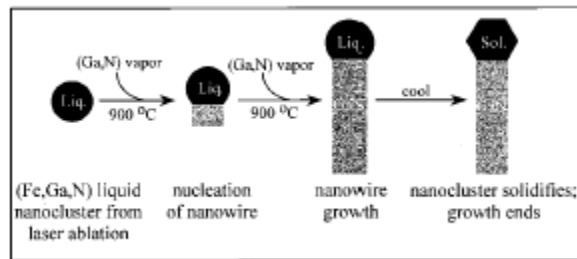


Fig. 11 – Overall evolution of nanowire growth following the generation of the catalytic nanocluster by laser ablation.

Fusing the Disciplines – InGaN nanowires for solid state white lighting

First of all, why do we want to involve InGaN in the down-conversion process? And second of all, why bring nanowires into the mix? These are both good questions, since doing either represents a significant materials challenge. However, it will be seen that the benefits of doing so could enable extremely efficient white light devices.

To answer the first question, Indium Gallium Nitride (InGaN) is a narrow bandgap material which, when sandwiched between layers of GaN (or different In mole fraction In_xGaN), is ideally suited to MQW applications for short wavelength LEDs. Yoshimoto et al. were the first to grow high quality InGaN films on a sapphire substrate.⁶¹ This same principle applies to a 1D wire of InGaN surrounded by a GaN cladding layer (as will be addressed). InGaN has a direct bandgap tunable by In mole fraction from 3.4 eV to 2.0 eV (calculated using Vegard's law). However, recent results have challenged the long-standing band gap value for InN (~2 eV) and asserted 0.9 eV as the true band gap for high quality InN films.⁶² This alone makes InGaN a promising material for blue/violet emission (and even a candidate for deep UV and infrared [IR] emission). To be more precise, the band gap of the ternary alloy $\text{In}_x\text{Ga}_{1-x}\text{N}$ can be approximated by the parabolic form:⁶³

$$E_g(x) = x \cdot E_{g, \text{InN}} + (1-x) \cdot E_{g, \text{GaN}} - b \cdot x \cdot (1-x) \quad (2)$$

where b is the bowing parameter.⁶⁴ From this, it is seen that if In_xGaN 's In mole fraction can be successfully tuned from 0 to 1, InGaN represents a ternary alloy capable of emitting photons from 0.9 eV to 3.4 eV – that is, from GaN's UV emission (~365 nm) to InN's infrared emission (~1380 nm). This gives us a remarkable material capable of spanning the entire visual spectrum and more.

Then, answering the second question, nanowires have the capacity to be extremely efficient simply based upon their 1D quantum wire nature. Viable solid state white light applications must satisfy two fundamental conditions: 1) there must be an efficient input source (e.g., optical pumping, electrical pumping), and 2) the down-conversion media must also be very efficient. We have already addressed the first condition. The second condition, however, is open for discussion. An ideal down-conversion medium would only experience heat loss (i.e., $E_{\text{in}} - E_{\text{out}}$), but non-radiative recombination loss through traps often hinders efficiency. Phosphors are generally not very efficient, as described above; especially in the context of blue-pumped yellow YAG phosphors, an appreciable fraction of the light is not even absorbed. Nanowires might offer a solution to this, while providing the tunable bandgap benefits inherent in the nitrides. And whereas conventional GaN and InGaN growth often suffers from dislocations due to lattice mismatch with sapphire or Silicon Carbide (SiC) substrates, InGaN nanowires have the potential for negligible non-radiative recombination loss because of ultra-low dislocation densities. This is perhaps the most important point – the efficiency of down-conversion in nanowires is much higher than in bulk GaN/InGaN. There are several reasons for this. First, because the overlap between electrons and holes is strong. Second, threading dislocations (TDs) are all but non-existent in nanowires. TDs arise in bulk GaN and InGaN due to lattice mismatch with the substrate. However, since the growth mechanism for nanowires is completely different, TDs are not a problem at all, and there is the potential for defect-free nanowires. This is excellent, since TDs function as non-radiative recombination centers, and non-radiative recombination hinders light output efficiency. However, non-radiative recombination still exists at surfaces and interfaces. Therefore, because nanowires have more surface than bulk, it is important that surface related non-radiative recombination seems to be low in the nitride system. However, even if surface recombination were high in the nitrides, we could conceivably circumvent this problem by employing a GaN cladding layer.

Surface recombination has the potential to absolutely decimate the efficiency of bulk GaN and GaAs optoelectronic devices. External quantum efficiency depends on this surface recombination, so we must take steps to insure that its effect is minimized. This can be solved by employing a GaN cladding layer that completely surrounds the InGaN nanowire. Since $E_{g, \text{GaN}} > E_{g, \text{InGaN}}$, carriers would be confined in the nanowire and not allowed to escape to the surface, where non-radiative recombination occurs. This would be like creating an effective 360 degree heterojunction so that carriers *could not* escape to the surface. Several authors have confirmed this in the recent nanowire literature^{65,66,67} – because of the large bandgap and structural confinement of GaN nanowires, the fabrication of visible and UV optoelectronic devices with relative low power consumption is potentially feasible. This GaN cladding layer is transparent so that we would not have to worry about the material absorbing any input pump light, or output white light emission. Thus, recombination in GaN-coated InGaN nanowires could be extremely efficient.

Thus, I have proposed to investigate Indium Gallium Nitride (InGaN) nanowires to determine whether they are viable and efficient down-converters of optical pumping sources relative to existing phosphors. If InGaN nanowires can function as efficient semiconductor-based down-converting media, they could be employed to generate white light for the next generation of solid state lighting applications. In this research I wish to replace the phosphors with nanowires of InGaN which could have much higher down-conversion efficiency. As stated, InGaN nanowires are extremely versatile in this application because their emission spectrum can be tuned from UV to IR based on In mole fraction. Also, the nitrides are resistant to chemical etching. This should allow GaN/InGaN-based devices to be operated under harsh environments, and may lead to devices with superior reliability.⁶⁸ Perhaps even more attractive for this application, these nanowires could have the ability to duplicate natural light spectra. As discussed above, natural light (sunlight) consists of a full wavelength spectrum, not discrete additions of red, green and blue. While it's true that the eye detects these ternary mixtures as "white," the eye can also tell that it is not natural, warm light. We, on the other hand, hope to produce this natural light using what we like to call the "cognac approach."

Fine makers of Cognac liquor are able to guarantee consistency and reliability of their products by crafting many different batches, and then combining all of them together. This combined mixture is then used as the source liquor, which is then bottled individually and distributed. Small variations in one batch of Cognac could be detected by a savvy connoisseur, but by averaging out any defects through hundreds of other batches, an extraordinary level of quality and consistency can be achieved. We hope to accomplish the same with InGaN nanowires. If we can devise a method of reliably growing tunable bandgap InGaN nanowires, it would be possible to grow 100 different batches, each with a different mole fraction ranging from 0 to 100%. These batches would represent nearly every conceivable spectral color between ~365 and 1380 nm. By then combining (averaging) and mixing these batches of nanowires, we would have created an omni-spectral phosphor-like down-conversion medium which, due to the 1D quantum nature of the InGaN nanowires, would be ultra-efficient. Practically speaking, these averaged batches of InGaN cognac would be ground into a fine pseudo-phosphor powder which could then be mixed into any LED-coating epoxy resin. This resin could potentially have an even emission spectrum from UV to IR, thus nearly replicating natural light.

As one might guess, my proposed research requires a reliable way to grow InGaN nanowires. We are then left to wonder: which, if any, of the GaN nanowire growth methods described above can be applied to InGaN nanowire fabrication? We think there are several likely candidates to accomplish this growth: VLS growth using In as a catalyst, InGaN nanorod growth inside carbon nanotubes, and/or laser-assisted VLS.

G. Cheng and I are currently investigating the feasibility of VLS growth of InGaN nanowires. Unfortunately, no conclusive results have yet emerged.

Another approach to growing InGaN nanowires would be to synthesize them through a carbon nanotube-confined reaction. This would involve preparing InGaN nanorods on a small scale using carbon nanotubes as a template. GaN nanorods have been successfully grown using this technique.⁶⁹ We are currently investigating a collaboration with Dr. Rao of the Indian Institute of Science (IISc) who is growing both GaN and InGaN nanorods via this technique. His recent work has demonstrated InGaN nanowires successfully grown in carbon nanotube templates.

Additionally, Dr. Martin Moskovits, dean of the Division of Mathematical, Life, and Physical Sciences and professor of physical chemistry here at UCSB, is currently researching GaN and InGaN nanowire growth, highly-ordered carbon nanotubes for electronic applications, and composite nanostructures based on template-grown boron nitride nanotubes. It also happens that G. Cheng is a postdoctoral student working for Dr. Moskovits. Thus our collaboration is obvious and beneficial.

Ultimately, I intend to examine the morphology of these InGaN nanowires using field emission scanning electron microscopy (SEM). PL spectrum analysis would give clear indications as to whether our nanowire growths were yielding the expected light emission. To further characterize the structure of our material, I would likely employ transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX).

Besides our "cognac approach" to natural white light, there are numerous other applications of this technology. With InGaN nanowires successfully grown, there are several other ways I could employ them to achieve less "pure" white light emission. Both methods optically pump the system, wherein blue light incident on the nanowires would be of the form $h\nu_{incident} > E_g(\text{red, green, or yellow})$ to enable excitation and emission. Given relatively even excitation, I would then expect $h\nu_{out}$ to be mixtures of E_{g_i} , where $i = 1, 2, 3 \dots N$ and N is the number of color-tuned nanowires. These mixtures of E_{g_i} , when balanced in the right proportions, would then constitute the desired white light emission. For the first method, I would use an InGaN-based blue source to pump a yellow-tuned InGaN nanowire to generate yellow down-converted light. This yellow light would mix with the blue pump to generate white light in a method analogous to that using YAG-based phosphors. For the second method, I would

use an InGaN-based blue source to pump an arrangement of red-tuned and green-tuned InGaN nanowires to generate red and green down-converted light. When mixing with the blue pump, this ternary arrangement would produce white light.

The crucial element of this material would then be its efficiency. To achieve the most efficient device, I would optically pump at the highest possible wavelength to minimize the Stokes Shift Loss (i.e., pump at the longest possible wavelength without sacrificing absorption loss in the nanowires). While pumping I would measure the efficiency of the radiative recombination as a function of the InGaN-based pump power.

Many advantages of InGaN nanowires in solid state white lighting applications have been discussed above. Several potential disadvantages must be addressed, however. No one has successfully grown InGaN nanowires to date, and having not successfully done so ourselves, we can conclude that they will likely be difficult to fabricate. Once fabricated, it also might be difficult to develop an equivalent nanowire resin that would coat pump LEDs prior to epoxy coating.

Conclusion

This paper has developed the motivations behind my current research at UCSB by describing the history of solid state white lighting and current problems in the field, reporting on the evolution of GaN nanowire growth, and demonstrating how these two areas of research can be beneficially fused. By adapting GaN nanowire growth techniques to InGaN nanowires, I hope to use ultra-efficient InGaN nanowires to replace current phosphors as down-converters in white LEDs, thus increasing the efficiency of white LEDs and making them even more attractive and viable for commercial applications. On a personal level, “re-lighting the world” with much more efficient (and more spectrally appealing) solid state devices appeals to my environmental ethic – less energy wasted through incandescent light bulbs corresponds to less polluting through coal-burning.

A fundamental outcome of this research would be to understand the physical properties of one dimensional nanoscale materials and their potential application in constructing nanoscale optoelectronic devices. This is an area of great potential for discovery. Further, if InGaN nanowires can function as efficient semiconductor-based down-converting media, they would satisfy the stated condition for a viable solid state white lighting device and could be employed in the next generation of these devices. This would be a major advance towards the goal of inexpensive and efficient next-generation white light sources. Additionally, it would carry the current realm of nitride semiconducting devices to a new level of theoretical sophistication and complexity.

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¹ Collaborators:

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 - Dr. Guosheng Cheng; postdoctoral researcher (Chemistry) for Dr. Moskovits
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