BASIC RESEARCH NEEDS FOR
SOLID-STATE LIGHTING

Report of the Basic Energy Sciences
Workshop on Solid-State Lighting
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On the Cover:

Solid-state lighting relies on the conversion of electricity to visible white light using solid materials. By taking advantage of direct electricity-to-light conversion rather than processes in which light is the by-product of another conversion, as with traditional incandescent and fluorescent lighting, it promises unprecedented, near-100% conversion efficiency.

Today's solid-state lighting technology, however, requires a fifteen-fold improvement to achieve such conversion efficiencies. The reason is that, to become the standard light source of the 21st century, conversion efficiency must be improved while *simultaneously* achieving low cost and "high quality" (a human visual experience similar to that provided by sunlight).

The front cover is an artistic stylization of a "chromaticity diagram," a common tool that can be used to describe how colors can combine to create the human visual impression of white. White can be produced from as few as two colors, but "high-quality" white requires many (e.g., red, yellow, green, and blue) colors. The tessellation overlaid on the chromaticity diagram is suggestive of photonic crystals (nanometer-scale periodic modulations of optical materials that can affect the directionality of light), a frontier area of interdisciplinary science being applied to solid-state lighting.

This report outlines basic research needs that could enable solid-state lighting to achieve its potential. The research needs support two overarching challenges: (1) fundamental understanding of light-emitting materials and nanostructures leading to solid-state lighting structures *rationally designed from the ground up* and (2) control of the competing pathways by which electricity is converted into light not heat so that *every injected electron produces a useful photon*. Successfully addressing these two challenges promises to enable energy-efficient, cost-effective, high-quality white light that will save energy and benefit the environment.

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Report of the Basic Energy Sciences Workshop
on
Solid-State Lighting

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This report is available on the web at *http://www.sc.doe.gov/bes/reports/files/SSL_rpt.pdf.*

CONTENTS

NOTATION

ACRONYMS AND ABBREVIATIONS

AFUE	annual fuel utilization efficiency
(Al)(In)GaN	GaN and its alloys with aluminum and indium
Cat-CVD	catalytic chemical vapor deposition
CCRD	Cross-Cutting Research Direction
CCT	correlated color temperature
CIE	Commission Internationale de l'Éclairage
COL	Cost of Light
CRI	color rendering index
DBR	Distributed Bragg Reflector
DOE	Department of Energy
DOS	density of photon states
EQE	external quantum efficiency
ET	energy transfer
ETL	electron transport layer
FET	field effect transistors
f_T	current-gain cutoff frequency
F-V/SMS	fluorescence-voltage single molecule spectroscopy
FWHM	full-width half maximum
GaN	gallium nitride
GC	grand challenge
HBT	heterojunction bipolar transistors
HFET	high-electron-mobility field-effect transistor
HID	high-intensity discharge
HIL	hole-injection layer
HOMO	highest occupied molecular orbital
HPLC	high performance liquid chromatography
IQE	internal quantum efficiency
IQE	internal quantum efficiency
IR	infrared
ISC	inter-system crossing
ITO	indium tin oxide

LDA	local-density approximation
LED	light-emitting diode
LER	luminous efficacy of radiation
LUMO	lowest unoccupied molecular orbital
MBE	molecular beam epitaxy
MLCT	metal-ligand charge transfer
MOCVD	metal-organic chemical vapor deposition
MOVPE	metal-organic vapor phase epitaxy
NC	nanocrystal
OLED	organic light-emitting diode
OVJP	organic vapor jet printing
PBG	photonic bandgap
p-HEMT	pseudomorphic high electron mobility transistor
PhOLED	phosphorescent OLED
PLED	polymer OLED
PRD	Priority Research Directions
PS	photonic structure
PVD	Physical Vapor Deposition
QCL	Quantum Cascade Laser
QD	quantum dots
QE	quantum efficiency
QW	quantum well
QWIP	Quantum Well Infrared Photodetector
RYGB	red + yellow + green + blue
SE	singlet exciton
SEM	scanning electron microscope
SM-OLED	small-molecule OLED
SOLED	stacked OLED
SPD	spectral power distribution
SSL	solid-state lighting
STEM	scanning transmission electron microscopy
TE	triplet exciton

TEM	transmission electron microscopy		$^{\circ}$C	degree Celsius
			DC	Direct Current
UV	ultraviolet		GW	gigawatt
			GHz	gigahertz
VCSEL	vertical cavity surface emitting laser		K	Kelvin
			kWh	kilowatt hour
			lm	lumen
WOLED	white OLED		Lm/W	lumens per Watt
WPE	wall-plug efficiency		m	meter
			nm	nanometer
YAG	Yttrium aluminum garnet $Y_3Al_5O_{12}$		s	second
YAG:Ce^{3+}	YAG doped with cerium		Tlmh/yr	Teralumen hours per year
			TW	Terawatt
			TWh	Terawatt hour
			W	Watt
			µm	micrometer
			yr	year

UNITS OF MEASURE

A	ampere
Cd	candela
cm	centimeter

EXECUTIVE SUMMARY

Since fire was first harnessed, artificial lighting has gradually broadened the horizons of human civilization. Each new advance in lighting technology, from fat-burning lamps to candles to gas lamps to the incandescent lamp, has extended our daily work and leisure further past the boundaries of sunlit times and spaces. The incandescent lamp did this so dramatically after its invention in the 1870s that the light bulb became the very symbol of a "good idea."

Today, modern civilization as we know it could not function *without* artificial lighting; artificial lighting is so seamlessly integrated into our daily lives that we tend not to notice it until the lights go out. Our dependence is even enshrined in daily language: an interruption of the electricity supply is commonly called a "blackout."

This ubiquitous resource, however, uses an enormous amount of energy. In 2001, *22% of the nation's electricity, equivalent to 8% of the nation's total energy,* was used for artificial light. The cost of this energy to the consumer was roughly $50 billion per year or approximately $200 per year for every person living in the U.S. The cost of this energy to the environment was approximately 130 million tons of carbon emitted into our atmosphere, or about 7% of all the carbon emitted by the U.S. Our increasingly precious energy resources and the growing threat of climate change demand that we reduce the energy and environmental cost of artificial lighting, an essential and pervasive staple of modern life.

There is ample room for reducing this energy and environmental cost. The artificial lighting we take for granted is *extremely* inefficient primarily because all these technologies generate light as a by-product of indirect processes producing heat or plasmas. Incandescent lamps (a heated wire in a vacuum bulb) convert only about 5% of the energy they consume into visible light, with the rest emerging as heat. Fluorescent lamps (a phosphor-coated gas discharge tube, invented in the 1930s) achieve a conversion efficiency of only about 20%. These low efficiencies contrast starkly with the relatively high efficiencies of other common building technologies: heating is typically 70% efficient, and electric motors are typically 85 to 95% efficient. About 1.5 billion light bulbs are sold each year in the U.S. today, *each one an engine for converting the earth's precious energy resources mostly into waste heat, pollution, and greenhouse gases*.

SOLID-STATE LIGHTING

There is no physical reason why a 21st century lighting technology should not be vastly more efficient, thereby reducing equally vastly our energy consumption. If a 50%-efficient technology were to exist and be extensively adopted, it would reduce energy consumption in the U.S. by about 620 billion kilowatt-hours per year by the year 2025 and eliminate the need for about 70 nuclear plants, each generating a billion Watts of power.

Solid-state lighting (SSL) is the *direct* conversion of electricity to visible white light using semiconductor materials and has the potential to be just such an energy-efficient lighting technology. By avoiding the indirect processes (producing heat or plasmas) characteristic of traditional incandescent and fluorescent lighting, it can work at a far higher efficiency, "taking the heat out of lighting," it might be said. Recently, for example, semiconductor devices emitting infrared light have demonstrated an efficiency of 76%. *There is no known fundamental physical barrier to achieving similar (or even higher) efficiencies for visible white light, perhaps approaching 100% efficiency.*

Despite this tantalizing potential, however, SSL suitable for illumination today has an efficiency that falls short of a perfect 100% by a factor of *fifteen*. Partly because of this inefficiency, the purchase cost of SSL is too high for the average consumer by a factor ten to a hundred, and SSL suitable for illumination today has a cost of ownership *twenty* times higher than that expected for a 100% efficient light source.

The reason is that SSL is a dauntingly demanding technology. To generate light near the theoretical efficiency limit, essentially every electron injected into the material must result in a photon emitted from the device. Furthermore, the voltage required to inject and transport the electrons to the light-emitting region of the device must be no more than that corresponding to the energy of the resulting photon. It is insufficient to generate "simple" white light; the distribution of photon wavelengths must match the spectrum perceived by the human eye to render colors accurately, with no emitted photons outside the visible range. Finally, all of these constraints must be achieved in a single device with an operating lifetime of at least a thousand hours (and preferably ten to fifty times longer), at an ownership cost-of-light comparable to, or lower than, that of existing lighting technology.

Where promising demonstrations of higher efficiency exist, they are typically achieved in small devices (to enhance light extraction), at low brightness (to minimize losses) or with low color-rendering quality (overemphasizing yellow and green light, to which the eye is most sensitive). These restrictions lead to a high cost of ownership for high-quality light that would prevent the widespread acceptance of SSL. For example, Cree Research recently (June 2006) demonstrated a 131 lm/W white light device, which translates roughly to 35% efficiency but with relatively low lumen output. With all devices demonstrated to date, a very large gap is apparent between what is achievable today and the 100% (or roughly 375 lm/W) efficiency that should be possible with SSL.

Today, we cannot produce white SSL that is *simultaneously* high in efficiency, low in cost, and high in color-rendering quality. In fact, we cannot get within a factor of ten in either efficiency or cost. Doing so in the foreseeable future will require breakthroughs in technology, stimulated by a fundamental understanding of the science of light-emitting materials.

THE BASIC ENERGY SCIENCES WORKSHOP ON SOLID-STATE LIGHTING

To accelerate the laying of the scientific foundation that would enable such technology breakthroughs, the Office of Basic Energy Sciences in the U.S. Department of Energy (DOE) convened the Workshop on Basic Energy Needs for Solid-State Lighting from May 22 to 24, 2006. The charge to the workshop was to examine the gap separating current state-of-the-art SSL technology from an energy efficient, high-quality, and economical SSL technology suitable for general illumination; and to identify the most significant fundamental scientific challenges and research directions that would enable that gap to be bridged.

This report is a summary of that workshop. It reflects the collective output of the workshop attendees, which included 80 scientists representing academia, national laboratories, and industry in the United States, Europe, and Asia. Workshop planning and execution involved advance coordination with the DOE Office of Energy Efficiency and Renewable Energy, Building Technologies program, which manages applied research and development of SSL technologies and the Next Generation Lighting Initiative.

The Workshop identified two Grand Challenges, seven Priority Research Directions, and five Cross-Cutting Research Directions. These represent the most specific outputs of the workshop.

GRAND CHALLENGES

The ***Grand Challenges*** are broad areas of discovery research and scientific inquiry that will lay the groundwork for the future of SSL. The first Grand Challenge aims to change the very paradigm by which SSL structures are designed — moving from serendipitous discovery towards rational design. The second Grand Challenge aims to understand and control the essential roadblock to SSL — the microscopic pathways through which losses occur as electrons produce light.

Rational Design of SSL Structures. Many materials must be combined in order to form a light-emitting device, each individual material working in concert with the others to control the flow of electrons so that all their energy produces light. Today, novel light-emitting and charge-transporting materials tend to be discovered rather than designed "with the end in mind." To approach 100% efficiency, fundamental building blocks should be designed so they work together seamlessly, but such a design process will require much greater insight than we currently possess. Hence, our aim is to understand light-emitting organic and inorganic (and hybrid) materials and nanostructures at a fundamental level to enable the rational design of low-cost, high-color-quality, near-100% efficient SSL structures from the ground up. The anticipated results are tools for rational, informed exploration of technology possibilities; and insights that open the door to as-yet-unimagined ways of creating and using artificial light.

Controlling Losses in the Light-Emission Process. The key to high efficiency SSL is using electrons to produce light but not heat. That this does not occur in today's SSL structures stems from the abundance of decay pathways that compete with light emission for electronic excitations in semiconductors. Hence, our aim is *to discover and control the materials and nanostructure properties that mediate the competing conversion of electrons to light and heat, enabling* the *conversion of every injected electron into useful photons*. The anticipated results are ultra-high-efficiency light-emitting materials and nanostructures, and a deep scientific understanding of how light interacts with matter, with broad impact on science and technology areas beyond SSL.

RESEARCH DIRECTIONS

The ***Priority and Cross-Cutting Research Directions*** are narrower areas of discovery research and use-inspired basic research targeted at a particular materials set or at a particular area of scientific inquiry believed to be central to one or more roadblocks in the path towards future SSL technology. These Research Directions also support one or both Grand Challenges.

The Research Directions were identified by three panels, each of which was comprised of a subset of the workshop attendees and interested observers. The first two panels, which identified the Priority Research Directions, were differentiated by choice of materials set. The first, LED Science, focused on inorganic light-emitting materials such as the Group III nitrides, oxides, and novel oxychalcogenides. The second, OLED Science, considered organic materials that are carbon-based molecular, polymeric, or dendrimeric compounds. The third panel, which identified the Cross-Cutting Research Directions, explored cross-cutting and novel materials science and optical physics themes such as light extraction from solids, hybrid organic-inorganic and unconventional materials, and light-matter interactions.

LED Science. Single-color, inorganic, light-emitting diodes (LEDs) are already widely used and are bright, robust, and long-lived. The challenge is to achieve white-light emission with high-efficiency and high-color rendering quality at acceptable cost while maintaining these advantages. The bulk of current research focuses on the Group III-nitride materials. Our understanding of how these materials behave and can be controlled has advanced significantly in the past decade, but significant scientific mysteries

remain. These include (1) determining whether there are as-yet undiscovered or undeveloped materials that may offer significant advantages over current materials; (2) understanding and optimizing ways of generating white light from other wavelengths; (3) determining the role of piezoelectric and polar effects throughout the device but particularly at interfaces; and (4) understanding the basis for some of the peculiarities of the nitrides, the dominant inorganic SSL materials today, such as their apparent tolerance of high defect densities, and the difficulty of realizing efficient light emission at all visible wavelengths.

OLED Science. Organic light emitting devices (OLEDs) based on polymeric or molecular thin films have been under development for about two decades, mostly for applications in flat-panel displays, which are just beginning to achieve commercial success. They have a number of attractive properties for SSL, including ease (and potential affordability) of processing and the ability to tune device properties via chemical modification of the molecular structure of the thin film components. This potential is coupled with challenges that have so far prevented the simultaneous achievement of high brightness at high efficiency and long device lifetime. Organic thin films are often structurally complex, and thin films that were long considered "amorphous" can exhibit order on the molecular (nano) scale. Research areas of particularly high priority include (1) quantifying local order and understanding its role in the charge transport and light-emitting properties of organic thin films, (2) developing the knowledge and expertise to synthesize and characterize organic compounds at a level of purity approaching that of inorganic semiconductors, and understanding the role of various low-level impurities on device properties in order to control materials degradation under SSL-relevant conditions, and (3) understanding the complex interplay of effects among the many individual materials and layers in an OLED to enable an integrated approach to OLED design.

Cross-Cutting and Novel Materials Science and Optical Physics. Some areas of scientific research are relevant to all materials systems. While research on inorganic and organic materials has thus far proceeded independently, the optimal material system and device architecture for SSL may be as yet undiscovered and, furthermore, may require the integration of *both* classes of materials in a single system. Research directions that could enable new materials and architectures include (1) the design, synthesis, and integration of novel, nanoscale, heterogeneous building blocks, such as functionalized carbon nanotubes or quantum dots, with properties optimized for SSL, (2) the development of innovative architectures to control the flow of energy in a light emitting material to maximize the efficiency of light extraction, (3) the exploitation of strong coupling between light and matter to increase the quality and efficiency of emitted light, (4) the development of multiscale modeling techniques extending from the atomic or molecular scale to the device and system scale, and (5) the development and use of new experimental, theoretical, and computational tools to probe and understand the fundamental properties of SSL materials at the smallest scales of length and time.

SUMMARY

The workshop participants enthusiastically concluded that the time is ripe for new fundamental science to beget a revolution in lighting technology. SSL sources based on organic and inorganic materials have reached a level of efficiency where it is possible to envision their use for general illumination. The research areas articulated in this report are targeted to enable disruptive advances in SSL performance and realization of this dream. Broad penetration of SSL technology into the mass lighting market, accompanied by vast savings in energy usage, requires nothing less. These new "good ideas" will be represented not by light bulbs, but by an entirely new lighting technology for the 21st century and a bright, energy-efficient future indeed.

INTRODUCTION

INTRODUCTION

THE ENERGY CHALLENGE

Meeting predicted worldwide energy consumption needs over the next hundred years will require fundamental changes in how we generate and use energy. Approximately 8% of the energy and 22% of the electricity consumed in the U.S. are transformed into artificial lighting [Navigant 2002]. Assuming reasonable growth rates, by the year 2025 the U.S. may be using as much as 1,000 Terawatt-hours (TWh) of electricity for lighting every year (1 TW is 10^{12} W or 1 trillion Watts). Worldwide, the energy used for lighting is estimated to be three to four times greater.

Given the ubiquity of lighting, it is somewhat surprising that 42% of the electricity used for lighting in the U.S. is consumed by light bulbs that use technology invented in the nineteenth century to heat a filament to above 3,000 °C. By a process known as incandescence, the filaments in such light bulbs convert more than 95% of the supplied energy into heat, with less than 5% actually emerging as visible light (see Appendix 1 for a more detailed discussion). New materials, first developed in the 1960s, however, allow the direct conversion of energy to light via the manipulation of electrons in a solid at room temperature. There is a range of systems (Figure 1) now exploiting these materials for visible light. Those systems that aim to produce white light for illumination purposes are collectively termed solid-state lighting (SSL).

Figure 1 Applications of LEDs and solid-state lighting. (Left) Monochrome LEDs already generate significant energy savings in traffic signal and indicator light applications. (Right) The biggest energy impact, however, lies in the illumination of building spaces by solid-state white lighting, as illustrated in this "concept" room. Source: Osram
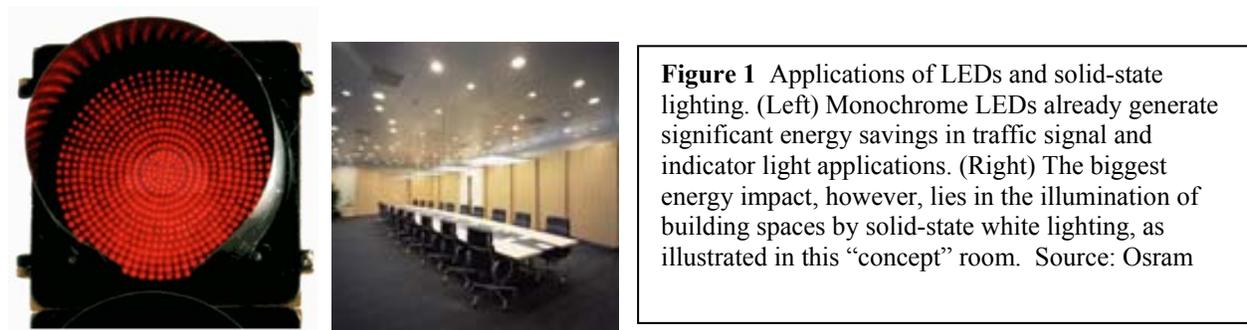
SSL has enormous potential. Solid-state devices have recently achieved electrical-to-optical power-conversion efficiencies of 76% at infrared wavelengths [Peters 2006]. Unlike incandescent and fluorescent lighting, for which indirect processes (electricity to heat, electricity to gas discharges) limit efficiencies, there is no known fundamental physical barrier to SSL achieving similar (or even higher) efficiencies for bright white light.

Even if "only" 50% efficient SSL were to be achieved and displaced current white-lighting technologies completely, the impact would be enormous. The electricity used for lighting would be cut by 62%, and total electrical energy consumption would decrease by roughly 13%. In the U.S. alone, consumers would save around $42 billion each year in electricity cost by 2025, and energy consumption would decrease by 620 TWh/y, or 70 GW (gigawatts) less average power. In other words, the U.S. *could forego building 70 nuclear power plants* (at roughly 1 GW per plant). These estimates do not take into account the *further* energy savings from the reduced heat load on air-conditioning systems as a result of improvements in inefficient lighting in hot climates.

The savings in energy production that could be enabled by SSL would also have an important impact on the environment. Currently, the U.S. emits approximately 10^6 tons of carbon to the atmosphere for every 6 TWh of electrical energy consumed. If the nation continues to produce its electricity with roughly the

same mix of technologies, the energy saved in 2025 through SSL would reduce carbon-equivalent emissions by about 100 Megatons per year.

CONVENTIONAL AND SOLID-STATE LIGHTING

Human vision is uncompromisingly selective about what constitutes acceptable illumination. The human eye is sensitive to light with a wavelength between only about 400 nm and 700 nm, with a distinct sensitivity peak at 555 nm as shown at the top of Figure 2. This curve essentially defines the conversion between watts of optical power and lumens (the unit of light intensity *perceived* by the human eye), and hence is the maximum luminous efficacy possible for a radiation source as a function of wavelength. A high-efficiency source suitable for general lighting applications should have a wavelength distribution that is as wide as possible but contained within the maximum luminous efficacy curve. A substantially narrower or noncentered wavelength distribution results in a light perceived as colored, and objects illuminated with such a source will not have their true colors "well-rendered." Moreover, light outside the wavelength range of the luminous efficacy curve represents wasted energy.

In the case of incandescent light bulbs, the basic technology, invented by Edison and others in the late nineteenth century, uses electricity to heat a coiled tungsten-based wire encapsulated in an evacuated glass bulb. When heated, the wire begins to glow red, yellow, and ultimately white, as its temperature increases. Most incandescent light bulbs operate at a temperature of 3,000–4,000 K to achieve a balance between light output and useable filament lifetime.

The spectrum of radiation from a realistic incandescent light bulb is shown as the dashed line at the bottom of Figure 2. Its spectrum is very broad (fills the entire wavelength range of high human eye sensitivity), so it renders colors extremely well. Indeed, a standard measure in the lighting industry is the color rendering index (CRI), which basically quantifies how well a light source renders colors compared to an ideal light source. The CRI is a number between 0 and 100, and incandescent light bulbs typically have a CRI approaching 100. As also seen in Figure 2, however, the incandescent bulb's spectrum is *too* broad (overfills the wavelength range of high human eye sensitivity). Most of its energy, some 95%, is emitted in the infrared as heat, beyond the response of the human eye; only a small fraction (roughly 5%) of the input energy is converted to visible light.

In the case of fluorescent tubes, which were commercialized in the middle of the twentieth century, ultraviolet (UV) light is generated by striking an electrical discharge in a glass tube containing a low pressure of a gas such as mercury, argon, or a mixture of gases. The electrical discharge excites electrons in the gas, and UV light is emitted when the electrons subsequently relax. UV light is absorbed by a mixture of phosphors coating the inside of the glass tube. The phosphors emit longer wavelength light in response to the UV illumination, and this is the light emitted from the fluorescent tube.

The spectrum of a typical fluorescent tube is shown as the dotted line at the bottom of Figure 2. It is made up of pronounced peaks in the blue, green, and red. While early fluorescent tubes achieved relatively high luminous efficacy, they had low CRI and poor color rendition properties because of the narrow line width of available phosphors. The CRI has steadily improved through new phosphor development, but overall efficiencies have barely increased for decades and are still (including ballast losses) roughly in the 20% range. The sources of the inefficiencies appear to be a combination of the excitation of the plasma itself, the conversion of plasma excitation to ultraviolet light, and the conversion of ultraviolet to visible white light.
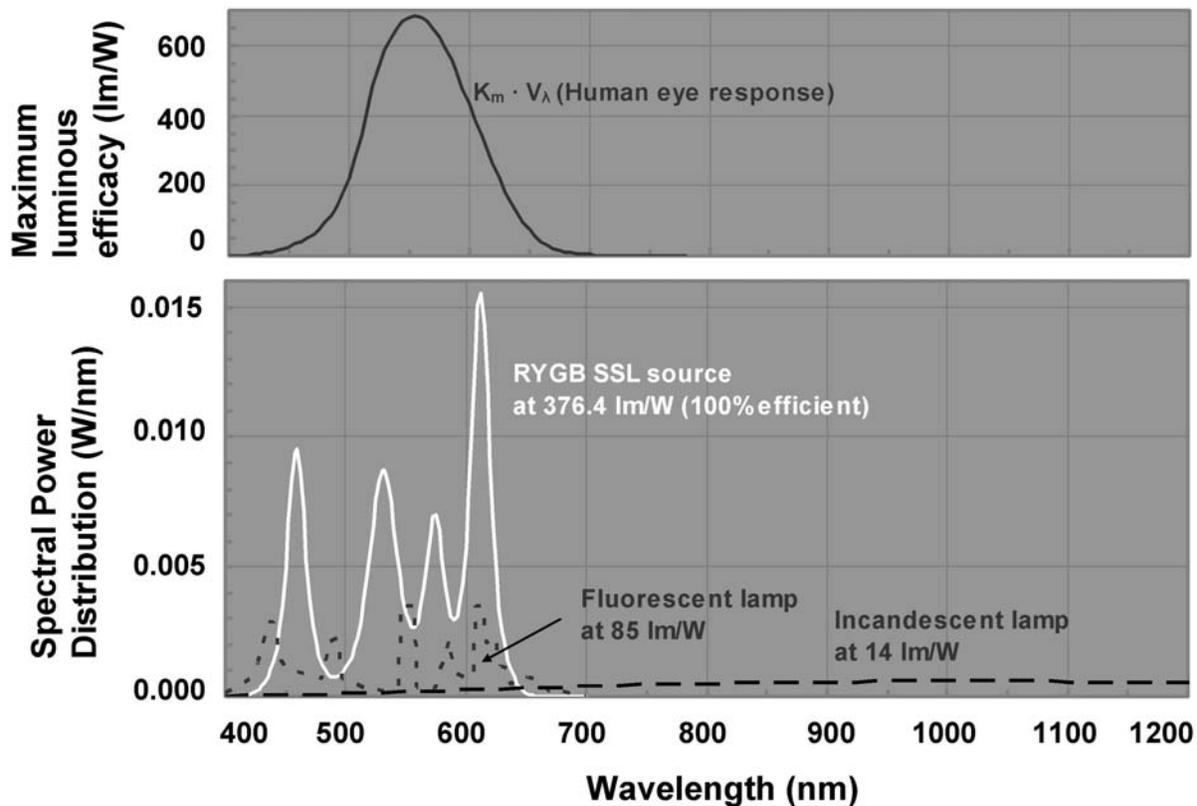
Figure 2 (Top) A plot of the maximum luminous efficacy possible for a radiation source as a function of wavelength. This curve is essentially the human-eye response function, explained more fully in Appendix 1. (Bottom) Plot of the spectral power distributions (SPDs) for three sources: an incandescent lamp, scaled to a luminous efficacy of 14 lm/W; a fluorescent lamp, scaled to a luminous efficacy of 85 lm/W; and a hypothetical four-color 100%-efficient high-color-rendering-quality RYGB SSL white light source, scaled to a luminous efficacy of 376.4 lm/W.

New materials designed to convert electricity directly to visible light *at room temperature* without the generation of heat would allow far higher lighting efficiency at high CRI, perhaps approaching the theoretical limit. Such materials were originally demonstrated in the early 1960s in inorganic [Holonyak and Bevacqua 1962] and organic crystals [Pope, Kallmann, and Magnante 1963] (see next section). In both cases, subsequent development led to a range of colored light sources known as light-emitting diodes (LEDs) and organic light-emitting diodes (OLEDs). The efficiency of these single color devices now exceeds that of filtered incandescent and even fluorescent lamps and there does not appear to be any fundamental physical reason why they could not span the visible with near-100% efficiency. The prospect of inexpensive, 100%-efficient SSL for general illumination is a compelling new horizon for reducing energy use and greenhouse gas emissions.

A hypothetical 100%-efficient four-color (red, yellow, green, blue) SSL white-light source with good color rendering (CRI 90) is shown as the white line at the bottom of Figure 2. The luminous efficacy of the SSL source is 4.4 times greater than that of the fluorescent lamp and 27 times greater than that of the incandescent lamp so its power spectrum dwarfs both. *This, then, is the quantitative promise of SSL: efficiency that dwarfs that of fluorescent and incandescent lamps, with both high CRI and low cost of ownership.* To achieve such SSL, however, significant challenges must be overcome. Among these, as

discussed throughout this report, are the understanding and control of the materials that mediate the competing conversion of electrons to light and heat at the nanoscale, enabling the conversion of every injected electron into useful photons.

Lighting is used in a wide range of applications, each with different requirements for color, brightness, and directionality. Single-color lamps are suitable for applications such as status indicators, including traffic signals, where LED arrays are already replacing filtered incandescent lamps with large resulting savings in energy and maintenance cost. The largest energy impact, however, lies in general illumination for buildings, and this requires high-quality white light. Neither OLEDs nor LEDs can produce acceptable white light from a single material today. This leads to scientific challenges that are unique to lighting applications.

Most solid-state white-light devices use one of two approaches (Figure 3): a combination of two, three, or even four single-color subelements, either side by side or in a vertically stacked geometry; or use of a blue or UV device to stimulate fluorescent or phosphorescent light emission of a different color in other materials. Both approaches face challenges: the first will require efficient LEDs over the full range of visible wavelengths; while the second must overcome energy losses associated with the wavelength down-conversion. A more detailed description of white-light characteristics is given in the Technology Perspective in Appendix 1.

Figure 3 It has thus far not proven possible to generate acceptable quality white light from a single inorganic or organic LED with high efficiency. Techniques for generating white typically fall into two categories: combining two (yellow and blue) or more (e.g., red, blue, and green) devices, shown on the left, or absorbing part of the light from a blue or ultraviolet device in a phosphor that subsequently generates light of other colors (e.g., yellow).

Both incandescent and fluorescent lamps require a diffuser (such as a lamp shade) to prevent the dazzle that would otherwise result from a small, high-intensity light source. This, together with reflectors and electrical fixturing, is collectively known as the luminaire. This part of the optical system can result in a 20% to 50% power efficiency loss, which can increase further as the diffuser accumulates dust. For efficient energy conversion, *system* efficiency is the critical parameter. As this report shows, some SSL technologies might allow the elimination of the luminaire. Further opportunities are created by spectrally tunable SSL that could, for example, vary the quality of a lamp to match the human circadian rhythm. Such desirable advantages cannot be achieved with conventional incandescent and fluorescent lighting, although there is ongoing debate as to the impact of such human factors on worker productivity and quality of life.

MATERIALS FOR SOLID-STATE LIGHTING

SSL materials fall into three broad categories, illustrated in Figure 4. Many of the scientific challenges (e.g., light production) associated with SSL depend strongly on the material category, while other challenges (such as light extraction) cut across the various material categories.

Inorganic Materials

Conventional semiconductor electronics is almost exclusively comprised of inorganic materials, the most common being silicon. Elemental semiconductors such as silicon, however, have indirect bandgaps (Streetman and Banerjee 2005), making it hard to use these materials to generate photons without heat. In contrast, many compound semiconductors have direct bandgaps, making photon production far more efficient. Early work on visible light emission from a compound semiconductor used the three component system gallium arsenide phosphide (GaAsP) [Holonyak and Bevacqua 1962]. The most efficient visible-light-emitting materials today are drawn from three-and-four component systems such as aluminum indium gallium phosphide or nitride (AlInGaP or AlInGaN). Light-emitting devices (most commonly diodes) made from these and other inorganic materials are known as light-emitting diodes, or LEDs. The number of possible light-emitting three- and four-component semiconductors is daunting. It is possible, perhaps even likely, that a superior SSL material remains undiscovered. Perhaps, indeed, the success of ceramic superconductors suggests that adding still more components to the semiconductor alloy will lead to dramatic improvement. How we choose the most likely candidates and prove that we have found the optimum material is a challenge of the highest order.

Compound semiconductors that emit light are generally single-crystal materials grown as thin films at very high purity using layer-by-layer growth processes such as molecular beam epitaxy or metal-organic chemical vapor deposition. The word "epitaxy" implies that the crystallographic order and orientation of the thin film is strongly correlated with that of the substrate. Conventionally, the thin film is grown "homoepitaxially" on a carefully prepared and cleaned substrate surface of the same material. If the thin film is grown "heteroepitaxially" on a different material, the two lattice constants must normally be very similar. A lattice constant mismatch of only a few percent leads to a rapid buildup of strain in the growing thin film, ultimately causing the formation of defects that usually degrade device performance. However, some light-emitting materials, particularly the nitrides, can (and in some cases must) be grown on highly mismatched substrates such as sapphire and can accommodate a surprising density of defects while still producing efficient LEDs. The reasons for this mysterious defect tolerance are not well understood and is a major fundamental science challenge for SSL.
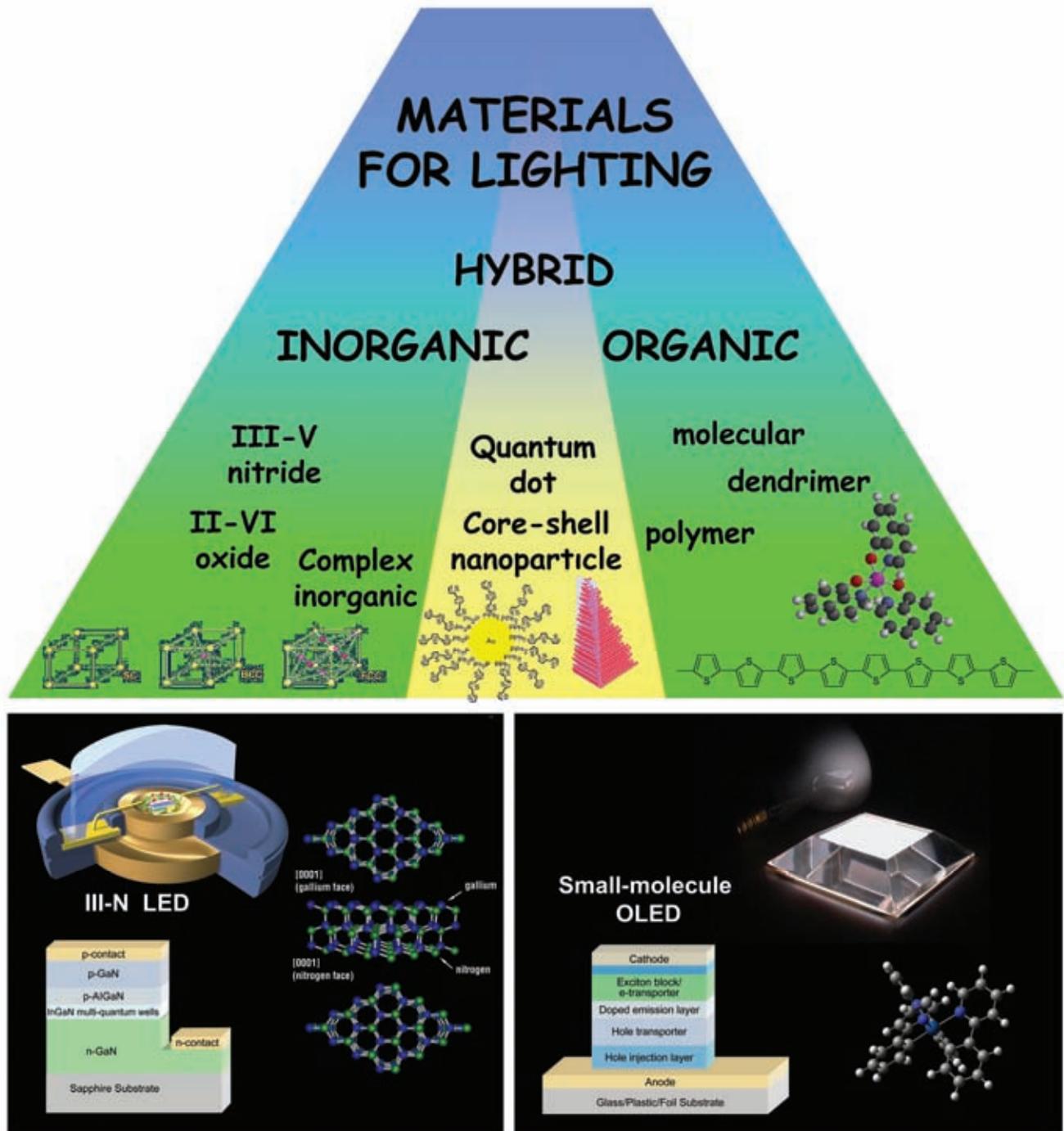
Figure 4 Materials for SSL span a wide range from crystalline inorganic semiconductors (left) to waxy organic materials (right) to hybrid structures (middle) such as core-shell nanoparticles combining both material sets into engineered structures. The white OLED (bottom right) is 25 cm^2 in area and optically coupled to an acrylic luminaire. Phosphorescent materials are employed to achieve 30 lm/W at 1,000 cd/m^2 normal emission. An incandescent lamp is shown in the background. (OLED photograph courtesy Universal Display Corporation.) Inorganic LED chips made from AlInGaN compound semiconductors (bottom left) are typically 1 mm^2 or smaller in area and may be coated with phosphors to generate white light. A schematic cross-section of a packaged Luxeon[TM] LED chip made by Philips Lumileds Lighting Company is shown (encapsulation removed to reveal LED chip).

Sophisticated growth techniques and the development of three (ternary) and four (quaternary) component systems allow for the fabrication of complex multilayer structures. Electrical charge carriers, both negative (electrons) and positive (holes), are confined in conduction and valence bands, respectively, and their allowed energy states can be adjusted by fine tuning both the composition and thickness of the various multilayers. Simultaneously, light can be manipulated in the multilayer structure by arranging the refractive indices of the layers to form, for example, a waveguide. In total, the available toolkit of materials and growth techniques enables the creation of layer structures a few microns thick that allow for the efficient injection of charge, conversion to light, and, finally, extraction of light back into the outside world. Even so, a significant fraction of the energy introduced into these structures never emerges as light. Understanding the causes for these energy losses is the crucial precursor to one day eliminating them.

Two key characteristics of LEDs based on inorganic materials are small size and high brightness. Typically, they are a square millimeter or less in area. And, because of the robustness and high thermal conductivity of inorganic semiconductors (GaN, for example, can be considered a refractory ceramic material), they may be "driven" very hard. The brightness (or luminance) of the emitting surface of current commercial LEDs is already as high as 2×10^8 cd/m^2 (more than 400,000 times brighter than the 200–500 cd/m^2 of a typical video screen), and there does not appear to be a fundamental physical reason why it could not be ten times brighter still. At this brightness, a single mm^2 chip would produce the same amount of light now produced by a 60 W to 75 W incandescent light bulb! At these power levels, however, light-emission efficiencies can decrease significantly and, worse, defects can form, thus shortening the lifetime of the device below levels acceptable for SSL. An understanding of the fundamental mechanisms that give rise to the formation of these defects is a crucial precursor to controlling their creation and achieving bright devices and long lifetimes simultaneously.

Two additional important consequences of the small size and high brightness of LEDs are that (1) LED costs (per unit chip area) may be relatively high and (2) their light cannot be looked at directly but must be diffused and distributed by an optical system before use.

Organic Materials

Organic semiconductors are carbon-based solids that may be discrete molecules, often called "small molecules" although the molecular weight typically exceeds 400 [Tang and Van Slyke 1987], long chain polymers [Burroughes et al. 1990], or dendrimers [Halim et al. 1999]. The first OLED was demonstrated in single crystals of anthracene, although the operating voltage was extremely high. Low-voltage devices have subsequently been demonstrated using amorphous materials engineered into extremely thin films, typically only a few tens of nanometers thick. The molecular structure of one efficient organic light emitter, consisting of three phenylpyridine moieties chelated to an iridium ion [Baldo 1999] is shown in Figure 4.

The properties of organic semiconductors are very different from those of inorganic semiconductors. Charge carrier mobilities are orders of magnitude lower and are strongly voltage and temperature dependent. Conduction and valence bands have little meaning for charge transport and are replaced by lowest unoccupied and highest occupied molecular orbitals (LUMO and HOMO, respectively). In the amorphous materials, injected charge tends to quickly localize around an individual molecule. Crystalline organic materials such as pentacene can have higher mobilities of up to 15 cm^2/Vs and may exhibit band-like conduction, but thus far do not emit light. Just as for inorganic semiconductors, however, the relevant energy levels for charge transport and light emission can be adjusted, though the means of doing so are different, in this case via chemical changes to molecular structure. Given the seemingly unbounded

versatility of carbon chemistry, an enormous diversity of molecules can be synthesized and integrated to optimize charge transport, light emission, color-tunability, or other desirable properties. This very diversity presents a challenge, however, since exploring all possible materials would be difficult. Can a sufficient scientific understanding of the factors governing the properties important for SSL be developed so that the most promising organic materials and structures can be identified *before* they are fabricated?

Although light-emitting organic materials are often characterized as amorphous, the thin-film structure on the molecular scale is not well understood, and local order may influence the properties of the solid. In the case of polymers, dispersity in molecular weight and conjugation length adds further complexity. Structural and optical isomers of an organic molecule may be *chemically* identical but *electronically* distinct, and the further presence of molecular fragments makes the assay of purity and quantification of the role of impurities a complex task. Thus, an understanding of the roles of purity and degrees of order in light-emitting organic materials as they relate to SSL is necessary. It is also highly probable that an understanding will need to be gained of how to produce organic materials at a level of purity that is unimaginable today. Progress in these areas can be anticipated to lead to OLED lifetimes that are sufficient for large-scale deployment in the consumer market.

Two key characteristics of OLEDs based on organic materials are large size and moderate brightness. Because there is no requirement to lattice match amorphous organic films to an expensive single-crystal substrate, OLEDs can in principle be deposited inexpensively (using vacuum deposition or printing techniques) on large areas of any suitably flat surface including glass, plastic, and metal foils. Also, because OLEDs appear to be limited in how hard they can be "driven" with a long operating lifetime, their brightness will be moderate: although a brightness in excess of 10^6 cd/m^2 has been demonstrated, operating lifetimes decrease with brightness and lifetimes on the order of thousands of hours have only been demonstrated at a brightness less than 10^4 cd/m^2. Still, this brightness is in the right range for general white lighting: at a brightness of 1,000 to 2,000 cd/m^2, roughly one square meter would be sufficient to produce the same amount of light now produced by a 60 W to 75 W incandescent light bulb. This is also a brightness that would enable large OLED panels not only to illuminate, but also to be viewed directly without discomfort, eliminating the need for a light-wasting luminaire. If we can simultaneously achieve long device lifetimes and high energy efficiency in devices of this sort by addressing the scientific challenges, SSL based on OLEDs could become a formidable economic force.

Hybrid Materials

Hybrid combinations of inorganic and organic materials may also play a role in SSL. For example, inorganic semiconductors have excellent carrier transport properties (e.g., high electron and hole mobilities), while organic semiconductors have excellent light-emission properties (e.g., high-luminescence quantum yield and color tunability). Hence, one might imagine a structure within which charge injection and transport occur first in an inorganic material, followed by charge transfer to an organic material, followed finally by luminescence and light extraction into the world [Agranovich et al. 1998].

Alternately, for example, inorganic nanoparticles (or quantum dots) of semiconductors such as cadmium selenide are well known for their efficient luminescence that can be tuned by changing the size of the particle, but phenomena such as surface quenching can swallow almost all their potential light emission. By "capping" these inorganic nanoparticles with organic molecules, it is possible to improve both fluorescence efficiency and ease of fabrication. The resulting structures could be used as down-conversion media (i.e., to convert UV or blue light into longer wavelength color via fluorescence), and recent work has demonstrated that they can, in principle, be incorporated into the light-emitting structure

of an OLED. The exploration of hybrid materials for SSL is in its infancy. Developing a deep understanding of the unique capabilities of these materials may offer as yet unimagined routes to revolutionary SSL.

SOLID-STATE LIGHTING OUTLOOK

SSL using any of the materials (inorganic, organic, or hybrid) discussed above has the *potential* for unprecedented efficiencies. Indeed, solid-state devices have recently achieved electrical-to-optical power-conversion efficiencies of 76% at infrared wavelengths [Peters 2006], and there does not appear to be any fundamental physical reason why they could not span the visible with near-100% efficiency. The large efficiency gap between the theoretically possible and the practically achieved (Figure 5) demonstrates that despite its greater than 40 year history, SSL still faces enormous technical challenges that are likely to be surmounted only with dramatic increases in scientific understanding.
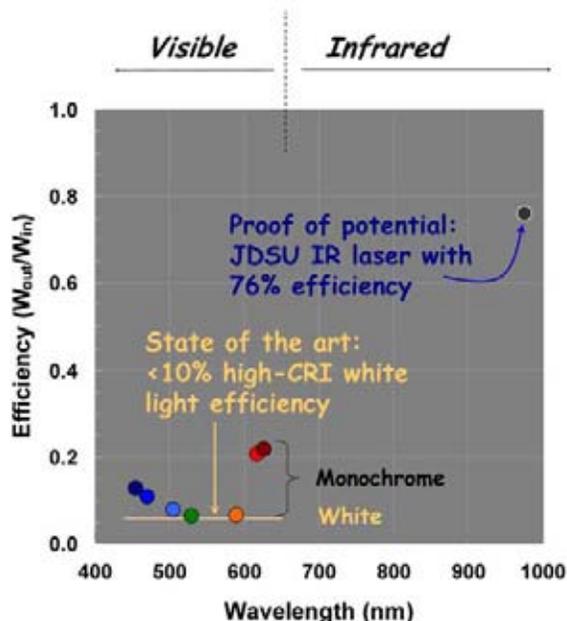
Figure 5 Power efficiency as a function of wavelength for commercially available monochrome LEDs compared to a state-of-the-art infrared laser (IR) [JDS Uniphase Corporation, Peters 2006]. The beige line represents the efficiency of commercial white LEDs designed for high color rendering quality and low cost-of-light. Higher efficiency devices have been demonstrated in research laboratories but at lower color rendering qualities and/or higher costs-of-light.

As discussed in more detail in Appendix 1, the efficiencies of state-of-the-art commercial devices designed to produce light with a low "cost-of-light" (the total cost of light to the consumer, including purchase, maintenance, and operating costs) and a high CRI are very low. This is illustrated in Figure 5, which shows efficiencies for such devices for various visible wavelengths. High efficiency across the visible wavelength range is needed for SSL, but as can be seen, efficiencies are on the order of 10% in the blue and still lower in the rest of the visible spectrum. Thus, there is a major gap between current SSL performance and the theoretical near-100% efficiency *potential* of SSL. Hence, while incremental improvements in technology will be important, a revolutionary jump in performance is needed to achieve high-efficiency SSL and a concomitant savings in energy usage and greenhouse gas emissions. Such a jump will be accelerated by a focused effort on fundamental research into the materials and mechanisms of light emission in semiconductors.

The opportunity for breakthroughs in the fundamental science of light emission occurs now because of several recent scientific and infrastructural advances:

- A new ability to control the structure of matter all the way from the nanoscale to the microscale allows the confinement of both electrons (to ensure only electronic transitions giving rise to light emission are allowed in the structure) and photons (to restrict light emission only into those optical modes that usefully couple light out of the system). This level of control will accelerate the achievement of near-100% conversion efficiency devices.

- Rapidly advancing capabilities to see the atomic structure, chemical composition, and properties (e.g., the ability to convert electricity to light) of materials at the nanoscale are enabling new insights into the structure of matter and its interactions with light.

- Recent advances in theoretical techniques to predict material properties with unprecedented accuracy, coupled with dramatic increases in computational power, are enabling new modeling techniques to rationally design semiconductor or molecular light-emitting materials. There is, however, still a significant gap between our ability to model important properties of a single material and the need to model an entire SSL device.

- Continuing progress in the synthesis and purification of SSL materials is beginning to enable separation of extrinsic and intrinsic phenomena and improve device performance. The ability to prepare high-quality crystalline silicon enabled the electronics revolution of the past 50 years — the technical community must now learn how to do the same for organic and inorganic materials for SSL. In particular, despite impressive progress in recent years, the purity of organic materials relevant to SSL remains more than three orders of magnitude poorer than for common inorganic semiconductors.

- Advances in the ability to probe in real time the structure of surfaces and thin films. For example, very high brilliance synchrotrons have made it possible to do in situ X-ray characterization of materials synthesis by metalorganic chemical vapor deposition, the most common (yet poorly-understood) process for producing inorganic LEDs. Such in situ studies are key to understanding growth modes, surface and interface structures, elemental incorporation, and defect generation at the atomic level, and to providing the foundation for creating new heterostructures for light generation.

THE WORKSHOP ON SOLID-STATE LIGHTING

The U.S. Department of Energy (DOE) Office of Basic Energy Sciences held a Workshop on Basic Science Challenges in SSL from May 22 to 24, 2006, in Bethesda, Maryland, to determine and prioritize science challenges and opportunities that might accelerate the development of energy-efficient SSL. The workshop brought together 80 participants, including experts in a range of scientific disciplines related to light emission in solid-state materials (Appendix 2 contains the full list of participants). Participants were drawn from academia, industry, and national laboratories in the U.S., Europe, and Asia, with expertise spanning organic and inorganic materials, and physics, chemistry, and modeling. Their charge was to identify basic research needs and opportunities underlying SSL technologies, with a focus on new or emerging science challenges with potential for significant long-term impact on energy-efficient and productivity-enhancing SSL. The workshop generated a set of priority research directions (PRDs) and cross-cutting research directions (CCRDs) aimed at scientific breakthroughs that would enable revolutionary, not evolutionary, progress in SSL. Two "grand challenges" (GCs) were also identified.

These are wide-ranging and longer-term "discovery science" initiatives that have the potential to fundamentally change the way we think about generating light-matter interactions in the solid state.

The workshop was comprised of panels that examined light-emitting materials from three perspectives. Two of these perspectives, LEDs and OLEDs, resulted from a natural division between crystalline nitride, oxide, carbide, and similar inorganic materials used in LEDs, and the largely amorphous polymeric and molecular carbon-based compounds used in OLEDs. A third perspective resulted from a desire to identify cross-cutting and out-of-the-box research directions such as light extraction and hybrid organic-inorganic nanomaterials. The chairs of the panels were drawn from universities and national laboratories.

Patricia Dehmer, Director of DOE's Office of Basic Energy Sciences, launched the opening plenary session of the workshop, presenting the charge to participants and the scope. Experts from academia and industry set the stage with plenary talks on the potential of SSL and the status and perceived roadblocks for lighting using inorganic and organic materials. James Brodrick, from DOE's Office of Energy Efficiency and Renewable Energy Buildings Technology Office, briefed the participants on the accomplishments and outlook for its SSL technology initiative. The chairs of the workshop panels then outlined specific scientific questions, the answers to which could generate game-changing advances in electricity-to-light conversion.

Following the opening plenary session, the participants divided into individual panels examining LED, OLED, and cross-cutting science (see Appendix 3 for the workshop programs). Each of these panels invited experts to analyze the grand challenges and scientific routes to achieve them. The panels then developed a set of high-priority research directions with the potential to produce revolutionary breakthroughs in materials and processes for SSL. The panel chairs also gathered emerging cross-cutting research directions which became candidates for GCs. Selection and development of the GCs occurred at additional workshop-level meetings between the panel chairs and conference chairs. These PRDs, CCRDs, and GCs are the major output of the workshop and comprise the bulk of this volume.

OUTLINE OF REPORT

This report presents information on several levels. This Introduction describes the motivation and challenge of reducing the energy used by lighting while simultaneously developing new lighting products to improve quality of life. The Broader Impact of SSL describes the influence that the core knowledge foundation of SSL optoelectronic materials and physics has had and is likely to continue to have on other broad areas of science and technology. The reports from the panels give overviews of the scientific basis of each of the panel areas, and describe the research challenges that must be met for SSL to compete with incandescent and fluorescent lighting.

The GCs describe overarching, longer-term research thrusts in broad areas of discovery-based science that would fundamentally change the way we think about converting stored energy to light. The associated PRDs and CCRDs represent the collective ideas of the workshop and are its most specific output. They identify high-priority science with the potential to clear away current technological roadblocks and generate revolutionary progress in bringing SSL to its full potential. These PRDs and CCRDs are promising routes to achieving the GCs.

A brief Conclusion sums up the main body of the report and is followed by five Appendices that provide additional information helpful in understanding the workshop and this report. Appendix 1 contains a technology assessment that describes the current state of commercial technology for conversion of electricity to light. It also presents a high-level overview of the various technological gaps associated with SSL. Appendices 2 and 3 list the participants of the workshop, and the workshop plenary and breakout

agendas. Appendix 4 contains a reading list that will be helpful in learning more about the science and technology of SSL. Appendix 5 is a list of SSL science issues generated before the workshop to stimulate the thinking of workshop participants.

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BROADER IMPACT OF BASIC RESEARCH FOR SOLID-STATE LIGHTING

BROADER IMPACT OF BASIC RESEARCH FOR SOLID-STATE LIGHTING

Optoelectronic materials and physics represent a deep and broad foundation of knowledge that has had an impact on a wide range of important areas of science and technology and that has, in turn, been deepened and enriched by those areas. Solid-state lighting (SSL) is among the most recent of these areas, emerging as a concept only in the past decade, with the sudden (almost shocking) development in the mid-1990s of blue and green light-emitting diodes (LEDs) [Nakamura et al. 1994], and with the increase in brightness of red LEDs to the point where outdoor applications, such as traffic lights, became possible.[1]

Today, as SSL, faced with daunting challenges, emerges as a new focus for basic research, it is poised to catalyze a further deepening of foundational knowledge in optoelectronic materials and physics. That foundation, in turn, will have continued wide impact: both in science, as SSL becomes a platform for exploring new science concepts in areas ranging from rational design of materials and nanostructures to electronic-excitation decay pathways in disordered materials; and in technology, as science concepts guide synergistic advances in technology areas ranging from high-speed communications to displays and from solar cells to bio-agent detection.

This section is a brief survey, by no means comprehensive, of the wide-ranging science and technology impact of basic research in areas foundational to SSL (Figure 6).
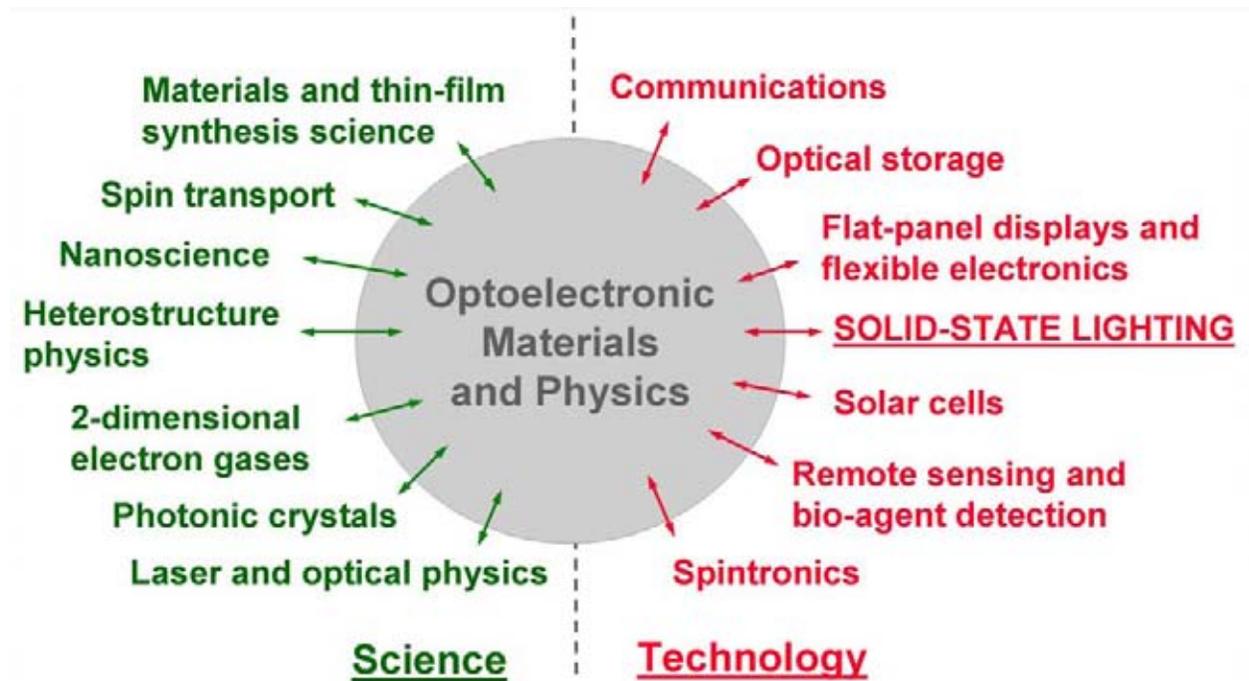

Figure 6 Mutual interdependencies and synergies between foundational knowledge in optoelectronic materials and physics, and a broad array (by no means comprehensive) of science and technology areas, including the emerging area of SSL.

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[1] These advances, of course, rested on even earlier advances. The first practical LED was invented in 1962 [Holonyak 1962] and was considered revolutionary. The first OLED was invented at about the same time, although the field received little attention until 1987, with the publication by C. W. Tang and S. A. Van Slyke [1987] of a thin-film architecture, which enabled small molecule organic electroluminescence *at low voltage*.

LED SCIENCE AND TECHNOLOGY

An important example of the broader impact of the foundational science and technology underlying SSL is the use of heterostructures in optoelectronic and electronic devices. A semiconductor heterostructure consists of two or more layers with different energy bandgaps, formed by changing the composition of the material. Examples include GaAs/AlGaAs and GaN/AlGaN in the III-V compound semiconductors, and Si/SiGe, alloys of elemental semiconductors in column IV of the periodic table. In general, the use of heterostructures allows the energy and flow of electrons in a device to be controlled in a sophisticated manner unobtainable in a single material. By incorporating materials with differing refractive indices, the confinement of photons can also be controlled. These two effects in combination enable the semiconductor laser. The principle of the heterostructure laser was suggested in 1963 by H. Kroemer [Kroemer 1963], and independently by Zh. Alferov and R. Kazarinov [1963, see also Alferov 2001] and has become the basis for light sources used in applications as diverse as high-bandwidth fiber-optic telecommunications, high-density optical storage (digital video disks, DVDs), and missile targeting. The concept of quantum wells (a special case of the double heterostructure) and the use of quantum confinement to control electron energy levels arose through a parallel experimental effort to create new types of semiconductor optical emitters.

Equally critical to these science and technology advances was the ability — developed in a tightly coordinated parallel effort in the 1970s — to synthesize semiconductor structures with atomic precision. The ability to epitaxially grow heterostructure layers with low defect densities was enabled by the emergence of several layer-by-layer epitaxial growth methods, including molecular beam epitaxy (MBE, developed by A. Y. Cho and others [Cho 1971, Cho and Arthur 1975]) and Metal Organic Chemical Vapor Deposition (MOCVD, developed by H. Manasevit and others [Manasevit 1968, see also Coleman 1997]). These methods were developed hand in hand with the heterostructure concepts and optoelectronic devices they enabled, and today they are mainstays of the entire compound semiconductor industry worldwide. They were also the foundation for both new generations of materials — filling out nearly the entire range of colors that could be emitted, from the infrared to the visible and even into the ultraviolet — and for new and predictive understanding of the structure and dynamical evolution of surfaces and thin films of these materials.

In the subsequent decades, the use of heterostructures, combined with deepening physical insights into their properties, led to an explosion of novel "bandgap-engineered" device concepts [Capasso 1987]. Examples include the vertical cavity surface emitting laser (VCSEL), quantum well infrared photodetectors (QWIPs), and quantum cascade lasers (QCLs). These latter devices represent a new class of heterojunction devices that operate in previously inaccessible wavelength regions by using electron transitions solely in the conduction band. Previously, devices exclusively utilized electronic transitions between the conduction and valence bands of a semiconductor; device characteristics were therefore dominated by the bandgap of the material. By incorporating new physical concepts and approaches (and of course new materials), nature's bandgap tyranny has been gradually rolled back, and new spectral regions have become available.

The advances in high-purity growth of ultra-low-disorder heterostructures over the last fifty years has led to a number of advances in our fundamental understanding of the electronic phases of condensed matter, particularly the behavior of two dimensional electron systems. These include the discovery of the integer quantum Hall effect at high magnetic fields by K. von Klitzing (Nobel Prize 1985) [Klitzing, Dorda, and Pepper 1980] and of the fractional quantum Hall effect at even higher fields by D. Tsui and H. Stormer

(Nobel Prize 1998) [Tsui, Stormer, and Gossard 1982]. It has also become possible to further confine electrons leading to one- and zero-dimensional structures, enabling to the discovery of new phenomena such as quantized conductance in one-dimensional wires, single-electron tunneling, and electronic structure in zero-dimensional quantum dots. These continue to be active areas of fundamental research enabled by semiconductor technology that is intimately associated with LED science.

The development of 2D electron layers in heterostructures made it possible to expose the role of disorder and localization in electron systems in different dimensions. For example, the theory of weak localization of the electronic wavefunction in a random potential was developed in the late 1950s by P. W. Anderson (Nobel Prize 1977) [Anderson 1958]. This phenomenon can be regarded as the prototypical manifestation of quantum coherence in a condensed matter system, and is considered by many to rival superconductivity in its significance as an embodiment of quantum coherence at the macroscopic scale. Experimental tests of later, more generalized versions of the theory [Abrahams et al. 1979] only became possible with the advent of low-disorder 2D electron systems.

Obvious examples of the application of heterostructures and quantum wells can be found in electronics, particularly high-frequency compound semiconductor electronics. The same physics underlying quantum confinement and strained semiconductor growth that enhanced the performance of LEDs and laser diodes has been applied to pseudo-morphic high-electron mobility transistors (p-HEMTs), in which a strained quantum well carries a high-density, high-mobility electron layer enabling very high frequency and high-power operation. Quantum confinement in the base layer of heterojunction bipolar transistors (HBTs) dramatically improves their performance. Such high-frequency devices are a key enabler of wireless communications (the amplifiers in today's ubiquitous cell phones, for example).

Advances in the understanding and control of GaN-based materials have enabled new technologies in two areas beyond solid-state lighting. The first of these is in deep ultraviolet (UV) LEDs, which provide a highly compact, robust, reliable, and portable alternative to mercury lamps and are being considered for fluorescence-based detection of chemical species and biological agents. The fundamental knowledge enabling the development of semiconductor UV emitters is also being applied to the development of UV detectors — both photodiodes and avalanche detectors. These are of particular interest in monitoring chemical reactions, and in detecting missile launch plumes and other related defense and national-security applications.

Materials advances in GaN have also had significant impact on high-power, high-frequency electronics. The electron saturation velocity in GaN is high, and since the bandgap is large, the breakdown voltage of the material is also very high. As a result, these high-power, high-frequency transistors are being introduced in state-of-the-art radar systems to replace the large, heavy tube sources used in the past. GaN transistors can also operate in high-temperature environments, where electronics made from conventional materials cannot reliably perform.

OLED Science and Technology

For organic light-emitting devices (OLEDs), a similar story is evolving, although commercial products are only just beginning to appear and much revolutionary technology is still in the laboratory demonstration phase. Here, the technology has been driven primarily by flat panel display applications, in particular the search for a full-color, high-resolution, and power-efficient information display for portable electronics. The resulting increase in our understanding of the electronic properties of organic materials has led to single-color OLEDs with efficiencies well in excess of 100 lm/W [Werner et al. 2006], and such results are encouraging a new development thrust in white OLEDs for lighting. The need for high-

resolution patterning at low cost has led to the development of materials amenable to ink-jet and other forms of printing. The sensitivity of organic molecules and cathode materials to moisture, particularly in films only a few nanometers thick under high electric fields and current injection, has driven the development of new encapsulation techniques. These now enable OLEDs to operate continuously for years without unacceptable degradation. Advances continue to this day, with one of the most recent being the ability to harness light emission from both singlet and triplet states by managing the diffusion of excitons in the organic material [Sun 2006].

The thin-film device architecture that rekindled interest in OLEDs in the late 1980s emerged from work on organic heterostructures used to make solar cells at Eastman Kodak [Tang 1986]. Subsequently, the lack of lattice-matching constraints in organic thin films was exploited to permit the vertical stacking of multiple OLED with different colors [Shen et al. 1997]. The property has since been applied to both high-brightness OLEDs [Liao, Kublek, and Tang 2004] and higher efficiency organic photovoltaic cells [Yakimov and Forrest 2002]. Thin-film organic solar cells now have demonstrated conversion efficiencies above 5%, which comes with the promise of low cost and low energy deposition over large areas. It is conceivable that a science-driven initiative to better understand structure and transport in organic thin films will one day lead to organic solar cells rivaling the performance of amorphous silicon at significantly lower cost. In a closely related technology, organic photodetectors have been shown to have attractive performance characteristics for high bandwidth operation [Peumans, Bulovic, and Forrest 2000].

The discovery of high efficiency phosphorescence in organic semiconductors was driven by the search for improved display materials, but also pointed to a route for achieving 100% conversion of electricity to photons in a lighting device. It also directly drove fundamental research into the nature of spin-dependent processes in organic semiconductors and led to an ongoing discussion on the nature of spin statistics in polymers. The focus on spin has led to renewed interest in using organic materials in spin-based electronics (known as spintronics), and giant magnetoresistance in thin films of an organic semiconductor has already been demonstrated [Xiong, Vardeny, and Shi 2004].

Organic lasers (essentially a solid state analog of the well-known dye laser) have been demonstrated using identical materials to those used in OLEDs. An electrically pumped organic laser, however, has yet to be achieved (an early claim of success was subsequently retracted). The manner in which injected charge changes the optical properties of the organic material makes such a device extremely challenging [Baldo, Holmes, and Forrest 2002]. The potential for easy integration of coherent organic light sources in photonic circuits, however, is a huge potential payoff; the improved understanding of light-matter interactions central to this volume will be similarly essential for the successful demonstration of the organic laser.

Finally, organic materials are now being investigated as the active semiconducting layer in thin-film transistors [Ling and Bao 2004]. Because of the weak intermolecular bonding in organic materials, they can be placed on curved or even flexible surfaces, enabling "macro" electronics to be integrated with fabrics and building materials. Ultra-thin electronic circuits may be embedded in various media and can be applied in a conformal surface coating in almost any imaginable geometry. These technologies together are leading to a new class of electronics known as organic photonic integrated circuits, and a better understanding of the fundamental building blocks of organic thin films will have an impact across this class.

PROSPECTS FOR FUTURE BROAD IMPACT

As research in SSL deepens and enriches our foundation of knowledge in optoelectronic materials and physics, it will almost surely have broad impact. The two overarching Grand Challenges articulated in this report — rational design of SSL structures and controlling losses in the light-emission process — address issues of broad interest in optoelectronic materials and physics.

Further understanding of the photoluminescence properties of quantum dots and nanoclusters, for example, may lead to the use of these nanostructures in high-specificity, high-sensitivity tagging applications, and may enable new techniques in bio-identification and bio-assays. Improved photonic crystals and plasmonic structures developed to aid the escape of light from the device may revolutionize communications technologies, producing ultra-compact components for the routing and manipulation of optically transferred data, as well as new capabilities for imaging and detection systems.

A particularly significant synergy exists between SSL and solar energy. Many of the same fundamental issues regarding the efficient production of visible light in SSL have their counterparts in solar cells.[2] Low-resistance charge transport and charge injection in LEDs and OLEDs are matched in solar cells by the need to efficiently collect charge carriers after electron-hole pairs are created by absorption of photons. The efficient emission of photons from LEDs and OLEDs, perhaps throughout the visible spectrum using multiple quantum well/organic layer structures, is paralleled by the need in photovoltaics to utilize as much of the solar spectrum as possible. Issues of light extraction in LEDs and OLEDs are paralleled in photovoltaics by the need to get as much solar radiation as possible to enter the cell. Surface texturing and photonic lattice approaches are likely to benefit both. The same detailed nanoscale understanding of how materials properties — including charge transport, nanoscale material composition fluctuations, defects, oscillator strengths, photonic density of states, and selection rules — affect the emission of photons from light-emitting devices, will doubtlessly provide invaluable and perhaps revolutionary guidance to the attainment of nano-engineered high-efficiency devices for harvesting solar energy.

In sum, the basic research needs for SSL articulated in this report address issues of broad interest in optoelectronic materials and physics, and vice versa. We can anticipate that the future technology advances that will shine most brightly will be the result of shedding light on the most fundamental science issues that underpin these interrelated fields.

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[2] There are also obvious differences. For example, lighting cares only about visible photons; solar cells need to utilize the entire solar spectrum (some in the UV and much in the infrared). Lighting, in large part, is an indoor technology; solar modules must be exposed to the elements.

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NOBEL PRIZES

Solid-state lighting has benefited from a steady accumulation of scientific knowledge associated with the physics and chemistry of light-emitting materials and structures. Here, we call attention to two especially important contributions that were awarded Nobel Prizes: one in physics and one in chemistry.

Physics

In 2000, Zhores I. Alferov (A.F. Ioffe Physico-Technical Institute, St. Petersburg, Russia) and Herbert Kroemer (University of California at Santa Barbara) were jointly awarded one-half the Nobel Prize in Physics "for developing semiconductor heterostructures used in high-speed and opto-electronics." (The other half of the prize was awarded to Jack S. Kilby, of Texas Instruments, "for his part in the invention of the integrated circuit.")

The 10 October 2000 press release from the Royal Swedish Academy of Sciences stated that Alferov and Kroemer "have invented and developed fast optoelectronic- and microelectronic components based on layered semiconductor structures, termed semiconductor heterostructures. Fast transistors built using heterostructure technology are used in e.g. radio link satellites and the base stations of mobile telephones. Laser diodes built with the same technology drive the flow of information in the Internet's fibre-optical cables. …With heterostructure technology powerful light-emitting diodes are being built for use in car brake-lights, traffic lights, and other warning lights. Electric bulbs may in the future be replaced by light-emitting diodes."

The advent of heterostructures, both conceptually and with concomitant advances in growth technology, enabled unprecedented control over electron, exciton, and photon behavior inside devices. They enabled control over electron and hole pathways in Heterostructure Biopolar Transistors (HBTs), enabling a thinner base layer and lower resistance-times-capacitance time constants, and dramatically increased operating frequencies. Heterostructures also resulted in the ability to make high-mobility electron layers sufficiently thin that they can be depleted by electrostatic gates, resulting in the invention of High Electron Mobility Transistors (HEMTs). These devices have achieved operating frequencies as high as 600 GHz and have enabled cellular telephone technology.

In optoelectronics, heterostructures enabled quantum confinement of carriers in LEDs and laser diodes, enhancing oscillator strengths and increasing efficiency. In addition, heterostructures provided waveguiding and confinement of photons within the laser structure, further enhancing efficiency. The principle of the double heterostructure laser was suggested in 1963 by Kroemer[1] and independently in a patent application by Alferov and R.F. Kazarinov.[2] Work on double heterostructure laser designs culminated in the first continuously operating room temperature semiconductor laser in 1970, demonstrated independently by groups led by Alferov at the Ioffe Institute and by Mort Panish at Bell Labs. Modifications of the same basic design are used in high-brightness LEDs today, as well as in high-end solar cells.

Chemistry

In 2000, Professor Alan J. Heeger (University of California at Santa Barbara), Professor Alan G. MacDiarmid (University of Pennsylvania) and Professor Hideki Shirakawa (University of Tsukuba, Japan) were awarded the Nobel Prize in chemistry "for the discovery and development of electrically conductive polymers."

Polyacetylene is one of the simplest organic polymers consisting of only carbon and hydrogen. A backbone of alternating single and double bonds forms a system of continuously overlapping orbitals known as a conjugated molecule. Polyacetylene was generally prepared from acetylene via a catalytic process. While the polymer normally forms as a nonconductive black powder, in 1974 Shirakawa and co-workers found that it appeared as a silvery film if prepared using a large excess of the catalyst. Despite its metallic appearance, the electrical conductivity of the silver film was still very low, characteristic of most polymers. In 1977, however, Shirakawa, MacDiarmid and Heeger[3] discovered that oxidation with chlorine, bromine or iodine vapor increased the conductivity of the polyacetylene films by a factor of a billion. This "doped" form of polyacetylene[4] had a conductivity of 10^5 Siemens per meter, which was higher than that of any previously known polymer and even within range of some metals (copper, for example, is one of the very best conductors and has a conductivity of 10^8 S/m). No light emission is observed from polyacetylene, and its rapid oxidation in air renders it impractical for use in devices.

Conductive organic materials had been previously known. Small molecule salts called charge transfer complexes[5] had been studied in the 1960s and an electrical device had even been made using biologically extracted melanin.[6] The prize-winning work on polyacetylene, however, was significant in that it revealed for the first time the physical mechanisms of charge transport in a controlled polymeric structure. This work has in excess of 1,000 citations at the time of writing, and clearly laid the foundations which ultimately led to the development of more complex organic polymeric materials for light emitting devices in the 1990s.
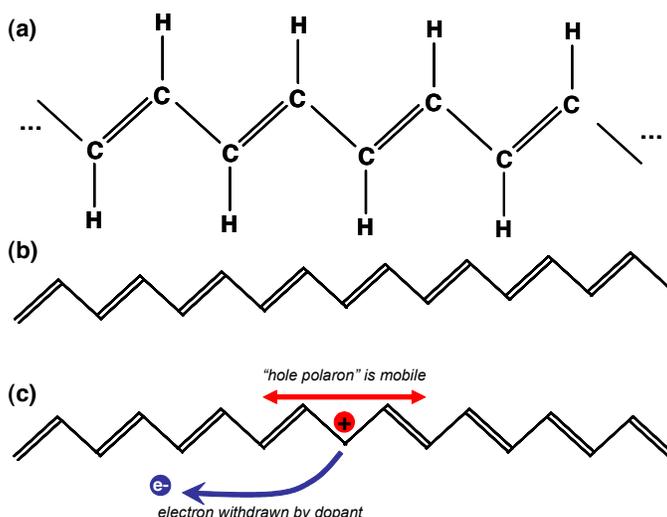
(a) Fragment of the infinitely repeating polyacetylene chain showing the bonding between carbon and hydrogen, which are the only atomic constituents of this polymer. (b) The same molecule in a different representation. Chemists often use this simplified structure showing only the chemical bonds without explicitly representing the carbon or hydrogen atoms. In theory, the bond conjugation extends throughout the entire molecule, although in practice, kinks in the chain restrict conjugation to a handful of units. (c) Doping the structure, e.g., using iodine pulls an electron off the polymer chain. The resulting positively charged "hole" causes a local deformation of the bond conjugation analogous to a weight on a mattress. The hole and its surrounding deformation are collectively called a "polaron" and it is this mobile species that gives rise to electrical conductivity.

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Reports of the Panels on Basic Research Needs for Solid-State Lighting

LED SCIENCE OVERVIEW AND RESEARCH CHALLENGES

BACKGROUND

Light-emitting diodes (LEDs)[1] are designed semiconductor structures within which electrical energy is converted to light through a complex sequence of steps. At each step in the sequence, energy can be, and is, lost. The physical mechanisms for the energy losses depend on the particular materials and structures and are known in some cases but not in others. Elucidating the mechanisms for these energy losses is key to controlling and reducing them.

To put these energy loss mechanisms in context, we consider here the sequence of steps involved in converting DC electrical energy from a battery (or from an AC electrical outlet converted to DC by a transformer) to a mixture of photons that appears white to the human eye and that ***accurately*** renders the colors of real-world objects. This sequence of steps can be thought of as "the life cycle of the photon," although, at the point at which the sequence starts (electrical energy in the battery), there is as yet no photon (an analogy to the pupa stage of a butterfly's life cycle might be appropriate).

At each stage in the photon life cycle, inefficiencies and parasitic processes cause energy to be lost, so the final amount of energy in the form of photons illuminating real-world objects is a small fraction (as low as a few percent) of the initial energy. As illustrated in Figure 7, the major stages in the photon life cycle are as follows:

1. Injection and transport of negatively charged electrons and positively charged holes;

2. Electron and hole radiative recombination to form a photon within the LED chip;

3. Extraction of photons from the LED chip into the surrounding matrix (either encapsulant or air);

4. Mixing of these photons (e.g., blue) with similarly produced photons of other colors (e.g., green and red), or conversion (and mixing) of these photons (e.g., ultraviolet or blue) into photons with longer wavelengths (e.g., blue, green, yellow, red).

CHARGE INJECTION AND TRANSPORT

The photon life cycle begins with energy provided to the LED from the electricity in the workplace or home, for example, or from a battery or a newly developed fuel cell.

The first step is injection of electrons and holes — the charges — into the negatively doped (n-type) and positively doped (p-type) contact layers of the LED, respectively. The injection takes place through metallic contacts, typically of different materials with electronic characteristics specifically suited for n-type and p-type. Typically, the injection is not 100% efficient because contact resistance leads to resistive losses in the process of injecting charge from the metallic contact into the semiconductor. For the technologically important GaN-based materials, this is more of a problem with p-type contacts. These typically have substantially higher resistances than n-type contacts, which can lead to significant energy losses. It is also often desirable to use a metallic contact that is transparent to the emitted light, although this may involve trade-offs in resistivity.

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[1] The nomenclature LED often refers broadly to semiconductor materials of any type—both inorganic and organic. However, in this Report, LED will usually refer specifically to inorganic LEDs, while OLED will usually refer specifically to organic LEDs.
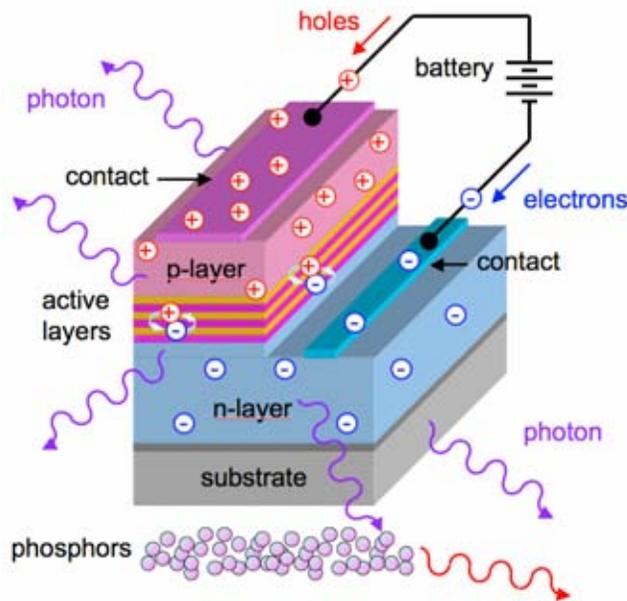
Figure 7 A schematic of a generic LED structure illustrating the major stages in the photon life cycle from initial electrical energy from a battery to a mixture of photons that appears white to the human eye and that accurately renders the colors of real-world objects.

The second step is the lateral spread of these electrons and holes to access all portions of the LED's active layer. These semiconductor "current-spreading" layers also need to have very low resistance so that resistive losses do not siphon off a portion of the input energy. Again, for GaN-based materials, p-type spreading layers present much more of a problem than n-type, and reducing their resistivities has been a long-standing concern.

In this stage of the photon life cycle, *an improved understanding of doping, and especially p-doping, in wide-bandgap semiconductors represents a major research challenge*.

One potential avenue of attack is to seek new classes of light-emitting visible bandgap semiconductor material and dopant combinations, particularly through computational design methodologies, that enable p-type doping to high concentrations. Such material and dopant combinations would need to behave somewhat differently than "simple" combinations (in which the material and dopant are closely lattice-matched and chemically similar) behave. For such simple combinations, the energy needed to ionize an electron or hole from a dopant impurity scales linearly with the effective mass of the electron or hole, and as the inverse square of the dielectric constant of the material. And, typically, effective masses increase, and dielectric constants decrease, with bandgap. Hence, ionization energies typically increase roughly as bandgap cubed, as illustrated in Figure 8. Wider-bandgap semiconductors are more difficult to dope than narrower-bandgap semiconductors, and since holes are heavier than electrons, p-type doping is more difficult than n-type doping.
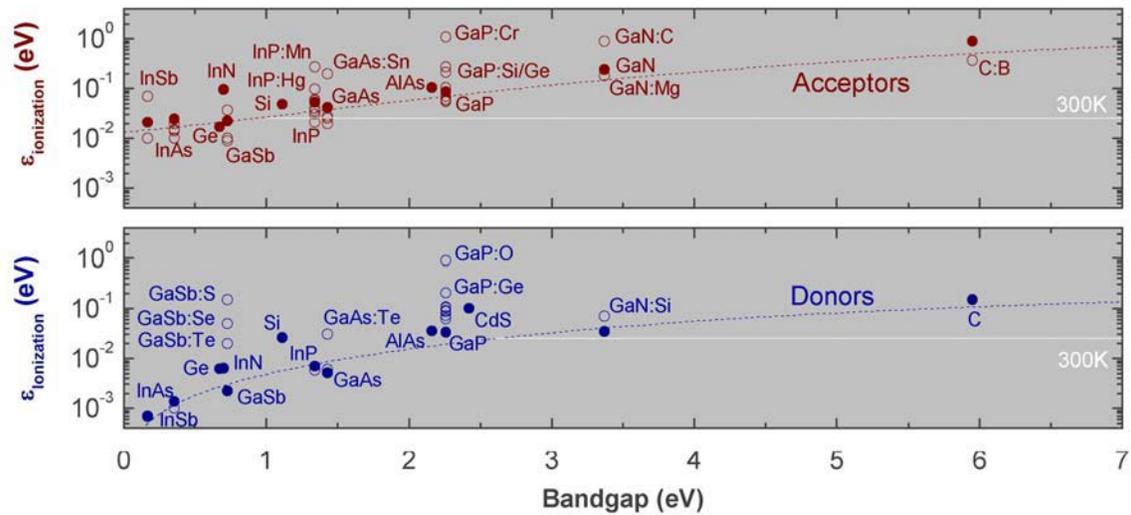
Figure 8 Ionization energies of electrons (bottom) and holes (top) from various dopants in elemental and binary compound semiconductors of various bandgaps [unpublished compilation by J. Y. Tsao]. The open circles are experimental data points; the filled circles are predictions from a simplified "hydrogenic" model assuming the material and dopant are closely lattice-matched and chemically similar, and hence for which there are no so-called "central-cell" local energy corrections.

Another approach is to exploit the properties of heterostructures constructed from polar materials such as InGaN. Such heterostructures have become the basis for an emerging class of electronic devices (high-electron-mobility field-effect transistors) in which there is no impurity doping, but very high sheet charge densities can nonetheless be achieved [Higashiwaki, Matsui, andMimura 2006]. It is possible to envision such "artificial" doping without impurities in optoelectronic devices as well.

RADIATIVE RECOMBINATION OF ELECTRONS AND HOLES

The next stage in the photon life cycle marks the end of the gestation period and the actual birth of the photon. Electrons and holes move into the active layer, typically a series (three or four) of quantum wells, layers of lower-bandgap semiconductors into which electrons and holes are attracted. Electrons and holes then annihilate each other, with their net energy being given up as a photon or light particle. This process is referred to as *radiative recombination*.

As implied by the term, another type of electron-hole recombination exists: *nonradiative recombination*. In this case, the electron and hole also annihilate each other, but instead of producing a photon, they produce unwanted heat, in the form of vibrations of the lattice of atoms in the crystal. This energy is wasted and reduces the overall efficiency of the LED. Nonradiative recombination is usually stimulated or initiated by a defect in the LED crystal; electron-hole pairs that encounter the defect will often nonradiatively recombine. The process is not fully understood but has been studied in many different semiconductor systems. In general, a clear correlation between nonradiative recombination and the density of defects in the material is observed.

Within the active layer of an LED, radiative and nonradiative recombination processes compete with each other. The efficiency of radiative recombination is given by the relative percentage of electrons and holes that radiatively recombine. The overall goal is to *enhance* the radiative recombination rate and *suppress* the nonradiative recombination rate. Parameters having an effect on these rates include extended and

point defect densities, alloy composition fluctuations, polarization fields in quantum wells, quantum well interface roughness, incomplete confinement of charge carriers in the active region, and many other factors. The competition between radiative and nonradiative recombination is not well understood, particularly in the GaN-based materials that hold great promise for LED-based solid-state lighting. A number of questions abound. For example, why are nonradiative recombination rates in GaN-based materials not greater than those observed, given the extraordinarily high defect densities? Why do the longer wavelength, GaN-based LEDs emitting in the green and yellow (and hence containing large amounts of In) have lower radiative efficiencies than those emitting in the blue and near-ultraviolet (with small amounts of In)? And finally, why do the radiative efficiencies of GaN-based materials drop at high current injection densities?

In this stage of the photon life cycle, *quantitatively unraveling the various radiative and nonradiative processes operating in GaN-based materials is a major research challenge*.

One particularly important avenue of attack is the study of InGaN materials and heterostructures, widely regarded as the most promising materials and heterostructures for SSL. Indeed, in many ways, the promise of SSL is largely because of the remarkable development of LEDs based on this alloy system. However, despite more than a decade of research, InGaN materials that emit light efficiently at the high electron-hole injection densities critical to white-light illumination, and at the green-yellow wavelengths critical to human visual perception, have proven elusive. The origins of these limitations are not well understood, though they may be speculated to arise from the complex interplay of a range of materials properties including compositional disorder, high defect densities and the presence of strong piezoelectric fields.

Another research direction for overcoming this problem is the study of polar materials and heterostructures. Because bandgaps tend to increase with bond polarity (the sequence Ge, GaAs, ZnSe is a good example), most known inorganic semiconductors with bandgaps wide enough to emit light in the ultraviolet (UV) and visible are polar. Indeed, GaN, the semiconductor that is central to current SSL technology, is among the most polar of the III-V semiconductors [Ambacher et al. 2002], and any inorganic semiconductor that might displace GaN in SSL is also likely to be polar. Because polar materials and heterostructures are characterized by internal electric fields, which can cause spatial separation of electrons and holes, they can suffer from lower radiative recombination rates. Hence, to fully exploit materials and heterostructures for SSL, it will be important to gain a fundamental understanding of the electronic and optoelectronic properties of polar materials and heterostructures, and to develop methods for their manipulation.

Another direction of approach is the enhancement of light-matter interactions, through nanoscale optical materials and structures wherein the resonant interaction between the electronic and photonic degrees of freedom is significantly stronger than the perturbation interaction regime typical of today's light-emitting devices. In the extreme limit, internal generation and external extraction (discussed below) of photons, traditionally thought of as sequential processes, become intimately integrated. Such new regimes of enhanced light-matter interactions could lead to new opportunities for ultra-high-efficiency SSL sources.

PHOTON EXTRACTION

Once a photon has been born in the active layer of the LED, it is still a long way from being useful for illumination. The next stage in the photon life cycle is its extraction from the LED. This extraction is relatively inefficient. Typically, only a fraction of the photons produced within the LED active layer escape from the semiconductor crystal into the surrounding air. Rather, a large fraction is totally internally reflected upon encountering the boundary of the crystal. This phenomenon occurs because of

the high refractive index of the LED crystal relative to the surrounding air. It is the same phenomenon that makes it difficult to see to the bottom of a lake unless one is looking nearly straight down. Indeed, in a simple rectangular LED chip, most photons bounce around within the crystal until they are eventually absorbed by a crystal defect, a surface state, or metal contact surfaces. Light-extraction efficiencies for most LED structures are less than 50% and depend very little on wavelength.

Light-extraction efficiency does depend significantly on chip size, however, as illustrated in Figure 9. As a consequence, there is typically a trade-off in chip design: larger chips produce more light, but allow less of the light to escape. Said another way, smaller chips will have higher overall efficiency, but will emit less light.

The approaches to improving light-extraction efficiency from LEDs range from the pedestrian to the exotic. Early approaches included shaping the LED chip so that it is trapezoidal rather than rectangular. With the proper angles, internally reflected photons tend to funnel towards corners of the trapezoid, where they can escape. A related approach is to randomly texture the surface of the LED to produce random internal reflectance angles, eventually enabling, after multiple bounces, most of the photons to escape.
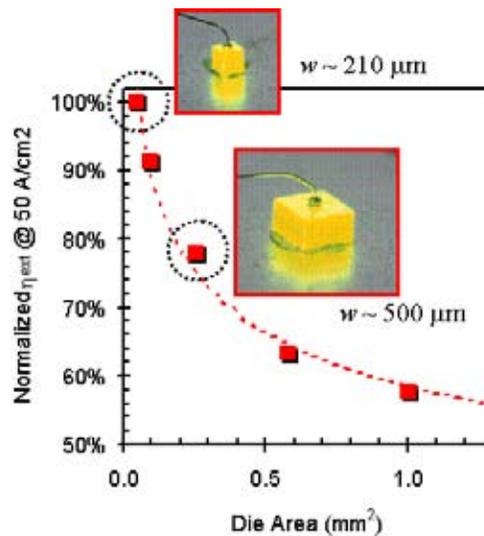

Figure 9 Extraction efficiency from LED chips is strongly correlated with the ratio of total surface area to active-layer area (a manifestation of the 2nd Law of Thermodynamics). In these "transparent substrate" LEDs, where lossless processes and light scattering should result in near-100% light extraction, the existence of internal optical loss mechanisms (though small) result in strong effects on external quantum efficiency because of die shape and size. For the case shown, one may think of the larger-area chip as having its side escape cones "clipped," so would-be side light has to bounce multiple times within the chip (experiencing additional loss) before escape. For the small chip, this is not the case, and higher extraction efficiencies are anticipated and in fact measured. [Courtesy of M. R. Krames, Philips Lumileds Lighting Company]

More exotic approaches include engineering the device structure so that when the photons are created in the active layer they are already highly directional. Indeed, the most efficient solid-state light-emitting devices are high-power laser diodes in which emission is parallel to the top surface of the device. The efficiencies of these devices have been steadily increasing and have now reached 76% [Peters 2006], albeit in materials systems that emit only in the IR. To obtain emission perpendicular to the LED top surface, it is possible to use partially transmitting mirrors to create a vertical resonant cavity. Another approach involves the use of photonic lattices. For example, by imprinting a periodic nano-pattern close to the active layer, the photonic density of states can be modified so that photons are preferentially emitted perpendicular to the surface.

In this stage in the photon life cycle, *exploring novel approaches to photon manipulation and extraction, and improving our understanding of the physics of photon-matter interaction are major research challenges*.

One important avenue of attack is to understand how to manipulate the fundamental photon modes that directly influence the brightness, directionality, polarization, and efficiency of emitted light [Yablonovitch 2001]. Recent advances in nanotechnology, particularly in creating photonic/plasmonic structures, present an unprecedented opportunity to explore strong photon-structure interaction and to manipulate such photon modes. Such innovative photon management is a new frontier in optical science, leading to a new era in smart control of light.

A related research direction is, as mentioned above, the enhancement of light-matter interactions. Again, in the extreme limit of very strong interactions, photon generation and photon extraction "merge," and these two stages in the photon life cycle must be considered together, rather than separately.

PHOTON CONVERSION

Even though a photon has been extracted from the LED crystal, it may or may not be at a wavelength (or color) optimal for illumination purposes. For general illumination, it is necessary to produce white light (i.e., light composed of a mixture of photons that appears white to the human eye and that accurately renders the colors of real-world objects). The final stage in the photon life cycle involves converting the wavelengths (or colors) of photons into those suitable for such white light. Here we summarize the two current approaches (discussed in more detail in Appendix 1).

The first approach, illustrated on the left side of Figure 10, is to use several LEDs of different wavelengths (or colors), mixing them together to produce white. This approach has advantages and disadvantages. An advantage is that it is very efficient—photons are mixed but not converted. A disadvantage is that the human eye is sufficiently sensitive to color imbalances that the brightness of the LEDs must be carefully controlled to achieve the proper balance. Because different color LEDs typically age at different rates, they would likely need feedback control circuitry, raising the costs of the system. The advantage in this approach, however, is that by adding control circuitry, the color temperature of the white light can be tuned and tailored in real time to the specific application.

The second approach, illustrated on the right side of Figure 10, is to use photon conversion materials, including phosphors or semiconductors [Mueller-Mach et al. 2005]. These materials absorb some or all of the photons directly emitted from the LED and then re-emit new photons at longer wavelengths. In this way, for instance, a blue LED can be converted to a white LED by coating its surface with yellow phosphors. A portion of the blue light is transmitted, while the rest is absorbed by the phosphor and re-emitted as yellow. Mixed together, the light appears white. This approach also has advantages and disadvantages. A disadvantage is that, because their wavelengths are longer, the re-emitted photons have

a lower energy —some of the original energy is wasted as heat in the photon conversion material. This is referred to as a *Stokes shift loss*. An advantage is that the approach is simple and relatively inexpensive. It is the dominant approach used with most commercially available white LEDs now, such as those found in flashlights. Currently, photon conversion materials suffer from less-than-ideal efficiencies on the order of 70% to 80%. Efficiencies are even lower for phosphors that emit in the red, but red is a necessary component of white lighting that accurately renders the colors of real-world objects.
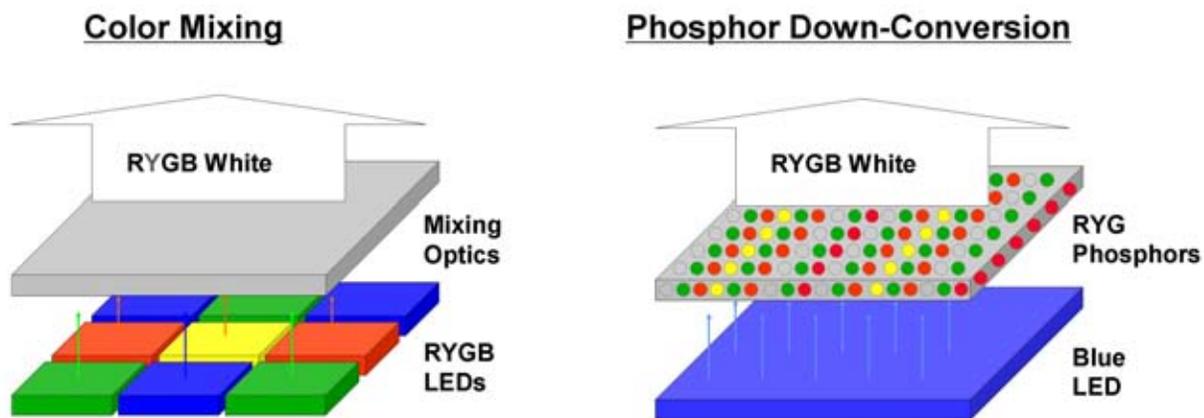
Figure 10 Schematic illustrations of the two approaches to producing white light from monochromatic LEDs.

In this stage of the photon life cycle, *exploring new materials and approaches for photon conversion is a major research challenge*. New phosphor materials need to be explored, but because the range of possible materials is large, a deeper physical understanding of the light absorption and re-emission process, along with simulation and modeling tools, is necessary to facilitate such exploration. Exotic new approaches also need to be explored, including the use of nanoclusters (or quantum dots), whose optoelectronic properties can be tailored by controlling size (hence quantum confinement) and surface ligand coverage. A related approach is the insertion of secondary "photon recycling" quantum wells within the LED, which would absorb primary photons and re-emit them at longer wavelengths within the LED crystal itself. In the quantum dot approach, recent results indicate that it is possible to transfer energy directly from an LED active layer to the quantum dots without a photon intermediary — the electronic excitation in the quantum well is transferred to the quantum dot, where radiative recombination takes place, thereby potentially avoiding Stokes shift losses.

DESIGN, SYNTHESIS, AND CHARACTERIZATION OF LED MATERIALS AND STRUCTURES

Although not part of the photon life cycle itself, underlying all of the stages in the photon life cycle discussed above are research challenges associated with the design, synthesis, and characterization of the materials and structures that comprise the LED. Indeed, as suggested in the sidebar on the National Medal of Technology, advances in materials have been intimately linked with advances in LED performance.

For example, to understand how radiative and nonradiative recombination processes (in stage 2 of the photon life cycle) depend on materials nanostructure, one must also be able to control the formation of the materials nanostructure during its synthesis. This includes not only the composition of the material (e.g., how much indium in InGaN), but the abruptness of the interfaces, the spatial distribution of the doping, the formation of nanoscale composition fluctuations, the formation of dislocations and point defects, and

the incorporation of impurities. These characteristics are all sensitive functions of the synthesis conditions. For the case of chemical vapor deposition, these conditions might include temperature, precursor gas flow rates, residual impurities in the growth reactor, substrate material, and film stress. Both ex situ and in situ monitoring, especially at the nanoscale, will help achieve better control of materials nanostructure. The development of new experimental tools for the nanoscale characterization, as well as new multiscale modeling techniques for predicting the macroscale properties that emerge from nanoscale characteristics, would accelerate progress.

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THE NATIONAL MEDAL OF TECHNOLOGY

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In 2002, Professor Nick Holonyak, Jr. (University of Illinois), Dr. M. George Craford (Philips Lumileds Lighting), and Professor Russell Dean Dupuis (Georgia Institute of Technology) were awarded the National Medal of Technology "for contributions to the development and commercialization of light-emitting diode (LED) technology, with applications to digital displays, consumer electronics, automotive lighting, traffic signals, and general illumination."

The dominant family of materials for optoelectronics today are the III-V compound semiconductors. In this family of materials an element from Column III (e.g., Al, Ga, In) of the periodic table is combined with an element from Column V (e.g., N, P, As, Sb) of the Periodic Table to form compounds such as GaAs, InP, and GaN. These materials are used to fabricate the lasers that drive our modern high-bandwidth communications infrastructure, the lasers that drive the optical storage (CDs, DVDs, HD-DVDs) we take for granted, and the light-emitting diodes that are the subject of this workshop report. They are the basis for today's most efficient solid-state converters of sunlight to electricity (39%)[1] and of electricity to light (76%).[2]

It was not so long ago, however, that these materials were considered too difficult and complex to fabricate into useful devices. This was particularly true for the wider-bandgap alloys that emit light in the visible, such as gallium arsenide phosphide (GaAsP), aluminum gallium indium phosphide (AlGaInP) and gallium indium nitride (GaInN).

In the early 1960s, however, at a time when other researchers focused on infrared light, Nick Holonyak used a new method, vapor-phase epitaxy, to synthesize the first III-V semiconductor alloys, specifically, GaAsP alloys. Using these alloys, he and his group at the General Electric Company crafted the first visible semiconductor laser and the first visible (red) LED. This seminal work paved the way for low-power applications, particularly for indicator lamps and for digital displays for calculators and wristwatches. In the early 1970s, George Craford and his group at Monsanto used nitrogen doping to extend the light emission of GaAsP into the yellow. In the early 1980s, he and his group at Hewlett-Packard pioneered the use of AlGaInP materials that enabled the first "power" LED applications, such as traffic lights and signage.

To harness the full power of the III-V compound semiconductors, however, new crystal-growth techniques were required. In the late 1970s, Russell Dupuis, then at Rockwell International, pioneered the use of a new technique, metal-organic chemical vapor deposition (MOCVD), for the growth of III-V heterostructure devices. This technique enabled vastly improved control over alloy thickness and composition, as well as the growth of the important Al-containing III-V alloys. In 1977, he demonstrated that the technique could be used to grow high-quality semiconductor thin films and devices, including LEDs, lasers, and solar cells. Today, MOCVD is the dominant materials synthesis technique for compound semiconductor optoelectronics, including visible LEDs.waq

All these developments combined paved the way for further developments, such as the pioneering work in Japan of Isamu Akasaki and Hiroshi Amano, and of Shuji Nakamura, in extending the accessible wavelengths into the blue through yet another III-V material, GaInN. In 2005, the market for high-power visible LEDs was $4B,[3] and if SSL for general illumination comes to pass, will be much larger still.

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OLED SCIENCE OVERVIEW AND RESEARCH CHALLENGES

BACKGROUND

Organic light-emitting diodes (OLEDs) have attractive properties for solid-state lighting (SSL). These include ease of processing, which can lead to large-area devices manufactured at low cost, and the ability to tune device properties via chemical modification of the molecular structure of the thin-film components. This has led to molecules with very high-luminescence efficiencies and the necessary spectral characteristics to generate white light. Indeed, OLEDs that emit white light with an efficiency of 30 lm/W have already been demonstrated, and the potential for improvement is great. Equally great are the challenges. Light-emitting organic materials are not routinely synthesized at the levels of purity typical of conventional semiconductors, and lighting applications require operation at higher brightness than has been developed for flat panel displays thus far. Achieving high brightness while maintaining long operating lifetimes will require fundamental advances in how we build and operate organic devices, starting with chemical synthesis and progressing through processing to the final integrated device structure.

CHARACTERISTICS OF OLEDS

OLEDs based on thin films are relatively new to the electronic-device world, having been under development for only two decades for applications in flat-panel displays. They are composed of organic films (made from small molecules or polymeric semiconductors) that have a high degree of structural disorder. Understanding the influence of disorder on the fundamental physical processes that take place in an OLED and finding ways to exploit order to improve device performance are essential for further increases in efficiency and lifetime. Furthermore, OLEDs are complex devices. Light emission is a result of a cascade of several physical processes that include charge injection, transport, recombination, and light extraction. The rich variety of chemistry based on carbon compounds leads to a potentially infinite number of organic semiconductors that can be synthesized. The ab initio design of multifunctional molecules, however, is difficult.

The performance of OLEDs degrades with time, and the processes that lead to this degradation are not well understood. Tools for understanding materials degradation under device-relevant conditions and for preparing organic semiconductors with improved stability are lacking. Indeed, apparently small changes in molecular structure can produce large effects on the efficiency and lifetime of not only the layer containing the molecule, but of other device layers as well. A holistic approach to the design of OLEDs that spans materials synthesis to device-architecture development is therefore required.

FUNDAMENTAL PHYSICAL PROCESSES IN OLEDS

As in LEDs, the emission of light from an OLED is the result of a cascade of fundamental physical processes. To maximize the efficiency of these processes, state-of-the-art OLEDs employ multiple organic layers between two electrodes (Figure 11). The first process that takes place upon application of a bias voltage in an OLED is the injection of electrons and holes from the electrodes (cathode and anode, respectively) into the adjacent organic films. The next step is charge transport, where the electrons and holes drift towards the active region in the middle layers of the OLED. If and when electrons and holes meet somewhere inside the organic films, neutral excitons form. The excitons can be singlet or triplet, and they can recombine radiatively to produce photons, or in a nonradiative fashion, via energy transfer to phonon modes, that is, wasted as heat.

The three processes (charge injection, transport, and recombination) give rise to the phenomenon of electroluminescence, observed in both organic and inorganic light-emitting diodes (LEDs). The contrast between the two materials sets is reflected in the physics of these processes, which is different because of the nature of electronic excitations in organic and inorganic materials. Organic thin films are extremely thin, typically on the order of 100 nm thick, and therefore, even low-voltage devices operate at extremely high electric fields, on the order of 10^8 V/m. This is partly because of the low charge carrier mobility of organic thin films. Under these conditions, charge carriers essentially move perpendicular (and not parallel) to the electrodes, and only the OLED area covered by an electrode emits light. In contrast to inorganic LEDs, current-spreading layers are not required.

An additional process that needs to take place for light emission into the outside world is the extraction of photons produced inside the organic layer. As a result, OLEDs employ at least one transparent electrode, through which some of the photons are transmitted.
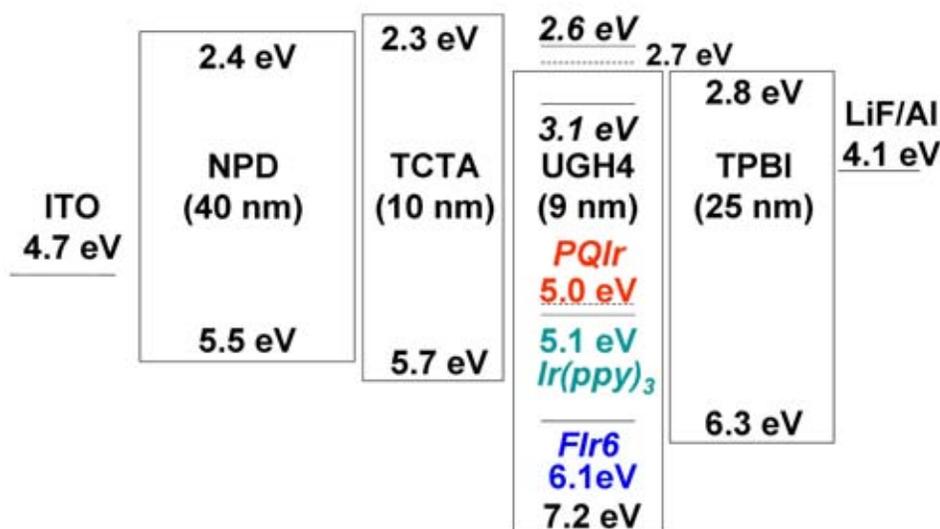

Figure 11 Energy-level diagram of a multilayer OLED. The horizontal lines indicate the highest occupied molecular orbital (HOMOs) (lower) and lowest unoccupied molecular orbital (LUMO) of the various organic layers and the Fermi levels of the metal electrodes. [For a more complete discussion of the terminology in the figure, see D'Andrade et al. 2004.]

Several metrics are important for the application of OLEDs in SSL, as discussed in more detail in Appendix 1. One metric is the efficiency with which OLEDs convert electrical power to photons. As light emission is a cascade of the processes discussed above, the efficiency of an OLED will be the product of the efficiencies of the individual processes. As a result, to improve OLED efficiency, it is important first to understand the physics of each process, then to synthesize materials that maximize the efficiency of each process, and finally to build the materials into device architectures that harmonize all processes for maximum overall efficiency. Another metric of OLEDs for SSL deals with the color of the emission and requires a deeper understanding of charge recombination and light extraction. Yet another metric involves the fact that OLED lifetime is also dependent on these fundamental processes; the more inefficient they are, the higher the chance that the energy carried by the injected charge will be released in a way that is detrimental to the organic materials, rather than as visible photons.

Charge Injection and Transport

The processes of charge injection and transport in OLEDs are not well understood outside a few highly studied systems. The disordered nature of organics makes generalization and reconciliation of the various published models a challenge. Improving charge injection and transport to optimize charge balance in the light-emitting layer with the minimum necessary applied voltage would dramatically enhance device performance. Replacement of the commonly used anode material indium tin oxide (ITO) by a more stable and higher efficiency material also appears to be highly desirable, partly to enhance device stability but also because there is no known method of depositing ITO at sufficiently low cost to make large area OLED lighting viable. While much progress has been achieved using PEDOT:PSS (a conducting polymer deposited from aqueous solution on ITO to improve its surface properties), much remains to be done. For example, it was shown that PEDOT:PSS attacks ITO and releases In and O that degrade the device.

On the other side of the device, low work function cathodes are used to inject electrons. We would like to be able to use interface modification schemes such as dipoles to achieve efficient electron injection from high work function metals and, while much in this direction has been achieved, a general design principle for stable, ohmic organic-inorganic interfaces is not available. Design rules for molecules that are effective electron- or hole-transporters, as well as blockers, would be a further important addition to the design toolkit. Whether both high-mobility and high-luminescence efficiency can be achieved in the same material remains unclear. There are some indications, for example, that discotic materials might result in increased carrier mobility in devices but, in general, our understanding of how the local (molecular) environment influences charge transport and light emission is incomplete, and our ability to design such environments in a complex multilayer device architecture remains primitive.

Recombination

Understanding the detailed dynamics of excitons in OLEDs is important. The dynamics of singlet excitons (SEs) and triplet excitons (TEs) in mixed fluorescent/phosphorescent devices was recently exploited to achieve a highly efficient white OLED. This was done by forcing the SEs to recombine in a blue-emitting fluorescent layer while the TEs were able to diffuse to layers doped with green and red phosphorescent molecules [Sun et al. 2006]. The design of molecules with control of SE and TE levels is important. Also important are the engineering of materials with small exciton binding energies to minimize energy loss from polarization, as well as the design of molecules with 100 percent photoluminescence (PL) quantum yield in neat films [Murata, Kafafi, and Uchida 2004]. Moreover, the design of molecules with controlled disorder will allow control of the branching ratio to polarons and SEs. For example, in solubilized polyphenylenevinylene-based materials, this branching ratio is acutely solvent dependent; it is also dramatically different in regioregular and regiorandom polythiophenes [Österbacka et al. 2000]. Finally, we need molecules that are efficient blue phosphors. Currently, the only commercially available efficient blue phosphor is FIrpic [Adachi et al. 2001], and no hosts with high TE states and good charge transport properties exist. It remains a challenge to achieve higher triplet energies without sacrificing charge transport.

Device Architecture and Lifetime

Because of the losses to the substrate and the metal cathode, only a small portion of the photons generated can escape from the substrate. Several approaches have been used to enhance light extraction from OLEDs, and most of these approaches are based on physical optics such as lens arrays, shaped substrates, and silica gels. More recently, quantum optics approaches have been demonstrated using perforated metal

film electrodes [Liu, Kamaev, and Vardeny 2006], where light transmission in 2D hole arrays is enhanced because of coupling to plasmons. Further investigation of these approaches is needed to improve light-extraction efficiency substantially.

Difficulties arise when trying to achieve chemical purity and to control conjugation lengths in polymers. Understanding defects, both intrinsic and extrinsic, in small molecular and polymer OLEDs is challenging. Degradation processes are complex because they depend on device architecture. For example, in some cases, spreading the emitting layer into a wide zone not only increases the device efficiency, because of reduced bimolecular recombination, but also dramatically increases the device lifetime because of the finite number of charging cycles that each molecule can tolerate. This finding also leads to the development of stacked OLEDs, where complexity is increased as a trade-off for enhanced lifetime [Kido et al. 2003].

Important issues related to novel device architectures also emerge. Past examples of novel architectures have included the following:

- top-emitting OLEDs, which result in high apertures;

- microcavity OLEDs, which result in narrower emission spectra and higher efficiency; and

- Stacked tandem OLEDs (SOLEDs), where the peak efficiency is shifted to higher total brightness at lower current but higher total voltage.

In addition, photonic crystal-type architectures in which the phosphorescence lifetime might be controlled by changing the radiative transition cross-section can also be explored to enhance light emission.

RESEARCH APPROACHES

The issues discussed above represent major research challenges for OLEDs. Three broad avenues of attack can be envisioned, through which both scientific and technological progress is most likely to be made.

Managing and Exploiting Disorder in Organic Films

A first broad avenue of attack lies in the management and exploitation of disorder in organic films. Disorder at a molecular scale is an intrinsic feature of OLEDs based on organic thin films, but the influence of this disorder on properties of light-emitting devices remains poorly understood, and our ability to control it is primitive. It is known, however, that disorder can either improve or degrade device performance, depending on its location within the thin film structure. Energetic disorder and local polarization fields near interfaces can improve charge injection. Morphological and conformational disorder in both conjugated polymers and small molecules can affect charge transport and exciton diffusion. The further addition of molecular and ionic dopants, and the structure of both metal/organic and organic/organic interfaces increases the morphological complexity.

New science, both experiment and theory, is needed to quantify this disorder and to understand its influence on device performance. It is anticipated that this understanding will enable disorder to be exploited, and will in turn enable breakthroughs in OLED performance. For example, although disorder reduces carrier mobility, it typically increases photoluminescence quantum yield by weakening the nonradiative pathways that result from intermolecular coupling. In that respect, disorder is already exploited in a primitive manner in existing devices. Far more accurate control of disorder, down to

molecular dimensions, would allow unprecedented control of the OLED architecture and would likely result in breakthrough increases in efficiency and lifetime.

Understanding Purity and Degradation in OLEDs

A second broad avenue of attack lies in a systematic understanding of purity and degradation in OLEDs. There is now significant evidence indicating that the purity of starting components, as well as degradation mechanisms that occur during device operation, seriously limits device efficiency and lifetime. In many cases, however, identifying the impurities and degradation byproducts that affect performance is currently impossible; hence major advances in analytical chemistry will be required. Moreover, the ability to quantify impurities is just the first step in learning to control or eliminate them. Other breakthroughs, focused on the development of advanced synthetic and purification techniques, will then be needed to eliminate defects in starting materials. To prevent the formation of defects during device operation, a comprehensive approach that relates the degradation mechanisms to materials properties will be required to design materials that ultimately avoid these detrimental pathways.

Among the particular issues associated with this broad approach are the following:

- understanding materials degradation under device-operating conditions;

- identifying the elementary processes responsible for degradation;

- understanding charge traps and quenchers;

- molecular aggregation;

- developing novel ultra-sensitive chemical analyses techniques,

- replacing problematic electrodes such as ITO and low work-function cathodes; and

- developing materials that are less sensitive to the environment and purification, and are more stable regarding morphological changes.

An understanding of these and other issues will help enable the development of an efficient, affordable large-area OLED on a low-cost substrate suitable for SSL.

Integrated Approaches to OLED Design

A third broad avenue of attack lies in a holistic approach to OLED optimization that goes beyond individual layers. General illumination has performance requirements that demand higher efficiency, longer operating lifetime, and lower cost than the display applications that are the current focus of OLED development. To meet these performance requirements, it is necessary to ensure that (1) essentially all electrons and holes injected into the structure form excitons, (2) the excitons recombine radiatively with high probability, (3) the light from these recombinations is efficiently coupled out of the device, (4) the drive voltage required to establish a given current density in the device is minimized, and (5) the material and device are stable under continuous operation. In distinct OLED designs, each of these five requirements has been satisfied, *but it has proven difficult to satisfy all the requirements simultaneously*.

This general approach would aim to elucidate the fundamental physical properties of organic electronic materials in realistic device structures. It would enable the OLED research community to move beyond an empirical Edisonian approach to a predictive science-based approach to new OLED designs. For example,

organic electronic materials are a condensed phase of π-conjugated molecules. Intermolecular interactions are critical in determining the properties of condensed phases of these molecules — the fundamental physical properties of isolated molecules or of single polymer chains are significantly affected by their environment. Therefore, a holistic molecule-film-device approach is necessary: one that integrates understanding of the fundamental physical properties of organic materials, thin films of these materials, and composite films comprising multiple materials, and devices made from these films.

Among the science questions and opportunities associated with this broad avenue of attack are the following:

- global modeling and optimization of injection, transport, and recombination for enhanced device performance;

- direct measurements of charge injection and spin relaxation rates of electronic excitations in a device-relevant architecture; and

- synthesis of new materials, in parallel with modeling their role in practical device architectures.

A common theme in these science questions and opportunities is the development of new methods to measure fundamental processes in *relevant device structures* rather than just in isolated material structures, combined with global OLED device models with injection, recombination, and out-coupling.

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COMPLEXITY OF ORGANICS

Isomeric "Defects"

mer-Alq₃ green emitter

fac-Alq₃ blue emitter

Oligomeric "Defects"

Organic Ligand + Zn⁺²(OAc)₂ → Organic Metal Chelate Structure?

Monomer

Dimer

Trimer

Tetramer

Or Mixture?

Morphological "Defects"

β-phase of _mer_-Alq₃ – <u>several</u> additional polymorphs and mixtures have been identified.

Chemical "Defects"

Polyfluorene

Unknown amounts of oxidized ring structures result in unwanted emission and likely effect charge transport.

[Courtesy P. E. Burrows]

Organic molecular structure determines functionality in more complex ways than the chemical composition of an individual molecule. Compositional analysis to the standards expected of inorganic semiconductors is not possible; indeed, there are no available techniques capable of quantifying the presence of chemical impurities or molecular defects at levels below 0.01% in organic starting materials. Many of these impurities or defects may, in fact, make no difference to the efficiency or stability of a device, but others most certainly do. Without appropriate assaying techniques, we cannot discover which are important.

The way organic molecular building blocks in small molecules, polymers, or dendrimers are chemically linked (i.e., how the atoms are connected and arranged in space) or physically linked (i.e., how the molecules are arranged in the solid state) ultimately determines their properties. This structural complexity of organic materials complicates our ability to build in functionality. For example, many small molecule organics when synthesized can form isomers [i.e., molecules with the same atomic composition, but with either a different connectivity of atoms (geometric isomer) or different arrangement of atoms in space (optical isomer)] or mixtures of oligomers (i.e., monomers, dimers, trimers, etc.). The archetypical electroluminescent material, aluminum tris(8-hydroxyquinoline (Alq₃), exemplifies some of these complexities [Brinkmann et al. 2000]. It has two geometric isomers: _mer_-Alq₃, which emits green light, and _fac_-Alq₃, which emits blue light [Cölle and Brütting 2004]. Because of the lack of symmetry of _mer_-Alq₃, it also exists as a 1:1 mixture of optical isomers that exhibit a strong influence on solid-state packing. In fact many organic molecules pack in different ways in the solid state (many times leading to polymorphism), depending on processing conditions, and this may ultimately determine the charge transport properties of the solid. In the case of organic polymers, the molecular building blocks are linked together with varying block lengths, depending on the type of polymer and how it was synthesized. Many of these polymer chains have been shown to contain chemical defects (e.g., oxidized defects in polyfluorene or PPV) [Sims et al. 2004], which can trap charge or excitons.

Note that many of the isomeric, oligomeric, and chemical impurities may or may not be present in "purified" starting materials but may appear upon processing by thermal evaporation or solvation (in the case of spin coating). Oligomeric mixtures of small molecules present similar problems associated with broad molecular weight distributions in polymers [Sapochak et al. 2002]. Ultimately, the size and shapes of molecules or long polymeric chains dictate how the molecules pack in the solid state, affecting both photophysical and charge transport properties. An additional layer of complexity is introduced by energetic disorder, which reflects differences in the local environment which arise because of reasons that include noncrystallinity, interfaces, and dopants. Energetic disorder strongly affects both photophysical and charge-transport properties. The "purity" of an organic material is clearly a very different concept from the purity of an inorganic semiconductor and involves higher degrees of complexity. A better way to quantify "chemical purity" is needed.

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CROSS-CUTTING AND NOVEL MATERIALS SCIENCE AND OPTICAL PHYSICS OVERVIEW AND RESEARCH CHALLENGES

BACKGROUND

The LED Science and OLED Science Overview and Research Challenges sections outlined issues that were specific to solid-state lighting (SSL) based on inorganic or organic active materials, respectively. There are a number of issues, however, that can be considered cross-cutting — that apply regardless of whether the active material is inorganic or organic. These issues include the discovery of new hybrid inorganic/organic materials and structures, the increased understanding required for the control of elementary excitations in the active material, advanced strategies for photon management and manipulation, and the development of the tools necessary to probe and understand the fundamental properties of materials relevant to SSL. The cross-cutting and novel materials science/optical physics panel used these issues as a starting point to define the current state of the art and the present and future research challenges.

From these discussions emerged five areas that represent cross-cutting research directions with the potential to have a significant impact on SSL: (1) The need for control of elementary excitations requires research on "new functionality through heterogeneous nanostructures." (2) The importance of extracting light from the SSL device structure led to a call for research on "innovative photon management" using approaches suggested by recent advances in optics such as photonic bandgap materials. (3) In calling for research on "enhanced light-matter interaction," the panel recognized that discoveries in the strong coupling limit of photon-material coupling could lead to revolutionary approaches to SSL. (4) To provide the understanding and guidance to exploit these research opportunities, significant effort on "multiscale modeling for solid-state lighting" is required. (5) Finally, meeting the challenges of these research directions necessitates the development of the experimental and theoretical tools to enable "precision nanoscale characterization."

NEW FUNCTIONALITY THROUGH HETEROGENEOUS NANOSTRUCTURES

The revolution in nanoscale materials suggests several exciting possibilities for SSL research. Materials structured at the nanoscale are of particular interest because of the ability to control important opto-electronic properties by tuning composition, size, shape, and quality (defect density). The breathtaking pace of advances in nanoscience over the last decade has enabled synthesis and manipulation of nanostructured materials with unprecedented fidelity and control. In particular, control of functionality at the nanoscale may enable increased efficiency and enhanced color quality of light sources. It is envisioned that the most effective results will emerge from interdisciplinary activity that spans the fields of physics, chemistry, materials science, and engineering.

An example of the current state of the art in the synthesis of high-quality nanostructured materials is shown in Figure 12. These inorganic semiconductor nanowires [Yang 2005] represent one class of important nanostructures for solid-state lighting (SSL) that could potentially outperform their thin film counterparts. These nanowires have several unique characteristics important for SSL: (1) their compositions can be any of the SSL-important semiconductor materials, including InGaP, InGaAs, and InGaN; (2) their diameters can be controlled precisely from 2 to 200 nm in width (potentially enabling quantum confinement effects to be utilized for optimization of the output wavelength and emission quantum efficiency); (3) their size and surface properties permit solution processing for easy integration into device architectures, (4) their electronic and conductive properties — including crystal structure,

doping density, mobility, and bandgap — can be exactly defined; and (5) their lattice structure is a near-perfect single crystal.

Because of the nature of free-standing nanowire growth, these nanowires and their heterojunctions are usually dislocation free and can readily accommodate large lattice mismatch, unlike superlattice thin films. Therefore, semiconductor nanowire growth also enables direct integration of optically active semiconductors (e.g., III-V compounds) onto silicon substrates. The luminescence wavelength of the nanowires is tunable over the visible and near-infrared spectrum because of different available compositions and quantum size effects similar to that seen with semiconductor nanocrystals (quantum dots). The dislocation-free nature of these semiconductor nanowires is expected to have significant impact on the emission characteristics, and, most importantly, the quantum efficiency. To obtain both n-type and p-type nanowires of the same material, light-emitting diodes and laser diodes rely on the ability to synthesize nanowires with complementary doping.

Figure 12 Patterned GaN nanowire arrays grown via a metal organic chemical vapor deposition (MOCVD) process. [Yang 2005]

Light emission at various wavelengths has been observed at the p-n nanowire junction [Sirbuly et al. 2005]. Additionally, nanowire lasers have also been demonstrated [Huang et al. 2001; Johnson et al. 2002].

INNOVATIVE PHOTON MANAGEMENT

A key goal for SSL is ultra high-efficiency light extraction. This extraction is determined by the fundamental photon modes that directly influence the brightness, directionality, polarization, and efficiency of emitted light. Recent advances in nanotechnology, particularly in creating photonic/plasmonic structures, present an unprecedented opportunity to explore strong photon-material interaction and to manipulate photon modes. Such innovative photon management is a new frontier in optical science, with the potential for extraordinary energy benefit and a new dimension in smart control of light.

An interesting example of such innovative photon management is illustrated in Figure 13. In its traditional implementation, SSL involves a color-conversion step in which a high-energy photon emitted by a light-emitting diode (LED) is absorbed by a phosphor that re-emits a lower-energy photon. Significant energy savings can be obtained if the light source activates the phosphor directly via nonradiative energy transfer (ET), which removes several of the intermediate steps involved in color conversion (e.g., emission of a primary photon, extraction of this photon from the LED, and photon absorption by the phosphor). This reduction in the number of steps would thereby eliminate several sources of energy loss. A proof of principle for the ET mechanism was demonstrated in which ET from an optically excited InGaN/GaN quantum well (QW) was utilized to activate emission from CdSe nanocrystals (NCs) [Achermann et al. 2004]. In these experiments, it was shown that at sufficiently close NC-QW separations, ET could successfully compete with both radiative and nonradiative decay in the QW, leading to high transfer efficiencies in excess of 50%.

Recently, a practical implementation of high-efficiency color conversion in an electrically pumped LED using nonradiative ET was reported, as illustrated in Figure 13 [Achermann et al. 2006]. Based on a new LED design that offers both strong ET coupling and efficient carrier injection, it was shown that a hybrid structure comprising of a single monolayer of CdSe NCs assembled on top of an InGaN/GaN QW provides nearly 10% color conversion efficiency. This value is significantly higher than that for a traditional absorption-re-emission color-conversion scheme in a similar device structure. Furthermore, these hybrid devices can also provide improved efficiencies, not only compared to phosphor-based structures, but also to standalone LEDs.
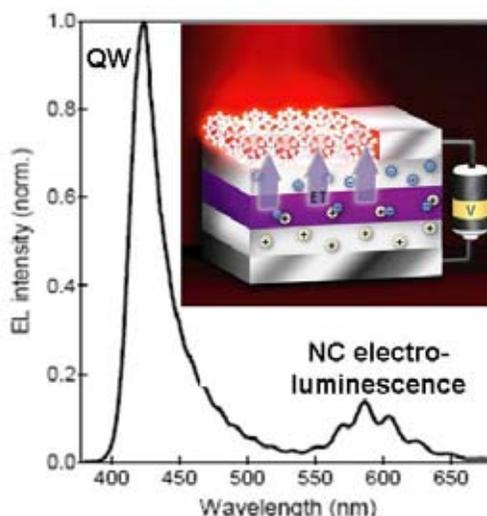

Figure 13 Electroluminescence spectrum from a nanocrystal/quantum well hybrid device (shown in inset). [Achermann et al. 2004]

In other words, the combined steps of primary photon emission, photon extraction from the LED, and phosphor absorption, were replaced with a single direct-energy transfer to the phosphor. This, combined with other possibilities for light control (such as photonic bandgap structures, nano-optical devices, etc.), offer entirely new routes to control of light extraction.

ENHANCED LIGHT-MATTER INTERACTIONS

Traditionally, the operation of a light-emitting diode (LED) or an organic LED (OLED) is viewed as the efficient internal generation of photons by electronic excitations in a semiconductor, followed by useful extraction of those photons to the device exterior. The engineering optimization of these individual processes forms the key objectives for high-efficiency SSL device development.

An alternative approach focuses on the fundamentals of light-matter interactions with the goal of discovering and implementing approaches by which the sequential processes involving conversion of electronic energy to light become intimately integrated. The idea is to identify material and device configurations in which the distinction between internal end external quantum efficiency merges to a unitary figure of merit. This new strategy is heavily based on discovering and designing nanoscale optical materials and structures wherein the resonant interaction between the electronic and photonic degrees of freedom is significantly stronger than the perturbative interaction regime typical of today's light-emitting devices.

An example of how this can be applied to increase the efficiency of SSL is illustrated in Figure 14. This example illustrates the application of photonic bandgap structures to inhibit emission in undesirable regions of the spectrum. This is a frontier area of research, but the opportunity to change the physical parameters of light-matter interaction and modify electronic excitation dynamics offers novel approaches to improving the efficiency of SSL systems. It is based on work from more than sixty years ago, when Purcell discovered that photon states surrounding an emitter could have a strong influence on its spontaneous emission rate [Purcell 1946], and on internal radiative quantum efficiency. If the density of photon states (DOS) is increased, the radiative recombination rate is enhanced.

Using modern nanofabrication techniques, it has now been found possible to create just such an increased DOS environment, using a photonic structure such as the one shown in Figure 14(b). Achieving strong emission enhancement will require the placement of emitters inside a photonic structure to ensure a strong photon-material interaction. Thus, an embedded emitter is most desirable for achieving the ultimate control of emission.

The Purcell effect applies equally well to emission suppression and recycling. If the DOS decreases, the recombination rate of an embedded emitter is suppressed. If the DOS completely vanishes over a specific frequency band (i.e., photonic bandgap or PBG) and for all angles, light emission will be quenched. One excellent example is the use of a PBG structure to quench infrared radiation (heat loss) from a filament [Lin et al. 2003]. This leads to improved energy efficiency, as illustrated in Figure 14(a). An initial demonstration of complete elimination of light emission in the mid-infrared has been illustrated using a 3D photonic crystal. Enhanced near-infrared and white-light emission has been achieved as shown in Figure 14(c).

Another very promising approach is to surround a filament with a PBG material that simultaneously rejects and recycles infrared photons. Simultaneously, it can fully transmit visible light. A preliminary energy-flow calculation of this recycling design indicates that an ultrahigh energy efficiency of 417 lm/watt is theoretically possible. An added advantage of this approach is that the PBG material experiences a much lower temperature (~1,000–1,500 K) than that of a filament, as it is remote from the filament.
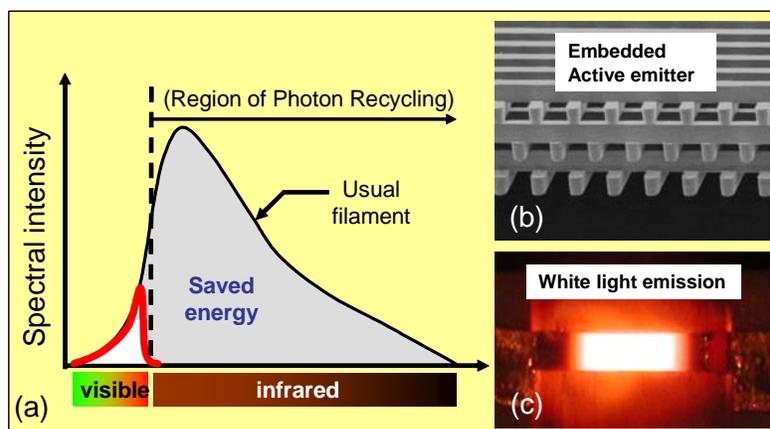
Figure 14 (a) spectral distribution of thermal source (gray shaded area) and a source inside photonic structure that limits emission (white shaded area); (b) SEM of photonic bandgap structure with embedded light emitted; (c) white-light emission from device. [Lin et al. 2003]

MULTISCALE MODELING FOR SOLID-STATE LIGHTING

To synthesize, characterize, design, and fabricate the materials and structures for advanced SSL architectures, it is clear that advances are needed in chemistry, physics, and materials science and also in our theoretical understanding of optoelectronic materials and optical systems. SSL structures will generally have processes occurring on many different length and time scales, all of which need to be understood and modeled to provide feedback to experimentalists for the optimization of efficiencies. Hence, there are opportunities for new approaches to modeling over such multiple length and time scales.

It can be anticipated that these approaches would be hierarchical, making relevant approximations based on the length and time scales, materials system, and functional properties to be described. On sub-nm and sub-ns scales, ab initio quantum mechanical methods would be employed. These ab initio calculations would provide the input parameters for semi-empirical models (often still quantum-mechanical) that can address larger scale interacting systems, such as coupling electronic excitations to optical modes, lattice dynamics, defects, and quantum transport. At the next scale, kinetic equations will be developed to describe transport, excitation decay channels, electrical and optical pumping, and nonequilibrium dynamics. On the largest length and time scales, continuum models will be used that are suitable for integrated device design. Making the necessary connections between the various models on the different length and time scales of this hierarchical approach is a particularly critical and challenging theoretical task.

Ultimately, these predictive models would need to be compared with fundamental measurements. Then, it would be desirable to make direct connection with experiment on as many levels of the hierarchy of models as possible. For example, a series of molecules could be studied, where some aspect of their molecular structure is systematically varied. By measuring properties of both the isolated molecules and of condensed-phase thin-film aggregates of the molecules, an improved understanding of structure-property relationships can be gained.

The exponential advances in computation capability combined with advances in nanoscale material synthesis and assembly suggest the pursuit of an "adaptive design" approach to SSL issues. Here, ideally, one would like to specify the desired properties and then determine the optimal components and structure. With advanced algorithms and extreme computational power, nonintuitive structures to provide optimized

function might be obtained. Such machine-oriented approaches could provide a higher level of abstraction in design. An example of the use of adaptive design to control the direction of electromagnetic radiation has recently been published [Gheorma et al. 2004]. As illustrated in Figure 15, the input design goal was to optimize power into the 30 to 60 degree direction. The output photonic structure was aperiodic and highly nonintuitive. The design was verified in the long-wavelength prototype structure shown on the left of Figure 15. Note how the device fulfills the design target properties as illustrated on the right.
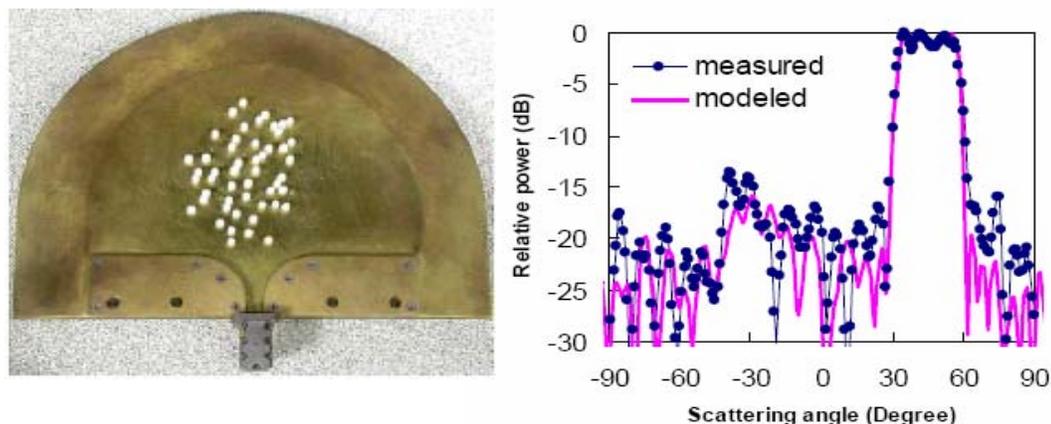

Figure 15 (Left) An aperiodic photonic structure for long-wavelength electromagnetic waves. Note the highly aperiodic nature of the design. (Right) Experimental and model scattering properties showing that the device efficiently scattered into the designed 30 to 60 degree window. [T. Levi, private communication]

PRECISION NANOSCALE CHARACTERIZATION

SSL devices rely now, and are expected to rely in the future, on complex organic and inorganic material nanostructures within which a variety of complicated, interacting phenomena (charge transport, recombination pathways, and photon extraction) occur. Understanding these nanostructures and phenomena necessitates precise characterization at levels beyond those currently possible. A key catalyst for advances in SSL is therefore the development of new, structurally sensitive tools.

For example, it is desirable to measure both elemental composition and chemical state because of the sensitivity of materials properties to both. These measurements need resolutions spanning the entire range of relevant length scales from individual molecules or dopant atoms to integrated heterostructures and functional devices. In essence, we would like to know the position and chemical state of every atom or molecule in a light-emitting material. A further challenge is to accomplish this in *operating* SSL devices. This would allow determination of local nanoscale properties under the precise conditions relevant to the basic phenomena behind electroluminescence. Novel in situ techniques for monitoring materials synthesis will also drive improvements in materials properties.

Recent progress in nanoscale characterization methods suggests that these ambitious goals are achievable. Optical and infrared spectroscopies, photoluminescence, scanning probe microscopies, electrical characterization, and structurally sensitive techniques employing energetic beams of ions, photons, and neutrons continue to improve and provide new insights into the relevant materials and devices. State-of-the-art advances in several techniques are particularly relevant for meeting the characterization challenges of SSL materials and devices:

- near-field scanning optical methods,

- single-molecule spectroscopy,

- electron-beam methods with enhanced energy and spatial resolution for improved sensitivities and methods that mitigate artifacts due to sample damage,

- neutron and x-ray scattering, fluorescence, and spectroscopy, including in situ microscopy, ultrafast time resolved scattering and spectroscopy, and inelastic scattering, and

- tools for the assay of organic materials.

Taken together, these advanced experimental and theoretical capabilities promise to enable unprecedented and in some cases simultaneous high resolution in energy, time, space, chemical composition, and other parameters.

A recent example of precise nanoscale characterization of both structure and optical properties (spectroscopy) in the carbon nanotube family of materials is illustrated in Figure 16 [Sfeir et al. 2006]. Carbon nanotubes are a promising class of materials and have been used to fabricate the smallest electrically controllable light source [Misewich et al. 2003]. However, an issue in this family is that carbon nanotubes can occur in a wide variety of structures characterized by a chiral vector (n,m) where the indices n and m determine the diameter and helicity of the nanotube and therefore determine the electronic and optical properties. There is a high sensitivity of the properties on the structure and therefore a need for nanoscale characterization of the structure and related properties. In this example, the structure of an individual carbon nanotube was determined by advanced electron microscopy. The nanotube was suspended in air between two slits and an electron beam in a transmission electron microscope was incident on the nanotube, creating the diffraction pattern illustrated in part "A" of Figure 16. A theoretical model of the diffraction pattern shown in "B" uniquely determines the structure. The chiral vector indices (n,m) were determined to be (16,11) for this particular nanotube. The optical spectrum was determined on the same individual nanotube via Rayleigh scattering as shown in panel "D." The sensitivity of important physical properties on subtle structural changes in this nanomaterial illustrates the need to develop precise characterization techniques.
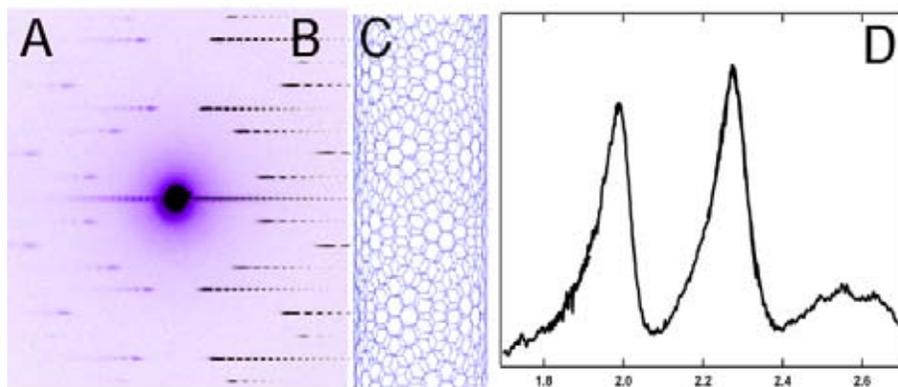

Figure 16 (A) Experimental electron diffraction pattern from a single carbon nanotube. (B) Theoretical model of diffraction pattern for a (16,11) nanotube. (C) A model of the (16,11) carbon nanotube. (D) Rayleigh scattering optical spectrum from the same individual carbon nanotube. [after Sfeir et al. 2006].

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HYBRID ORGANIC WHITE-LIGHT QD-LEDS

A quantum dot (QD), also called a semiconductor nanocrystal or an artificial atom, is a semiconductor crystal whose size is on the order of just a few nanometers. They are typically made from inorganic semiconductors, and they are a promising material for conversion of light of one wavelength to light of another wavelength. Recently, these inorganic QDs have been embedded in organic LED structures, thereby creating hybrid organic-inorganic QD-LEDs [Coe Sullivan et al. 2005]. LED color emission across the visible part of the spectrum and from 1.3 μm to 1.6 μm in the infrared was demonstrated with attractive power-consumption properties.

Moreover, white color emission can be achieved by composing the QD monolayer of a mixture of QD materials with different color-emission properties. Akin to mixing colors in a paint shop, the solutions of QD-LEDs can be precisely mixed to achieve any desired spectrum. This is a unique capability of QD-LED sources that surpasses the tunability of the best OLEDs, and it originates from the simplicity of the QD-LED design and the color purity of QD materials. A recently demonstrated QD-LED with a mixed QD-emitter layer is shown in the figure. The combined emission spectrum generates the appearance of white light with CIE coordinates of (0.41, 0.43). After Coe-Sullivan, S., J. S. Steckel, W.-K. Woo, M.G. Bawendi, V. Bulović, "Large Area Ordered Quantum Dot Monolayers via Phase Separation During Spin-Casting," *Advanced Functional Materials* 15, 1117 (2005), and references therein.
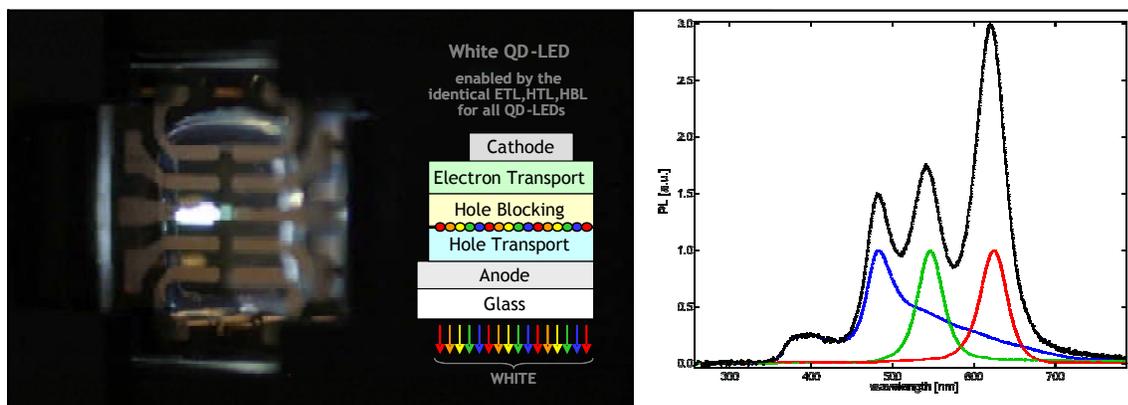
(Left) Picture of a white QD-LED in operation and a schematic cross section of a white QD-LED indicating that the QD monolayer consists of a mixture of different (multicolor) QD materials. The spectral emission is optimized by adjusting the QD composition ratios. (Right) Spectral emission of the white QD-LED on the left, which incorporates three types of QDs [Anikeeva, Bulović et al. 2006].

GRAND CHALLENGES

THE GRAND CHALLENGES

The successful realization of solid-state lighting will be accelerated by advances in our understanding of the fundamental properties of light-emitting materials, and of the physical processes that take place during the conversion of electricity to light. Workshop participants identified two scientific Grand Challenges (GCs) — science questions so broad and fundamental that significant progress towards their understanding and solution would be foundational to any future SSL technology. Workshop participants also identified a number of Priority Research Directions (PRDs) and Cross-Cutting Research Directions (CCRDs). The PRDs and CCRDs are also areas for fundamental scientific inquiry, but are not as overarching and are more focused on a particular approach to solid-state lighting, or a particular scientific challenge. The relationship between the PRDs, CCRDs, and GCs is such that success of the PRDs and CCRDs, as illustrated in Figure 17, is expected to contribute significantly to the success of the GCs.
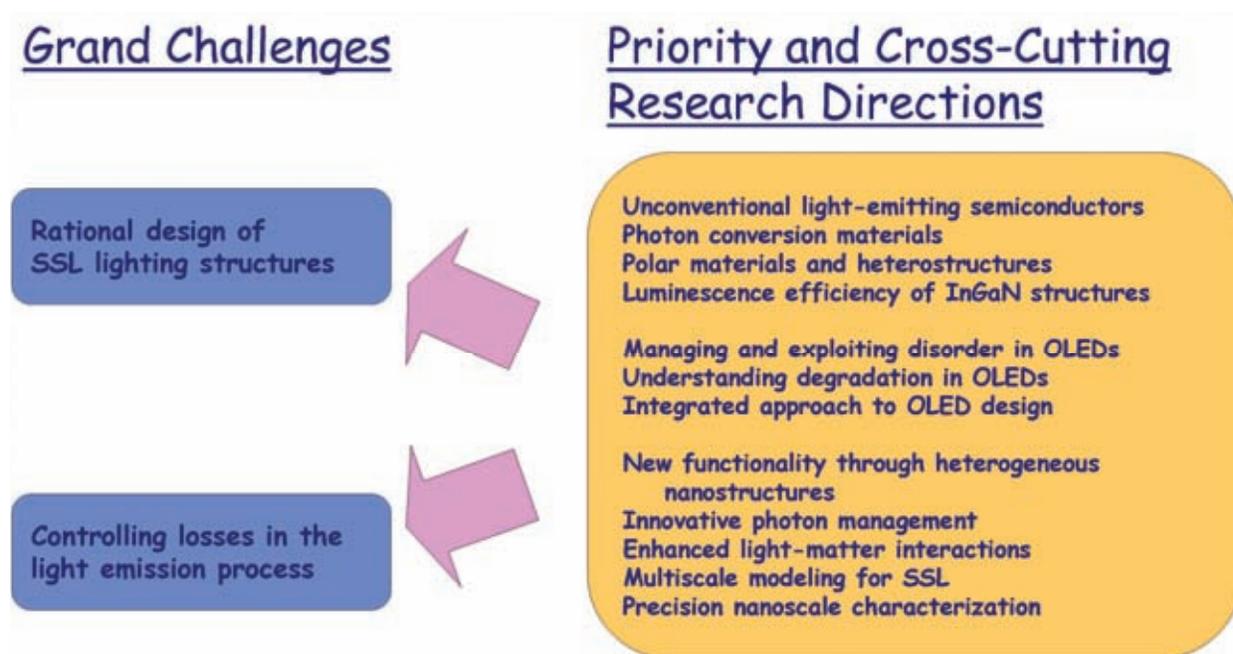

Figure 17 The relationship between the Grand Challenges and the Priority and Cross-Cutting Research Directions. The Grand Challenges are overarching "discovery research" themes believed key to any future SSL technology. The Priority and Cross-Cutting Research Directions are "discovery research" and "use-inspired basic research" themes relevant to particular approaches to SSL or to particular scientific challenges. Their success will contribute to the success of the Grand Challenges.

RATIONAL DESIGN OF SOLID-STATE LIGHTING STRUCTURES

Significant savings in energy consumption would be achieved with novel solid-state lighting structures that approach the thermodynamic limit in efficiency. Rational design approaches would optimize control and maximize the efficiency of such structures. Such approaches have been elusive, however, and the groundwork of fundamental science that would provide such a toolkit is yet to be laid. Rational design for solid-state lighting (SSL) requires that we have a deep understanding of many issues including the physical properties of the candidate components of an SSL architecture, capabilities for reproducible chemical synthesis of the components, strategies for assembly of the components with the required precision, and a capability to model the entire system predictively.

The prospects for rational design of SSL structures are promising, however, in large part because of the recent and ongoing scientific revolution in nanoscience and computation. Nanoscale synthesis and low-dimensionality offer the means to tune materials properties for optimal performance, while unprecedented computational power and novel methodologies offer the means to model many materials properties relevant to SSL, such as excited states, complex heterostructure behavior, and nonequilibrium transport over length scales that have traditionally been challenging for the theoretical community. With the emergence of these new scientific capabilities, it is possible to envision a path toward rational design for SSL. This path also inspires a number of Priority Research Directions, each of which represents an important avenue of attack toward meeting this grand challenge.

BACKGROUND AND MOTIVATION

The long-term goal of rational design is to provide the fundamental scientific understanding and capability that enables rational design of SSL architectures that are not only highly efficient, but that produce the properties of light desired for general illumination in terms of color rendering quality, color temperature, brightness, and spatial/temporal distribution.

The components of such a futuristic architecture are schematically illustrated in Figure 18, which shows a structure made from components of specific functionality. The electronic components include green boxes that represent hole-transporting components and blue boxes that represent electron-transporting components, both of which are connected to a battery. The optical components include the gold sunburst symbols that represent lumophores and the red circles that represent optical control components (which could represent photonic bandgap structures, microcavity elements, or nanoplasmonic structures).

These components are envisioned to be self-assembled (as illustrated in this figure), or they could be fabricated through more conventional techniques, although at an unprecedented level of control. In either case, the material components would be robust with respect to thermal or photo-induced degradation, or they would be designed to be self-healing. It should be noted that the separate electronic and optical components might well be materials that perform both functions rather than separate materials. We envisage a high level of integration of what are now separated components.

These materials would be designed to provide the necessary physical properties when assembled into the final structure. The electronic properties would be optimized for efficient charge injection and transport — for example, high mobilities and good contact to the power source. The optical components would provide means to enhance the desired radiative rates and suppress parasitic processes — these might include high-Q resonators to strongly couple excitons and photons. Finally, the optical properties of the assembly would efficiently couple the output light to achieve the design lighting parameters (color-

rendering quality, color temperature, brightness, and spatial/temporal distribution). Multidimensional modeling would guide the researcher to the optimal materials and structure to meet the design goals.
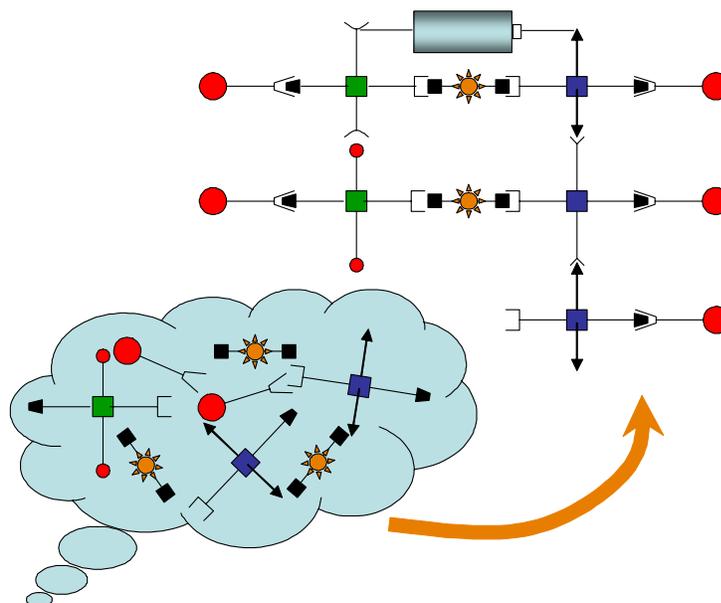

Figure 18 A rationally designed SSL system self-assembled from component materials: the green boxes are hole transporting materials, the blue boxes are electron transporting materials, the gold sunbursts are lumophores, and the red circles are optical components to control radiative properties. The complementary geometric figures attached to the colored components represent a directed self-assembly strategy for the system. [Burrows, unpublished]

The path toward rational design of SSL systems requires that strategies be developed to tailor precisely the basic physical properties of materials. While many recent scientific advances are pertinent to this issue, perhaps the most compelling reason to propose this challenge is the explosive worldwide growth in research at the nanoscale. Recent research has demonstrated increasingly precise control over the size, composition, and shape of optoelectronic nanomaterials. This has been accompanied by an improved understanding of the emergence of novel properties because of lowered dimensionality in nanostructured materials. These advances in nanoscale physics, chemistry, and materials science have demonstrated unprecedented control over materials structure and properties.

Advances in computational methods and algorithms and inexorable growth in computer power parallel the extraordinary advances in nanoscience and materials technology. Driven partly by research in complex materials, the theoretical understanding of the properties of strongly interacting systems has advanced, and a challenge is now to drive the applications of those models into large-scale, complex and inhomogeneous materials systems. Because the science extends from nanoscale to macroscopic, modeling efforts need to be integrated over all scales.

SCIENCE QUESTIONS AND OPPORTUNITIES

A number of fundamental materials science questions must be addressed before rational design of SSL structures can be successful. Broadly speaking, these materials science questions involve materials chemistry, physics, assembly, and theory, and each of these areas offers a exciting research opportunities.

Materials Chemistry. At the foundation of rational design is a requirement for advances in materials synthesis techniques. Materials need to be synthesized with extreme degrees of control over size, shape, and chemical composition. A device design could call for inhomogeneous composition profiles, such as the core-shell structures characteristic of some approaches to quantum dots. Strategies for the control of composition profiles therefore need to be developed. The density of defects needs to be controlled and possibly eliminated. Unpaired chemical bonds on the surface of the material might need to be passivated. Molecular systems need to be designed for improved stability to ambient conditions, especially in the reduced, oxidized, and excited states.

Materials Physics. The control of basic physical processes relevant to the operation of optoelectronic materials is another broad area where advances are required to meet the challenge of rational design for SSL. Objectives include the control of radiative and nonradiative recombination rates in optoelectronic materials (discussed further in the companion grand challenge), investigation of the opportunities afforded by entering the strong coupling limit in light-matter interactions, and optical mode tailoring. In addition, a better fundamental understanding of the electrical properties of semiconductors, including charge injection, transport, and trapping, is required to decrease the operating voltage and increase the conversion efficiency of SSL sources.

Materials Assembly. Designs for optimized SSL structures are expected to require the precise placement of different components. One example is the rational arrangement of molecules to increase outcoupling efficiency. Another example is the precise placement of an "antenna" in the vicinity of a molecule to provide electric field enhancement for the modulation of fluorescence [Anger et al. 2006]. The extension of traditional directed-assembly techniques, such as e-beam lithography, is one path toward assembly with the extreme nanoscale precision required to build rationally designed SSL systems. However, emerging self-assembly techniques are a promising alternative path.

In some cases, directed- and self-assembly techniques may also be profitably combined. Semiconductor nanocrystals, for example, are an attractive class of self-assembling chromophores that combine size-controlled emission colors with high emission efficiencies, but the challenge is to incorporate them into an electrically driven light emitting device. Recently, this has been accomplished in the device structure shown in Figure 19 [Mueller et al. 2005]. This structure can be viewed as a GaN p-i-n light-emitting diode (LED), in which the nanocrystals form the intrinsic layer sandwiched between p- and n-type GaN injection layers. In this case, encapsulation of nanocrystals into the GaN without degrading them required the development of a new technique called energetic neutral atom beam lithography/epitaxy [Mueller, Akhadov, Hoffbauer 2006]. This technique allows for the deposition of polycrystalline semiconducting nitride films at sufficiently low temperatures to preserve the high emission efficiency of the nanocrystals. One- and two-color electroluminescent structures were fabricated in which monolayers or bilayers of nanocrystals were incorporated into the p-n junctions formed by doped GaN injection layers.

Theory. Rational design implies the ability to predict properties of a structure before it is made. Such an ability will require advances in theoretical understanding of basic physical properties and in modeling capability for complex assemblies whose components have spatial dimensions spanning the molecular, nanoscale, and ultimately macroscopic, length scales.
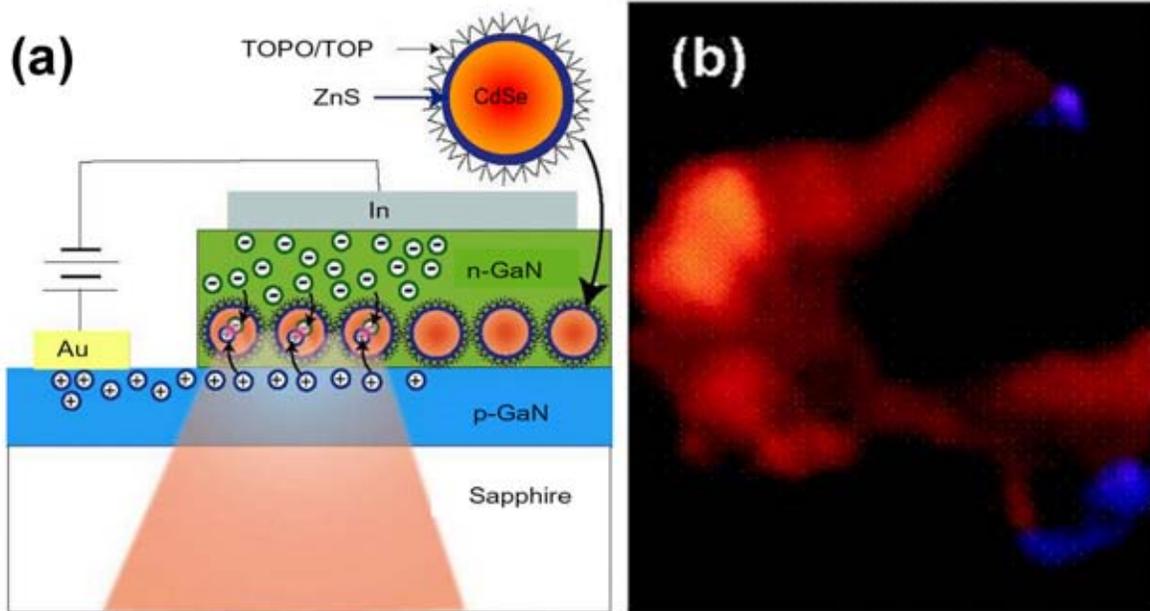
Figure 19 (Left) A proof-of-concept hybrid nanostructured LED recently demonstrated by Mueller et al. [2005]. The nanocrystals consist of a cadmium selenide core surrounded by a zinc sulfide shell capped with organic solubilizing ligands. A monolayer of these nanocrystals is deposited on p-type GaN using the room-temperature Langmuir Blodgett technique. An n-type GaN layer is added using a novel atomic beam deposition technique. (Right) Photograph of light emission from the device as it operates in air at room temperature [Mueller et al. 2005]. The red color originates from the nanocrystals that emit near 620 nm. The blue light emission is from the GaN and results from carrier leakage through the nanocrystal layer. This, and the overall nonuniformity of the light, illustrates the extremely fine degree of control required to turn this into a practical technology.

CONCLUSION

Success in this Grand Challenge would enable the rational design and fabrication of optimized SSL devices and systems by considering from the beginning the complex interplay of the different materials and components in a structure. With sufficient scientific understanding, we expect to use experimentally validated computational modeling to guide us towards the most promising materials and structures for optimal performance. The anticipated results include dramatic decreases in the time between articulation of desired device properties and actual fabrication, and as-yet-unimagined new materials and structures for SSL, with dramatic increases in performance.

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CONTROLLING LOSSES IN THE LIGHT-EMISSION PROCESS

Starting from the source of electricity, opportunities abound for power loss enroute to usable light emission from a semiconductor. The most fundamental and important of these occur after electrical charges (electrons and holes) have been injected into the semiconductor. Ideally, these electrons and holes will recombine radiatively, accompanied by the emission of usable light. Enroute, however, they may also recombine nonradiatively, ultimately accompanied by the generation of nonusable heat. Understanding and controlling these nonradiative losses enroute to light emission is the sine qua non of high-efficiency solid-state lighting (SSL).

For the semiconductors currently most relevant to SSL, recombination processes are strongly influenced by various types of disorder. This disorder ranges from crystalline defects and compositional/structural variations in inorganic semiconductors to the much higher degree of energetic, structural and orientational disorder of organic films. Hence, it is especially important to understand radiative and nonradiative recombination processes in disordered semiconductors. Insight into the role of disorder will lead to new opportunities to tailor the competition between radiative and nonradiative recombination, rendering materials defect tolerant by restricting no-radiative pathways or enabling dramatic enhancement of radiative processes through the use of artificially structured materials. Success would yield unprecedented control of losses in light-emission processes and enable the high optical efficiencies needed for practical SSL.

BACKGROUND AND MOTIVATION

An enduring scientific puzzle relevant to SSL is that several of the most critical materials in light-emitting diodes (LEDs) and organic LEDs (OLEDs) are able to emit light at appreciable brightness levels despite the fact that they are disordered. For inorganic LEDs, key materials for SSL include wide bandgap nitride semiconductors — gallium nitride, GaN, and its alloys with aluminum and indium, (Al)(In)GaN. These materials have an extraordinarily high density of dislocation defects, typically around 1 billion per square centimeter. This defect density is so high that it is surprising that GaN LEDs emit any light at all. (The behavior of these III-N materials is very different from that of other compound semiconductors — an LED made from any other compound semiconductor material containing this many defects would have extremely low light-emission efficiencies.)

Currently, the nanoscale physics that enables electrons and holes to recombine radiatively in these defect-tolerant materials is poorly understood. In LED materials, the underlying mechanisms include the complex interplay of extended defects such as threading dislocations, electron and hole transport, nanoscale structure, quantum confinement effects, point defects, carrier localization and screening, spontaneous polarization and piezoelectric field effects, and alloy compositional variations. In general, this complexity leads to the formation of many different channels or pathways by which electrons and holes recombine. In some cases, the recombination is radiative, resulting in emission of a photon, while in many others the recombination is nonradiative and acts as a parasitic drain on the efficiency of the LED. By developing a fundamental understanding of the nanoscale physical mechanisms and how they depend on structural characteristics of the material, we can identify approaches to controlling and tailoring the recombination pathways to achieve greater light output and higher efficiencies.

In OLED materials, the issue of disorder is perhaps even more central to achieving a more complete understanding of the physical mechanisms underlying the luminescence behavior. The films used in OLEDs are in general not crystalline, but highly disordered. Electron and hole wavefunctions do not extend across multiple lattice sites, but rather tend to be localized around individual molecules.

Understanding the physical properties of organic light-emitting materials lies midway between the scientific disciplines of quantum chemistry and conventional solid-state physics, and hence requires a new hybrid approach. Of particular interest are how singlet and triplet exciton binding energies, energy transport, charge transport, exciton dynamics, decay pathways of excited states, and spin dynamics all depend on material parameters, molecular structure, and each other. Identifying which material attributes (at both the molecular level and in a thin film matrix) and which mechanisms enhance radiative recombination rates and quench nonradiative recombination pathways is a major scientific challenge at one of the frontiers of condensed matter physics whose solution could have enormous technological impact on both the efficiency and stability of OLEDs.

SCIENCE QUESTIONS AND OPPORTUNITIES

The challenge we have described involves both science questions and opportunities. First, we face the challenge of achieving a fundamental and global understanding of radiative and nonradiative recombination processes in the presence of the disorder found in SSL-relevant organic and inorganic semiconductors. While the exact nature and impact of such disorder may appear to be quite different for these two types of semiconductors, we anticipate that this broad-ranging research will find important commonalities regarding how disorder can impact recombination processes in semiconductor materials, and consequently the efficiency of the resulting devices. Second, these global insights into recombination pathways will provide exciting opportunities to tailor the recombination mechanisms themselves — revealing new approaches to manipulating electronic-to-photonic energy conversion processes and providing insight into the ultimate limits of radiative efficiencies and device stability that can be achieved in semiconductors.

UNDERSTANDING RADIATIVE AND NONRADIATIVE RECOMBINATION PROCESSES

In the quest to understand and control the performance of semiconductor light-emitting materials, we must find answers to key scientific questions regarding their radiative and nonradiative pathways. For III-N semiconductor materials, the competition between radiative and nonradiative recombination may be influenced by a range of phenomena that are directly coupled to the unique microstructural characteristics of these materials but are poorly understood. One example of this unique microstructure is the predicted existence of compositional inhomogeneities and phase separation in InGaN alloys [Ho and Stringfellow 1996]. Carrier localization at In-rich regions of the InGaN alloy has long been thought to be a key factor in mitigating nonradiative recombination at defects in these materials [Chichibu et al. 1996]. In turn, the existence and nature of compositional inhomogeneities is thought to depend strongly on materials growth conditions and is expected to become more pronounced at the high indium compositions needed for deep green alloys. However, the precise determination of compositional profiles has been hindered by the tendency for materials to degrade during post processing and characterization using e-beam microscopy techniques [Smeeton et al. 2003], as well as the inability of less direct techniques, such as cathodoluminescence, to unambiguously determine the spatial distribution of indium. Fundamental questions still remain regarding the "as-grown" indium compositional profile and its dependence on growth conditions as well as the way in which particular indium distributions impact radiative efficiency.

The radiative recombination of III-N semiconductors is also strongly impacted by the spontaneous and piezoelectric polarization that is inherent to these wurzite semiconductors. These effects can create large (>1 MV/cm) electric fields in the quantum-well (QW) active region of InGaN-based light-emitting devices, resulting in strong band bending that reduces the electron-hole wavefunction overlap and thus decreases the radiative recombination rate. These effects are especially pronounced for higher indium composition alloys because of increased strain and the related piezoelectric field. Recently, the ability to tailor the polarization fields in the active region has been enabled by the growth of InGaN QW structures

and light-emitting devices on substrates with both nonpolar and semipolar crystal orientations [Kamiyama et al. 2005; Neubert et al. 2005; Sharma et al. 2005]. While the efficiency of LEDs grown on these nontraditional crystal orientations is still relatively poor, such approaches offer a unique opportunity to gain deeper insight into the impact of polarization fields on radiative performance of InGaN materials.

A third potential factor in the recombination processes of III-N materials is the presence of high densities of both extended and point defects. Threading dislocations, primarily resulting from lattice mismatch with the sapphire or SiC substrates, exist at levels of $\sim 1 \times 10^9$ cm^2 — more than four orders of magnitude higher than in typical III-V semiconductors. Although the III-N materials demonstrate significantly greater tolerance to dislocations than other III-V semiconductors, these defects have been identified as nonradiative recombination centers and may, in fact, limit optical efficiency. Beyond their direct impact as nonradiative centers, threading dislocations have also been associated with the initiation of distinct morphological defects, known as "v-defects" (Figure 20). The factors contributing to v-defect formation are not entirely clear, but growth conditions including temperature, indium composition and related strain, and carrier gas used during growth are potentially critical factors. The impact of these morphological defects is still not completely understood.
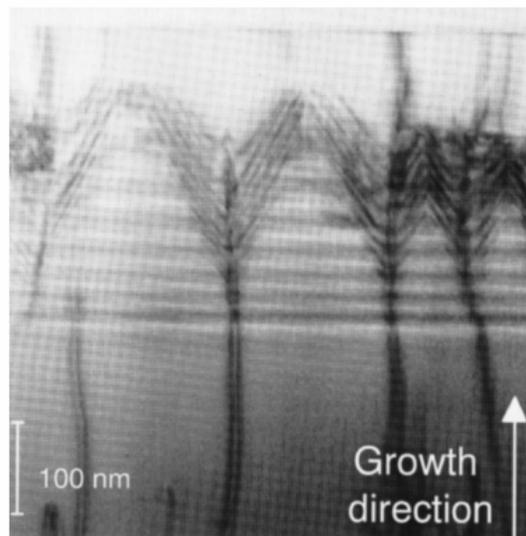

Figure 20 Scanning transmission electron micrograph of threading dislocations dressed by "v-defects" in InGaN/GaN multi-quantum well structure [Scholz et al. 1997].

In addition to extended defects, III-N materials typically contain a range of point defects, such as nitrogen vacancies, as well as impurities, such as oxygen. As in other III-V semiconductors, point defects and impurities have the potential to act as nonradiative recombination centers. To date, however, their role in nonradiative recombination in InGaN alloys is not well characterized, and their impact may be masked by the effects of threading dislocations at this stage of material development. Importantly, the incorporation of higher indium compositions in the InGaN alloys requires lower growth temperatures, which are expected to contribute to higher point defect and impurity concentrations. Thus, for green and longer visible wavelength materials critical for SSL, the impact of point defects on recombination processes may be far greater than for shorter wavelength materials.

For organic semiconductors, disorder has a strong effect on the light-emission process, influencing carrier transport, electron-hole polaron pair formation, exciton formation, and radiative and nonradiative recombination channels. As the deposited organic active layers are not crystalline in nature, the structural disorder, and particularly the nanoscale morphology of some films, may be controlled to varying degrees by the deposition parameters. Depending on the film morphology, the quantum efficiency for the formation of an exciton from a pair of polarons may change from 100% in disordered films to about 50% in ordered films that form lamellae. This reduced efficiency with increased order is a striking effect, and it is contrary to what is seen in typical inorganic semiconductors. Since the excitons in organic semiconductors tend to be localized, delocalization that is brought about by increased order may actually lower the exciton formation cross section and its radiative transition probability. This has been well demonstrated in films of poly(3-hexyl thiophene) (P3HT) with various degrees of regio-regularity, as the

photoluminescence (PL) quantum efficiency of regio-regular P3HT in which lamellae are formed is less than 1%, whereas regio-random P3HT films have PL quantum efficiency in excess of 20%. In addition, the radiative transition probability of the excitons after they are formed may depend on the film morphology. It has been documented that certain arrangements of small molecules may lead to PL quenching. This has been explained by aggregate formation, in particular on whether the configuration and dipole coupling for nearest-neighbor chromophores is parallel or anti-parallel: in one configuration, the lowest coupled exciton state is nonemissive (dark), and this may be devastating for device performance. Thus, understanding the fundamental rules governing aggregate formation is a primary challenge for organic semiconductors.

Just as for the inorganic semiconductors, for organic semiconductors the competition between radiative and nonradiative pathways is crucial for determining internal quantum efficiencies of organic materials. The radiative lifetime of singlet excitons in polymers is on the order of 1 ns [Frolov 2000], and if nonradiative processes with shorter lifetimes are operative, substantial reduction in internal quantum efficiency (IQE) will result. Nonradiative recombination routes include chain defects and impurities, intersystem crossing to a triplet manifold that is not radiative, and proximity to the device electrodes. The intersystem crossing time depends on the polymer backbone structure and atomic constituents and is ~5 ns in polythiophene, which has a backbone structure that includes sulfur atoms. In other polymers such as PPV and PFO that include only hydrogen, carbon, and oxygen, the intersystem crossing time is much longer, on the order of microseconds. The effect of the metal electrode may be reduced by including electron blocking and hole blocking layers so that the radiative recombination occurs mainly in the active organic layer. Another important nonradiative recombination channel is the quenching of excitons by various other excited states that are formed simultaneously in the emitting layer upon current injection. These excited states may include polarons and polaron pairs, triplet excitons, and exciplexes. The singlet exciton interactions with these excitations have not been sufficiently elucidated, and the further study of these interactions, especially at high-excitation densities, is an important area for future research.

Additional sources of light in organic semiconductors include aggregates, exciplexes, and charge transfer excitons. These excitations have low radiative transition rates and thus act to decrease the overall emission efficiency of the organic semiconductor. These recombination pathways may play an important role in the flow of light in an OLED, since carriers may visit many "defected" regions in the organic active layer, where such photoexcitations are easy to form. It is thus expected that the transient recombination of these excitations may be of practical use.

Finally, film purity is of great concern in organics. Oxygen, carbonyl, and other groups are nonradiative recombination centers that reduce the PL quantum efficiency (QE). In fact, the OLED device degradation is thought to be principally affected by the diffusion of these defects into the emitting layers. Therefore, the study of electroluminescence degradation as a function of defect density is a research direction that merits further study.

TAILORING RADIATIVE AND NONRADIATIVE RECOMBINATION PROCESSES

In optimizing the recombination pathways of semiconductors, one would ideally like to design and synthesize materials for maximum radiative efficiencies. Achieving the ideal light emitter would require control of the electronic transitions and their matrix elements to enable efficient radiative recombination at desired wavelengths, elimination or mitigation of nonradiative recombination pathways as well as implementation of effective means to out-couple the light from the semiconductor with 100% efficiency.

For III-N semiconductors, the unique materials properties afford a range of options for modifying carrier localization as well as radiative and nonradiative recombination. For example, the propensity for indium compositional variations could be harnessed to provide controlled engineering of uniform arrays of In-rich quantum dots for effective carrier capture and localization, thereby effectively eliminating the potential for carriers to reach nonradiative defects. As another example, the electronic properties of v-defect structures could be designed to form an effective energy barrier in the vicinity of threading dislocation cores (Figure 21), repelling carriers from such killer defects.
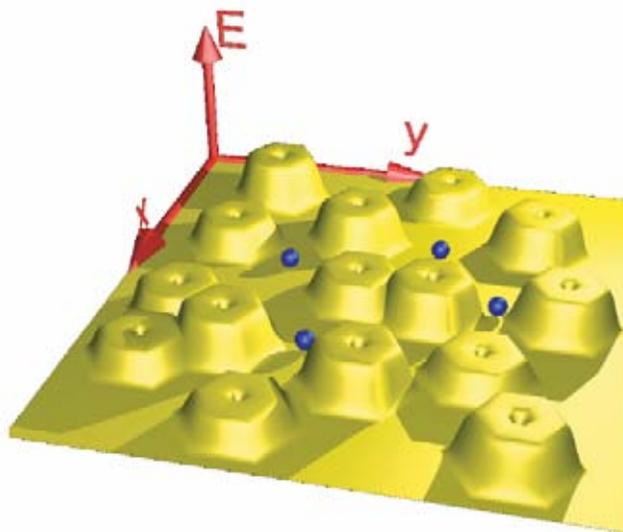

Figure 21 Proposed energy landscape of dislocations decorated with v-defects in InGaN/GaN QW structures. Increased bandgap in the v-defect sidewalls may provide an energy barrier to nonradiative recombination at dislocations. [Hangleiter 2005]

Even greater tailoring of recombination processes could be achieved with the development and synthesis of new types of inorganic semiconductors, beyond the more conventional III-V compounds. In materials such as the oxychalcogenide LaCuOS, intentional hybridization of constituent atomic orbitals provides a means to tune band energies and band offsets in heterostructures and control a range of properties, including the dynamics of exciton stability and transport scattering. The potential to design an inherent defect tolerance may also be possible through minority carrier lifetime engineering or the alteration of the electronic properties of the defects themselves.

Organic semiconductors also present an array of possibilities for tailoring recombination processes. A research approach that employs nanoscale characterization techniques to measure the film morphology in concert with in-depth studies of the radiative characteristics of the organic active layers may yield fundamental insights on approaches to improving light-emission efficiencies of OLEDs. Controlling the spin state of an injected polaron pair using spin aligned current injection is fundamentally challenging but would also provide intriguing opportunities for manipulating recombination processes. It is well known that the spin relaxation rate of most organics is slow. This property results from weak spin-lattice interaction, since organics are composed of light atoms and also weak hyperfine interaction because of the π-electron wave function properties in conjugated polymers, oligomers, and molecules. Recently, spin valve devices using Alq3 as an intermediate layer were demonstrated [Xiong et al. 2004], verifying the possibility of spin aligned carrier injection into organic semiconductors using ferromagnetic electrodes. This strategy may enable enhanced formation of singlet or triplet excitons in the organic emitting layer and may dramatically impact OLED efficiency for SSL.

For both organic and inorganic materials, a common goal is to effectively manage the competition between radiative and nonradiative pathways such that radiative recombination is the dominant process. Opportunities to selectively enhance radiative recombination rates in both material systems may be realized in a number of ways that are enabled through exploiting both materials science and optical physics on the nanoscale. These approaches include the development of nanoscale quantum confined organic and inorganic semiconductor structures, including quantum dot or quantum wire systems, which may yield enhanced oscillator strengths and improved radiative recombination rates. Heterogeneous integration, possibly including both organic and inorganic materials in the same structure, may be employed to enable low-loss energy transfer mechanisms (e.g., Förster energy transfer) providing excitation exchange on a time scale far shorter than typical nonradiative processes. Tailoring of the local environment of light-emitting materials through nanoscale structuring of active or passive elements may enable strong coupling of electronic and photonic excitations, for example, through resonant cavity, photonic lattice, and plasmonic systems. A striking example of the ability to influence light-emission processes through nanoscale modification of the local environment is seen in recent studies of the fluorescence rate of a single molecule interacting with a laser-irradiated gold nanoparticle [Anger, Bharadwaj, Novotny 2006] (Figure 22). Further study of these strong interaction regimes may lead to novel approaches for dramatically enhanced radiative efficiency of semiconductor materials and LEDs.
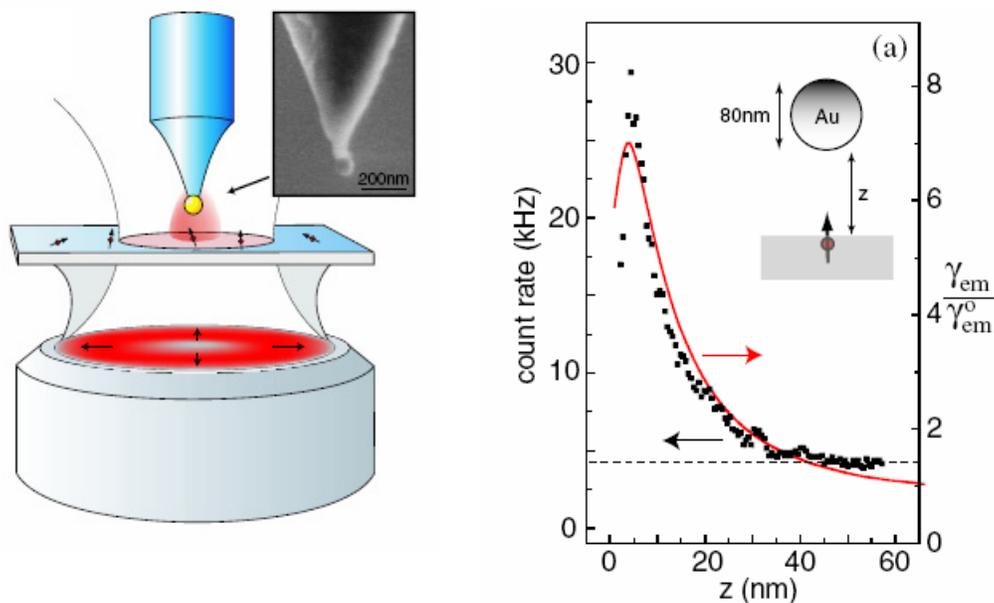
Figure 22 Left: High precision scanning probe near-field enhancement experiment. A fiber tip with a nanoscale gold particle (or "antenna") enhances the electric field to modulate the optical properties of a single molecule. Right: Fluorescence rate as a function of nanoparticle-surface distance for a vertically oriented molecule (solid curve: theory, dots: experiment). [Anger, Bharadwaj, Novotny 2006]

CONCLUSION

Success in this Grand Challenge would yield a deep and global understanding of the nature and impact of disorder on the radiative and nonradiative recombination pathways in both inorganic LED materials (particularly III-Nitrides) and organic OLED materials. There is little doubt that a striking increase in

scientific understanding of electron-hole and/or exciton recombination processes would lead immediately to strategies to tailor and control these recombination mechanisms for dramatic enhancements in luminous efficiency. By focusing on the complex role of disorder in both organic and inorganic materials, we have the potential to advance the performance of a wide range of light-emitting materials and to provide not only the high energy efficiency needed for practical SSL, but unparalleled control of light emission that will truly make SSL a disruptive and revolutionary lighting technology.

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RADIATIVE AND NONRADIATIVE RECOMBINATION IN DISORDERED MATERIALS

Point defects

e ① e ②

Quantum Well

× ②

h h

Path ① : radiative
Path ② : nonradiative

Extended defects
(threading dislocations)
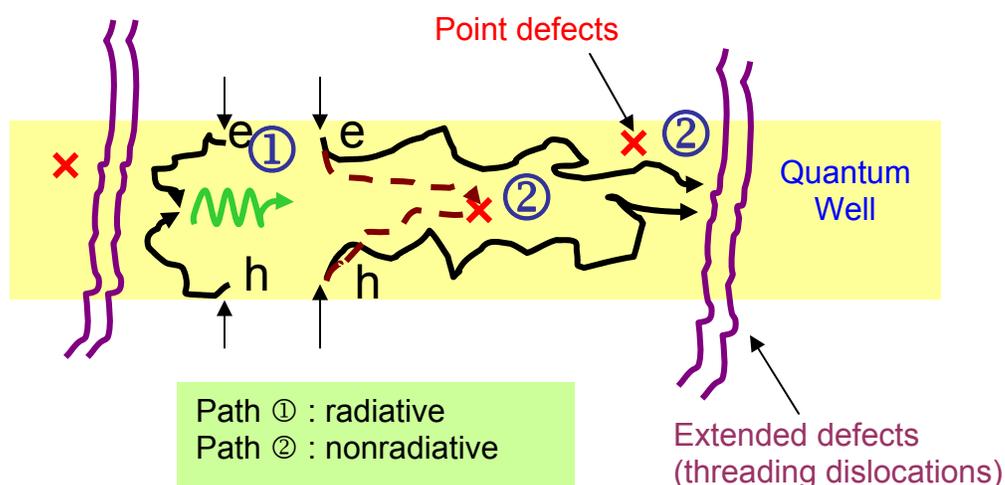
The efficiency of a light-emitting diode (LED) or organic light-emitting diode (OLED) is determined by the fraction of electrons and holes that recombine to emit a photon ("radiative recombination"), compared to the fraction that recombines without emitting a photon, in which case the energy is wasted in the form of heat ("nonradiative recombination"). Electrons and holes injected into an active layer of the device, such as a quantum well, may follow either radiative or nonradiative pathways.

Typically, material defects —including defects that extend over some distance of the material such as threading dislocations and more localized point defects such as vacancies and impurities — act as centers of nonradiative recombination. Whether electrons and holes recombine radiatively, or instead become trapped at a nonradiative center, is then largely related to the density of defects, the carrier diffusion lengths, and the radiative lifetimes of charged carriers. For materials with reasonably high carrier diffusion lengths and high densities of defects, it is likely that charged carriers will become trapped at nonradiative defects before they have a chance to recombine radiatively.

Less typically, but in some important cases, disorder can actually decrease nonradiative recombination rates and increase radiative recombination rates. For instance, compositional variations in materials can create regions of reduced bandgap where carriers can become localized, reducing the probability of encountering defects that would otherwise cause nonradiative recombination. Moreover, nanoscale quantum-dot-like structures in the LED can bring electrons and holes together more efficiently, increasing their radiative recombination rate. The overall physical picture of how radiative and nonradiative recombination rates depend upon a variety of material parameters (including many different types of disorder) is extremely complex and is the focus of this Grand Challenge.

SPIN STATISTICS IN OLEDS

POLARONS   *EXCITONS*
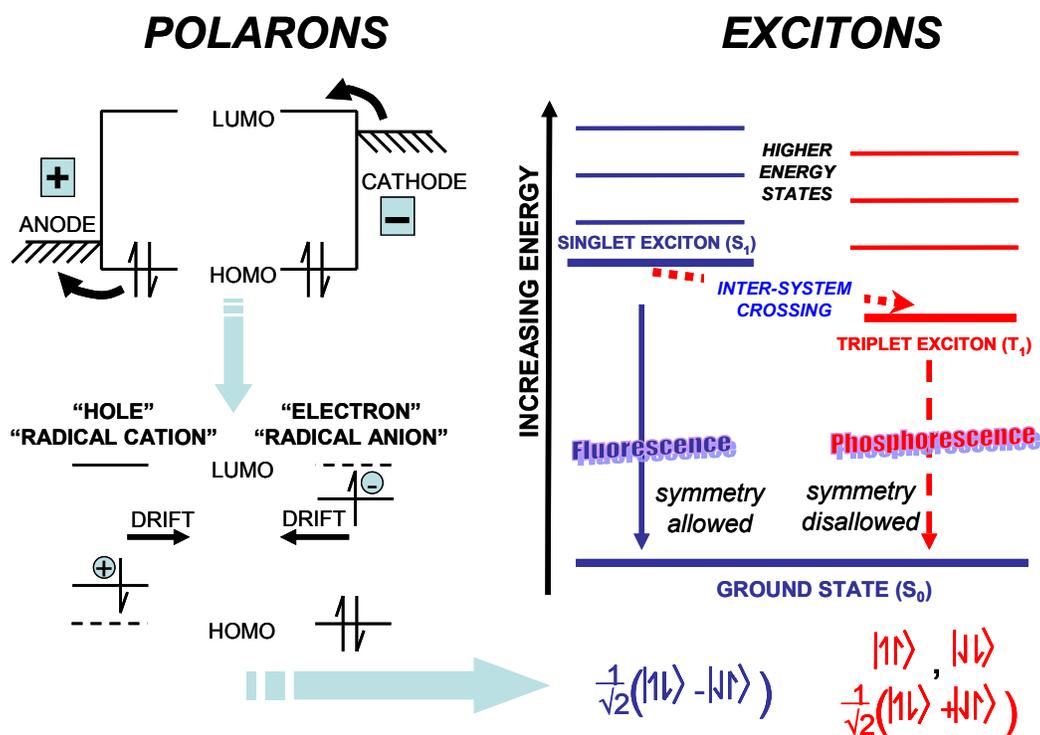
The "life-cycle" of excitations in an organic semiconductor. Most organic materials have a pair of electrons with zero net spin in the ground state (top left). Under the influence of an electric field, electrons are injected from the cathode and holes from the anode [a "hole" is of course a theoretical construct corresponding to the removal of an electron from the highest occupied molecular orbital (HOMO) to the anode]. Relaxation of the local molecular structure around the injected charge usually results in a localized state known as a polaron (bottom left). Since these are molecular systems, the semiconductor terminology of electron and hole, however, further correspond to chemical transformations into radical anions and cations, respectively. As these charged species drift together under the influence of the electric field, they form neutral bound particles called excitons (right). Singlet or triplet excitons may form, depending on the relative spin of the electron and hole. The transition from T_1 to S_0 does not conserve spin and is therefore slow and inefficient. While light emission usually occurs from the lowest energy excited states (S_1 for fluorescence or T_1 for phosphorescence), a manifold of higher energy states exists that may also play a role in excitation or inter-system crossing effects.

Most organic materials have a highest occupied molecular orbital (HOMO) comprising a pair of electrons with opposite spins, known as a zero spin ground state. In optically pumped fluorescence, excitons are created via absorption of an ultraviolet photon, which raises an electron from the HOMO to the lowest unoccupied molecular orbital (LUMO), leaving a positively charged "hole" in the HOMO. The electron and hole then relax to form an exciton. This is a spin-conserved process and therefore only results in net zero spin "singlet" excitons. In the absence of spin-flipping interactions known as inter-system crossing, singlet excitons therefore radiatively recombine with very high efficiency back to the zero spin ground state. This is the process that can give 100% quantum efficiency (QE) in fluorescent down-conversion (described in Appendix 1).

Electrical injection of electrons and holes, however, gives very different exciton spin statistics if the charge carriers are uncorrelated. In the language of quantum mechanics, four different exciton wavefunctions ($|\psi_{TOT}\rangle$) can result from the combination of spin-up and spin-down electrons and holes, denoted by $\uparrow$ and $\downarrow$: $|\psi_{TOT}\rangle = |\uparrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$, $1/\sqrt{2}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$ and $1/\sqrt{2}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$. Of these, only the last example represents a singlet exciton, and in organic materials, the three spin-symmetric wavefunctions form a set of distinct, lower energy states known as triplets. Recombination of triplet excitons to a singlet ground state is forbidden by the spin conservation rules of quantum mechanics, and triplet light emission, known as phosphorescence, is therefore usually slow and inefficient. If all four excitons are created in equal proportion, the efficiency of an organic LED (OLED) is limited to the 25% singlets.

The exciton recombination rules can be broken, however, in the presence of sufficient spin-orbit coupling, usually from a heavy metal atom. While external heavy atom effects, where the metal is not chemically bound to the molecule, have long been known, building an organic molecule around a metal ion such as Ir, Pt or Os in a chelated structure has recently been shown to perturb the organic system to such an extent that a metal-ligand charge transfer state is created. Such spin-mixed excitons have been shown to give 100% QE of phosphorescence with a radiative lifetime of about a microsecond. This is compared to a few nanoseconds for spin-conserved fluorescence. The most efficient OLEDs made today use this mechanism.[1]

Two paths to maximizing OLED efficiency have therefore emerged. Phosphorescent OLEDs use rapid inter-system crossing to transform all generated excitons into triplet or metal-ligand charge transfer states with subsequent high efficiency phosphorescence. Fluorescent OLEDs utilize only singlet excitons and hopes for high efficiency rest on engineering the material to change the ratio of excitons formed in favor of singlets. There is an ongoing controversy in the literature as to what the singlet-triplet ratio is in a certain organic semiconductor and whether it may be possible to alter the formation rates of singlet and triplet excitons from polaron pairs by methods completely unknown today. Such approaches to control the emission properties of organic materials represent an extraordinary research opportunity.

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[1] In *inorganic* semiconductors, strong spin orbit coupling mixes states in the valence band such that "pure" spin states are no longer present. The various valence band states (e.g., heavy-hole band, light-hole band) are therefore not characterized by electron spin alone, but by the total angular momentum. Spin selection effects alone do not, therefore, determine light-emission properties.

PRIORITY RESEARCH DIRECTIONS

UNCONVENTIONAL LIGHT-EMITTING SEMICONDUCTORS

Understanding how one might design and synthesize light-emitting semiconductor materials with properties that are tailored for conversion of injected charge into light is significant for solid-state lighting. Progress in computational science and theory, as well as thin film and bulk synthesis, allows for the possibility of designing materials with specific hybridized band structure, exciton states, transport properties, and doping characteristics. This requires a fundamental understanding of how structure and solid-state chemistry dictate properties that are relevant to electroluminescence based on minority carrier injection and radiative electron-hole recombination. This Priority Research Direction (PRD) seeks to exploit opportunities in designing unconventional light-emitting materials that have properties tailored to elucidate and/or exploit electroluminescent-related processes.

BACKGROUND AND MOTIVATION

Inorganic semiconductors are among the most studied classes of materials known to mankind. However, the ever-growing field of semiconductor-based technology is primarily based on a handful of relatively simple elemental and binary inorganic materials dominated by oxides and Group III nitrides. While this limited set of materials has yielded extremely valuable technologies, it is increasingly recognized that complexity in structure provides opportunities to enhance, and in some cases revolutionize, the functionality of electronic materials. To understand and optimize the conversion of electricity to light, one would ideally like to design and construct materials that have targeted properties (Figure 23). For example, imposing electronic anisotropy allows one to manipulate the energetics of band-to-band transitions, change the dynamics of exciton stability, separate dopants from conduction channels, and dictate transport scattering [Ueda 2006]. Intentional hybridization of constituent atomic orbitals provides a means to "tune" band locations and band offsets [Kamiya and Hosono 2005]. Selection of surface termination impacts electronic coupling across interfaces with dissimilar materials.

Figure 23 Schematic illustration of the energy band diagram and crystal structure for the oxychalcogenide LaCuOS, a wide gap semiconductor for which p-type conduction is designed into an oxide material through the hybridization of the oxygen 2p orbital with Cu 3d and S 3p orbitals. [Ueda, K.; Hiramatsu, H.; Hirano, M.; Kamiya, T.; Hosono, H., Thin Solid Films, 496 (1), 2006, pp. 8-15]

To design materials with specific characteristics, one must understand the fundamental mechanisms dictating the properties of interest, as well as have significant insight into the stability of the proposed structures and the means by which the structure may ultimately be formed.

The emerging tools in computational materials science, along with atomic-scale control of thin-film deposition provides the basis for the design and synthesis of new semiconductor materials and structures with novel transport and/or optical properties directly relevant to electroluminescent phenomena. In some cases, these materials can assist in our understanding of the complex interplay of charge transport, recombination, and optical transitions in converting electrical current into photon emission. In other

instances, new materials may enable novel device concepts that could have significant impact on both the efficiency and cost of electricity-to-light conversion.

This PRD seeks to exploit these opportunities in designing light-emitting materials that are unconventional in terms of structure and crystal chemistry, but have properties that are tailored to elucidate and/or exploit electroluminescent-related processes. Activities of significant interest include design of new direct wide-gap semiconductors, tailoring of anisotropic electronic properties, and the realization of bipolar doping. Layered semiconductor structures yield shifts in the optical transitions because of electron wave confinement. Bipolar doping (achieving both n- and p-type doping) is difficult to achieve in most wide-gap semiconductors [Zunger 2003], but necessary in the formation of p-n junctions. The development of candidate direct wide-gap materials amenable to bipolar doping, along with rational approaches to achieving bipolar doping in known but lesser used materials through structure or metastable substitution, is of interest. In addition, the suite of direct wide-gap semiconductors with exciton states that are stable at or above room temperature is limited. The design of materials with large exciton binding energy would be of interest for fundamental studies and applications where the stability of the exciton could be exploited for elevated temperature light-emitting diode (LED) performance.

In recent years, examples have emerged in which the enhanced capabilities in computational materials science, theoretical insight into materials properties, and advanced synthesis techniques have led to new materials with unique functional properties. In semiconductor materials, a long-standing issue in wide-gap materials has been the inability to dope most wide-gap semiconductors p-type. However, by designing oxide-based crystal structures for which the oxygen 2p orbitals are intentionally hybridized with cations containing active 3d orbitals, a new class of p-type transparent oxides has been developed (Figure 24). In addition, the ability to control the growth of compound materials has progressed to the point where materials with remarkably complex crystal chemistry and structure can be grown as epitaxial structures with atomic layer control of the growth process.
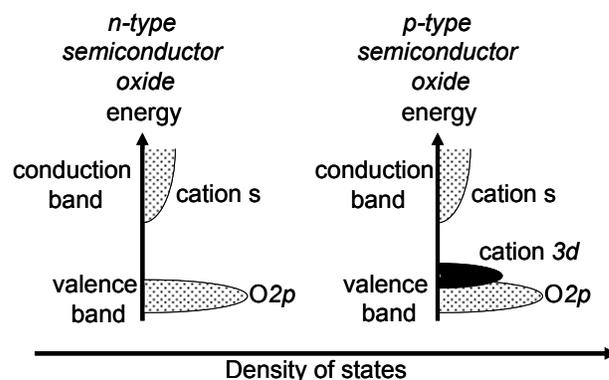
Figure 24 In typical wide-gap oxide semiconductors, the conduction band minimum is primarily composed of the cation s orbitals and valence band maximum of the O 2p orbitals. The relatively deep energy position of the resulting valence band favors n-type doping, but not p-type. If the O 2p orbital can be hybridized with active 3d states (as is available with Cu), the valence band maximum can be raised in energy, making the material more amenable to p-type doping. [Kamiya, Toshio, and Hosono, Hideo, *International Journal of Applied Ceramic Technology* 2 (4), 285-294 (2005)]

SCIENCE QUESTIONS AND OPPORTUNITIES

The ability to tailor the properties of semiconducting crystal structures, either by manipulation of known materials or the construction of entirely new phases, presents opportunities to address a number of fundamental issues that have direct bearing on electroluminescent phenomena. Specific examples include the following:

- Can metastable doping configurations be predicted and implemented for bipolar doping in wide-gap semiconductors? Bipolar doping is a serious limitation for several interesting direct wide-gap semiconductors, including ZnO, where electroluminescence research is limited by a lack of robust dopants. Can new materials be designed that are amenable to bipolar doping?

- Can self-assembled inorganic structures be used in a predictable manner to achieve specific direct-gap optical transitions? Epitaxial film growth provides a means of creating abrupt, layered structures in the form of superlattices and quantum wells for which quantum modification of macroscopic properties are observed. These structures are particularly advantageous for light emission. However, highly anisotropic crystal structures containing "sub-units" of semiconducting layers can also be realized as bulk materials. Can these structures be designed to have desirable properties for efficient electroluminescence?

- Can semiconductors be designed with tailored band offsets and surface chemistries that provide attractive candidates for organic/inorganic hybrid structures? Multiple concepts have been proposed whereby interfacing organic and inorganic semiconductors yield interesting channels for light emission. However, the realization of these ideas is often limited by band offsets and/or surface chemistry that adversely dictate interface properties. Nevertheless, the chemical specificity of electronic interface states in novel semiconductors may perhaps be harnessed to create new pathways for excitation transport and recombination.

- Can electronic structure theory be predictive? In wide-gap materials where excitons are strongly bound, they may be confined on the length scale of an atomic layer (in contrast to the several nm scale of quantum wells in III-V materials), and the simple paradigms of semiconductor quantum wells are displaced by the Mott physics of strong Coulomb interactions.

- Can novel semiconductor materials be designed with high tolerance to defects? It is well recognized that some semiconductor materials can support functioning minority carrier device constructs even with a high density of extended defects. Specific examples include GaN-on-sapphire LEDs and chalcopyrite-based polycrystalline photovoltaics. If one can understand the origins of this apparent tolerance for defects and design the characteristic into new materials, one has the possibility of realizing inorganic LED structures that do not require epitaxy on expensive single crystal substrates.

- Finally, what new synthetic processes and techniques are needed for novel compound development? New strategies for synthesis of metastable compounds and heterostructures are essential for creating novel photoluminescent materials (Figure 25). Coupled to this, improved in situ probes are required for both understanding and controlling the growth process. New approaches to structural and chemical characterization are also needed to understand composition-structure-property relationships, for example, to quantify the chemical state of dopants in new material systems.
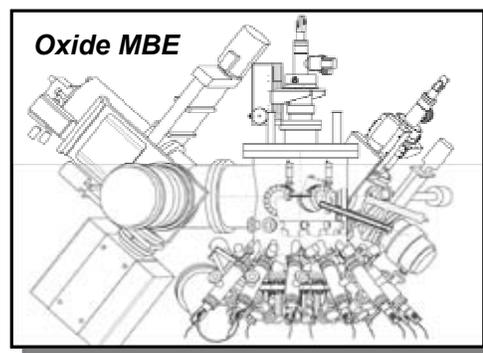
Figure 25 Advances in film growth technology such as molecular beam epitaxy of oxide materials enable atomic-layer control of complex materials. [Courtesy of DCA Instruments and Argonne National Laboratory]

POTENTIAL RESEARCH APPROACHES

The design and synthesis of semiconductor materials with unconventional crystal structure and chemistry, with specific electronic and interface properties, will require the use of computational methods, theoretical modeling, and novel synthesis techniques. Activities within this PRD may include the following:

- Advanced ab initio theoretical methods for predicting material properties – Wide-gap materials allow electron and exciton confinement on short length scales, but conventional band theory fails in these cases under the challenge of strong Coulomb interactions. At short length scales, electronic states, especially at interfaces, and exciton binding are not parameterized by effective carrier masses, nor are Coulomb interactions parameterized by an effective dielectric constant. An accurate full electronic structure of the ground state, enhanced by methods to calculate excitations that can incorporate strong Coulomb and polaron correlations, will be needed.

- Rational approaches to exploring synthesis of complex semiconductor materials – Techniques include epitaxial stabilization of metastable phases; bulk synthesis; electron, x-ray, ion, and optical scattering and spectroscopic investigations of growth processes; designed precursor and surface chemistries for atomic-level control in chemical vapor deposition, physical vapor deposition, metastable substitutions and phase formation; and combinatorial methods.

- Atomic layer control of complex semiconductor materials and structures – In wide-gap materials, the character of electronic states, and hence the electronic band offsets and electrical transport, is determined at the atomic level.

- Experiments to quantitatively establish relationships between photoluminescence, band structure, and microstructure, and to explore the formation of interface and defect states in heterogeneous materials – This includes utilization of electron beam methods (EELS, STEM), optical techniques (PL, Raman, ellipsometry and reflectance-difference), and x-ray scattering, EXAFS/XANES, and photoemission. These experiments also give additional feedback on growth, and further inform and refine the electronic structure computations.

HOW WILL SUCCESS IMPACT TECHNOLOGY?

Most current LED technologies are based on the III-V semiconductor family of materials, yielding impressive electroluminescent performance over a wide-wavelength spectrum. Despite this success, many attractive device concepts are limited by the lack of appropriate electroluminescent materials. Opportunities where superior material properties may yield revolutions in LED technology include defect-tolerant semiconductors for polycrystalline inorganic LEDs, tailored band offsets and surface chemistry for organic/inorganic hybrids, and large exciton binding energy for LEDs with high operating temperatures and high output power. In some cases, the properties of existing semiconductor materials may be altered to provide the necessary functionality. In other cases, entirely new materials need to be designed and synthesized. The outcome of this PRD will include an enhanced palette of electroluminescent materials for novel device concepts (inorganic/organic hybrids, polycrystalline LEDs, and higher temperature operation), and a significantly better understanding of the relationships between structure and electroluminescent-relevant processes.

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Zunger, A., "Practical Doping Principles," *Appl. Phys. Lett.* 83, 57 (2003).

BANDGAPS AND DOPING IN WIDE-GAP SEMICONDUCTORS

Semiconductors do not conduct electricity at the absolute zero of temperature because all the electrons are used for bonding between atoms and are not free to move in the material. Only when additional energy (in the form of photons or heat) is added to the material can electrons gain enough energy to escape the localized inter-atomic bonds (valence band) and become free to move in the crystalline lattice (conduction band). When this occurs, the semiconductor conducts electricity via two carriers of charge: (1) the excited free electron and (2) the unfilled bonding site left behind, referred to as a "hole." The amount of energy needed for the electron to "escape" the localized bonding site is known as the energy gap (or bandgap) of the semiconductor. If this bandgap is large (i.e., wide-bandgap semiconductors), then very few electrons can gain enough energy to make this jump at room temperature.

However, electrical conduction can also be induced by a process known as doping, where an impurity atom is substituted into one of the semiconductor's lattice sites, and where the impurity has one too many (known as a donor) or one too few (known as an acceptor) electrons for normal bonding. The discrepancy in the number of electrons at the dopant site can introduce either an extra electron or hole (vacant bond) for conduction. However, for an "extra" electron to become mobile and contribute to conduction, it must escape (be ionized) from the dopant atom. Similarly, the dopant with one too few electrons for normal bonding must be able to "steal" an electron from a neighboring atom to create a charge-conducting hole. Both of these processes require an energy that depends on how well the atomic size of the dopant matches the normal crystal lattice and on the relative energies of bound and mobile electrons in the semiconductor material itself (see figure). In wide-gap semiconductors, achieving both electron and hole doping in the same material is difficult because of the relative energies of the bound (valence band) and excited (conduction band) electrons. A significant challenge is to identify dopant/semiconductor combinations for which both electrons and holes can be created, as this is needed to realize a light-emitting p-n junction (which relies on recombination of electrons and holes).

A conduction band with high electron energy makes it difficult to generate mobile electrons

A valence band with low electron energy makes it difficult to generate mobile holes

In wide gap semiconductors, the intrinsic separation of the valence and conduction bands makes it impossible to avoid at least one of these conditions, hence the challenge in achieving both electron and hole doping in a wide gap semiconductor

(Zunger, A., "Practical doping principles," Appl. Phys. Lett. 83,(2003), 57)

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PHOTON CONVERSION MATERIALS

Light-emitting diodes (LEDs) based on wide-bandgap semiconductor materials produce ultraviolet (UV)/blue light and are the basis for most current inorganic solid-state lighting applications. Various combinations of these LEDs with materials that convert photons of one wavelength into photons of another wavelength can be used to produce white light sources. For example, a blue LED can be combined with either a yellow phosphor or a mix of green and red phosphors, or a UV LED can be used with a blend of three phosphors, red + green + blue (RGB). Photon conversion materials for solid-state lighting (SSL) are at an early stage of development, however, and it has not been easy to satisfy simultaneously all the stringent demands of SSL, particularly for white lighting applications requiring good color rendering quality. Two areas of science are believed important to significant further progress. The first concerns the discovery of new classes of phosphor materials, the second concerns the design and synthesis of new classes of binder matrices that contain and protect the phosphor grains.

BACKGROUND AND MOTIVATION

Light-emitting diodes (LEDs) based on wide-bandgap semiconductor materials such as GaN/InGaN produce UV/blue light (380–460 nm) [Nakamura and Fasol 1993], and provide the basis for most current solid-state lighting (SSL) applications. The emission from such LEDs can be converted into lower energy radiation by using the luminescent properties of photon conversion materials [Schlotter, Schmidt, and Schneider 1997]. For example, the first commercially available white LED was based on an InGaN chip emitting blue photons at around 460 nm combined with a $Y_3Al_5O_{12}:Ce^{3+}$ (YAG) phosphor layer that converted blue into yellow photons with an emission peak at ~540 nm [Schlotter, Schmidt, and Schneider 1997]. Other combinations of LEDs with phosphors can also be used to produce white light sources; for example, a blue LED can be combined with a mix of green and red phosphors [Mueller-Mach et al. 2002], or a UV LED can be used with a blend of three phosphors, red + green + blue (RGB) [Mueller 2000].

In this manner, photon conversion materials are believed likely to play a key role in SSL for white light illumination. They are, however, at an early stage of development, and it has not been easy to satisfy simultaneously all the stringent demands of SSL. Among the demands that they must satisfy are the following:

- High quantum efficiencies

- Excitation spectrum well matched to LED emission wavelengths and linewidths

- Fast photoluminescence lifetimes (to avoid saturation at high excitation intensities)

- Chemical tunability of excitation and emission wavelengths

- Thermal and photochemical stability consistent with long-term SSL goals, including operation for up to 100,000 hours under 100 W/cm^2 UV irradiation and at temperatures up to 200 °C (designs that use remote phosphors relax the temperature requirements)

- Stable color (position on the CIE chromaticity diagram over this range of excitation and temperature

- Absence of thermal quenching at operating temperature

- Ease of manufacture and low cost

- Nontoxic

Simultaneously satisfying these stringent requirements is likely to require the discovery of entirely new classes of photon conversion materials. Indeed, in addition to the need to meet the demands listed above, these materials must be developed over the entire range of colors necessary to provide a high color rendering index (CRI) (the standard CRI scale, discussed in Appendix 1, maximizes at 100 for an incandescent source or sunlight) over a range of correlated color temperatures (CCTs) (the standard CCT scale is also discussed in Appendix 1). While most current work is focused either on yellow or on combined green and red phosphors that can be excited by a blue LED, novel red, green, and blue phosphors that can be excited by a UV LED at 380 nm are also possibilities for future generations of white LEDs. A CRI increase from 70 with the so-called one phosphor setup to more than 90 with a multiphosphor system should be possible [Mueller 2000]. We note that CRIs >80 are generally acceptable today for indoor illumination by fluorescent lamps, and CRIs >90 are considered "deluxe" light sources. Unfortunately, very few red and green phosphor materials are available for blue or near-UV excitation, though recently some new phosphors have been developed exhibiting either a broad band emission [Mueller-Mach et al. 2006] or line emission [Neeraj, Kijima, and Cheetham 2004].

Along with the discovery of new classes of photon conversion materials, it is necessary to develop new classes of binder matrices for containing and protecting these materials, as well as for dispersing and attaching them to the LED. For the current generation of phosphors, this is normally achieved by the use of polymers based on epoxy or silicone materials. However, these encapsulants are themselves a source of reliability problems, since they degrade under the combined impact of high operating temperatures and intense UV or blue irradiation (i.e., photothermal degradation). This leads to both a breakdown in mechanical properties as well as a yellowing/browning of the polymers that alters color quality and decreases light output of the device. An additional constraint is that these materials should have high refractive indices in order to optimally couple light from the LED device into the photon conversion material.

SCIENCE QUESTIONS AND OPPORTUNITIES

Photon conversion materials themselves have a long history. One common set of photon conversion materials is phosphors used for fluorescent lighting or displays. These phosphors, however, are not an ideal starting point for a search for phosphors for SSL. Phosphors used for fluorescent lighting were optimized for excitation at the wavelength of a mercury discharge tube at ~250 nm. Phosphors used for television screens and other emissive displays were optimized for electron-beam excitation and, in addition, have sharp emission lines rather than the broad emission lines that, at least in the green and yellow, are desirable for high color rendering quality.

In the past few years, some phosphors have been developed specifically for SSL (as opposed to fluorescent lighting or display) applications. Most of these are based on either Eu^{2+} or Ce^{3+} activator ions. There are three reasons for this. First, Eu^{2+} and Ce^{3+} are the only common rare-earth ions for which the excitation and emission bands in the visible region involve 4f↔5d transitions that are parity-allowed and, therefore, intense. Second, the involvement of the 5d energy levels facilitates tuning of the excitation and emission wavelengths by modification of the crystal field environment (Figure 26). Third, the 4f↔5d transitions are characterized by broad lines (FWHM between 50 and 100 nm) that are well-matched to LED emissions and give access to higher CRI values by mimicking the broad emission of incandescent bulbs and/or the solar spectrum.
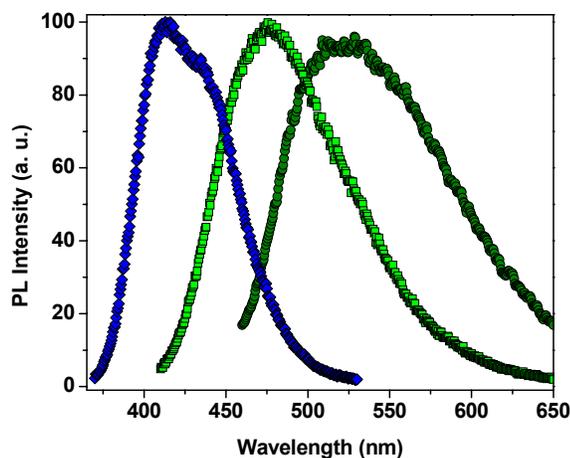
Figure 26 Control of emission energy in $Sr_{2-x}Ba_xSiO/N_4;Ce^{3+}$. [Le Toquin and Cheetham, pending]

However, there is a wide range of potential phosphors based on these ions, and their detailed properties are difficult to predict. Because of this, much current phosphor development is carried out by high throughput screening and combinatorial chemistry rather than on the basis of rational design [Sohn et al. 2006]. The first aim of this Priority Research Direction is, therefore, to carry out the science that will be needed to place the development of new phosphor materials on a much sounder footing. In particular, a major scientific challenge is to go beyond approaches based on empirical materials synthesis and characterization to approaches based on prediction and *design* of detailed properties (e.g., the energies and linewidths of the excitation and emission spectra).

These phosphors must ultimately be encapsulated, and in this area, the challenges can be considered equally urgent because the current materials simply fail under the potential operating conditions of today's high-power white LEDs much more quickly than the intrinsic lifetimes of the LEDs themselves. The second aim of this Priority Research Direction is therefore to develop entirely new classes of encapsulant materials. Research should not be limited to the class of polymers, but should also consider inorganic alternatives such as low-temperature glasses, for example.

Underlying both of these "materials discovery" challenges is the likelihood that theory and modeling, working in close collaboration with experiment, can make important contributions to materials design. For example, many photon conversion materials consist of an emissive dopant ion in a host material. Typically photo-excitations are first generated in the host and then transferred to the dopant, which emits a photon. If we can better understand the interplay between luminescent properties and the doping, structure, and the composition of the materials, we can effectively concentrate on promising material classes.

Understanding that interplay would involve, for example, understanding the electronic structure of the host and dopant ions, the position of energy levels of the dopant ion with respect to the band states of the host, the efficiency of energy/charge transfer from the host to the dopant ions, and the luminescence properties of the dopant ions. The properties of both host and dopant ions are important and could be studied using electronic-structure approaches such as density functional theory. In many cases, excited electronic states of the materials are of particular interest. This can present a theoretical challenge because some of the most successful electronic structure approaches, such as local-density approximation (LDA), are best suited for ground-state

properties. The host materials are often strongly ionic, and the electron-phonon interaction and resulting polaron physics can play an important role in determining the material properties. In many cases high spin states, resulting from Hund's rule state filling, occur on the dopant ions. Semiconductor quantum dots and large-gap insulator nanophosphors also present interesting new opportunities for novel photon conversion materials. Understanding electronic processes in these new nanoscale materials is an interesting theoretical challenge. Theory and modeling could be used to guide experimental material characterization and new material searches by using a combination of first- principles electronic structure approaches coupled with phenomenological models of key processes to understand important trends in the properties of different classes of photon conversion materials.

POTENTIAL RESEARCH APPROACHES

Phosphors Based Upon Rare-Earth Activator Ions

A range of factors determine the energies and linewidths of the absorption and emission wavelengths of the $f \rightarrow d$ and $d \rightarrow f$ transitions in systems based upon Ce^{3+} or Eu^{2+}. These include the following:

- The d-f separations and the manner in which these are altered by the host structure. In general, these separations are smaller for nitrides than oxides, which, in turn, are smaller than those of the free ions [Andriessen, Dorenbos, and van Eijk 2005]

- The splitting of the d levels of the excited state by the ligand field environment, which depends in the first instance upon the symmetry at the rare-earth site (Figure 27)

- The degree of disorder in the Ce^{3+} or Eu^{2+} environment, which affects the energy levels at individual sites and leads to line broadening (which may be advantageous or not, depending on the application)

- Substitution effects in the host lattice, which may shift the lines as well as broadening them

- The Russell-Saunders splitting of the ground state in the case of Ce^{3+} (this splitting is apparent in Figure 26 and also shown in Figure 27)

It is not intended that the quest for tunable phosphors should be restricted to Ce^{3+} and Eu^{2+} systems, or indeed to rare-earths in general, since there are other classes of materials that could prove to be equally attractive. Certain materials containing transition metal activators may prove to be of interest, such as the GdF_3: Ce^{3+}, Mn^{2+} system [Poort, Meijerink, Blasse 1997]. In this case, the LED emission would be harvested by the Ce^{3+}, and then transferred via the Gd^{3+} to the Mn^{2+} where it could be emitted in the green or red, depending on the site symmetry. However, in research and design of these materials, it is imperative that strong consideration be given to the energy transfer rate and number of available final transition states, to avoid shifting luminescence properties as a function of excitation level and/or temperature.

The challenge of designing tunable phosphors for SSL applications will require a multifaceted approach. On the experimental side, it will require systematic studies of families of oxides, nitrides, oxynitrides, and others in which the cation coordination numbers, site symmetries, and other parameters are varied in a systematic manner to elucidate the influence of these parameters on the excitation and emission spectra.
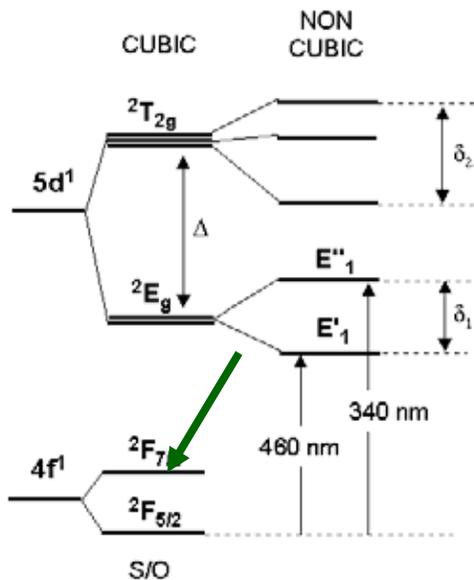
Figure 27 Energy level diagram for Ce^{3+} in a distorted cubic field. [Courtesy of A. K. Cheetham]

Quantum Dot Approach for Light Conversion

As discussed in the sidebar to this Priority Research Direction, as well as in the Cross-Cutting Research Direction on "New Functionalities through Heterogeneous Nanostructures," tunable photoluminescence can also be achieved by the use of quantum dots (QDs). In the case of ZnSe-capped CdSe QDs, for example, the emission can be adjusted continuously from the blue to the red by adjusting the size of the CdSe cores in the range 2–10 nm [Rohwer, unpublished results]. In principle, this appears to be a very attractive way of developing tunable phosphors, but there are several serious challenges that need to be addressed, including long-term stability under the LED operating conditions and, most importantly, toxicity. Also, QD materials must be designed with optical properties that are immune to the environment so that they may be dispersed in a wide range of binder materials and maintain their desired optical properties. Finally, because of the almost nonexistent Stokes shift for these materials, ultra-high quantum efficiencies (approaching 100%) are required to avoid cascading energy losses in light conversion when the QDs are densified to provide meaningful absorptive properties. In addition, there is an urgent need to develop new classes of QD materials systems that have all the attractive features of the CdSe systems but are environmentally benign.

We note that an alternative use for QDs is for refractive index modification of binder matrices. While many of the same requirements apply (e.g., robustness and dispersion) as for luminescent QDs, at least the necessity of high luminescence efficiency is relieved and, arguably, progress in this area could allow QDs to have an impact on SSL much sooner. We finally note that a combination of luminescent and non-luminescent (for passive optical property tailoring) QDs in suitable binder matrices opens up a wide range of possibilities for new optical materials for SSL. This is an important area for future research under this Priority Research Direction.

Phosphor Binder Matrices

Current binder matrices, or encapsulation materials (epoxy and silicone polymers) are unable to satisfy the needs of white LEDs in terms of temperature and radiation stability as well as mechanical performance. Rather than focusing on gaining a better understanding of the current materials (already being addressed by industry), we suggest that the development of new classes of materials is required. This approach might follow two quite different directions. The first would include the synthesis of new classes of polymers specifically designed for the UV application, such as thermally stable perfluoro polymers. These might require additional components such as titania nanoparticles to increase the refractive index. The second would involve the development of *low temperature* deposition processes for *inorganic* encapsulants such as silica. A prototypical process for such low-temperature deposition of inorganics has been developed by Symmorphix (www.symmorphix.com). The films, which are currently used for physical barrier, dielectric, and optical layer applications, are deposited using a wide-area, low-temperature Physical Vapor Deposition (PVD) process. Other classes of low-temperature glasses are also possibilities, and the unprecedented demands of SSL technology for such materials provide a basis for not only new research directions, but may potentially lead to new industries.

HOW WILL SUCCESS IMPACT TECHNOLOGY?

Success in the area of both photon conversion materials and binder matrices will bring benefits in all aspects of SSL — brightness, lifetimes, color rendering index, and energy efficiency. It is also important to recognize that the work done on phosphors for SSL is also likely to have important ramifications for display technologies. Equally, it is probable that new encapsulant materials that have the required thermal and optical properties and high refractive indices will find applications in other areas.

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TUNING THE COLOR OF SEMICONDUCTING NANOCRYSTAL QUANTUM DOTS

A quantum dot, also called a semiconductor nanocrystal or an artificial atom, is a semiconductor crystal whose size is on the order of just a few nanometers. Simple chemical techniques now exist that can be used to synthesize inorganic nanocrystalline quantum dots (QDs) at the laboratory benchtop. Electrons and holes occupy nearly discrete energy states within these QDs very similar to those for isolated atoms. The energy of these energy states depends strongly on the nanoparticle size, as can be seen from the shifts in the light absorption and emission energies for various sizes of CdSe particles illustrated in the figure. The energies can be tuned so much through size that QDs can be made to emit light *across the entire visible spectrum*. At the same time, the distribution in nanocrystal QD size can be made very narrow so that the wavelength range of the emitted light is <30 nm (that is, very pure in a particular color). Though the science of QD materials is still evolving rapidly, photoluminescence (PL) efficiencies of near unity have already been achieved, and QD materials have been demonstrated with several technologies, including efficient solar cells, light-emitting diodes, and photostable fluorescent tags in biological systems.

(Left) The absorption spectra of a series of different size (from 2 to 12 nm) CdSe nanocrystals indicating precise tuning of the lowest energy absorption peak from wavelength λ = 400 nm to λ = 650 nm [C.B. Murray et al., *J. Am. Chem. Soc.* 115, 8706 (1993)]. **(Right top)** Schematic cross section of a nanocrystal QD indicating the placement of the core and shell materials as well as of the organic ligands that surround the shell. The shell material typically has a wider bandgap than the core, and serves to confine the electrons and holes to the core. The organic ligands facilitate QD synthesis and QD dispersion in organic solvents. **(Bottom)** A series of luminescent vials containing solution of different sized QD lumophores.

POLAR MATERIALS AND HETEROSTRUCTURES

Because bandgaps tend to increase with bond polarity, most known inorganic semiconductors (including InGaN) with bandgaps wide enough to emit light in the ultraviolet and visible are polar. Hence, to fully exploit materials and heterostructures for solid-state lighting, this Priority Research Direction (PRD) proposes a concerted effort aimed at manipulating and understanding the electronic and optoelectronic properties of polar materials and heterostructures. These materials and heterostructures would include those based on GaN, the semiconductor that is central to current solid-state lighting technology, as well as other wide-bandgap polar semiconductors such as those based on ZnO.

BACKGROUND AND MOTIVATION

Because bandgaps tend to increase with bond polarity (the sequence Ge, GaAs, ZnSe is a good example), most known inorganic semiconductors with bandgaps wide enough to emit light in the ultraviolet (UV) and visible are polar. GaN, the semiconductor that is central to current solid-state lighting (SSL) technology, is among the most polar of the III-V semiconductors [Bernardini, Fiortini, and Vanderbilt 1997], and any inorganic semiconductor that might displace GaN in SSL is also likely to be polar. In other words, polar materials and heterostructures are a central feature of SSL.

Hence, to fully exploit materials and heterostructures for SSL, it is necessary to understand how to manipulate and understand the electronic and optoelectronic properties of polar materials and heterostructures. One aspect of polar materials and heterostructures, for example, is strain-induced piezoelectric fields. These fields cause spatial separation of electrons and holes in quantum wells and a decrease in radiative recombination rates, and thereby decrease the overall efficiency of radiative recombination. Moreover, these effects become more pronounced with increasing strain, and hence with increased In content in the InGaN alloys (discussed in the PRD "Luminescence Efficiency of InGaN Structures") needed for green-light emission.

Another aspect of polar materials and heterostructures, for example, is the ability to manipulate effective charges at the interfaces between materials with different polarizations, as illustrated in Figure 28. Recently, such manipulation has led to a new class of high-electron-mobility field-effect transistors (HFETs) in which there is no doping in the channel or the barrier, but sheet charge densities as high as 10^{13} cm^{-2} can nonetheless be achieved [Ambacher et al. 2002]. The result is high charge density combined with high mobility, since there is no charge scattering because of ionized dopant ions. The resulting product of sheet charge and mobility — key parameters for transistor performance — is higher than that in GaAs and over an order of magnitude higher than that in Si. Devices with very high frequency and high power have been demonstrated in this technology [Higashiwaki, Matsui, Mimura 2006].

In this PRD, we propose a concerted effort aimed at manipulating and understanding the electronic and optoelectronic properties of polar materials and heterostructures. These materials and heterostructures would include those based on GaN, the semiconductor that is central to current solid-state lighting technology, as well as other wide bandgap polar semiconductors such as those based on ZnO. The ultimate aim would be to understand how to mitigate those aspects of polar materials and heterostructures disadvantageous to SSL while exploiting those aspects advantageous to SSL.
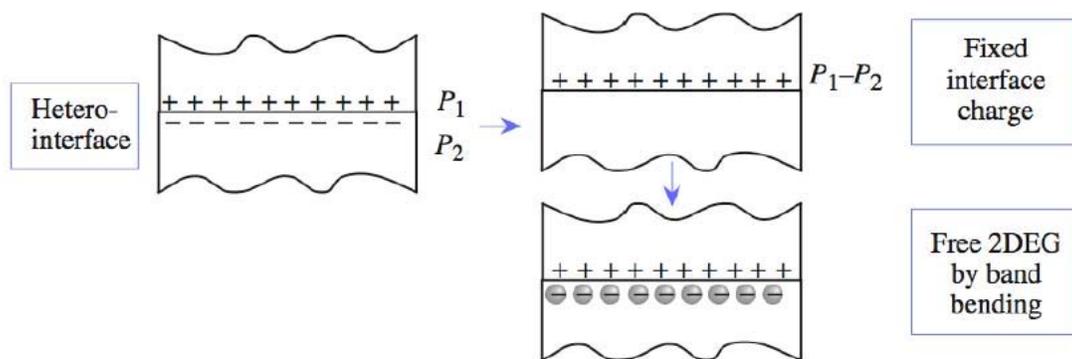
Figure 28 Spontaneous polarization and piezoelectric effects can be exploited in heterostructures to cause internal fields and induce free carriers. (Left) At a heterostructure interface between two materials with different polarizations, there will be an abrupt gradient, ΔP, in the polarization. (Top right) This polarization gradient leads to an effective "fixed" charge bound to the interface. (Bottom right) In n-type heterostructures, the fixed interface charge will in turn cause free electrons to accumulate, producing a free two-dimensional electron gas (2DEG). [Courtesy of J. Singh]

SCIENCE QUESTIONS AND OPPORTUNITIES

Our basic understanding of polar materials and their heterostructures is quite rudimentary. Moreover, it may not be possible to use our knowledge and understanding of nonpolar heterostructures to explain phenomena observed in polar heterostructures. As such, there are a number of broad classes of science questions and opportunities to explore in polar materials and material structures made from them.

One broad class of science questions and opportunities is very basic in nature, and includes the following questions:

- What are the energy band lineups of various polar materials, and how do these influence the magnitude of polar charges?

- How do dimensions influence the magnitude of polar charges; for example, if we have one or two monolayers of material, do the polar effects survive?

- How do polar surfaces alter the thermodynamic thin film growth modes (layer-by-layer, island formation, and the sequential combination of the first two modes) that are controlled by surface/interface energetics and the resulting structure of heterostructure interfaces? The growth mode may significantly alter the polarization values, since the distortions will probably be different.

- Conversely, how do the different thin film growth modes affect the polarization values? It is known that polar charges are different along different crystallographic directions and that a thin film of a given chemistry will nucleate and grow via different modes along different crystallographic orientations.

Another broad class of science questions and opportunities pertains to optoelectronic light-emitting structures of current practical importance. These structures would include those based on InGaN materials in which, as discussed in the PRD "Luminescence Efficiency of InGaN Structures," poor efficiency is observed at high electron-hole injection densities, or at high In content.

- What is the role of polar effects at InGaN/GaN interfaces in creating electric fields, and what is the role of electric fields in reducing electron-hole overlap and decreasing radiative recombination rates?

- How do the above effects scale with In content and strain?

- How do the above effects scale with electron-hole injection densities and the screening fields they provide?

- Can polar charge distributions be engineered so as to provide a built-in field to "funnel" the charge carriers into the active region and thereby enhance electron/hole recombination?

Yet another broad class of science questions and opportunities pertains to electronic properties, particularly those related to charge injection, transport, and capture.

- Can polar heterostructures be exploited to enable improved p-doping and hole mobilities?

- Can polar heterostructures be exploited to decrease p-type contact resistivities, which are normally two orders of magnitude higher than n-type contact resistivities?

- Can polar effects be exploited to achieve enhanced doping in the quasi-neutral region where significant power is dissipated, especially under high bias conditions?

The ultimate goal would be to eliminate all sources of inefficiency related to charge injection, transport, and trapping—energy loss at contacts; energy loss (especially under high injection) in the n- and p-regions of these devices; nonradiative energy losses in the active and quasi-neutral regions of the device; and energy loss because of carriers not captured in the active region. We note that such a goal is, in principle, attainable; an examination of GaAs and InP based light-emitting diodes (LEDs) indicates that there are nearly no inefficiencies related to charge injection, transport, and trapping.

POTENTIAL RESEARCH APPROACHES

The focus of this PRD is manipulating and understanding the electronic and optoelectronic properties of polar materials and heterostructures. A number of research approaches suggest themselves, though this listing is not intended to be inclusive.

One broad research approach would involve comparisons between polar and nonpolar structures. For example, because of the anisotropy of hexagonal (wurtzite) GaN-based materials, polar effects will change in magnitude, depending on the crystallographic orientation of the heterostructure. Crystallographic orientation can therefore be a powerful tool in understanding polar effects.

Another broad research approach would involve separating out the normally linked effects of composition and strain. For example, because of the composition-dependent lattice mismatch between InGaN and GaN, changes in composition are normally accompanied by changes in strain, and therefore changes in polar effects. If strain could be varied independently of composition, through lattice-constant-engineered substrates, the effects of strain and composition could potentially be unraveled.

Another broad research approach would involve purely electronic structures without the complication of light-emission processes. These structures might include those recently

developed for polar AlGaN/GaN heterojunction field effect transistors (FETs), as shown in Figure 29, or for polar heterojunction diodes, as shown in Figure 30.
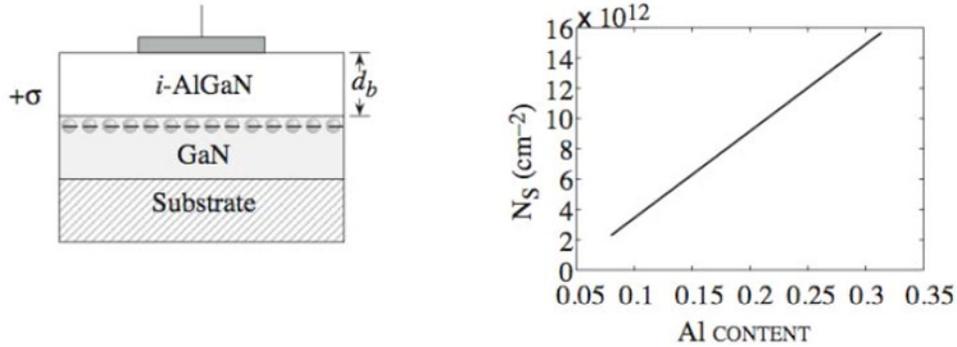
Figure 29 (Left) The device structure for an undoped high-electron mobility field-effect transistor showing a high sheet-charge density of electrons beneath the i-AlGaN/GaN interface. (Right)Graph of this electron density as a function of Al mole fraction in the AlGaN. [Wu, Singh, and Singh 2003]
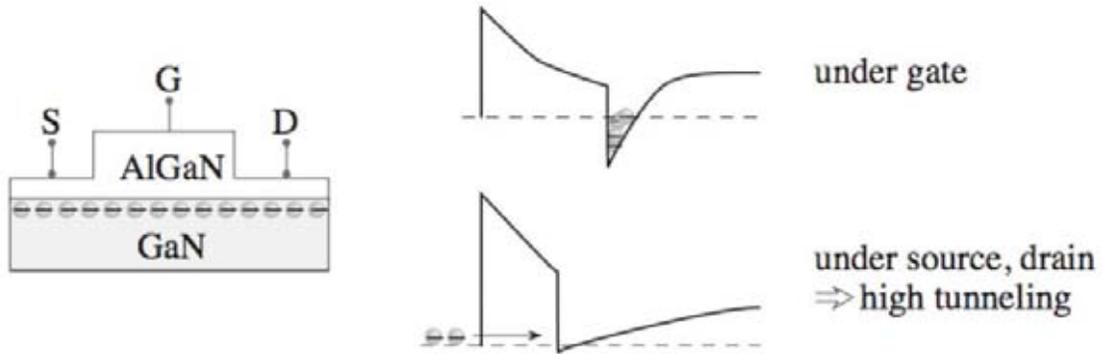
Figure 30 Tunnel junction structures for controlled vertical transport. The polar fixed charge at the interface causes band bending, which for thick AlGaN barriers can induce two-dimensional sheet charge (upper drawing) and for thin AlGaN barriers can enhance tunneling (lower drawing). [Wu, Singh, and Singh 2003]

A number of observations have already been made in such structures:

- Polar heterointerfaces can be used to create large electric fields inside devices *without the need for doping*.

- Polar heterojunctions can be used to induce free carriers leading to undoped electronic structures.

- Electrons induced in undoped polar heterostructures have high mobilities and do not suffer from impurity scattering. In other words, electron mobilities are as high as they would be in pure (or unintentionally doped) materials.

- Metal-semiconductor junction properties can be modified so that junction properties can span the range from Schottky to nearly ohmic behaviors without doping level changes.

This broad research approach would seek to extend these observations from electrons to holes, and from structures of value to electronic applications to structures designed for electronic applications to structures important for optoelectronic applications and light emission.

Yet another broad research approach would involve light-emitting structures. For example, it is widely believed that high densities of carriers ($\geq 10^{13}$ cm^{-2}) injected into the active quantum wells can mitigate some of the negative aspects of polarization, since the carriers can screen the polar field in the InGaN/GaN wells. Thus, radiative efficiency can improve with injection instead of degrading with injection. However, experimental results for power output of current LEDs [Higashiwaki, Matsui, and Mimura 2006] suggest that carrier densities in the well are typically too low (less than 10^{12} cm^{-2}) to screen the polar fields and to significantly influence radiative recombination rates [Jiang and Singh 2000]. If special-purpose structures capable of steady-state or transient carrier densities much higher than this could be constructed, it should be possible to observe, understand, and perhaps ultimately exploit, screening effects.

HOW WILL SUCCESS IMPACT TECHNOLOGY

In principle, LEDs should be able to convert electrical power to optical power with near 100% efficiency. Current nitride-based LEDs are quite far from this efficiency, especially for green-light emission and for high electron-hole injection densities. Research topics addressed by this PRD may make it possible for nitride-based LEDs to overcome nonradiative losses especially at high injection through better p-doping technology and through better channeling of charge into the active region. If one assumes nitride LEDs can be efficient at injection densities of 10^4 A/cm^2, we can expect light output powers of over 5,000 lm from a 1 mm diameter LED.

Semiconductor technology has relied on doping to create internal fields, charges, and contacts. This dependence on dopants limits the potential development of new semiconductors, particularly large-gap semiconductors where doping efficiencies are low because of high ionization energies. This PRD will have the additional and far-reaching benefit that it may allow one to understand the origins of polar charges at monolayer dimensions, which in turn will offer another tool in semiconductor technology. This will be especially useful for wide bandgap technology (materials ranging from diamond to a variety of oxides) and lead to undoped electronics and optoelectronics.

Finally, we also note that polar heterostructures, though relatively new in electronics and optoelectronics, have a longer history of use in sensors and in smart cards, so the understanding resulting from this PRD would likely have broad impact beyond SSL.

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LUMINESCENCE EFFICIENCY OF InGaN STRUCTURES

While a number of inorganic semiconductors have the potential to impact solid-state lighting (SSL), InGaN alloys stand out as being exceptionally promising. In many ways, the imminent revolution of SSL is largely because of the remarkable development of light-emitting diodes (LEDs) based on this alloy system. However, despite more than a decade of research, InGaN materials that emit light efficiently at the high electron-hole injection densities critical to white-light illumination, and at the green-yellow wavelengths critical to human visual perception, have proven elusive. The origin of these limitations is not well understood, though it may be speculated to arise from the complex interplay of a range of materials properties including compositional disorder, high defect densities and the presence of strong piezoelectric fields. This Priority Research Direction calls for a deeper scientific understanding of these limitations.

BACKGROUND AND MOTIVATION

InGaN-based semiconductors have tremendous potential for impacting solid-state lighting (SSL). The development of InGaN blue and green light-emitting diodes (LEDs) [Nakamura, Senoh, and Mukai 1993], in combination with AlGaInP-based red LEDs has enabled a red-green-blue (RGB) architecture for realizing high-performance inorganic LED-based white lighting. The further demonstration of white LEDs based on ultraviolet/blue InGaN LEDs coated with phosphors has provided another promising architecture that may expand the flexibility and performance of lighting systems. Perhaps the most distinctive property of InGaN alloys for lighting applications is their direct energy bandgaps that span the entire visible region of the spectrum through tuning of the indium composition of the alloy. The realization of full spectrum capability from a single semiconductor alloy system may provide substantial benefit for future SSL architectures and may ultimately be enabled by InGaN alloys.

Despite this potential, InGaN LEDs suffer from two severe limitations. The first limitation is the efficiency roll-off in the green. Currently, the most efficient electrical-to-optical energy conversion is obtained in the near ultraviolet (UV) to blue region (400–460 nm), where up to 70% internal quantum efficiency (IQE, or percentage of electron-hole pairs converted into photons) and up to 40% external quantum efficiency (EQE, extracted photons per electron) is obtained. However, for green InGaN-based LEDs [Wetzel et al. 2004], a steep decrease of efficiency occurs, dropping to about 5% external efficiency at 550 nm, near the peak sensitivity of the human eye (Figure 31). Amber and red light emission have also been demonstrated from this material system [Mukai, Narimatsu, and Nakamura 1998; Fuhrmann et al. 2006b], but efficiencies are typically significantly less than 5%.

The second limitation is the efficiency roll-off at high electron-hole injection densities. This effect is shown for state-of-the-art high-power InGaN LEDs in Figure 32. The observed efficiency roll-off places unacceptable limitations on the maximum obtainable optical power per unit area of the LED and the maximum power from a single source that can be employed in SSL applications.
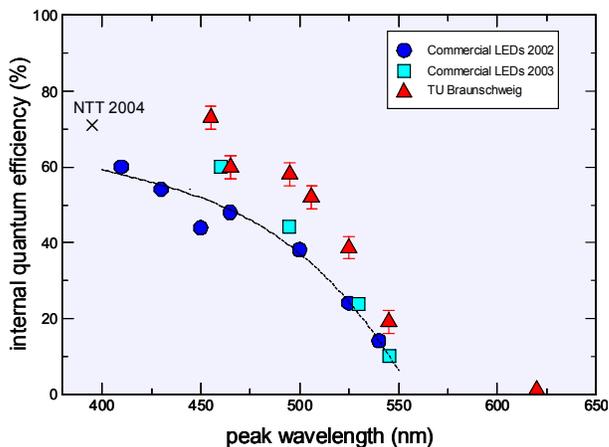
Figure 31 Wavelength dependence of the internal quantum efficiency of InGaN-based LEDs and materials. Commercial LED data (circles and squares) refer to estimated IQE from electroluminescence of LEDs. Data from the Technical University of Braunschweig (triangles) represent IQE data from photoluminescence of InGaN single-quantum well structures. [Furhmann et al. 2006a]
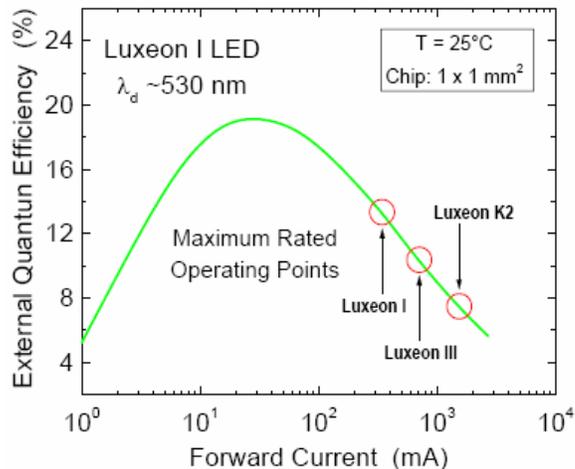
Figure 32 External quantum efficiency of Lumileds' Luxeon LEDs as a function of operating current. Maximum rated operating currents of three different Luxeon models are indicated. These devices employ InGaN multi-quantum wells with green emission at ~530 nm. [Krames 2006]

Despite more than a decade of InGaN materials and LED research, the physical mechanisms behind these two limiting behaviors are poorly understood. The III-nitride material system has proven to be extremely complex, with large internal polarization effects, alloy disorder, quantum well interface roughness, and high defect densities, all contributing to materials properties and LED performance. A further challenge is that these characteristics are strongly dependent on materials growth conditions (e.g., temperature, V/III ratio, growth rate), and optimal growth conditions are different for different indium compositions. Nevertheless, there seems to be no clearly established reason why InGaN-based structures should not be able to perform well in the green and even in the red spectral region, as well as at high current densities.

SCIENCE QUESTIONS AND OPPORTUNITIES

These performance limitations define two fundamental science questions that, if solved, could dramatically enhance the wavelength range and efficiency of InGaN-based LEDs, particularly at higher electron-hole injection densities needed for SSL applications. Below, we formulate these questions, and suggest a range of issues that must be explored.

- Why does the quantum efficiency of InGaN-based active regions and LEDs fall off dramatically at wavelengths beyond 500 nm?

Because of the complex properties of InGaN materials and devices, several issues must be examined to address this question. First, investigations must seek to determine to what extent the wavelength-dependent performance is driven by fundamental properties of InGaN alloys as their indium composition is increased for longer wavelength emission. In particular, when using a GaN template, higher indium composition alloys have increased strain, increased piezoelectric fields, and a greater tendency for compositional variations. These properties can have tremendous

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impact on carrier transport and recombination processes, and the precise dependencies must be better understood.

A second critical issue is the role played by materials growth processes. InGaN materials and LEDs are most often grown by metal-organic vapor phase epitaxy (MOVPE) or molecular beam epitaxy (MBE) techniques. These two techniques offer extremely different growth environments, but each approach must be optimized for a given alloy composition. For example, the incorporation of increased indium requires lower growth temperatures, which can lead to increased point defect incorporation, greater compositional variations, and the nucleation of morphological defects. The impact of growth conditions as well as the growth technique itself on the performance of higher indium composition InGaN LEDs is thus an issue of fundamental importance that warrants in-depth investigation.

Finally, it is essential to consider the InGaN materials as but one part of the entire LED structure. InGaN LED active regions often consist of InGaN QWs with GaN barriers, and the surrounding p-type and n-type regions also consist of GaN (and possibly AlGaN) epilayers. Since the optimal growth conditions of GaN and InGaN are quite different, the growth of structures incorporating both materials necessarily involves compromises. For example, the reduced quality of GaN barriers grown at lower temperatures and in nitrogen ambient appropriate for InGaN quantum wells (QWs) may detrimentally impact both carrier transport and radiative recombination processes. Optimized growth of p-type GaN layers typically requires higher temperatures that may degrade the quality of underlying InGaN QWs. Thus, the growth conditions and properties of all layers of the LED structure must be thoroughly examined to gain a complete understanding of wavelength dependent performance issues.

- What is the reason for the strong efficiency reduction in InGaN based LEDs at current densities greater than ~10 A/cm^2?

This current-dependent behavior is distinct from other III-V semiconductor LEDs, and its magnitude suggests that factors in addition to thermal limitations must be involved. Currently, it is unclear which of the unique properties of InGaN alloys and LED structures dominate in the higher carrier density regime. This regime can lead to a range of phenomena, such as the screening of internal polarization-induced electric fields, the creation of energetic carriers with reduced confinement, and possibly the saturation of nonradiative states. That some of these effects would appear to be beneficial to optical efficiency demonstrates the complexity of the problem.

The impact of high carrier densities on the nonradiative properties and global impact of extended and point defects are additional factors that are not well understood. However, as the desired operating current density of LEDs for SSL approaches that of InGaN laser diodes, it is anticipated that threading dislocations may play an increasingly detrimental role in device performance, as research on laser diodes has clearly demonstrated [Takeya et al. 2003]. Overall, the behavior of InGaN LEDs with increasing current density may involve a complex interplay of phenomena characteristic to InGaN alloys, and fundamental studies of InGaN LED structures are needed to provide insight into achieving high efficiency from high-power LEDs.

POTENTIAL RESEARCH APPROACHES

The long-standing nature of these performance limitations indicates that new approaches must be applied to unravel the complex phenomena in InGaN materials and LEDs. First, we need to develop greater insight into the nanoscale materials properties, both as they arise in real time through materials growth processes and also in how they specifically relate to device performance.

In addition, we must develop approaches to simplifying the light-emission process, achieving selective isolation or elimination of particular properties to enable greater insight into which processes are dominant in InGaN LEDs.

Achieving greater insight into InGaN materials properties will rely on the development and application of advanced characterization tools with improved performance in areas such as chemical sensitivity, spatial resolution, and real-time access. (Some of these advanced characterization techniques are described in the Cross-Cutting Research Direction "Precision Nanoscale Characterization"). A particular limitation in InGaN materials development, particularly for the MOVPE growth technique, has been the lack of a broad array of in situ monitoring tools to provide quantitative measurement of the evolution of InGaN film properties. The increasing availability of specialized x-ray characterization methods, including the in situ application of very high brilliance synchrotron x-ray sources [Stephenson et al. 1999] promises to provide unprecedented access to growth modes, surface and interface structure, defect generation, and the evolution of compositional instabilities in InGaN films. The further advancement and application of in situ x-ray techniques, as well as optical techniques, would contribute to fundamental insights into the relationship between growth parameters and materials properties and further reveal methods to tailor those properties in real time. Combining these in situ measurements with theoretical models of the growth process, including the coupled gas-phase and surface chemistry, fluid flow, and mass transport within the reactor, may provide the basic understanding that has been lacking throughout InGaN materials development.

Further development of ex situ characterization tools is also essential to advancing InGaN materials properties and LED performance. While a range of structural, optical, and electrical characterization techniques has been applied to InGaN studies, notable limitations have been identified. One example is the difficulty in unambiguously characterizing nanoscale properties including compositional variations of InGaN alloys and QW structures. The potential for InGaN alloys to demonstrate strong compositional variations, including the spontaneous formation of In-rich quantum dots, has been a subject of intense interest throughout InGaN development. Particularly for longer wavelength, high indium content alloys, carrier localization at In-rich regions has been reported to be a dominant factor in limiting nonradiative recombination, potentially providing an explanation for the unusually high performance of InGaN materials in the presence of high defect densities [Chichibu et al. 1996] . However, recent studies have revealed the tendency for InGaN materials to degrade during post-processing and characterization using e-beam microscopy techniques [Smeeton et al. 2003], frustrating the identification of "as-grown" compositional profiles. Advances in e-beam and ion-beam techniques to enable high-resolution measurements at lower, less-damaging beam energies, as well as the development of improved near-field optical and other scanning probe techniques would greatly contribute to insight into properties of InGaN materials and LEDs. As mentioned above, the application of theoretical models to predict materials properties, in concert with experimental efforts, would provide substantial benefit.

While these materials characterization advances will undoubtedly provide valuable insights, they may have limitations in revealing all the important factors in multilayer InGaN LEDs, particularly under high current injection conditions. Exciting developments in the nanoscale characterization of real-time processes of LEDs includes the application of single molecule spectroscopy to functioning organic LED (OLED) devices [Gesquire, Park, and Barbara 2004]. The development and application of related approaches to InGaN LEDs would provide unprecedented insight into the complex interplay of carrier injection and recombination processes, particularly under high injection conditions.

All of these material and device characterization approaches could benefit from the development of InGaN structures and growth strategies designed to reduce the complexity of processes operative in InGaN materials and devices. As an example, materials performance is clearly influenced by high densities of defects and the presence of strain in InGaN alloys. Threading dislocations in InGaN structures have been reported to act as nonradiative recombination centers [Shaguhara et al. 1998] and provide initiation points for morphological defects and compositional variations. On the other hand, so-called *v-defects* that decorate dislocations may even be highly beneficial [Hangleiter et al. 2005]. Strain in InGaN epilayers has been shown to modify the growth process, limiting indium incorporation through "composition pulling" effects [Larche and Cahn 1987] and may also contribute to compositional variations and defect formation. The development and study of InGaN materials on low defect density GaN templates, in addition to the development of strain-relaxed templates, would enable a clearer identification of the impact of extended defects and strain on InGaN materials performance. Achieving a strong reduction in extended defects may also more clearly isolate and identify the impact of point defects. Additional specialized structures and growth approaches, including growth on patterned or planar templates revealing nonpolar or semi-polar surfaces [Kamiyama et al. 2005; Neubert et al. 2005; Sharma et al. 2005], could provide control and minimization of internal piezoelectric fields that are known to affect transport and recombination processes [Takeuchi et al. 1998; Wetzel et al. 2000]. These examples are just a sampling of the strategies that could be employed to isolate and study individually the dominant factors that limit present-day InGaN LED performance.

HOW WILL SUCCESS IMPACT TECHNOLOGY?

Success in this PRD will require developing a fundamental understanding of the physical mechanisms leading to both the drop of emission efficiency at longer wavelengths and the decrease of efficiency at high current density. With the ability to mitigate the factors that dominate these InGaN LED performance limitations, up to a fivefold increase of the efficiency of green LEDs becomes possible, which will enable lighting applications with unprecedented energy efficiency. Moreover, the development of high-efficiency InGaN LEDs across the entire visible spectrum will enable RGB white light emitters on a single material base, potentially providing advantages in chip integration and color stability of white-lighting systems. Finally, the ability to achieve high efficiency at high operating currents will supply the high powers critical for wide-scale adoption of energy-efficient LED-based white lighting in general illumination applications.

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WIDE-BANDGAP NITRIDE SEMICONDUCTORS
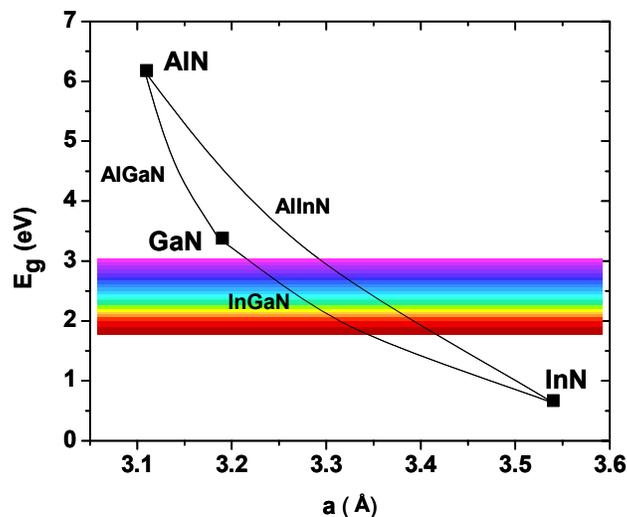
Energy bandgap versus lattice-constant diagram for wurzite nitride semiconductors. Figure adapted from Wu, J., W. Walukiewicz, K. M. Yu, J. W. Ager III, S. X. Li, E. E. Haller, H. Lu, and W. J. Schaff, "Universal Bandgap Bowing in Group-III Nitride Alloys," *Solid State Comm.* **127, 411 (2003).**

Wide-bandgap nitride semiconductors include AlN, GaN, InN, and their mixed-composition alloys. This family of materials has direct bandgaps that span a tremendous range of energies, enabling light emission from the near-infrared to the deep-ultraviolet region of the spectrum. Nitride-based LEDs for SSL applications employ light emission from $In_xGa_{1-x}N$ quantum wells (QWs) with $In_yGa_{1-y}N$ or GaN barriers. Emission wavelengths of these LEDs can be tuned across the entire visible spectrum (see figure) by varying the indium composition of the QW. Other structural parameters, such as the thickness of the QW and barrier layers, in addition to the strain and piezoelectric fields of the QW, can also affect the emission wavelength. To date, the most efficient InGaN LEDs emit in the near-UV to blue region, using QWs with relatively low indium compositions. LEDs with higher indium compositions emit at green and longer wavelengths, but have significantly lower efficiencies. While the origin of this reduced efficiency is not well understood, it is speculated to arise from the complex interplay of a range of material properties, including localized variation in composition, high defect densities, and the presence of strong piezoelectric fields. Achieving high-efficiency emission across the entire visible region with InGaN alloys is one of the fundamental challenges for SSL. The realization of full-spectrum capability from a single semiconductor alloy family would provide substantial benefit for future SSL architectures and may ultimately be achieved using InGaN alloys.

MANAGING AND EXPLOITING DISORDER IN ORGANIC FILMS

Disorder is an intrinsic feature of organic light-emitting diodes (OLEDs) based on organic thin films. The influence of molecular scale order on properties of light-emitting devices remains poorly understood, and our ability to control it is primitive. It is known, however, that disorder can either improve or degrade device performance, depending on its location within the thin film structure. Energetic disorder and local polarization fields near interfaces can improve charge injection. Morphological and conformational disorder in both conjugated polymers and small molecules affect charge transport and exciton diffusion. The further addition of molecular and ionic dopants, and the structure of both metal/organic and organic/organic interfaces increases the morphological complexity. New fundamental science is needed to understand, quantify, and control ordering in molecular thin films. Experimental tools to quantify disorder on the nanoscale need improvement. Quantifying the effect of disorder on critical device parameters requires new modeling capabilities. Such techniques will lead to breakthroughs in OLED efficiency and also have cross-cutting impact on other fields of organic electronics that use thin films.

BACKGROUND AND MOTIVATION

State-of-the-art OLEDs are composed of many thin film layers that serve diverse functions such as charge injection, transport, and recombination. These films are often described as amorphous. However, such a description is inadequate at small (few nanometer) length scales, where the local environment has significant and varying effects on the electronic structure of a molecule and significant correlations exist between the position and orientation of neighboring molecules. There are many indications that "amorphous" organic thin films contain significant degrees of local order that can sensitively depend on how the film was made. In addition, local order might evolve by exposure of the film to the ambient or exposure during device operation.

Structural disorder reflects the noncrystalline nature of both molecular and polymeric films. A major distinction of organic materials is that structural disorder is not associated with broken bonds as, for example, in the case of amorphous silicon. A consequence of structural disorder is that electronic excitations and charges are spatially localized in organic thin films, either on individual molecules or on conjugated segments in polymers. Since charge transport takes place via hopping between localized states, the mobility is related to transfer mechanisms that depend sensitively on *positional* and *orientational* disorder between neighboring molecules. The structure of polymeric semiconductors is even more complex, as chains can come together and form crystallites that are usually small and dispersed in the otherwise amorphous polymer film.

Energetic disorder reflects differences in local environment that can arise for reasons including noncrystallinity, interfaces, and dopants. A widely adopted model for transport in organic materials postulates that energetic disorder causes a Gaussian distribution in the energy of hopping sites, with a FWHM (full-width half maximum) on the order of 100 meV [Bassler 1993]. As a result, the mobility increases with electric field and temperature. Similar concepts have been applied to excitons. Energetic disorder can be correlated, leading to the potential energy profile landscape shown in Figure 33.

Interfaces can introduce additional contributions to disorder because of surf

ace dipoles, polarization, and roughness on a longer length scale of 10 nm that is a substantial fraction of the film thickness. Moreover, metal/organic and organic/organic interfaces introduce different contributions to disorder and call for different characterization techniques. Managing

and exploiting disorder is not limited to OLEDs but applies to all organic electronic devices, such as solar cells or transistors whose architectures are based on thin films.
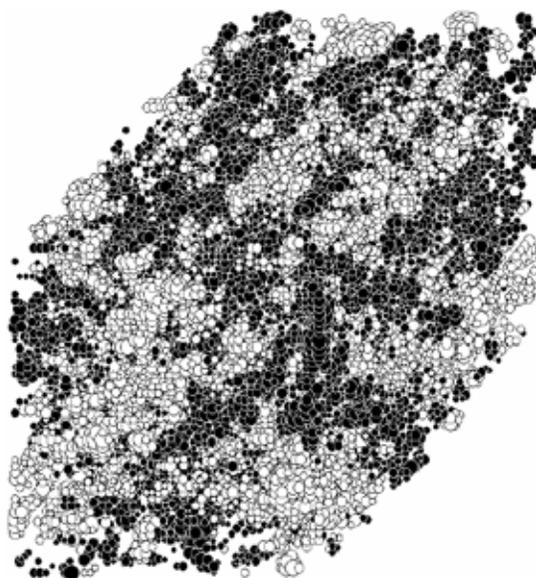
Figure 33 Energy landscape for an organic film with correlated disorder in a cubic lattice. White (black) circles correspond to hopping sites with energy above (below) the average hopping site energy. Dipoles are randomly distributed over the lattice. Since the energy landscape seen by any one charge depends on the locations of the other charges, the charge hopping rate cannot be assumed to be constant. [Novikov 2003]

SCIENCE QUESTIONS AND OPPORTUNITIES

OLEDs are molecular solids whose electronic excitations are particularly challenging to model. Neither the quantum chemistry of individual molecules nor the powerful methods of band theory for semiconductor physics is directly applicable to molecular materials. Electronic states are strongly coupled to intramolecular vibrations whose energies may be a significant fraction of the optical gap. In contrast to wide-bandgap inorganic semiconductors with almost equal optical and charge transport bandgaps, the transport gap for injecting an electron and hole in organic crystals typically exceeds the optical gap for a singlet exciton by 500 meV or more. Disorder can further perturb electronic excitations and charge carriers that are already localized. It is a major challenge for theory and experiment to relate changes in fundamental electronic processes and their dynamics to specific kinds of disorder.

The photophysics of spin-coated conjugated polymers varies with solvent or processing conditions. The interpretation involves conjugation lengths arising from conformational defects and interchain interactions in films from solvents that favor extended conformations. More quantitative interpretation at the molecular level calls for new or improved characterization tools, for both conjugated polymer and small molecular films. Synchrotron x-ray diffraction can help characterize local order in nominally amorphous organic semiconductors. Photophysical signatures reflect local energetic disorder and can be used to quantify it. Energetic and positional disorder in molecularly dispersed polymers, the photoconductors used in xerography, have been modeled using a distribution of site energies and a random distribution of active sites on a lattice [Sin and Soos 2003]. Similar Monte Carlo simulations are appropriate for much higher concentrations of charges in OLEDs under working conditions.

Limited mobility is associated with a small overlap of wave functions. Improved local order, for example, in discotic liquid crystals (composed of disk-like molecules), increases the mobility significantly. Opportunities exist to improve OLED performance through increased local order and to demonstrate greater wave function overlap experimentally. Surface techniques have been widely applied to characterize metal/organic and organic/organic interfaces [Salaneck et al. 2001]. Scanning probe microscopy can also be employed to obtain information on local electrostatics. Buried interfaces in OLEDs present new challenges and opportunities. The desired goal is simultaneous structural and electrostatic information at nanoscale resolution in an OLED.

POTENTIAL RESEARCH APPROACHES

Managing and exploiting disorder in OLEDs will require a multipronged approach, first, to understand the nature of the disorder and its effect on device performance and second, to optimize the degree and type of disorder for highest device performance. High-priority research approaches include the following:

Experimental Techniques for Quantifying Disorder. The combination of existing and novel techniques aimed at quantifying structural and energetic disorder because of noncrystallinity, interfaces, dopants, conjugation lengths, etc., is important. Structural tools, such as synchrotron x-ray diffraction, can help us understand local structure in organic semiconductors and provide information about alignment of chains/molecules along interfaces. Scanned probe microscopy techniques can allow imaging of trapped charge and electrostatic potentials across an organic film. High-resolution photoelectron spectroscopy might be able to measure energetic disorder directly. Optical spectroscopy and micro-Raman spectroscopy are other tools to quantify local energetic disorder. The combination of several techniques on the same sample will help to quantify disorder and understand its influence on electronic processes and OLED performance.

Theoretical Techniques for Understanding the Influence of Disorder. Monte Carlo techniques have been very useful in understanding the role of disorder on charge transport. This is by no means a subject that is fully understood, as the relative importance of sources of disorder on charge transport is still debated. Exciton migration in the presence of disorder can also be modeled using these tools, and a deeper understanding of this process is needed. Experimentally determined structural data and energetic landscapes need to be taken into account in these models.

Simulations can elucidate the influence of interfaces on fundamental physical processes, such as charge and exciton transport across an interface and in the bulk of a film. For example, the role of disorder on charge injection across a metal/organic interface is currently not understood. Modeling approaches that predict the effect of various interface modification layers will help develop schemes that optimize charge injection in OLEDs.

NEW MATERIALS AND PROCESSES

Control of positional and orientational order represents a major opportunity for improving the performance of OLEDs. Order can be controlled by rational materials design that leads to self-assembly and also by deposition and processing techniques. Self-assembly, such as in discotic liquid crystals, should be pursued as a way to improve transport and increase device performance. Disorder should be used as an additional degree of freedom to tune charge and exciton transport processes and control the location of recombination inside an OLED.

Interface modification schemes, especially to improve charge injection across metal/organic and organic/organic interfaces, can be developed. Self-assembled monolayers, doping, and interface texturing are examples of avenues leading to improved injection. Of special interest is exploiting

these schemes to be able to inject electrons from air-stable metals. Controlled alignment and/or chemical tethering of the organic semiconductor molecules at an interface can influence disorder and should also be pursued as a way to manipulate charge and exciton transport across interfaces.

HOW WILL SUCCESS IMPACT TECHNOLOGY?

Since disorder is pervasive in organic films, immediate improvements in OLED performance are likely to be achieved upon understanding the relative impact of the various kinds of disorder. Quantifying disorder will lead to a better understanding of its origin and will enable the community to design materials that help inject and transport charge more efficiently. Improved modeling will help guide materials synthesis and device development efforts.

Controlling energetic disorder will improve charge injection and transport in the bulk of the films and also help confine excitons away from quenchers, both of which lead to higher OLED efficiency. Achieving injection from air-stable metals will enable devices with reduced encapsulation requirements and reduced manufacture cost. Finally, control of disorder will benefit not only OLEDs, but also other organic electronic technologies, such as solar cells.

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UNDERSTANDING PURITY AND DEGRADATION IN OLEDS

While organic light-emitting diodes (OLEDs) have begun to penetrate the display market, their performance is not suitable for solid-state lighting applications. Importantly, a fundamental understanding of OLED degradation remains elusive. The research that has been done indicates that the purity of starting components, as well as degradation mechanisms that occur during device operation, seriously limit device efficiency and lifetime. In many cases, simply identifying the impurities and degradation byproducts that affect performance is currently impossible and will require major advances in analytical chemistry. The ability to quantify impurities is just the first step in learning to control or eliminate them. Other breakthroughs, focused on the development of advanced synthetic and purification techniques, will then be needed to eliminate defects in starting materials. To prevent the formation of defects during device operation, a comprehensive approach that relates the degradation mechanisms to materials properties will be required to design materials that ultimately avoid these detrimental pathways. This in turn will enable the development of an efficient, affordable large-area OLED on a low-cost substrate suitable for solid-state lighting.

BACKGROUND AND MOTIVATION

In both small molecule and polymer OLEDs, there is a need to improve lifetime and operating voltage if these technologies are to be used in solid-state lighting (SSL) applications. To date, little is known about the mechanisms that limit lifetime. Polymer-based OLEDs (POLEDs) commonly use a polyfluorene-based polymer to achieve blue light. It has been known for several years that as the device ages, the spectrum of the emitted light shifts from blue to green. Many researchers initially attributed this shift in emission to excimer formation as a result of chain aggregation during device operation. Now it is known that the green shift can be attributed to the formation of fluorenone (Figure 34) defects in the chain [Bliznyuk et al. 1999; Lupton, Craig, and Meijer 2002; Gamerith et al. 2004]. This discovery has resulted in the design of new polymers that prevent the formation of the fluorenone defect [McKiernan, Towns, and Holmes 2005; Perepichka et al. 2005]. Scientists spent years discussing the cause of the green shift, in part because of the lack of tools capable of analyzing the formation of a small density of defects in an operating device. Electroluminescence itself is currently the most sensitive tool available for measuring degradation, but it does not provide any information on *which* species *causes* the degradation or what is formed during degradation. Tools capable of providing this type of information will enable dramatic advancement of the field.

Ultra-sensitive analytical tools are also need to establish the fundamental structure/property relationships essential to the advancement of OLEDs for SSL. Today it is not possible to measure variations in conjugation length between polymer chains or within different segments of a chain, yet it is known that such differences impact POLED performance [Menon et al. 2002]. Devices based on inorganic materials, such as GaAs transistors, use starting materials of >99.9999% purity, and the electronic properties of impurities at that level are understood. The significance of chemical, isomeric, and morphological defects in organic semiconductors cannot be related to fundamental physical processes or device performance because of our inability to identify and quantify their existence below 0.1% in an otherwise pure material.
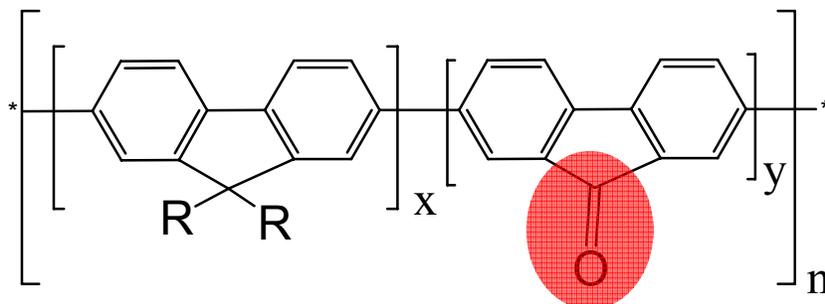
Figure 34 Structure of polyfluorene with an oxygen-containing fluorenone "defect." This light-emitting polymer consists of very long chains of fluorene molecular chromophores. Upon exposure to high temperatures, UV irradiation, and electrical stress, some of the chromophores are oxidized to form fluorenone moieties (labeled red) within the molecular chain. These "defects" are known to trap carriers and affect luminescent properties, resulting in device degradation. [Courtesy F. So]

Another aspect of degradation involves changes in the structure of organic films by exposure to the ambient (for example, water-induced crystallization), and/or by device operation (crystallization assisted by heating of the device under driving conditions). The formation of crystallites is accompanied by the formation of voids, which deteriorate charge transport and might also quench light emission. Chemical degradation of molecules might also be accompanied by the formation of structural defects in the films, and understanding the relationship between these two degradation mechanisms and their influence on device performance is important.

Many of the anodes and cathodes used to inject carriers are further impediments to OLED SSL. Indium tin oxide (ITO) is used as the anode in many devices because it is transparent and conductive and it can be patterned. It is, however, a major source of degradation in OLEDs [Scott et al. 1996; de Jong, van Ijzendoorn, and de Voigt 2000]. Furthermore, it is too expensive for use in large-area OLEDs for lighting applications and, being a brittle glass, is also a barrier to the fabrication of flexible devices. For these reasons, ITO will need to be replaced before OLED SSL is pervasive. To inject a sufficient quantity of electrons, today's devices rely on the use of low-work-function metal cathodes such as calcium or barium. These metals are highly reactive with water and oxygen, so hermetic sealing of an OLED is required to achieve long operational lifetime. Encapsulation, while achievable on rigid glass substrates, remains a significant challenge on flexible plastics or foils, which may be required because of cost and weight constraints in organic SSL applications. An alternative approach that would enable the utilization of water-stable, higher work function metals would reduce or eliminate the need for encapsulation.

SCIENCE QUESTIONS AND OPPORTUNITIES

The scientific challenge of this PRD can be summarized as the discovery of general trends across material classes — small molecule, dendimer, and polymer — that will allow for the design of stable materials and devices. The structural diversity of carbon-based materials lies at the heart of this problem. In a crystalline two-, three- or even four-component inorganic semiconductor, elemental impurities tend to stand out against a low background in analysis techniques such as those based on mass spectrometry. In a carbon-based system, however, molecular fragments, isomers, and oligomers exist in addition to elemental impurities. These can even have identical empirical formulae and are therefore very difficult to quantify at low concentration. The result is that, whereas defects in Si are known to affect device performance at the parts-per-million levels and below, defects in organic semiconductors are often not even quantifiable below 1%

concentration. This leaves us ignorant about which impurities and degradation products are important and unable to draw meaningful structure-property relationships to guide the design of stable materials.

A specific bottleneck to white-emitting OLED efficiency is the stability of blue fluorescent or phosphorescent emitters. Red and green emitters are far more stable; the fundamental reasons for this are not well understood.

POTENTIAL RESEARCH APPROACHES

Specific science opportunities naturally group themselves according to the defect source to be investigated.

Purity of Starting Materials

We must be able to define and analyze chemical impurities at levels that are orders of magnitude more sensitive than standard techniques such as chromatography and nuclear magnetic resonance. If accomplished, this will enable correlation of impurities to device performance and degradation. We must also be able to quantify structural defects such as conjugation length in polymers, structural isomers such as *cis* vs. *trans* linkages, head-to-tail vs. head-to-head couplings in polymers, *fac*-Alq$_3$ vs. *mer*-Alq$_3$, and similar isomeric and oligomeric impurities in small molecules. These, too, must be related to device performance. Clearly, the development of new ultra-sensitive analytical tools and a methodology to quantitatively determine the purity of an organic compound and to measure the conjugation length and conjugation length distribution within a polymer is required. New methods to identify isomers and oligomers in both organic and inorganic materials are also needed to allow device properties to be related to the quality of the starting materials.

In addition, new synthetic and purification techniques are required that will afford structural control and purity at a level common in inorganic semiconductors, but unprecedented in organic materials. Such techniques could help reduce the need for post-synthesis purification. For example, the ability to synthesize an electroactive polymer with the level of control available in living and biological polymerization would allow us to deliver organic compounds with purity levels approaching those of inorganic semiconductors.

Morphological Defects

We must understand how morphological defects impact OLED performance. We need to define quantitatively the morphology of a thin organic film and relate that morphology to charge injection, transport, and luminescence. Morphological defects include variations in the extent of molecular overlap, polymer chain and small molecule aggregation, and local packing effects. Experimental tools are needed to identify and quantify morphological defects at length scales from the nanoscale to the macroscale to relate their presence to device performance and device degradation.

Materials Stability under Device-Relevant Conditions

Defects that impact device performance may be introduced at every stage of device fabrication and operation. Some are present as a result of the synthetic method used to make the organic compounds themselves. Others are a result of the processing techniques used to fabricate the device. Still more are introduced via reactions during device operation. It is critical to be able to identify all these species, quantify their concentration, and determine their impact on the device

efficiency. This will enable the improvements in device efficiency and operating lifetime that are required for OLED SSL.

Electrode Degradation

The charge-injecting electrodes offer further potential for innovation. New transparent conductors are needed that are chemically stable during device operation and can be printed or patterned to reduce cost. The design of highly conducting polymers that are stable and transparent and that can inject carriers may allow the elimination of reactive metal electrodes, enabling devices that have reduced encapsulation requirements. Using dipoles, self-assembled monolayers or other interfacial layers might allow efficient injection of electrons from high-work-function metals.

HOW WILL SUCCESS IMPACT TECHNOLOGY?

The importance that defects and degradation processes play in OLEDs cannot be overstated. The challenges outlined in the previous sections need to be addressed immediately if this field is to advance. Only when it is possible to characterize and quantify defects and the mechanisms of degradation will it be possible to design and fabricate low cost, large area OLEDs for SSL. The development of new analytical techniques will better enable scientists to understand which defects are detrimental, and that, in turn, will allow them to design better materials and device structures. As new analytical and characterization techniques develop, improved materials will be synthesized. It is very likely that improved materials and devices will create a need for even better analytical tools that will lead to different materials, devices, and theoretical knowledge. The iteration of this process should ultimately allow for commercialization of OLED SSL.

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INTEGRATED APPROACH TO OLED DESIGN

Much of the research on organic light-emitting diodes (OLEDs) has focused on display applications. General illumination, however, has performance requirements that demand higher efficiency, longer operating lifetime, and lower cost. To maximize efficiency, it is necessary to ensure that (1) essentially all electrons and holes injected into the structure form excitons, (2) the excitons recombine radiatively with high probability, (3) the light from these recombinations is efficiently coupled out of the device, (4) the drive voltage required to establish a given current density in the device is minimized, and (5) the material and device are stable under continuous operation. In distinct OLED designs, each of these five requirements has been satisfied, but it has proven difficult to satisfy all the requirements simultaneously. Because of the very large material and device structure phase space, there is a critical need for basic scientific research on the fundamental physical properties of organic electronic materials in realistic device structures. It is essential to move beyond an empirical Edisonian approach to a predictive science-based approach. Organic electronic materials are a condensed phase of π-conjugated molecules. Intermolecular interactions are critical in determining the condensed phase properties, and the fundamental physical properties of isolated molecules or of single polymer chains are significantly affected by their environment. Recent breakthrough results for OLEDs have highlighted the need for a holistic molecule-film-device approach that integrates understanding of the fundamental physical properties of organic materials, thin films of these materials and composite films comprising multiple materials, and devices made from these films. This global understanding of the fundamental processes in organic LEDs is crucial to their development for solid-state lighting.

BACKGROUND AND MOTIVATION

The performance of OLEDs is currently much lower than their theoretical potential [Sheats 2004]. The Edisonian approach to the development of new materials and device structures has led to distinct OLED designs that satisfy some of the various requirements for general illumination, but it has not been possible to satisfy all of them simultaneously [D'Andrade and Forrest 2004; Duggal et al. 2004]. Figure 35 shows a recent device structure for a high-performance white OLED [Kanno 2006]. The complexity of this device structure highlights the importance of developing a global molecule-film-device approach that will enable a science-based predictive design of organic molecules, films, and device architectures to optimize the performance of OLEDs for solid-state lighting (SSL). Satisfying these requirements will likely require more complex device architectures to increase efficiency and optimize spectral properties while decreasing drive voltages. Cost and lifetime constraints for SSL, however, will require *simpler* manufacturing processes and reduced materials sets to avoid differential aging. A science-based design approach will be crucial to balancing these opposing requirements.
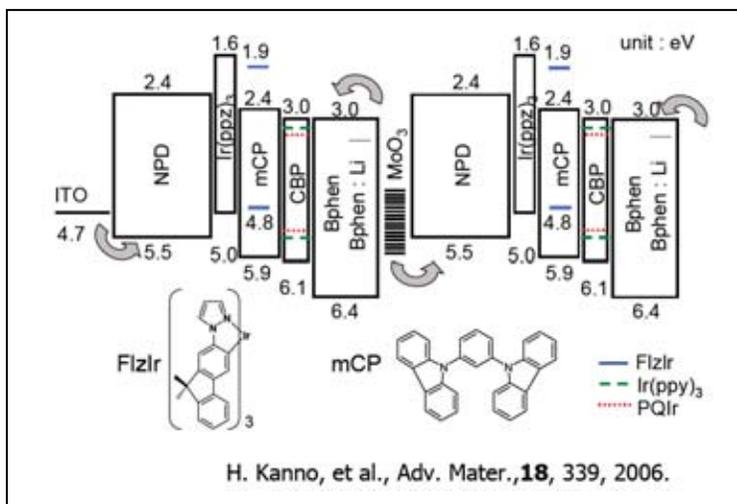
Figure 35 Device structure for a high-performance white OLED.

There are many parasitic processes that can occur in organic light emitting diodes that must be eliminated by material and device design. For example, in addition to forming excitons, it is also possible that injected electrons or holes traverse the device and are collected at the opposite contact. This is a process that leads to energy dissipation without light emission. Approaches to minimizing this parasitic process include matching electron and hole densities via control of charge injection and mobility and the use of organic/organic heterojunctions. Nonradiative recombination of excitons is also a parasitic process that reduces OLED quantum efficiency. Formation of triplet excitons, which are both lower in energy than singlet excitons and do not fluoresce, are of particular concern. The incorporation of organometallic molecules, which contain a heavy metal atom with strong spin-orbit coupling that mixes singlet and triplet states, can be used to overcome this problem. However the singlet-triplet energy split presents another loss mechanism if the organometallic materials and their organic hosts are not chosen carefully to ensure the direct formation of a triplet state.

Reduced drive voltages can be achieved by improved charge injection from contacts and carrier mobility in the organic thin films. Reduction of OLED drive voltages is especially critical for general illumination. Reduced drive voltages will not only improve OLED efficiency, but will increase operating lifetimes because the materials are less heavily stressed. There can be trade-offs in material and structure design choices between improving quantum efficiency and reducing drive voltages to improve power efficiency. For example, the use of multilayer structures to maximize exciton formation can increase drive voltages. To meet the requirements of SSL, these issues will all have to be simultaneously optimized in an integrated molecule-film-device approach.

SCIENCE QUESTIONS AND OPPORTUNITIES

An integrated approach to OLED design will require the development of new methods to measure fundamental processes in relevant device structures and of global OLED device models including injection, recombination, and out-coupling. The developments will be crucial in enabling the design and optimization of new tailor-made materials and lighting-specific device architectures.

New materials are needed for white OLEDs (e.g., for blue emission, charge transport, etc.). Equally important, the *interplay* of materials in complex, multimaterial OLEDs is not yet well understood. For example, the lifetime of white OLEDs can exceed the lifetime of blue OLEDs even if both devices use the same blue-light emitting materials. The introduction of a new material in a multilayer device may cause degradation in another layer, and the energy levels of an organic "dopant" molecule can depend on the host matrix in which it is placed. An integrated approach to OLED fundamentals should include the ability to design new organic materials for a variety of desired physical properties including the following:

- appropriate energy levels for minimal energy loss during transport of carriers from the electrodes to the recombination layer,

- minimal exciton binding energies and singlet-triplet exchange energy,

- high carrier mobilities for electron and hole transport layers, and

- equal electron and hole mobilities for simple single layer devices.

New and existing measurement methods and global models must be applied to understand fundamental physical processes of organic materials in realistic device structures. An ideal global model would use the molecular structure of the materials comprising an OLED to determine the physical properties of these molecules (using quantum chemistry), of pure and composite materials made from condensed phases of these molecules (using condensed matter physics), and of heterostructures and devices of these materials (using device models that include injection, transport, recombination, and out-coupling). Measurements such as exciton dynamics and energetics; charge transport in organic materials and composites, and across interfaces; energy transfer between components in devices; field and carrier distributions across complex devices; and morphological changes of materials in relevant device structures will be needed to validate the global models. The global device models will be crucial to understand the complex interactions that determine the electrical properties, optical properties, and stability of organic materials in realistic device architectures. This understanding will be crucial to the science-based development of new organic materials and device architectures for SSL.

New device architectures are also needed for SSL applications. Current OLED designs have mostly grown out of designs for display applications. The cost constraints for lighting may require architecture innovations such as novel substrates (metal foils, for example), down-conversion (or up-conversion) phosphors external to the OLED, air-stable materials that reduce or remove the need for encapsulation, and reduced complexity single or few layer devices. An integrated global approach to OLED device architecture design will enable devices with minimal complexity and optimal performance.

POTENTIAL RESEARCH APPROACHES

The research approaches needed to develop a global approach to OLED design can be categorized as (1) global modeling and optimization of injection, transport, recombination, and outcoupling for enhanced device performance, (2) direct measurements of fundamental physical processes in device-relevant architectures, and (3) integrated approaches to the development of new device architectures.

Global Modeling for Device Optimization

An ideal global molecule-film-device approach to OLED operation and design will require development and eventual integration of models on several scales. Molecular-scale models will be needed to determine physical properties (such as energetic, optical, and structural properties of the ground and excited states) of isolated molecules starting from their molecular structure and local environment. The physical properties (such as charge transport, energetics and dynamics of ground and excited states, and structural and optical properties) of condensed phases of organic molecules will require modeling at a variety of length scales, from several molecules through films with single or multiple molecular components. Device-scale models will also be needed that use input from molecular and material scale models (or from fundamental measurements of molecules and materials) to calculate operation of complex devices and include all relevant physical processes (e.g., charge injection, charge transport, exciton formation by sequential charge capture or by energy transfer, exciton energetics and dynamics, degradation mechanisms, and photon out-coupling. Research is needed to develop the components of such models and eventually to integrate these models into global device models that can be used for the development and optimization of new device architectures.

Direct Measurement of Fundamental Processes in Device-Relevant Structures

The development of molecular and materials scale models will require fundamental measurements for their verification. For example, a series of molecules could be studied in which some aspect of their molecular structure is systematically varied. By measuring the physical properties of isolated molecules (in several inert hosts) as well as in thin films, a better understanding of structure-property relationships will be gained to guide the development of molecular- and material-scale models, as well as the development of new materials with tailored physical properties. These physical properties could include molecular ground and excited state energetics and dynamics, or charge transport in materials.

An important component of the development of a global approach to OLED design is an improved understanding of fundamental physical processes in device-relevant structures. These include measurements in such structures of charge injection from electrodes, charge transport, charge transport across organic heterointerfaces, exciton formation, energy transfer, exciton energetics and dynamics, and photon out-coupling. These measurements will guide the development of global device models as well as the development and optimization of device architectures.

Integrated Approaches to Design of New Device Architectures

The development of efficient OLEDs will require the synthesis of new materials with improved properties such as high electron and hole mobilities, reduced exciton binding energies, and reduced singlet-triplet exchange energy. It will also require the synthesis of molecules or composites with equal electron and hole mobilities for efficient single-layer devices. Additional advances should be achieved for the development of effective, low-cost electrodes. Replacing one type of molecule in an OLED layer affects multiple physical processes. Therefore, the development of new materials should be done in concert with global device measurement and modeling and necessarily requires a collaboration between synthetic chemists and device physicists.

At the same time, new device architectures that take advantage of novel materials should emerge. For example, architectures that achieve reduced operating voltage will be enabled by molecules with occupied and unoccupied states optimized in both energy and space. Efficient devices with

reduced complexity, such as single-layer devices, might become possible via materials with equal electron and hole mobilities. Other avenues that should be pursued include device architectures that are insensitive to differential aging, that show more efficient outcoupling, and that are synergistically designed so that materials in one layer enhance the stability of materials in another layer.

HOW WILL SUCCESS IMPACT TECHNOLOGY?

An integrated approach to OLED fundamentals will impact OLED lighting technology by accelerating research and development through development of science-based design tools, enabling the development of novel organic materials with tailor-made properties, and introducing unique device architectures with low-cost, high-efficiency white-light emission.

The development of new materials should impact technology within a few years. The development of stable high-efficiency blue materials and high-mobility transport materials would improve the lifetime and power efficiency of white OLEDs. Materials with reduced exciton binding energies and singlet-triple splittings would enable more efficient devices and reduce the difficulty of blue emission. Materials with equal electron and hole mobilities would permit simpler device architectures, reducing costs.

Measurements of fundamental physical processes in device-relevant structures will provide immediate feedback to the optimization of current OLED designs, as well as providing validation necessary for the development of global device models. Longer term, these global device models will enable science-based development of novel device architectures for cheap, efficient white light.

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CROSS-CUTTING RESEARCH DIRECTIONS

NEW FUNCTIONALITIES THROUGH HETEROGENEOUS NANOSTRUCTURES

The breathtaking pace of advances in nanoscience over the last decade has enabled synthesis and manipulation of nanostructured materials with unprecedented fidelity and control. With this accumulated knowledge and growing understanding, we can now envision disruptive technology advances enabled by nanoscience. In this Cross-Cutting Research Direction, techniques of nanoscale synthesis are applied to the formidable challenge of solid-state lighting. In particular, control of functionality at the nanoscale may enable increased efficiency and enhanced color quality of light sources. It is envisioned that the most effective results will emerge from interdisciplinary activity that spans the fields of physics, chemistry, materials science, and engineering.

BACKGROUND AND MOTIVATION

At nanoscale dimensions, materials adopt new configurations, shapes, and compositions that lead to unique and controllable size-dependent properties. This tailoring of properties (see sidebar "Light-Emitting Carbon Nanotubes") leads to new degrees of freedom that can be exploited to control the fundamental physical and optoelectronic processes important for solid-state lighting (SSL). For example, the electronic and optical properties of nanostructures strongly depend on their size. Light-emission wavelength and efficiency can therefore be tuned by the size of the nanostructure, a capability that does not exist in traditional bulk materials. Such size-tunable properties occur in all dimensions: one-dimensional confinement in semiconductor quantum wells, two-dimensional confinement in quantum wires, and three-dimensional confinement in quantum dots. In addition, nanoscale materials can have other intriguing physical properties of relevance to SSL, such as the ability to achieve simultaneous ambipolar transport as illustrated in the sidebar on light-emitting carbon nanotubes.

At the same time, the astonishing rate of advances in nanoscience over the last decade has enabled synthesis and manipulation of nanostructured materials with unprecedented fidelity and control. In this Cross-Cutting Research Direction, these techniques are applied to the challenge of SSL.

SCIENCE QUESTIONS AND OPPORTUNITIES

Several science questions and opportunities are key to the development of new SSL functionalities through heterogeneous nanostructures. They are broadly divided into three areas: synthesis and self-assembly issues, understanding and control of radiative and nonradiative processes, and integration into SSL structures. Ultimately, the priority research approaches summarized here follow from these issues.

Synthesis and Assembly Issues. Building on the advances of the past decade, we must continue to explore novel approaches to synthesis and assembly of nanostructures. Although a number of fascinating physical properties have been discovered in nanomaterials, synthesis efforts have explored only a relatively small number of materials systems, suggesting enormous opportunities for discovery from the synthesis of a broader range of nanomaterials. Because of the sensitivity of physical properties on nanomaterial structure, it is also expected that synthesis advances that increase the uniformity of nanomaterial structure will benefit SSL research. Finally, the advanced functionality needed for SSL might require the precision alignment of nanomaterials, and thus advances in the science of assembly are expected to have great impact. It is from the accumulation of knowledge and from our growing understanding of how to manipulate matter at the nanoscale that disruptive SSL nanotechnologies not yet imaginable may flow.

Structuring Materials to Control of Radiative and Nonradiative Processes. Among the key physical properties of relevance in SSL are the radiative and nonradiative lifetimes. Since efficiency is paramount, it is important to optimize the radiative processes relative to the nonradiative channels. The fundamental science issues to be addressed include the coupling of fundamental excitations in complex heterostructures and optical mode control. An understanding of these basic issues, coupled with precise synthesis and assembly of heterogeneous nanostructures, offers a new path toward unprecedented control of the relative radiative and nonradiative rates for optimal efficiency of SSL.

Integration into SSL Structures. A final challenge is to integrate the carefully designed, synthesized, and assembled heterogeneous nanostructures with optimized radiative efficiency into SSL structures. In any SSL device, interfaces with the nanostructures will inevitably be present, including electrical contacts, electron or hole blocking layers, organic/inorganic interfaces, etc. This gives rise to a need to understand the properties of the interface to heterogeneous nanostructures. Recent work has demonstrated that novel light-emitting devices utilizing heterogeneous nanostructures are feasible (Figure 36). However, there remain fundamental science issues, including the behavior of arrays of heterogeneous nanostructures (since practical devices will involve large arrays of nanostructures rather than a single nanostructure), the mechanical and thermal properties of nanostructures, the stability of nanostructures, and, potentially, the interface of functional heterogeneous nanostructures with other materials (i.e., hybrid systems).
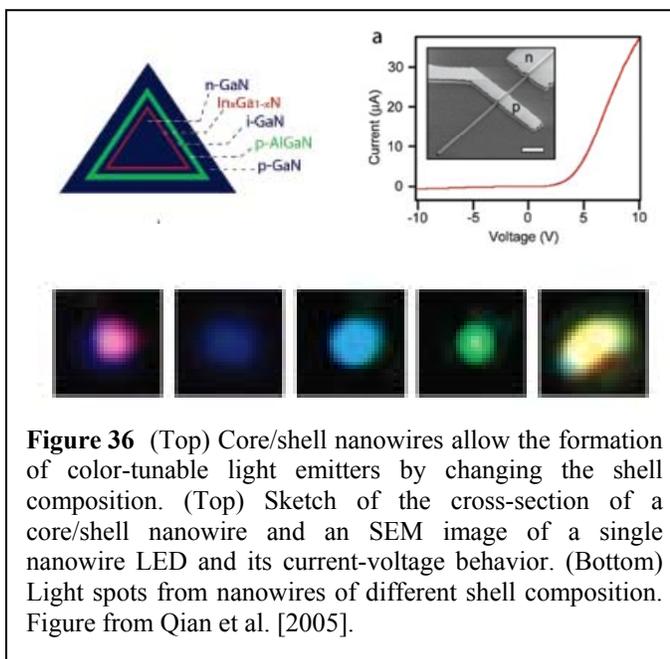

Figure 36 (Top) Core/shell nanowires allow the formation of color-tunable light emitters by changing the shell composition. (Top) Sketch of the cross-section of a core/shell nanowire and an SEM image of a single nanowire LED and its current-voltage behavior. (Bottom) Light spots from nanowires of different shell composition. Figure from Qian et al. [2005].

POTENTIAL RESEARCH APPROACHES

Synthesis and Assembly Issues

Nanomaterial Synthesis for Controlled Size, Composition, Passivation, and Shape. Today's chemical synthesis techniques provide unprecedented control of the size, shape, and composition of designed nanostructured materials. The controlled growth of semiconducting and metallic nanostructures as small as 1 nanometer has been demonstrated. The size of the smallest nanostructures can strongly affect the energy levels of the confined electrons, fine-tuning the optical bandgap and consequent luminescence properties of the nanomaterials. In metal nanoparticles, plasmon resonances have been shown to depend on the size of nanoscale domains within a particle. These and other nanoscale effects can be used to benefit the SSL effort through their ability to tailor the color, efficiency, and perhaps even directionality of the emitted light. This will become possible only as we develop an understanding of the role of each of the "knobs" (size, composition, passivation, shape) and the interplay among them. Greater understanding should enable us to design (and fabricate) exactly the nanomaterials that will deliver the performance required.

Environmentally Acceptable Nanomaterials. Nanostructured materials containing cadmium, lead, and mercury are unlikely to be permitted to enter the world market in electrical devices, although today's

most efficient nanostructured lumophores are cadmium-based. If nanostructured materials are to play a role in SSL technologies, it is necessary to develop chemistries for nanostructure synthesis that utilize environmentally acceptable materials. While some work has been done on luminescent material sets such as ZnS, ZnSe, ZnTe, as well as III-V semiconductors, the level of effort on those materials has been only a small fraction of the effort on cadmium- and lead-containing semiconductors. A concerted effort to develop still more environmentally acceptable nanostructured materials is necessary. The theoretical limits of performance of these materials is equivalent to that of the better known cadmium-containing materials, but the more difficult synthetic routes have, to date, discouraged research from occurring at a fast pace.

Assembly of Nano-Elements into Enhanced Functional Forms. To utilize the superior physical properties of organic/inorganic nanostructures, we need to develop robust, reproducible, and scaleable methods for assembling large arrays of them. Additionally, ordered nanostructured arrays can give rise to enhanced functionality as demonstrated, for example, in plasmonic structures. Ordered plasmonic structures consisting of coupled spherical metal resonators have recently been shown to provide a sub-wavelength approach to light (energy) transport. Monolayer arrays of semiconducting nanocrystals have been used in macroscopic light emitting devices (see sidebar on efficient white light down-conversion using QD lumophores). These and other unconventional approaches for manipulating and generating light may give rise to new and superior approaches to SSL. To move beyond a "cut and try" approach to assembling nano-elements, however, detailed understanding of the behavior of the individual elements, as well as understanding of the behavior that emerges when the elements are combined, is essential

Structuring Materials to Control of Radiative and Nonradiative Processes

What Governs Quantum Efficiencies at the Nanoscale? A critical component to developing efficient SSL is to optimize quantum efficiencies. However, because of the novel physics at the nanoscale, many of the concepts that govern quantum efficiencies in bulk materials need to be revisited. For example, while the exciton binding energy is small in bulk inorganic materials, the poor electrostatic screening in quasi-one-dimensional systems leads to large exciton binding energies that dominate the optical properties. It is important to recognize that the electronic energy structure can be modified when the nanostructured material interacts with its immediate local environment. The fundamental science that governs radiative and nonradiative recombination at the nanoscale, spin statistics for singlet vs. triplet excitons, and the role of bandstructure and surface effects needs to be understood both from modeling and experimental perspectives.

Manipulating and Metering Photons, Excitons, Polarons, Phonons, and Plasmons in Nanostructures. Basic excitations (photons, excitons, polarons, phonons, and plasmons) govern the electronic processes at the nanoscale. To ascertain the dominant physical processes, it is highly desirable, and in many cases is essential, to monitor and meter these basic excitations. From the gained knowledge, the goal is to develop methods to manipulate the form of energy within the nanostructures to maximize performance.

Coupled Excitations in Nanostructures. In electronic devices, the coupling between excitations plays a crucial role in determining properties and performance. For SSL using heterogeneous nanostructures, many such excitation interactions exist, and their properties at the nanoscale must be understood. At the forefront are electron-photon interactions, particularly under nonequilibrium conditions where electron transport is coupled to light emission. A second example is electron-phonon interactions that affect both the electronic transport through the system and the light emission. While these coupled excitations are expected to govern behavior as in traditional devices, the coupled states can enhance the performance strikingly at the nanoscale. For example, for hybrid organic/inorganic

semiconductors, resonant coupling between the Frenkel excitons of organic molecules, and Wannier-Mott excitons in inorganic quantum wells may lead to enhancement of the resonant all-optical nonlinearity in the strong coupling regime [Tischler et al. 2005] and fast, efficient noncontact and nonradiative excitation energy transfer in the weak coupling regime [Anikeeva et al. 2006]. Both of these concepts, and many others that can arise from other couplings of excitations, suggest the possibility of novel designs of SSL devices.

Optical Mode Tailoring. Another perceived benefit of heterogeneous nanostructure integration is the development of devices with nanoscale features that efficiently control the creation and behavior of photons in inhomogeneous media. Nanoscience provides an overwhelmingly large number of experimentally accessible ways to configure the spatial position of atoms, molecules, and other nanoscale components to form such devices. The challenge is to find the best, most practical configurations that yield the highest-efficiency SSL devices.

Large gains can be made by manipulating the local optical density of states of poor and medium grade emitters in otherwise unattainable spectral ranges. In this regime, engineering the interaction between the nanostructured emitter and optical modes can enhance the radiative rates as well as the extraction efficiency.

Integration into SSL Structures

Array Behavior of Nanostructures. Arrays of nanostructured materials could exhibit cumulative or coherent effects due to electronic or nuclear excitation coupling across the array (see sidebar on extraordinary optical properties of J-aggregate thin films [Tischler et al. 2005]). Furthermore, the periodicity of perfectly ordered nanostructured arrays can result in enhanced physical properties, as is apparent in the optical and electronic properties of crystals. The advantage of nanomaterial tunability has already been suggested in recent studies where quantum dot arrays have been integrated into organic LED structures for enhanced performance [Coe et al. 2002]). As an example, ordered plasmonic structures consisting of coupled spherical metal resonators have recently been shown to provide a sub-wavelength approach to light (energy) transport [Maier et al. 2002].

Opportunities for Thermal/Mechanical Management. Thermoelectric and thermo-photovoltaic devices have recently utilized heterogeneous nanostructured materials to decouple electrons and phonons [Hsu et al. 2004]. This allowed for a three-fold increase of the power generation figure of merit, reflecting tighter confinement of thermal energy. The same types of heterogeneous nanostructures are inherent in many of the envisaged SSL designs. This points to the possibility of designing and fabricating semiconductor nanocomposites that enable the management of the thermal output of SSL devices.

Enhanced Operational Stability. Nanostructured luminescent materials such as semiconducting nanocrystal quantum dots (QDs) have, in some measurements, demonstrated remarkable environmental stability during the photoluminescence process as well as during storage. The very small number of studies that have considered the operating stability of luminescent nanostructured materials such as QDs is a reflection of the nascent stage of this research field [Zhong et al. 2004]. Further material stability studies are necessary to fully explore these intriguing results and the origin of the stability as it relates to SSL.

HOW WILL SUCCESS IMPACT TECHNOLOGY?

There has been remarkable progress in exploring the properties of light-emitting heterogeneous nanostructures. The first forays into device architectures that might have relevance for SSL have been

very intriguing. Future research is expected to give further insights into the structures and control of these materials. It is possible to envision two different scenarios for their impact on SSL: (1) an enhancement to one of the two general approaches to SSL that already have significant momentum or (2) an entirely different way of approaching broadly applicable, energy-efficient lighting. Determining which path will emerge as important awaits research embodied in this Cross-Cutting Research Direction.

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# EFFICIENT WHITE LIGHT DOWN-CONVERSION USING QUANTUM DOTS

A quantum dot (QD), also called a semiconductor nanocrystal or an artificial atom, is a semiconductor crystal whose size is on the order of just a few nanometers. The photoluminescence efficiency (the number of emitted photons divided by the number of absorbed photons) of the best nanocrystal quantum dots exceeds 90%. Such high performance can, in principle, be achieved for any visible QD luminescence color or combination of colors (including white). Consequently, photoluminescence down-conversion (conversion of a higher-energy photon to a lower-energy photon) using QDs and an efficient blue or UV pump-light source can create high efficiency white light sources with precisely tunable spectra. Previous attempts at implementing this idea, however, failed to produce high efficiency devices because of shortcomings in the QD chemistry and large (undesired) self-absorption of the light in the optical device structure. In a recent demonstration, shown in the figure, the down-conversion of light was accomplished using a single monolayer of QDs coated on an optical fiber that is pumped by a light from a blue LED (λ = 475 nm emission wavelength) directed into the fiber. The blue light propagating through the fiber is absorbed by the QD monolayer, resulting in QD re-radiation at λ = 610 nm and a mixed color signal. The absence of self-absorption in this geometry can potentially lead to higher efficiencies [Bulović et al., patent pending].
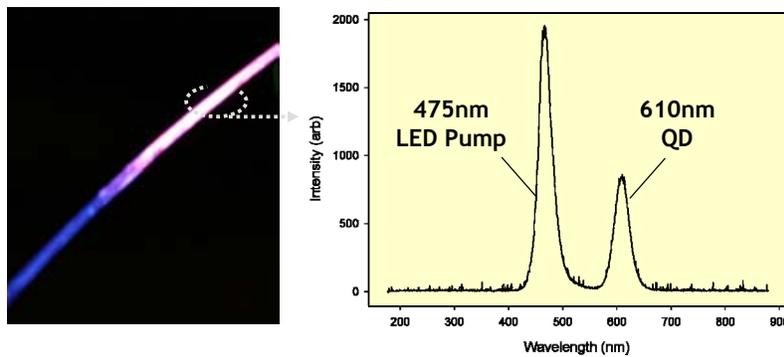
(Left) Photo of a luminescent fiber pumped by λ = 475 nm emitting inorganic LED. (Right) Spectral emission of the indicated section of the fiber showing QD luminescence at λ = 610 nm together with scattered blue LED light [V. Bulović, private communication].

# EXTRAORDINARY OPTICAL PROPERTIES OF J-AGGREGATE THIN FILMS

J-Aggregates are ordered arrangements of highly polar cyanine dye molecules in which the transition dipole moments of the individual molecules add to form a giant dipole oscillator and a new optical transition called a J-band. Relative to that of the monomer building blocks from which the aggregate is assembled, important J-band optical properties are enhanced, most notably the absorption/fluorescence spectrum is considerably narrower in energy (50 meV at room temperature). The lifetime of the J-band transition is also much faster (~ps). These enhancements are significant, since they can lead to an efficient fluorescence process. J-aggregates are the crystalline phase of the dye monomers, although not necessarily the lowest energy crystalline form. The enhancement of relevant optical properties is a quantum mechanical effect associated with an effectively larger "box" for the electrons in the J-aggregate relative to the monomer building blocks. It has recently been demonstrated that the exceptionally large optical cross section ($\alpha \sim 10^6$ cm^{-1}) and narrow absorption spectra (FWHM ~20 nm) of ordered J-Aggregate monolayers [Bradley, Tischler, Bulović, Adv. Mater. 17, 1881 (2005)] can result in a strong coupling between the J-Aggregate excitations and the optical modes of a microcavity. This drastically enhances the light-matter interaction [Tischler et al. Phys. Rev. Lett. 95, 036401 (2005)].

CRYSTAL DIFFRACTION	ABSORPTION / EMISSION	FLUORESCENCE

CRYSTAL DIFFRACTION

0.33 cm

Bragg Law: d = λ/sinθ
λ = 0.0251 Å, sinθ = 0.33cm/60cm
Spacing d = 4.56 Å

ABSORPTION / EMISSION

Absorption
Pk = 591 nm
FWHM = 17.5 nm

PL
Pk: 596 nm
FWHM: 13 nm

Stokes Shift: 5 nm

500 nm Excitation

Abs (log$_{10}$)

PL Counts

Wavelength (nm)

FLUORESCENCE
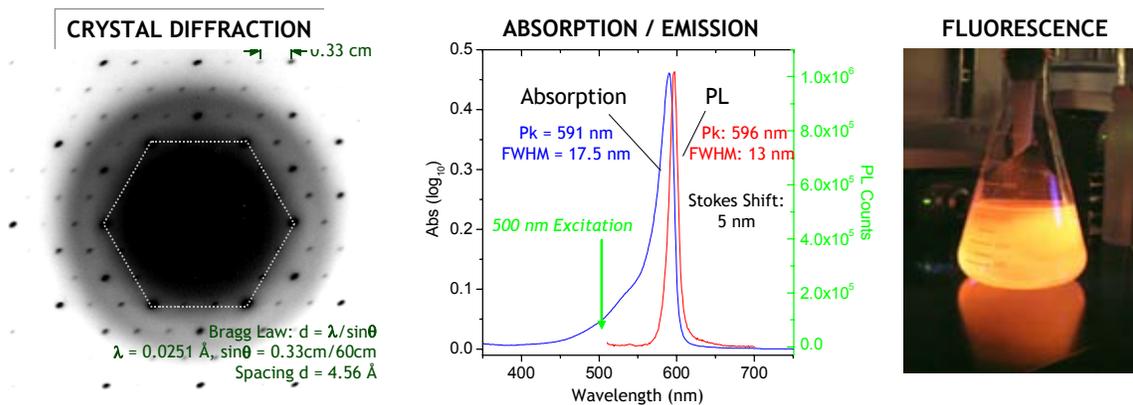
(Left) Electron diffraction pattern of a J-aggregate dispersed in polyvinyl alcohol. (Middle) Absorption and photoluminescence emission spectra under λ = 533 nm excitation of TDBC/PDAC J-Aggregate/polyelectrolyte bi-layers generated by dip-coating. (Right) Fluorescence of TTBC J-Aggregates in solution. PDAC is poly(diallyldimethylammonium chloride) and TDBC is a J-aggregate-forming cyanine dye.

LIGHT-EMITTING CARBON NANOTUBES

Recent progress in nanoscale science and technology has allowed the fabrication of nanometer-scale, solid-state light-emitting devices based on a carbon nanotube [J. Misewich et al., *Science* 300, 783, 2003]. In this device, a single carbon nanotube with a diameter of 1.4 nm acts as a semiconductor bridge between two electrodes (see Figure, left side). By appropriate choice of the voltages applied to the source, drain, and gate electrodes, both electrons (negatively charged carriers) and holes (positively charged carriers) can be injected into the carbon nanotube at the same time from opposite ends of the nanotube. This leads to emission of light when the injected electrons and holes recombine (see Figure, right side) in the middle of the nanotube. This is the smallest electrically controllable light emitting diode ever demonstrated. It also illustrates the opportunity in nanoscale systems with reduced-dimensionality systems for more efficient electronic transport and novel optoelectronic designs. This device is entirely controlled by electrostatics and does not require any dopants.
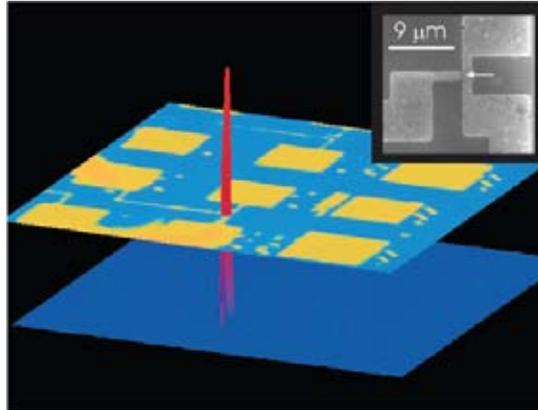
(Left) Schematic of a single carbon nanotube light emitting device. Two electrodes (source and drain) make contact with the single wall carbon nanotube while a field is applied via a gate electrode and gate dielectric (SiO$_2$). (Right) Top, Infrared image of chip. Bottom, IR image showing emission (red peak) occurring only in location of nanotube. The insert is a scanning electron micrograph showing details of the lithography, and an arrow pointing to the location of the nanotube.

INNOVATIVE PHOTON MANAGEMENT

A key to the success of solid-state-lighting is ultra high-efficiency light extraction. Basic research is needed to investigate fundamental photon modes that directly influence the brightness, directionality, polarization, and efficiency of emitted light. Recent advances in nanotechnology, particularly in creating photonic/plasmonic structures, present an unprecedented opportunity to explore strong photon-structure interaction and to manipulate photon modes. Such innovative photon management is a new frontier in optical science, leading to an extraordinary energy benefit and a new dimension in smart control of light.

BACKGROUND AND MOTIVATION

Solid-state lighting (SSL) involves the generation, extraction, conversion, and control of photons emitted from a light-emitting element. SSL technology has begun to impact our daily life in general illumination, traffic light, and display applications. However, we have not reached the full energy efficiency benefit of SSL, partly because of our inability to extract photons efficiently out of light-emitting layers into free space. Moreover, we have not taken advantage of recent advances in nanoscale photonic structures (PS) to tailor the quality of light at the most fundamental level of photonic states. Accordingly, the next frontier in SSL is to achieve significant enhancement in extraction efficiency to near 100% and to tailor the quality of light based on a strong light-material structure interaction.

Fundamental innovations are required to explore basic photon states and modal properties that enhance spontaneous emission, thermal emission, and light extraction. An artificially engineered PS offers a new pathway for creating photon modes with desirable characteristics. Today, the two best known structures are photonic crystals that support Bloch optical modes and metallic structures that support plasmonic modes. Exciting progress has been made in realizing PS at the nanometer scale and moderate extraction enhancement demonstrated by both optical [Erchak et al. 2001; David et al. 2006] and electrical [Wierer et al. 2003] pumping. However, these PS are typically spatially separated from active light-emitting elements, which requires coupling of emitted light (slab modes) into modes supported by a PS. In this context, basic research is needed to (1) design and realize an innovative PS that captures emission from all angles and both polarizations with little reflection; (2) design and incorporate a PS into an embedded active emitter, which totally eliminates the need for additional photon coupling. Exciting science opportunities also exist in tailoring the embedded design to influence the spontaneous emission rate, redirect light emission, and recycle thermal emission. Lastly, basic research in emitters with integrated lens capability and bio-inspired optics will pave the way for ultra-efficient photon distribution.

Embedded Emitter Photonic Nano-structures. An "embedded emitter photonic nanostructure" combines both light emission and light manipulation functionalities into one integrated structure (Figure 37). In this novel design, an emitter's intrinsic emitting properties are directly and locally influenced by the presence of photon-modes. Strong coupling between emitters and photon-modes is intrinsic. There is great flexibility in tailoring such photon-modes to enhance the spontaneous emission rate, to steer emission into a specific direction, to allow emission with certain polarization, and to recycle certain parts of the emission spectrum. Preliminary examples of the embedded structure include, but are not limited to, two-dimensional (2D) arrays of GaN nanorods, 3D arrays of self-assembled nanodots, and 3D photonic-crystal light emitters [Lin, Fleming, and El-Kady 2003].

Control Over Final Spectrum, Polarization, and Radiation Pattern. A new dimension in SSL is the smart control of radiation color, pattern, and polarization. A light source with controllable and tunable characteristics is needed to enable adaptation to specific requirements and environments. A photonic nanostructure closely coupled to active emitters will enable these new functionalities (Figure 38).

Bio-Inspired Optics and Biomimetic Approaches. Nature has inspired many developments in materials through synthesis, structure, and processing. Recently, there has been a change in the paradigm of how materials are used in the design of optical systems by emulating the way nature designs optical lenses in the eyes of various creatures [Zuccarello et al. 2002]. This scientific thrust has been called bio-inspired optics [Lee et al. 2005; Vukusic and Sambles 2003]. The ability to synthetically reproduce the components of a biologically inspired vision system, which demonstrates a level of performance well beyond the standard optics of today with reduced size and complexity, is an ongoing challenge. One example is the recent development of cylindrical, radial, and spherical GRIN (graded index of refraction) lenses using a highly flexible nanolayer extrusion processing technology [Baer et al. 2005]. Both cylindrical and radial GRIN lenses are completely
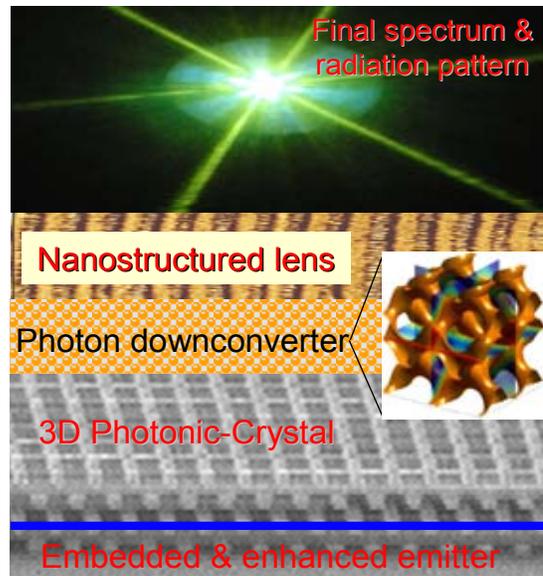
Figure 37 A schematic drawing showing the life cycle of photons in an integrated photonic nanostructure and its final, extracted radiation pattern. The embedded and enhanced emitter is inside a 3D photonic crystal. A photon down-converter and a nanostructured lens are also shown.
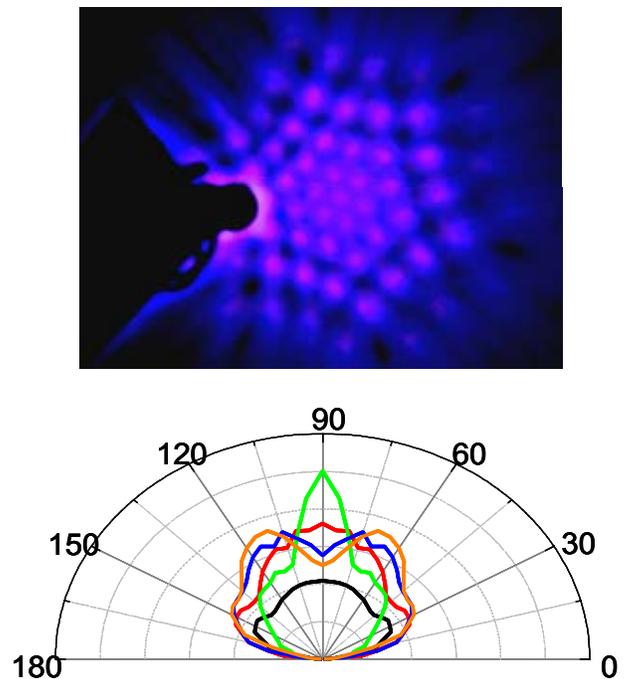
Figure 38 (Top) Image of light emission from a photonic structure. (Bottom) The different colors in the polar plot are patterns taken from different nanostructures. [Wierer et al. 2003]

flat, and the optical properties can be tailored on a scale as large as meters. This facile processing technique can produce large films with predetermined gradients of index that may provide truly innovative photon management for future concepts in SSL.

SCIENCE QUESTIONS AND OPPORTUNITIES

Ultra-High Energy Transfer into Extracted Light Spectrum. The life cycle of photons inside a light-emitting diode (LED) or an organic LED (OLED) follows a sequence, starting from photon generation, down-conversion, and collimation, and ending with the extracted light spectrum. Each event is, in essence, a photonic mode-transfer process, and energy loss, however small, is inevitable. The grand challenge of SSL is to maximize the energy efficiency of each process by innovative photon-mode management. To accomplish this goal, an exciting opportunity exists to create an integrated light-emitting photonic nanostructure. Photonic nanostructures, including photonic crystals, offer a fundamentally new mechanism for controlling photon modes at a sub-wavelength scale. To achieve near 100% extraction will require either an embedded emitter design or a 3D photonic crystal [Lin et al. 1998] that extracts light from all angles. Achieving significantly enhanced absorption and conversion will require enhanced photon mode density for light incident from all angles. Significant opportunity also exists in optical physics. Classical optics has limited applicability to describe photonic nanostructures at a sub-wavelength scale. This limitation calls for basic research in developing the theoretical framework and computational modeling capability for handling spatially complex photonic nanostructures.

Spontaneous Emission and Thermal Emission Modification. More than sixty years ago Purcell [Purcell 1946] made the fascinating discovery that photon modes can have a strong influence on spontaneous emission. This discovery had an important consequence on internal quantum efficiency of SSL devices. If photon modes are highly concentrated at a specific frequency and spatially and spectrally overlapped with emitters, the radiative recombination rate will be enhanced. To achieve strong spontaneous emission enhancement will require an integrated or embedded nanostructure-emitter design. Thermal emission of metals at visible wavelengths is an example of a spontaneous emission phenomenon with an equilibrium electron distribution. The Purcell effect is most useful to suppress infrared emission, recycle the energy [Lin et al. 2003], and achieve ultra-high emission efficiency of ~100% at visible wavelengths. To achieve this goal will require the design and synthesis of high-temperature nanostructures and systems for thermal emission.

Tailoring the Density of Photon Modes. It has been known that altering the refractive indices of the emitting environment can change the density of photon modes [Yablonovitch 1987; John 1987; Joannopoulos, Meade, and Winn 1995). For example, the photon density-of-states (DOS) can dramatically change in photonic crystals, where two material constituents with different indices are arranged in the form of a lattice. The photon-mode dispersion in such structures contains forbidden gaps in which light penetration is impossible [Joannopoulos, Meade, and Winn 1995]. At the edge of these gaps, the DOS reaches a large maximum. The extra DOS at the gap edges may dramatically influence the ability of an embedded chromophore to radiate light by changing its radiative transition rate, which may lead to mirrorless lasing [Shkunov et al. 2002]. An example of two materials that can give a drastic change in the DOS are an insulator with positive real dielectric constant, ε, and a metal with large negative ε. In these structures, not only is the radiative transition rate of an embedded chromophore changed, but they may also serve as effective electrodes. Such metamaterials (that do not exist in nature and so must be artificially fabricated) are also dubbed "transparent metals," which show high optical transmission in the visible in addition to electrical conductivity.

Photonic Coupling to Desirable Down-Conversion Media. SSL sources for daylight-illumination applications require high luminous-source efficiency. For a phosphor-based white LED or OLED, the phosphor arrangement must achieve the following objectives: (1) maximization of phosphor efficiency and (2) maximization of ultraviolet (UV) coupling to the phosphor. To achieve these goals will require an effective photon coupling to the down-conversion media. This calls for basic research in 3D photonic-crystal and related nanostructures to fully capture primary emission at all angles. To enhance the phosphorescent radiative recombination rate will require embedding nanoscale phosphors inside a porous photonic nanostructure [Lin et al. 1998]. Avoiding UV leakage will require the design of an all-angle UV blocker integrated into the phosphor package. The integration of such phosphors with photonic crystals promises new and ultra-efficient phosphor-based white LEDs.

Emitters with Integrated Lens Capabilities. Most of today's LEDs incorporate a primary lens element, typically made from transparent organic materials such as epoxies or silicones. The lens element serves two main purposes: (1) increase in light extraction by providing an "ambient" higher refractive index (n ~1.5) than air for the LED chip and (2) radiation pattern tailoring. However, the use of such lenses increases the étendue (i.e., optical extent) of the LED chip and tends to limit the operating power density of the LED because of photothermal degradation of organic materials under high-density, high-photon energy flux combined with high operating temperature.

Using photonic nanostructures incorporated into the LED, one can envision a design for very high light extraction (~90%) from the LED chip directly into air. This can be accomplished by designing a photonic structure that reduces or eliminates the number of guided modes that will couple to radiating dipoles within the LED active layer. Also, the photonic structure (or, perhaps a second one incorporated in conjunction) should allow manipulation of the radiation pattern of the LED chip [Erchak et al. 2001]. In this way, high light extraction and radiation pattern tailoring are provided by structures within the chip, providing a lower-cost, ultra-thin, and elegant solution for these requirements.

Although OLEDs are large-area devices, similar concepts could be developed to apply arrays of nanostructures to the emitting area if they can be scalably manufactured at reasonable cost.

New Luminaire Concepts Based on Large-Area Nanostructured Materials. The availability of efficient light sources with the large optical power density of today's LEDs is expected to result in a paradigm shift in the ways light sources are used in illumination applications. Conventional lamps are inherently large-étendue light sources which require sizeable secondary reflector systems to distribute light efficiently to the target illumination area. With high-luminance SSL sources, this situation changes completely. The small etendue of the optical sources (few mm^2-sr, or less) will allow very efficient secondary optics systems without requiring very large optical elements. Thus, cost-effective luminaire designs are envisioned with anticipated utilization efficiencies in the 90% regime. Novel luminaire designs are required. One concept is the use of nanotechnology (photonic structures) to provide light-manipulation structures in inexpensive optical media such as simple plastic sheets. Efficient light coupling to the plastic is made via the small étendue LEDs.

Bio-Inspired Optics for Large-Area Illumination. Innovative concepts for photon management represents a critical need for future applications of SSL. Creative approaches to putting specific types of light where and when needed will involve new insights into the engineering of luminaires. For example, color-changing lighting panels and lighted walls for

home and office could be fabricated using an approach similar to the layered features that form "structural colors" in butterfly wings [Srinivasarao 1999]. Light could be managed in quite different ways by the "luminaire" portion of the system. Spectrum and polarization may be tailored by "light walls" and will require facile manipulation of optical properties on a large material scale that would be particularly applicable to outcoupling enhancements from large area OLEDs. In the future, any surface could be an area of photon distribution for general illumination or specific purposes such as building-size murals for aesthetics or advertising.

POTENTIAL RESEARCH APPROACHES

Facile 3D Nanostructure Fabrication Techniques. Successful photon management depends critically on facile fabrication of 3D photonic nanostructures. Fundamental innovations are needed to create photonic nanostructure for ultra-efficient control and manipulation of photons. This has not been an easy task for two basic reasons. First, the nanostructure will be required to operate at visible wavelength, which requires a typical feature size of 40 to 100 nm. Second, facile fabrication is required for SSL applications because of cost limitations, and the following conditions must be met: spatial coherence, wafer-scale, low cost, and ease of fabrication. However, several innovative techniques are promising for SSL needs. As flexibility in making different types and symmetries of nanostructures as well microcavities is of prime importance to SSL applications, techniques described below are based on top-down fabrication approaches.

Nano-Imprint Approach. This is a printing technique, which is a fast and large-scale process. However, multilayer alignment at a large scale (4 to 6 inches) has not been demonstrated. Furthermore, layer planarization of each process is still required.

Laser Holography Approach. This is a large-area, low-cost, single-exposure process and is desirable for SSL applications. However, the technique requires precise optical alignment of four laser beams. Furthermore, no visible photonic nanostructure or photonic crystal has been demonstrated. Basic materials research is required to develop a coating to transfer the patterned structure into a high refractive index contrast structure.

Triple-Layer Phase-Mask Approach*.* This is a large-area, low-cost, single-exposure, and single-laser technique. Accordingly, this technique is most desirable for SSL applications. To achieve the goal will still require basic materials research for pattern transfer. It will also require comprehensive theoretical design and accurate fabrication of phase masks [Chan, Toader, and John 2006].

Full 3D Electromagnetic Wave (EM) Solvers Including Photonic/Plasmonic Structures for Efficient Photon Management. Maxwell's equations provide an accurate description of the behavior of EM fields in passive photonic/plasmonic nanostructures. However, many existing theoretical tools are not efficient enough for SSL design purposes where it is necessary to examine many different possibilities. There are needs in the following areas:

- Structural imperfections and defects in a photonic structure can lead to degradation of performance arising from scattering losses and/or absorption. This is especially important in plasmonic structures where the field is highly inhomogeneous. A key part in the design of useful photonic/plasmonic structures is the robustness of performance to imperfections/defects.

- Inclusion of active gain materials can lead to new functionalities and controllability of photonic/plasmonic structures. While many studies have been done in reduced dimension systems, efficient treatment of the problem in full 3D space is still lacking. In this case, again, the sensitivity of performance to structural imperfections is a key issue.

- Efficient treatment of the effects of photonic structure on spontaneous emission rates of embedded light sources.

Novel Materials for Photo/Thermally Stable Optical Packaging. As discussed above, typical optical materials used in today's LEDs for lensing, encapsulation, and optical coupling are organic materials such as epoxies and silicones, which exhibit photothermal degradation when simultaneously exposed to a high density of large energy photons and elevated temperature. The degradation results in breakdown in transparency, and this "yellowing" or "browning" eventually destroys the lumen maintenance of the LED. This problem is the primary limiter of operating power density in today's high-power LEDs. New classes of optical materials for such applications should be explored. One class of materials that has not received a great deal of attention for application to LEDs is low-temperature glasses. These inorganic materials, in principle, could be tailored to provide the necessary optical properties, and they should be robust against photon density and heat. Such low-temperature, inorganic materials might also be transformational for OLEDs by simultaneously simplifying and improving encapsulation while increasing light outcoupling.

HOW WILL SUCCESS IMPACT TECHNOLOGY?

The potential impact of success in the exploration of photonic nanostructures for innovative photon management will be ultra-efficient, high-power light sources. The availability of ultra-compact, high-power emitters will provide a paradigm shift with regards to design and manufacture of luminaires for SSL lighting.

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ENHANCED LIGHT-MATTER INTERACTIONS

This Cross-Cutting Research Direction (CCRD) presents an opportunity for innovative basic research for the development of high-efficiency light emitters that exploit new regimes of enhanced light-matter interactions. Traditionally, the operation of a light-emitting diode (LED) or an organic LED (OLED) is viewed as the efficient internal generation of photons by electronic excitations in a semiconductor followed by useful extraction of those photons to the device exterior. The engineering optimization of these individual processes forms the key objectives for high-efficiency solid-state lighting device development. While aiming at ever higher efficiencies, this CCRD focuses on the fundamentals of light-matter interactions with the goal of discovering and implementing approaches by which the sequential processes involving conversion of electronic energy to light become intimately integrated. The basic research endeavors to identify material and device configurations in which the distinction between internal end external quantum efficiency merges to a unitary figure of merit. This new strategy is heavily based on discovering and designing nanoscale optical materials and structures wherein the resonant interaction between the electronic and photonic degrees of freedom is significantly stronger than the perturbation interaction regime typical of today's light-emitting devices.

BACKGROUND AND MOTIVATION

The development of designed nanostructured materials represents a significant untapped resource for the development of ultra-high-efficiency solid-state lighting (SSL) sources. The tailoring of the electronic properties of quantum dots (QDs), rods, and other quantum confined structures offers the opportunity to manipulate optical oscillator strengths for accelerated radiative processes and to control the spectral content. Furthermore, configuring the dielectric properties of the "optical enclosure" of a light emitter using nanoscale, subwavelength features such as photonic crystals and resonant cavity emitters [Shakya, Lin, and Jiang 2004; Wierer et al. 2004; Chen and Nurmikko 2004; Song et al. 2000] has already given fresh impetus to novel visible LEDs based on the InGaN quantum well material system and is known to significantly change the light-emission properties of OLEDs [Bulović et al. 1998].

The key aim of this CCRD is to investigate the fundamentals of light-matter interaction in nanoscale structures, in which increased integration and convergence of the internal photon generation and its extraction from a device structure are achieved as a unified physical process. Such a convergence of photon generation and extraction would go beyond the current generation of light emitters, from LEDs to lasers, in which the interaction of electromagnetic fields with electronic excitations occurs in a regime in which the photon field presents only a very weak perturbation on the excited electronic states, and the device optical enclosure is a dielectric concentrator structure to guide those photons into specific spatial and spectral channels.

Several recent examples broadly connect and support the direction of this CCRD. Among them are developments in the field known as "atom optics," which show how two-level atoms in a (vacuum) microcavity (Figure 39 can reach the so-called strong coupling regime. Here, the hybridization of photon-electron states leads to coherent superpositions with exceptional physical attributes [McKeever et al. 2003]. Such enhanced light-matter interaction can potentially be exploited in light-emitting devices. A figure of merit, the so-called Rabi (or normal mode) splitting represents a measure of the light-matter interaction of the hybrid states. In the ultimate strong coupling regime, this can exceed thermal energy at room temperature for wide bandgap organic thin films [Lidzey et al. 2000, and Song et al. 2004] and II-VI semiconductor QW micro-cavities [Kelkar et al. 1997; Dang et al. 1998], making such hybrid excitations stable in practical devices. Another recent development relevant to this CCRD has roots in the physical characteristics of the efficient photo-

Figure 39 Schematic of an "artificial" atom trapped in a microcavity for enhanced light-matter interaction.

receptors that nature has developed using multichromophore systems in specific molecular constructs. In these systems, recent theory has shown how the local- or near- field optical interactions of adjacent, resonantly coupled chromophore sites respond together in a collective manner [Jang, Newton, and Silbey 2004], which greatly enhances the total oscillator strength of this coherently coupled Förster transfer system. Elsewhere, research on very tightly confined optical guided wave structures using collective electronic excitations in metals (surface and interface plasmons) suggest that opportunities exist in hybrid nanocomposites where metal and semiconductor nanoparticles interact to provide novel electromagnetic energy transfer pathways.

SCIENCE QUESTIONS AND OPPORTUNITIES

Key fundamental science questions in this CCRD are listed below. While they naturally fall into two interrelated topical groupings, overall synergy is envisioned as an important research strategy. In the first group, electromagnetic field confining structures are explored as a means to achieve enhanced light-matter interaction. In the second group, excitonic energy transfer processes that rely on Förster transfer and related near-field and photon tunneling processes are considered for enabling ultra-high-efficiency LEDs.

Integrated Photon Generation and Extraction

Strong Coupling in a Nanocomposite-Optical Microcavity System. The ultimate experimental and theoretical challenge is the realization of a strongly coupled system in an SSL device, in analogy to atom-field optics. The use of quantum dots and other quantum confined particles embedded within high-Q, 3D-nanocavities are sought in order to ultimately reach Rabi splittings exceeding the decoherence linewidths of both the nanocavity and the quantum dot.

Nanoplasmonic Enhancement. The ability to create size and shape-controlled noble metal nanostructures may offer an opportunity to employ metals in a dual role: to provide enhanced light emission via plasmon resonances while simultaneously being used to make electrical contact to a nanomaterial composite. The relative contribution of absorption and radiative scattering of a metal nanostructure dictates the conversion efficiency of incident photons to luminescent channels of optically active QDs/nanoparticles or within doped phosphor systems.

New Electromagnetic Pathways for Enhanced Emission. In tightly optically confined and guided structures on the nanoscale, light-matter interaction may acquire significant contributions beyond the electric dipole dominated regime. Magnetic dipole contributions are already in evidence, e.g., in rare earth phosphors. Nano-optical structures are envisioned as a means to further enhance these and higher order multipole processes for increasing total radiative cross sections in nanocomposite active media and phosphors.

Control of Exciton-Photon Energy Pathways in Heterogeneous Nanomaterials

Directed Förster Energy Transfer Pathways. Control of nanocrystal size and shape enables tuning of spectral content of emission for individual particles. For high-density assemblies of active media, photon coupling via tunneling through interparticle dipole-dipole energy transfer may enable designed distribution of electronic energy excitations for "smart" spectral tailoring of emission, including near-field induced optical transitions by embedded nanoscale antenna structures.

Coherent/Collective Processes. In dense assemblies of identical nanoparticles, local feedback by strong photon localization because of elastic scattering may augment the Förster energy transfer in a degenerate system. When acting cooperatively, these subwavelength proximity effects in resonantly coupled nanocomposites can potentially offer significant enhancement of functionality by coherent "multiple chromophore" effects in an LED device structure.

Organic/Inorganic Semiconductor Hybrid Nanostructures. The resonant coupling between Frenkel and Wannier-Mott excitons in spatially integrated organic/inorganic nanoparticles may lead to striking enhancement of the energy transfer and radiative rates from such novel hybrid electronic media, extracting a joint benefit from each constituent [Agranovich et al. 1998].

POTENTIAL RESEARCH APPROACHES

Design and Implementation of Hybrid Microcavity/Exciton Light-Emitter Devices

Optical microcavities in 3D confine light to subwavelength-scale volumes by resonant photon recirculation. Microcavities can induce quantum dots or other nanoparticles to emit spontaneous photons in a desired direction or can provide an environment where dissipative mechanisms such as spontaneous emission are overcome so that quantum coherent coupled states of light and matter are possible. The coupling can formally be divided into two regimes, depending on the balance between exciton oscillator strength and dissipative or dephasing damping rates of polarization.

In the weakly coupled regime, dissipation exceeds the coherent normal mode coupling dynamic. Here, the control of spontaneous emission through the "Purcell enhancement" has been demonstrated in various semiconductor planar microcavities [Baba and Sano 2003].

In the strongly coupled regime, which presents fundamentally new opportunities in basic SSL research, schematically shown in Figure 40, modification occurs from the usual irreversible spontaneous emission to a reversible exchange of energy between the emitter and the cavity mode. Using randomly distributed single InGaAs QDs, the strongly coupled regime has been demonstrated recently at cryogenic tempera-

$$\omega_{\pm} = \frac{\omega_{cav} + \omega_{ex}}{2} \pm \frac{1}{2}\sqrt{\Omega_R^2 + (\omega_{cav} - \omega_{ex})^2}$$

Figure 40 Schematic of exciton-microcavity interaction of the "strong" coupling regime, indicating the "Rabi" splitting of the normal modes.

tures by employing either Fabry-Perot waveguide or photonic crystal 3D microcavities [Reithmaier1 et al. 2004; Yoshie et al. 2004]. In wide-bandgap inorganic and organic semiconductors, which have stable excitons at room temperature and high excitation densities, such coherent coupling may provide a basis for ultra-high-efficiency LEDs. Strong coupling occurs when the emitter-photon interaction becomes larger than the combined atomic dipole decay rate and the cavity-field decay rate. Then the irreversible spontaneous emission process of the emitter is replaced by a coherent periodic energy exchange between the emitter and the photon, and the excitations are shielded from nonradiative pathways during the microcavity photon release time. Recent results at cryogenic temperatures with CdTe QW-based planar microcavities have clearly shown that the effects of a strongly coupled exciton-cavity polariton system is condensation to a macrosopically coherent state [Richard et al. 2005].

Ordered Nanocomposites for Collective and Controlled Energy Pathways

Aiming beyond established means of heterostructure engineering of electronic states (such as quantum wells or dots) and optical physics (such as photonic crystals), a new approach is to explore designed heterogeneous active semiconductor media with an internal organization on the nanometer scale, to serve as an efficient converter of electrons to photons in the visible range. An example is the search for chemical synthesis routes to achieve dense arrays of inorganic III-nitride and II-VI nanorods (density $>10^{10}$cm^{-2}, <10 nm in diameter) by "bottom-up", self-organized assembly for the formation of "nanotextured" active media. Such ordered inorganic structures can further act as the template for the creation of hybrid nanocomposites which structurally intercalate. One specific example is that of organic semiconductors (see below) combined with metal nanostructures for modulating local electronic and electromagnetic energy transfer couplings. One seeks to explore and exploit such novel nanocomposites for enabling efficient transport of photoelectronic excitation on the nanoscale while simultaneously providing electronic interconnects such as is shown schematically in Figure 41 with nanorods as the active medium. One motivation for
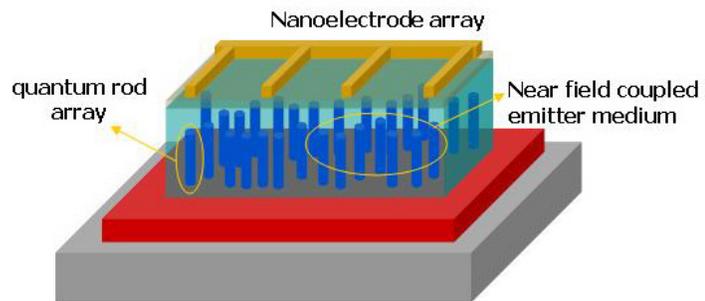
Figure 41 A schematic concept view of a coupled nanorod LED.

such two-component nanotextured media is the search for near-field enhanced optical phenomena. These include photon coupling via tunneling through inter-wire dipole-dipole energy transfer, in addition to local feedback by strong photon localization because of elastic scattering. This process is well known in random nanosale optical media. When acting cooperatively, these subwavelength-scale antenna effects in resonantly coupled nanostructures can potentially offer significant enhancement of functionality for light emitters by either coherent or incoherent "multiple chromophore" effects.

Organic-Inorganic Hybrid Photonic Device Structures

The combination of organic and inorganic materials in a single nanostructure may lead to novel light-emitter devices that combine the advantages of both classes of materials. Thin multilayer core-shell quantum dots or rods and other inorganic-organic hybrid structures can open the path to new types of coupled electronic excitations under conditions where the Frenkel excitons and Wannier-Mott excitons of the organic and inorganic constituents have nearly equal energies. The resonant coupling between Frenkel and Wannier-Mott excitons across interfaces in quantum-confined structures has been predicted theoretically to lead to striking enhancements of linear and nonlinear optical cross sections [Agranovich, La Rocca, and Bassani 1998; Agranovich, Benisty, and Weisbuch 1997]. Of specific interest to spectrally smart and high-efficiency LEDs is the prospect of fast, efficient near-field excitation energy transfer or wavefunction hybridization between the inorganic and organic nanoparticle components, leading to a broad spectrum and strong relaxation. For instance, such energy transfer would facilitate a hybrid LED in which the electrical injection into the inorganic semiconductor quantum well can efficiently enhance the organic material luminescence, or vice versa. Initial demonstrations have involved spatially separate organic and inorganic QW layers in a microcavity with polariton Rabi splittings [Forrest et al. pending]. Other recent results on planar InGaN/organic structures show initial demonstration of Förster-type energy transfer between excitons of the two materials [Heliotis et al. 2006], and electrical injection in such heterojunctions has yielded spectrally controlled electroluminescence [Song et al. pending].

Enhanced Emission from Novel Nanophotonic Device Structures

Recent advances in nanophotonics now provide an unprecedented ability to guide and manipulate light at ever smaller length scales. While it has been generally assumed that the interaction of light with matter is dominated by propagating far-field radiation, the importance of near-field interactions has become more apparent with developments in the ability to design, fabricate, and characterize optical structures with deeply sub-wavelength dimensions. Evanescent waves, such as the surface plasmon-polaritons supported by collective excitations along metal-dielectric interfaces, offer novel pathways for both the enhanced excitation and emission of light-emitting species. For example, the surface plasmon modes supported by small metal particles are well known for their ability to funnel light into small volumes, leading to dramatically enhanced electric field strengths. Recently, it has been shown that such particles can serve as local optical antennas and facilitate the efficient photo-excitation of light-emitting molecules to dramatically enhance luminescent efficiency [Anger, Bharadwaj, and Novotny, 2006]. Surface waves can also dramatically increase the number of radiative paths available for an excited emitter, and within certain regimes, they can provide a truly divergent density of optical states [Zia unpublished]. These additional states not only provide for more efficient emitters, but also allow one to engineer the emission spectra by modifying the selection rules for optical transitions. The rapid spatial variation of the electromagnetic fields associated with surface polaritons can greatly enhance higher order transitions beyond the electric dipole approximation. These transitions, such as the

590 nm magnetic dipole transitions in Eu^{3+}, are already important for rare-earth phosphors in LEDs, and recent results have shown that presence near a metal film can be used to selectively tune the 590 nm and 612 nm (electric dipole line) for spectral shifting [Zia unpublished].

HOW WILL SUCCESS IMPACT TECHNOLOGY?

The research opportunities and avenues outlined in this section represent a new set of approaches to light-emitter device design by focusing on light-matter interaction at a fundamental level. The basic research is anticipated to benefit the light-emitter performance of existing devices and materials, but it will be particularly important to exploit rapidly advancing nanoscale materials science. The ability to manipulate and synthesize new artificial active media opens entirely new avenues and design options for next generations of LEDs and related devices for SSL.

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ENHANCING LIGHT-EMISSION WITH NANOPLASMONIC OPTICAL ANTENNAS

It is well established that the efficiency of a light emitter can be artificially enhanced by coupling it to a secondary body. This principle is used in many radiowave and microwave applications such as cell phones or television. We refer to the secondary body as an antenna, which is a device that efficiently converts the energy of free-traveling radiation (propagating through the air) to localized energy and vice versa.

An antenna is a reciprocal device; that is, a good transmitting antenna is also a good receiving antenna. However, antennas do not radiate all the energy released by the coupled local emitter. Some of the energy is unavoidably absorbed in the antenna and ultimately converted to (or wasted as) heat.

To understand antenna-coupled light emission at the nanometer scale a group at the University of Rochester [P. Anger, P. Bharadwaj, and L. Novotny, *Phys. Rev. Lett.* 96, 113002 (2006)] used a single molecule as an elementary light-emitting device and studied the trade-off between fluorescence enhancement and fluorescence quenching. With an optical antenna in the form of a simple gold particle, the group achieved a 7- to 10-fold increase in emission efficiency. However, as shown in Figure (a), for very short distances between the gold particle and molecule, the fluorescence yield dropped drastically because of nonradiative energy transfer (or quenching) from the molecule to the particle. Hence, an optimum distance exists between molecule and antenna. Of course, a simple gold particle is not an efficient optical antenna, and it can be expected that favorably designed structures will yield much higher enhancement.

Ultimately, antenna-coupled light emission may have a number of uses. In addition to enhancing light emission for solid-state-lighting applications, they are able to localize (or confine) optical radiation to length scales much smaller than the wavelength of light, and hence can be employed as light sources for high-resolution optical microscopy and spectroscopy [Figure (b)].
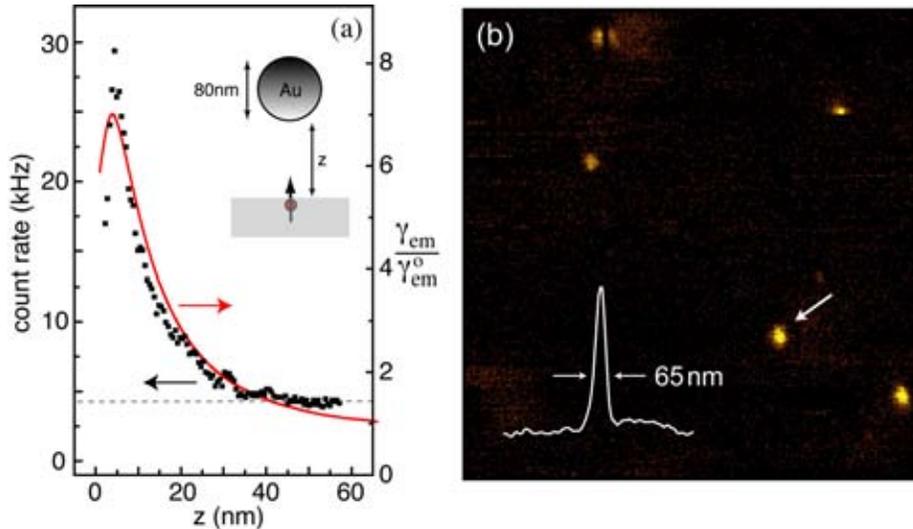
Enhancing the emission efficiency of a single molecule with a particle antenna: (a) fluorescence enhancement as a function of distance. (b) fluorescence imaging of single molecules. From Anger, Bharadwaj, and Novotny [2006].

MULTISCALE MODELING FOR SOLID-STATE LIGHTING

The creation of predictive models that reliably describe, and can be used to optimize, the behavior of heterogeneous optoelectronic materials and lighting devices fabricated from them is a critical research direction for solid-state lighting. Models must accurately capture the physical processes that determine behavior on a number of very different length and time scales. Quantum mechanical models, used to describe fundamental processes on an atomic scale, must be interfaced to semi-empirical mesoscale models, which must in turn connect to classical continuum models that describe behavior at the device scale. This hierarchical approach creates special research challenges, including developing a correct description of interactions between the different length scales in the set of models. Multiscale modeling exposes degrees of freedom that have to be optimized to find materials and device configurations that result in efficient light-emission properties. Successfully implementing a hierarchical multiscale physics theory and simultaneously determining a global optimization approach are the focus of this Cross-Cutting Research Direction (CCRD).

BACKGROUND AND MOTIVATION

Recent advances in theoretical methods, computational algorithms, and the rapid growth in computational power, parallel the extraordinary advances in nanoscience and materials technology. We now have the physical ability to construct microstructures and nanostructures of heterogeneous materials with exquisite control of physical structure. This CCD is concerned with providing the necessary theory and modeling capabilities to enable integrated materials and device design that can optimally utilize these new nanostructure synthesis and fabrication advances.

Theory and modeling methods will follow a hierarchical approach, making relevant approximations based on the length and time scales, materials system, and functional properties to be described. On sub-nm and sub-ns scales, ab initio quantum mechanical methods will be employed. These ab initio calculations will provide the input parameters for semi-empirical models (often still quantum-mechanical) that can address larger-scale interacting systems, such as coupling electronic excitations to optical modes, lattice dynamics, defects, and quantum transport. At the next scale, kinetic equations will be developed to describe transport, excitation decay channels, electrical and optical pumping, and nonequilibrium dynamics. On the largest length and time scales, continuum models will be used that are suitable for integrated device design. Making the necessary connections between the various models on the different length and time scales of this hierarchical approach is a particularly critical and challenging theoretical task.

The creation of predictive models for solid-state lighting (SSL) materials and devices will require comparison of theoretical results with fundamental measurements for validation of the models. It is desirable to make direct connection with experiment on as many levels of the hierarchy of models as possible. For example, a series of molecules could be studied, where some aspect of their molecular structure is systematically varied. By measuring properties of the isolated molecules and comparing with condensed phase properties in thin films, a better understanding of structure-property relationships can be gained. An improved understanding of fundamental physical processes in device structures is an important component of the development of a hierarchical modeling approach to SSL device design. Comparison of theory/modeling results with measurements of charge injection, charge transport, charge transport at internal interfaces, exciton formation, energy transfer, exciton energetics/dynamics, and photon out-coupling will be essential to validate the SSL device-design approach.

Adaptive quantum design is a new methodology involving optimization of parameters that control the predicted response of both ab initio quantum and hierarchical physical models. Using recent advances in control theory, the availability of computational resources, and the existence of realistic physical models, it is now possible to explore vast regions of a complex multidimensional configuration space and discover new, nonintuitive structures with unanticipated behavior. The use of adaptive quantum design to address critical needs in SSL is motivated in part by the fact that conventional ad hoc methods often fail to identify potentially important solutions and thus result in suboptimal behavior.

SCIENCE QUESTIONS AND OPPORTUNITIES

Optoelectronic materials utilized for SSL include inorganic semiconductors, organic semiconductors, and hybrid composites of the two. Each of these materials systems presents a class of theory/modeling challenges. In addition to understanding materials issues, it is also necessary to understand and control the basic device physics of SSL structures.

Inorganic semiconductors are crystalline materials that have been widely studied. However, most effort has been concentrated on a relatively small number of elemental (such as Si and Ge) and binary materials (such as GaAs and InP). New inorganic semiconductors with more complex structure provide opportunities for enhanced functionality. Impurities and defects are especially important in determining electronic processes in inorganic semiconductors, and improved understanding of their role is a very important and challenging theoretical task. Organic semiconductors are condensed phases of π-conjugated organic molecules that are typically highly disordered with strong intramolecular electronic interactions and weaker intermolecular interactions. However, the intermolecular interactions are critical for many condensed phase properties such as electrical and exciton transport. To describe these disordered molecular materials theoretically will require a new approach that lies between the traditional scientific disciplines of quantum chemistry, which relies on the comparatively small size of individual molecules, and condensed matter physics, which relies on the translational symmetry of crystalline solids. Hybrid composites of organic and inorganic semiconductors are an exciting new class of electronic materials with potentially important application to SSL. A main scientific hurdle to achieving high-quality hybrid composite materials is to understand/control interface properties such as charge carrier traps that decrease carrier lifetime, charged scattering centers that decrease mobility, and charged interfaces that decrease built-in potentials. Self-assembly approaches to modify and control interface properties are expected to be very important. The description of these disordered molecular and composite materials presents an exciting new theoretical challenge that will require the creation of new approaches.

Many experiments are done in device structures, and device-scale models are required to make contact with these measurements. Macroscopic device models typically consist of differential equations for the density of various excitations as functions of position and time coupled to Poisson's equation. Injection properties of various interfaces enter as boundary conditions for the differential equations. Microscopic theory provides descriptions of material parameters, such as carrier mobilities, that appear in the differential equations and descriptions of interface properties, such as injection behavior, that appear as boundary conditions. The device models are used to describe the position and time dependence of the densities of the various excitations, the electric field, the current, and the emitted light. The continuum device model description of the experimental structure provides a bridge between microscopic calculations and measurements for which macroscopic aspects of the experimental situation must be taken into account.

POTENTIAL RESEARCH APPROACHES

Adaptive Quantum Design

In recent years, a remarkable opportunity has emerged in which it is now possible to create optimal designs of structures whose operation and description is fundamentally quantum mechanical. Adaptive quantum design is now feasible because of advances in the description of inhomogeneous physical systems on multiple length and time scales, the availability of inexpensive computation power, and the existence of efficient optimization algorithms. Key to the success of the SSL initiative is the development of structures with nanoscale features that efficiently control the generation and behavior of photons in inhomogeneous media (Figure 42). Nanoscience provides an overwhelmingly large number of experimentally accessible ways to configure the spatial position of atoms, molecules, and other nanoscale components to form such structures. A challenge is to find the best configuration that yields the highest efficiency SSL device. In the presence of an enormous nonconvex search space, traditional ad hoc design methods will miss many possible solutions. The enabling approach to solving this difficult problem is to employ machine-based searches of configuration space that discover user-defined objective functions. Such an optimal design methodology aims to identify the best broken-symmetry spatial configuration of metal, semiconductor, and dielectric materials that produce a desired response. By harnessing a combination of modern computational power, adaptive algorithms, and realistic physical models, it will be possible to seek robust, manufacturable designs for SSL devices that meet previously unobtainable system specifications.
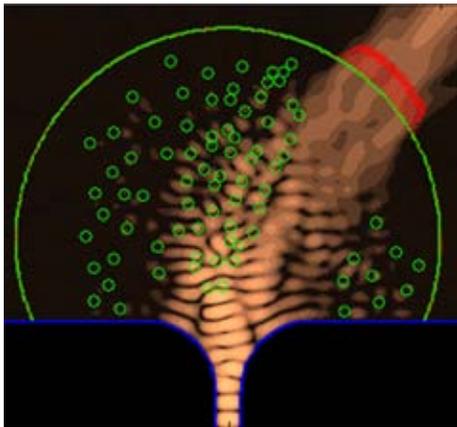
Figure 42 Aperiodic array of dielectric scatterers used to redirect and shape an electromagnetic beam. Image shows electromagnetic intensity incident from below on an array of dielectric cylinders whose position has been optimized to redirect more than 90% of power and uniformly illuminate the region of the circle shown with a red curve. The broken symmetry of aperiodic dielectric structures can provide functionality that is not accessible with conventional optics. After Gheorma, Haas, and Levi [2004] and Seliger et al. pending.

A Hierarchy of Models

At the fundamental quantum level, there is now an established and successful orthodoxy based on density functional theory that accurately describes electronic structure, atomic structure, and physical properties of large classes of materials in their ground state, even for assemblies of hundreds or thousands of atoms. Such ab initio models have been successfully integrated with classical atomic modeling (e.g., molecular dynamics) and continuum modeling (e.g., elasticity theory) to provide a basic toolkit that can be used to describe processes in which many scales are relevant, such as mechanics of solids [Csanyi et al. 2005], chemical catalysis, and ferroelectric devices.

However, for describing the physics underpinning SSL, these methods are much less advanced for several reasons. At each level of modeling, linking challenges present themselves.

- **Quantum nanoscale:** We must describe excited electronic states that require fundamental physics beyond the regime of density functional theory, where both traditional and novel methods of quantum chemistry, quantum Monte Carlo [Foulkes et al. 2001], Dynamical Mean Field Theory [Kotliar et al. pending], and exact methods for small systems [Szymanska, Littlewood, and Needs 2001] are now being developed that offer the opportunity to model realistic systems of great complexity. We must tackle energy spectra and interactions in complex molecules, quantum dots, and surfaces and interfaces to determine basic parameters to be used in the next scale.

- **Quantum mesoscale:** The physical interactions to be modeled are often long range, as in Coulomb-mediated Förster transfer, or in coupling of electronic excitations to confined optical modes. This complexity requires intermediate scale quantum models, where excitonic transitions are parameterized using simpler models of, for example, interacting dipoles coupled to light and to other elementary excitations of the system, such as lattice vibrations. The relevance of large scales here interferes with the complexity introduced by nanostructure inhomogeneity (which may include disorder intrinsic to materials, or structure deliberate to the design). In strongly coupled optical systems, modeling of the electromagnetic waves must be integrated at this stage. These quantum models themselves can be used to give insight into carrier and excitation transport, optical design, and macroscopic coherent properties [Marchetti et al. 2006].

- **Semiclassical mesoscale:** Lighting devices are driven, open, dynamical, and out of equilibrium. At this level, quantum or semiclassical kinetic equations emerge from the dynamics of the model Hamiltonian systems, coupled to external reservoirs. The models at this level are still statistical, for example Langevin dynamics, or (classical) Monte Carlo, but should nevertheless be based on fundamental physical principles, with parameters derived from higher design levels or from closely coupled experiments.

- **Device level models:** The statistical models provide an interface to device-level physics, either directly, or by abstraction into classical continuum equations, describing, for example, laser rate equations, and drift-diffusion equations for carrier, excitation, energy, and photon transfer. Many experiments are done in device structures, and device-scale models are required to make contact with these measurements.

HOW WILL SUCCESS IMPACT TECHNOLOGY?

Recent developments in nanoscience open up a very large range of new materials and device possibilities for SSL. There is a wide variety of both organic and inorganic semiconductors that are potentially valuable as SSL materials, and organic-inorganic hybrids offer a new class of exciting material-design possibilities. Predictive theoretical models are required to enable full exploitation of the opportunities provided by these new materials and device options. The space of material/device options is too large for an unassisted experimental search. It is important for theory to serve as a guide to experiment in investigating these options. The successful implementation of adaptive quantum design algorithms provides a natural path to efficiently transfer and optimize new nanoscale degrees of freedom for SSL needs. It is essential that theory and modeling efforts be closely coordinated with experimental efforts both to validate the

theory/modeling results and to ensure that the theory/modeling results are used to guide and interpret experiment.

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PRECISION NANOSCALE CHARACTERIZATION

The development of solid-state lighting (SSL) materials and devices has been driven on two fronts: by new materials and by new tools. Examples of the latter include the development of molecular beam (and other epitaxial deposition techniques) and electron microscopy, which enabled the fabrication and visualization, respectively, of complex, multilayer light-emitting structures. Achievement of the next breakthrough in performance to 50% power conversion efficiency (and beyond) will require a new generation of tools to characterize materials with an unprecedented degree of insight. As we approach the goal of atom-by-atom design of light-emitting materials, nanoscale characterization must illuminate the path forward.

BACKGROUND AND MOTIVATION

SSL structures rely now, and are expected to rely in the future, on complex organic and inorganic material nanostructures within which a variety of complex phenomena (charge transport, recombination pathways, and photon extraction) occur. Understanding these nanostructures and phenomena necessitates precise characterization at levels beyond those currently possible. A key catalyst for advances in SSL is therefore the development of new, structurally sensitive tools.

For example, it is desirable to measure both elemental composition and chemical state because of the sensitivity of materials properties to both of these. These measurements need resolutions spanning the entire range of relevant length scales from individual molecules or dopant atoms to integrated heterostructures and functional devices. In essence, we would like to know the position and chemical state of every atom or molecule in a light-emitting material. A further challenge is to accomplish this in operating SSL devices in ways that allow determination of local nanoscale properties under conditions relevant to understanding the basic phenomena behind electroluminescence. Novel in situ techniques for monitoring materials synthesis will also drive improvements in materials properties.

Recent progress in nanoscale characterization methods suggests that these ambitious goals are achievable. Optical and infrared spectroscopies, photoluminescence, scanning probe microscopies, electrical characterization, and structurally sensitive techniques employing energetic beams of ions, photons, and neutrons continue to improve and provide new insights into the relevant materials and devices. State-of-the-art advances in several techniques are particularly interesting for meeting the characterization challenges of SSL materials and devices:

- near-field scanning optical methods,

- single-molecule spectroscopy,

- electron-beam methods with enhanced energy and spatial resolution for improved sensitivities and methods that mitigate artifacts because of sample damage,

- x-ray scattering, fluorescence, and spectroscopy, including in situ microscopy, ultrafast time resolved scattering and spectroscopy, and inelastic scattering, and

- tools for the assay of organic materials.

SCIENCE QUESTIONS AND OPPORTUNITIES

Fundamental challenges include understanding stress distributions, the details of atomic arrangements at defects and interfaces, mesoscale heterogeneity, impurity and dopant chemistry, local structure, and the relationship of all these effects to efficient light emission. Meeting these challenges requires new approaches that enable simultaneous determination of structure and function in inorganic, organic and inorganic/organic hybrid materials. Opportunities exist for development of methods that are minimally invasive, that can image subsurface features and buried interfaces, that provide unprecedented levels of quantification for impurities and dopants in a host structure, and that can elucidate the three-dimensional structure of defects and elemental distributions in electroluminescent heterostructures.

We also need novel time-resolved techniques to understand local dynamics as charges are injected into a material; relax into bands, polarons, traps, or a combination of all three; diffuse through the material; and finally combine to produce a photon. These processes occur on timescales of picoseconds to milliseconds and longer. High and simultaneous spatial and temporal resolution could enable an unprecedented understanding of these processes.

Incorporation of organic materials as the heart of a functional device introduces new degrees of complexity that semiconductor science has not previously encountered. For example, as discussed in the OLED Science Overview and Research Challenges section, and in Priority Research Direction "Understanding Purity and Degradation in OLEDs," a recurring theme in OLED science is the difficulty in assaying an organic compound to the same degree as is routine for inorganic semiconductors. It is impossible to understand the role of defects on efficiency unless the nature and concentration of those defects can be quantified to an extremely high accuracy. In inorganic GaAs, for example, the role of electronically active defects at a concentration of $<10^{15}$ /cm^3 is well established. But for organics, it is not yet possible to exclude below 0.1% the fraction of isomers, oligomers, and molecular fragments present in the amorphous organic compounds used in most OLEDs.

A further challenge presented by organic light-emitting materials is the measurement of energy levels important to charge transport and light emission. While the energy of occupied states can be measured using various forms of photon spectroscopy, the experimental error is large (basically because the result is usually a small number obtained via the subtraction of two relatively large numbers). Furthermore, the measurement of the lowest unoccupied molecular orbital (LUMO) and higher-lying unoccupied states presents further difficulties because these are virtual states, and often disagreement exists with different approaches. We need to better characterize these states to improve our understanding of interfacial and bulk doping of charge transfer materials in OLEDs.

POTENTIAL RESEARCH APPROACHES

An array of potential research approaches may yield the high resolution in time and in real and reciprocal space needed to measure local function and structure in light-emitting materials. Chemical identification and three-dimensional reconstruction of features and interfaces buried within a multilayer structure are key challenges; a two-dimensional description of structure is insufficient to accurately link structure and property. Structural measurements should complement spectroscopic techniques. We need to develop ultrafast pump-probe spectroscopies performed in the near field that also provide local dynamic information.

More traditional approaches to probe materials synthesis and growth mechanisms need advancement across the broad range of environmental conditions of interest for SSL materials. This includes development of higher precision process metrology tools including: ultrasonic and infrared/optical methods for monitoring and control of source fluxes and gas-phase chemistry and reactions in vapor phase deposition; trace element measurement and purification techniques for organic materials synthesis; pyrometry for surface temperature determination of compound semiconductor systems; and optical methods that are sensitive to stress, layer structure, and surface behavior.

Here, we enumerate a list, by no means complete, of fruitful research directions in precision nanoscale tools.

Beyond the Diffraction Limit: Near-Field Optical Microscopy. This technique combines the high spatial resolution of scanning probe techniques with the chemical information provided by optical spectroscopy (Figure 43). While researchers have demonstrated near-field Raman microscopy and near-field infrared absorption microscopy on selected samples [Knoll and Keilmann 1999; Hartschuh et al. 2003], those techniques lack the sensitivity to be routinely applicable to more general problems. Exploring plasmon-enhanced optical antennas, for example, could lead to increased sensitivity. The key property of these optical antennas is to efficiently convert the energy of incident laser radiation into localized energy that is then used as an optical excitation source. Also, recent studies have shown that we can apply near-field optical techniques to subsurface imaging and tomography [Anderson et al. 2006; Carney et al. 2004].

Recent progress in near-field optics demonstrated that spatial resolution of 10 to 20 nm can be achieved while retaining the full power of vibrational spectroscopy [Novotny and Stranick 2006]. These new approaches make use of an optical antenna to localize external laser radiation to dimensions beyond the diffraction limit down to about half the wavelength of light. When this localized field is brought close to a sample surface, the response because of the local optical interaction is converted by the same antenna into propagating radiation and subsequently spectrally analyzed using standard optical instrumentation. A hyperspectral image of the sample surface can be recorded by guiding the antenna over the sample surface and recording an optical spectrum from each image pixel. Most commonly, a sharply pointed metal tip is used as the optical antenna, but other antenna geometries, such as particles and bowties, have also been studied. Examples include near-field Raman spectroscopy used to study defects in carbon nanotubes [Hartschuh et al. 2003] and for stress analysis of silicon devices. To make the technique applicable to SSL research, it is necessary to increase its sensitivity by exploring more efficient antenna geometries and materials.
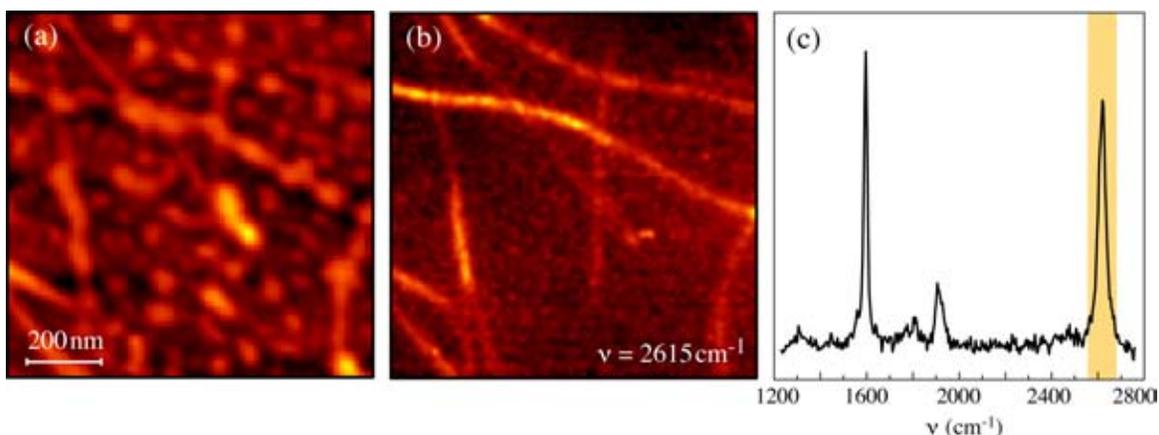
Figure 43 Near-field Raman imaging of a single-walled carbon nanotube sample: (a) topography showing a network of carbon nanotubes overgrown with water droplets, (b) Raman image of the same sample area recorded by integrating, for each image pixel, the photon counts that fall into a narrow spectral bandwidth centered around ν =2615 cm^2 (indicated by the yellow stripe in c), and (c) Raman scattering spectrum recorded on top of the nanotube. Adapted from Hartschuh et al. 2003.

Properties of Individual Molecules: Single Molecule Spectroscopy. Researchers have recently shown [Park et al. 2004; Gesquiere et al. 2004] that morphological features in organic thin films relevant to polymer LEDs can be revealed on the molecular scale. Details such as polymer chain folding, packing, and aggregation have been measured, as well as the diverse set of excitons, polarons, and defects present in such materials under charge injection. These advances have been achieved through the development of methods that combine fluorescence single-molecule spectroscopy with localized electric field enhancement or charge injection. For example, fluorescence-voltage single molecule-spectroscopy (F-V/SMS) is a powerful tool for "mapping" the photophysics and charge-transfer processes of conjugated polymers. In Figure 44, the fluorescence intensity of a single isolated conjugated polymer molecule is shown as a function of the bias voltage, V, applied to an organic multilayer. The F-V/SMS data reveal that a single positive charge injected within the capacitor-like hole injection device entirely quenches the light emission from the film, thereby potentially limiting the efficiency of a device based on these materials. To reach the next generation of single-molecule characterization, we need to combine atomic probe techniques with optical or Raman spectroscopy, optically detected magnetic resonance, or other nanometer resolution optical microscopy to create three-dimensional spatial profiles of key chemical, physical, structural, and dynamical properties that dictate device performance in realistic light-emitting diode (LED) structures.
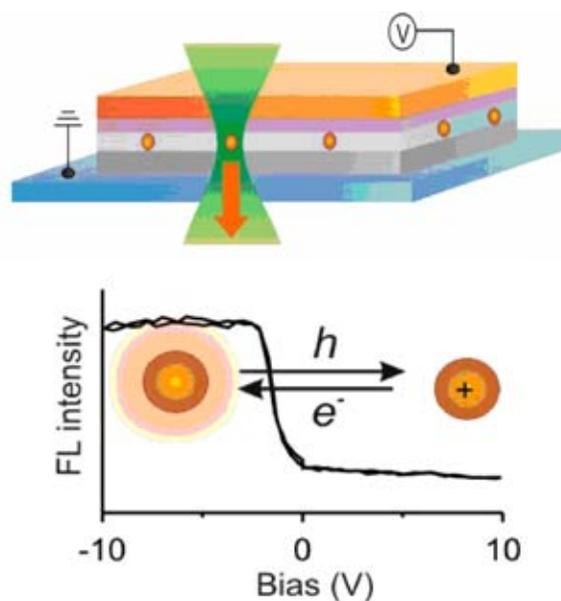
Figure 44 Schematic of the device structure used in the F-V/SMS studies, and the fluorescence changes measured under oxidation/reduction. (Left) Polymer MEH-PPV nanoparticles (orange dots), sitting on top of an insulating layer (grey), are close to or contacting a hole transporting layer (HTL, reddish purple), which is in turn interfaced with a gold electrode (orange) at which hole injection occurs. (Right) F-V/SMS data for a single electron-transfer involving a single MEH-PPV nanoparticle. Adapted from Gesquiere et al. 2004.

Toward Sub-Ångstrom Resolution: Electron Microscopy and Microspectroscopy.
These techniques are already indispensable tools for nanocharacterization. However, researchers are revolutionizing electron-beam methods by correcting electron-optic aberrations. Spherical aberration (C_s) correction has been successfully demonstrated for transmission electron microscopy [Haider et al. 1998] (TEM) and scanning transmission electron microscopy [Batson, Delby, and Krivanek 2002] (STEM) and is now commercially available [FEI web]. Chromatic aberration (C_c) correction is under development [Rose 2005] for these types of microscopes. Both C_s and C_c correction are available on scanning electron microscope (SEM) platforms [JEOL web]. C_s correction yields dramatic improvements in resolution and contrast transfer such that information limits below 1 Å can be achieved. C_s correction reduces information delocalization and, when applied to a microscope's condenser lens system, increases the beam current in a small probe (<0.1 nm) by one to two orders of magnitude. C_c correction improves probe profile and greatly reduces the effect of working distance (for SEM) or pole-piece gap (for TEM and STEM) on lens performance. It is important to note that the combination of C_s and C_c correction benefits not just high-resolution instruments, but is also poised to be a breakthrough technology for analytical electron microscopy. Microscopes corrected for both C_s and C_c will have significantly improved resolution and beam currents and thus higher analytical sensitivities, and can accommodate increased space around the sample for detectors and for in situ environments. Furthermore, reducing the accelerating voltage will not significantly degrade the electron-optical properties of such a microscope. This is highly advantageous, as lowering the accelerating voltage reduces the radiation damage done to a sample by an electron beam and increases analytical sensitivity. As a specific example, the near-term implementation of C_c correction in the transmission electron microscope will allow high-resolution elemental analysis at voltages below

155

100 kV, such that electron-beam damage and segregation in InGaN heterostructures may be greatly reduced. This will help resolve outstanding issues surrounding the possible existence of In clustering in this alloy system. The ultimate challenge is to be able to know the position and state of every atom or molecule in a multilayer structure.

Using Photons to Probe Structure: X-Ray Scattering and Spectroscopy. We need to advance x-ray scattering, fluorescence, and spectroscopy to provide new insight into materials structure and function. Laboratory systems have improved significantly in recent years, becoming easier to operate and equipped with more functional optics and detectors. For example, the availability of high-flux, high-resolution monochromators on laboratory four-circle diffractometers has made specular x-ray scattering and reciprocal space mapping workhorses for determining composition and strain in compound semiconductor systems [Pereira et al. 2002]. New advances in x-ray optics [Kang et al. 2006] hold forth the promise of focusing hard x-rays down to the nanometer level, opening up a range of scattering and fluorescence methods for application at high spatial resolutions. The increasing availability of user hours at existing very high brilliance synchrotron x-ray sources, with several new sources nearing completion or in the planning stages, has made specialized x-ray characterization methods that depend on such sources more accessible to the community. This is of particular interest, for example, for in situ characterization of materials synthesis by near-atmospheric metalorganic chemical vapor deposition [Stephenson 1999]; this common process produces inorganic LEDs. X-ray probing of this type of environment depends on the high flux and high penetrating power of the hard x-rays that are produced at undulator beamlines at a synchrotron. Such in situ studies are key to understanding growth modes, surface and interface structures, elemental incorporation, and defect generation at the atomic level, providing the basic foundation for creating new heterostructures for light generation.

Simpler, nondestructive methods are required that measure LUMO energies and how they change at interfaces. Inverse photoemission spectroscopy has been combined with ultraviolet photon spectroscopy to measure electronic energy levels [Sugiyami 1998], but there is some debate about how to interpret the data. The available techniques require the detection of weak signals from a secondary process, so data must be accumulated over long periods of time with great care to dissipate charging and avoid degradation of the organic material. Improved spectroscopy is needed to enable the measurement of occupied and unoccupied states in organic materials at high spatial resolution.

High Purity Materials: Tools for Organic Assay. Currently, when a new organic electronic material is reported, it is typically determined to be "pure" by NMR and elemental analysis standards. Impurities as high as 5%, however, might not be detected by these techniques. This is especially true if the impurity is an isomer, but also if it is a byproduct from the original synthesis reactions or a smaller fragment formed during film production. In very few cases do researchers report high-performance liquid chromatography (HPLC) results — and in cases where it is reported, the detection system is more commonly a UV-visible (diode array) detector, which can show that impurities are present but does not determine what the impurities are. Techniques such as liquid chromatography coupled with a high-resolution, quadrupole-time-of-flight mass spectrometer with electrospray in the positive ion mode can quantify impurities whether they are isomeric, oligomeric, or byproduct so long as they can be separated. However, not all compounds produce a response by electrospray positive ion mode mass spectrometry. New tools and advanced methods for organic separations and for detecting the separated species must be developed and then applied to amorphous molecular and polymeric light-emitting materials.

HOW WILL SUCCESS IMPACT TECHNOLOGY?

The outcome of these research directions will provide the basic information required to link structure/composition and function in LED and OLED materials and devices at the nanoscale. To connect experiment and theory for new predictive models for LED and OLED function and optimization, it is essential to develop these spatially-resolved experimental tools for unraveling the complex and heterogeneous structure and dynamics in functioning LEDs and OLEDs. This can only be achieved by simultaneous measurement of different physical properties (e.g., optical, structural, and electronic) in ways that allow for evaluating strategies of generation and extraction of photons. Success will also yield unprecedented feedback and control for improved growth and synthesis, and enable the design of novel heterostructures for highly efficient, cost-effective light emission.

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CONCLUSION

CONCLUSION

Almost every aspect of our modern lives depends on artificial lighting. If current technology remains dominant, however, the U.S. alone will use about a trillion kWh of electricity each year for lighting by 2025. All of the lighting technologies in current general use produce light as a byproduct of high-energy processes involving heat or plasmas, which places low limits on their attainable efficiency. Solid-state lighting, however, uses materials that directly convert electricity into light at room temperature and are capable of efficiencies near 100%.

The development of light-emitting diodes for displays, indicators, and monochromatic light sources over the past 40 years offers the basis of a new lighting technology that could dramatically slow or even roll back the growth in energy used for lighting. General lighting is a demanding application, however, and today's SSL devices cannot produce light with acceptable color rendering properties needed for general illumination at even close to the theoretically achievable efficiency. If we rely solely on technology driven improvements, previous experience with the development of incandescent and fluorescent lighting suggests that SSL suitable for general lighting and with high efficiency and low cost may remain a distant dream.

THE CHALLENGES

The direct conversion of electricity to light at room temperature can be accomplished in carbon-based organic materials, crystalline inorganic semiconductors, or nanostructured hybrid materials comprised of both organic and inorganic elements. Regardless of the materials set, however, generating light near the thermodynamic efficiency limit requires essentially every electron injected into the material to generate a photon that escapes from the material into the outside world. Furthermore, the voltage required to inject and transport the electrons to the light-emitting region of the device must be no more than that corresponding to the energy of the resulting photon. Finally, the distribution of photon wavelengths generated must match the spectrum perceived by the human eye to render colors accurately, with no photons generated outside the visible range. All these constraints must be achieved in a single device with an operating lifetime of at least a thousand hours (and preferably ten to fifty times longer) and at a cost of ownership comparable to or lower than that of existing lighting technology.

Compared to indicator lamps and niche applications such as accent lighting, the amount of light required for general illumination is large. A typical office lighting fixture (containing four fluorescent tubes) emits about 5,000 lm. In contrast, the best commercially available white inorganic LEDs generate a mere 80 lm at the time of writing. Organic LEDs have only just begun to penetrate the small display market and are not available as lighting products but, given that long-lived devices brighter than 1000 cd/m^2 have yet to be demonstrated, about two square meters of OLED would be required to generate the required 5000 lm. We are clearly far from reaching the potential of SSL.

The two Grand Challenges and twelve Priority and Cross-Cutting Research Directions presented in this volume represent scientific breakthroughs that could dramatically advance SSL, both by removing roadblocks to improving current technology and by discovery-driven science, which will enable as yet unimagined architectures for the conversion of electricity to light. In particular, the two inter-related Grand Challenges represent recurring themes that weave together the specific Priority and Cross-Cutting Research Directions.

Rational Design of Solid-State Lighting Structures. The revolutionary progress we envisage will be accelerated by a fundamental understanding of how the many atom-scale components of a light-emitting device work, both individually and in concert. We are unlikely to discover easily a 100% efficient lighting system by shuffling known materials into new sequences; but we can envisage a system that is designed *from the bottom up* through an understanding of charge transport and light emission in organic and inorganic semiconductors at a fundamental level.

Controlling Losses in the Light-Emission Process. At the core of any 100% efficient solid-state lighting material, the energy carried by electrons is converted into light without *any* of it converted into heat. To accomplish this, we must discover and control the materials and nanostructure properties that mediate the competing conversion of electron energy into light and heat, *enabling every injected electron to generate useful photons*.

OUTLOOK

The time is ripe for new fundamental science to beget a revolution in lighting technology. The demonstration of infrared lasers that convert electricity to light at 76% efficiency clearly shows both the potential that should be achievable at visible wavelengths and the deficiency of today's white SSL devices. The overarching message from the workshop is that bridging this gap will be accomplished much faster if the ability to *design* sets of materials with complementary properties of charge injection and transport, light emission, and optical out-coupling in a device architecture replaces our current methodology of attempting to combine *discovered* materials with poorly understood properties. Such an effort is timely because recent advances in nanoscale fabrication and characterization coupled with the exponentially increasing capacity of massively parallel computers for multi-scale modeling bring the goals within reach for the first time.

In addition to the potential for disruptive advances in SSL technology, the plenary and breakout sessions of the Workshop highlighted the potential wider impact of the emerging research directions. Solar power is the most obvious parallel beneficiary of new ideas developed for SSL, since both fields depend on a fundamental understanding of the interaction of light with matter (although in distinctly different regimes of operation). Indeed, the combination of solar power and efficient SSL has been proposed as the *only* rational lighting solution for the estimated 2 billion people worldwide who still rely on poor-quality, pollution-generating fuel-based lighting.[1] Other beneficiaries of new ideas developed for SSL, in particular the research priorities in materials design, modeling, and measurement described in this report, will include a wide range of novel semiconductor electronics and optoelectronics, where the properties of materials (and the lack of design rules for them) often limit device performance.

Implementing the Grand Challenges and Priority and Cross-Cutting Research Directions described in this report will potentially revolutionize how we think about artificial lighting, bringing SSL devices up to the efficiency standards that should be expected of an appliance that makes such a large demand on the electricity grid.

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[1] Mills, E., "The Specter of Fuel-Based Lighting," *Science* 308, 1263 (2005).

APPENDICES

APPENDIX 1. TECHNOLOGY PERSPECTIVE

As discussed in the introduction to this workshop report, solid-state lighting (SSL) may completely change the way we generate and use lighting in all aspects of our lives and, in doing so, enable significant savings in national and worldwide energy consumption. Significant advances in semiconductor science were key to enable the computer revolution in the last half of the twentieth century. Analogous advances are essential for SSL to fulfill its promise of unprecedented luminous efficacy combined with real-time digital control of intensity, chromaticity, and spatial placement.

The workshop identified basic research needs and opportunities underlying SSL lighting technologies. A broad view of SSL applications and technology provided a useful context for the identification of fundamental scientific challenges that must be understood and overcome, and potential research approaches to address them. Participants included both experts with strong scientific credentials within the general lighting and SSL communities, as well as scientists with other diverse but relevant backgrounds. This appendix provides a high-level overview of SSL technology to put the underlying scientific challenges discussed in the workshop into their broader technology context.

We set the stage with a brief overview of SSL's potential applications and impact on national/worldwide energy consumption and the human visual experience. There are a number of characteristics of SSL that will be important if it is to achieve its potential impact — as illustrated in Figure A-1. The quantitative metrics that underlie these features are summarized in the following section. The final two sections review the current state of the art of inorganic light-emitting diodes (LEDs) and organic LEDs (OLEDs), as well as their limitations.
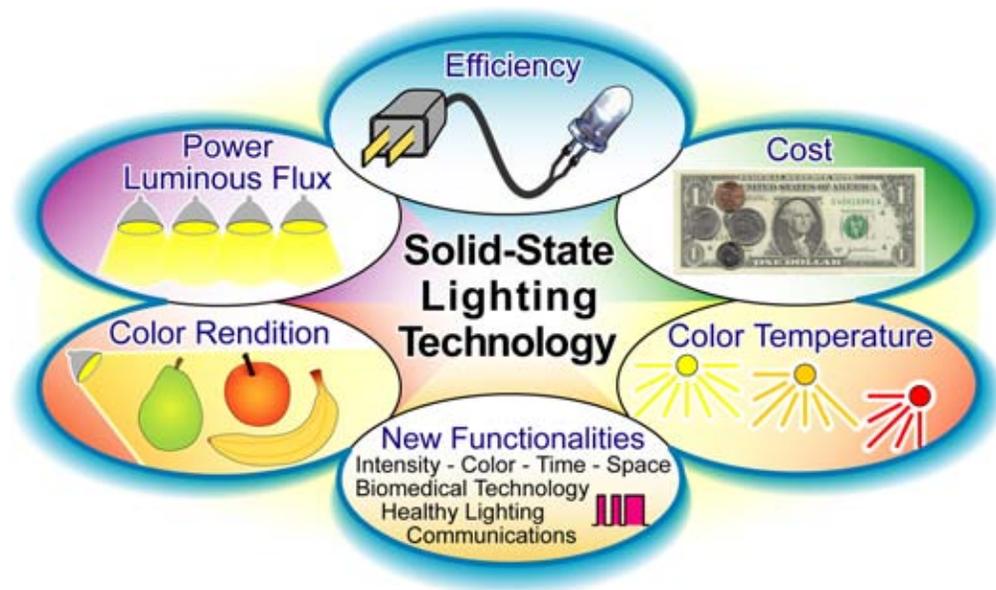

Figure A-1 Characteristics of SSL that will likely play important roles in SSL's ultimate impact on national/worldwide energy consumption and the human visual experience. [Schubert 2006]

APPLICATIONS AND POTENTIAL IMPACT

Applications

SSL uses LEDs and OLEDs to convert electricity into light for illumination.[1] Whereas 90–95% of the power input into a traditional incandescent light bulb is wasted as heat,[2] SSL has potential energy efficiencies of 50% or greater. In addition, SSL can offer ultra-long lamp lifetimes, rugged tolerance to mechanical stress, compactness, directionality, and tunability in its light characteristics (e.g., spectral power distribution, color temperature, temporal modulation).

Applications for high-brightness LEDs and SSL broadly fall into two categories, lighting for indication and for illumination (Figure A-2). Indication is the use of a self-luminous source that is to be viewed directly, such as signage. Illumination is the use of light to make other things visible by reflection from those objects, for example, the traditional incandescent light bulb commonly in residential use and fluorescent lighting employed in commercial and industrial settings.

Figure A-2 Current and near-term application using high-brightness LEDs and SSL.

As indicators, high-brightness LEDs have many benefits. This is particularly so for many monochromatic applications, in which LEDs are replacing extremely inefficient filtered incandescent light sources. Some initial applications of monochromatic LEDs for indicators have been [Haitz et al. 1999] traffic lights, safety/emergency lights, outdoor decorative lighting, automobile tail lights, outdoor displays, and backlighting for wide-color-gamut graphic displays. For example, LEDs have four distinct advantages over filtered incandescent sources for traffic signals: higher brightness and directionality, improved daytime visibility; lower operating costs saving up to $1,000 per intersection per year (derived from Navigant 2003); and an expected seven-year lifetime versus one year for incandescent lamps. A red LED traffic light quickly pays back the initial higher purchase cost (approximately $75 versus $3 for an incandescent source) with lower energy usage; the seven-year cost of ownership of a red LED traffic light is approximately one-third the cost of using an incandescent source [Navigant 2003].

As illumination sources, solid-state lights face much greater challenges, with an accompanying larger payoff. Replacement of all incandescent and fluorescent light sources with solid-state white lighting could

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[1] Although this is the normal usage, SSL could include generation of light from the conversion of nonelectrical energy (e.g., chemiluminescence or bioluminescence from chemical reactions).

[2] Note that other building technologies are much more efficient. Heating is typically 70% efficient, and ENERGY STAR qualified furnaces have an annual fuel utilization efficiency (AFUE) of 90% or greater (http://www.energystar.gov/index.cfm?c=furnaces.pr_furnaces). Electric motors are typically 85–95% efficient, and electric motors purchased for federal facilities must have an energy efficiency of 85% (or greater for larger motors), specified as the NEMA Premium efficiency levels (NEMA 2003).

have revolutionary global impact for energy savings and accompanying environmental benefits. However, current white-light LEDs are not yet up to the task. Today, white solid-state lights are mainly in specialized, low-flux applications, such as shelf lighting, stair/aisle lights, accent lights, landscape path lights, and flashlights.

Impact on Energy Consumption

The total energy consumption in the U.S. was about 9,200 Terawatt hours (TWh/y) in 2001. As illustrated in Figure A-3, 38% of that energy, or 3,450 TWh, was consumed as electricity, and of that, 22%, or 765 TWh, was consumed by lighting [Navigant 2002]. Thus, around 8.3% of total energy consumption was consumed by lighting. This is a significant fraction of total energy consumption and is an indication of the importance of lighting to human society. At $0.068/kWh, the electricity cost to the end user was about $53 billion [Navigant 2002].
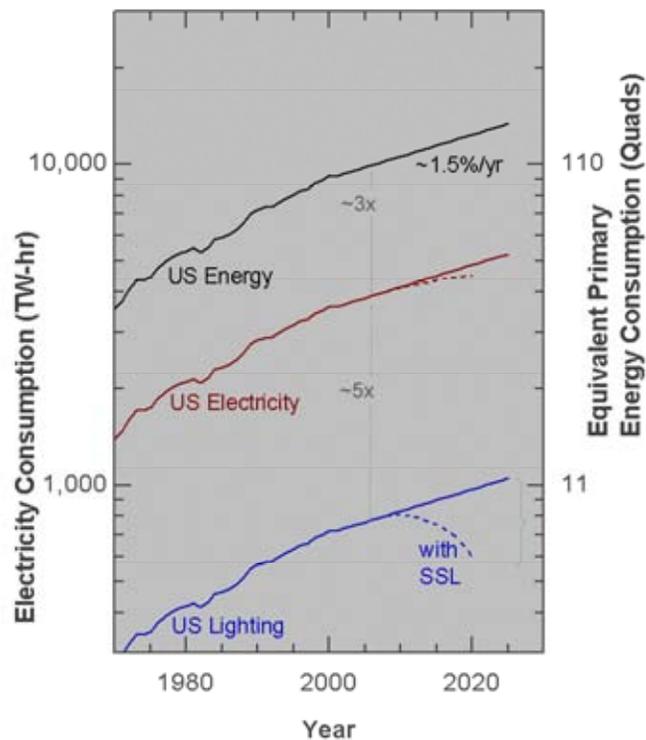
Figure A-3 Historical and projected U.S. energy and electricity consumption for all uses and for lighting, with and without SSL. Adapted from M. Kendall and M. Scholand, "Energy Savings Potential of SSL in General Lighting Applications." [U. S. DOE-OBT study by Arthur D. Little, 2001, and EIA Statistics]

Also as illustrated in Figure A-3, assuming reasonable growth rates, the U.S. may be consuming as much as 1,000 TWh/y of electricity for lighting by the year 2025 [Tsao 2003]. At $0.068/kWh, the electricity cost to the end user would be about $70 B/y. The worldwide trends are similar, with the consumption amounts increased by factors of three to four.

The electricity that was consumed by lighting in 2001 was consumed by three major classes of lamps. From a recent comprehensive inventory of lighting in the U.S. [Navigant 2002], it can be deduced that the aggregate[3] luminous efficacies (defined later in this Appendix) for these three classes of lamps, including ballast losses, were 14.0 lm/W for incandescent lamps, 70.7 lm/W for fluorescent lamps, and 96.2 lm/W for high-intensity-discharge (HID) lamps. That same inventory also found that the lumens consumed in the U.S. were 12% incandescent, 62% fluorescent, and 26% HID. From that mix, it can be deduced that the lumens-consumption-weighted aggregate luminous efficacy of lighting in the U.S. in 2001 was 70.6 lm/W.

As discussed later in this appendix, a 100%-efficient (zero-ballast-loss) four-color RYGB SSL lamp with a color-rendering index of 90 (high enough to satisfy practically all white lighting applications) and a color temperature of 4000 K (intermediate between common incandescent and fluorescent lamps) can be calculated using a spreadsheet simulator [Ohno 2002] to have a theoretical luminous efficacy of 376.4 lm/W. Thus, *in comparison to this ideal SSL lamp,* the lumens-consumption-weighted aggregate efficiencies are: 3.7% for incandescent lamps, 18.8% for fluorescent lamps, 25.6% for HID lamps, and 18.8% for all lamps.[4]

In other words, relative to the 100%-efficient RYGB SSL lamp, 18.8% of the electricity consumed for lighting is converted to useful visible light, while 81.2% is wasted. Of the 765 TWh of electricity used for lighting in 2001, about 145 TWh were useful, while about 620 TWh were wasted. Of the $53 billion electricity cost to the end user for lighting in 2001, about $10 billion paid for useful electricity, while about $43 billion paid for wasted electricity. Similarly, of the projected $70 billion electricity cost to the end user for lighting in 2025, about $13 billion would be projected to pay for useful electricity, while about $57 billion would be projected to pay for wasted electricity.

If, instead of an aggregate efficiency of 18.8%, lighting had an efficiency of 50%, as envisioned by the Department of Energy Energy Efficiency and Renewable Energy Solid-State-Lighting Roadmap [Navigant 2006] for white SSL lighting by 2025, the impact would be enormous.

- The electricity required to create a given number of lumens would be decreased by 1-(0.188/0.50), or 62%. In 2001, the 765 TWh at a cost of $53 billion would have been decreased by 475 TWh for a savings of $33B. In 2025, the 1,000 TWh at a cost of $70 billion would potentially decrease by 620 TWh for a savings of $42 billion. This 620 TWh, averaged over a year, translates to 71 GW of average power; at about 1 GW per nuclear power plant, this represents a savings of the equivalent of 71 nuclear power plants.

- The savings in energy production by SSL would also be important for its impact on a cleaner environment. Currently, the U.S. emits approximately 1 Megaton of carbon-equivalent emissions to the atmosphere for every 6 TWh of electrical energy consumed. With this "carbon intensity,"

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[3] Aggregate luminous efficacy of a class of lamps was calculated by summing the luminous efficacies of all individual lamps within that class, weighted by the fraction of lumens that lamp produced relative to all lamps in that class in the U.S. in 2001.

[4] Higher efficiencies can be deduced in other ways. Greater than 5% efficiencies for incandescent lamps can be deduced by comparing such lamps with blackbodies whose spectral power distributions are truncated in the visible (say, 400–700 nm), rather than with ideal SSL lamps whose spectral power distributions have been optimized to the human eye response. Greater than 20% efficiencies for fluorescent lamps can be deduced by not including ballast losses. Because the focus of this volume is on the potential benefit of SSL, however, all efficiencies (both traditional incandescent, fluorescent, and HID lamps as well as current SSL lamps) are calculated relative to that of an ideal zero-ballast-loss high-CRI SSL lamp.

the U.S. would have saved in 2001 about 80 Megatons, and would potentially save about 100 Megatons of carbon-equivalent emissions in 2025.

Although the DOE-EERE SSL Roadmap goal of 50% system energy efficiency is aggressive and will be challenging, there is no known fundamental physical (e.g., thermodynamic) constraint to cap the efficiency even at this value. If near-100% power-conversion efficiency could be achieved, the economic and environmental benefits above would be even greater.

Impact on Human Visual Experience

SSL could enhance in many fundamental ways the human visual "experience" with lighting, and thereby enhance human functionality, safety, and comfort. Potential improvements in the quality of white lighting include steady color output at all levels of illumination, the ability to continuously vary output color temperature, simplified and flexible design for mounting fixtures (including the elimination of lossy luminaries and diffusers), low voltage, and safe power distribution.

A host of novel applications could also be enabled by SSL, for example [Schubert and Kim 2005]:

- The ability to create large-area, diffuse lighting or, perhaps, weaving strands of light-emitting material into fabrics using OLED technology open up new architectural possibilities for room designs and clothing.

- New interior design concepts are possible, such as integration with distributed color/intensity sensors for optimization of an entire lighting space.

- Lighting could be "personalized" in real time according to the preferences of an individual entering a room; for example, tuning of color preferences might be important for an aging population.

- Lighting could also be tailored to emphasize those features of the environment that are more desirable to notice at a given time.

- Mood enhancement may be possible by programming interior lights to change room color temperature throughout the day, corresponding to outdoor circadian cycles.

- Lighting could also be tailored for photopic versus scotopic (i.e., normal lighting vs. low-lighting) conditions.

TECHNOLOGY CHARACTERISTICS

Characteristics of Visible Light

The visible light produced from all sources, including solid-state, can be characterized by various quantitative metrics. This section summarizes those most relevant to SSL.

The *Spectral Power Distribution* (SPD), $P(\lambda)$, is the radiant power emitted by a source at each wavelength or band of wavelengths over the entire spectrum (e.g., in units of W/nm). The SPD provides a complete description of the spectral properties of a light source.

The color of a light source can be described by the Commission Internationale de l'Éclairage (CIE) chromaticity coordinates, calculated as follows. Figure A-4a displays the three *Color-Matching*

Functions, $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$, which define the "1931 CIE Standard Observer." The function $\bar{y}(\lambda)$ was defined to be identical to the photopic *luminous efficiency function*, V_λ, which describes the brightness perceived by the human eye of light of a particular wavelength under day-brightness conditions (the scotopic luminous efficiency function, which we do not discuss here, is the perceived brightness under night-brightness conditions). The other two Color-Matching Functions, $\bar{x}(\lambda)$ and $\bar{z}(\lambda)$, do not have such simple physical interpretations [Fairman, Brill, and Hemmendinger 1997; Brill 1998] but, together with the first, are necessary to determine the color of light, as described next.
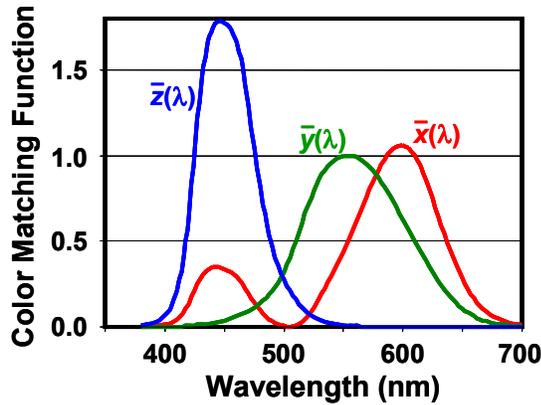
Figure A-4a CIE 1931 Color-Matching Functions.
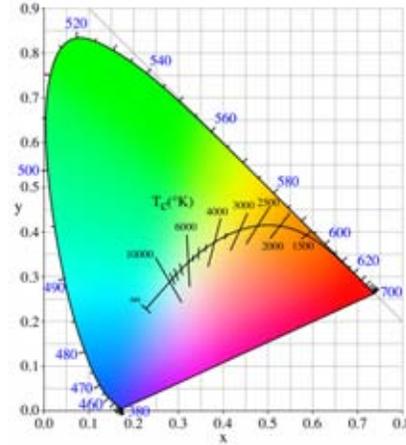
Figure A-4b CIE 1931 (x,y) Chromaticity Diagram.

The *tristimulus values X, Y*, and *Z* of a light source are defined as

$$X = k\int P(\lambda)\bar{x}(\lambda)d\lambda; \; Y = k\int P(\lambda)\bar{y}(\lambda)d\lambda; \; Z = k\int P(\lambda)\bar{z}(\lambda)d\lambda \;, \qquad (1)$$

where *k* is a proportionality constant. The *Y* value will be equal to one of the photometric quantities (such as luminous flux) of the light source if $k=K_m$ (K_m=683 lm/W) is used. The tristimulus values were derived such that *X=Y=Z* is equal-energy white.

The *chromaticity coordinates x,y* are calculated as *x=X/(X+Y+Z)* and *y=Y/(X+Y+Z)*. Any color of light can be represented on the CIE 1931 (*x,y*) chromaticity diagram, which is shown in Figure A-4b. The chromaticity diagram is a guitar-pick-shaped 2-D plot of all possible hue and saturation values of a light source, independent of luminance. The perimeter of the guitar pick is the locus of chromaticity coordinates for the spectral colors (i.e., monochromatic light, wavelengths in nm).

The black arc plotted in the interior of the chromaticity diagram gives the chromaticity coordinates of emission from a blackbody at temperatures between 1,000 K and infinity. It is called the Planckian locus and is a convenient way of representing a white light source. Positions along the Planckian locus can be specified by the temperature of the blackbody, called the *color temperature*, thereby reducing the hundreds of numbers in an SPD, or the two numbers of chromaticity coordinate, to a single number.

A nonblackbody source is often described by the *correlated color temperature* (CCT), which is the temperature of a blackbody radiator that most closely resembles the color from a source of equal brightness. Lines of a specified (constant) CCT would cross the Planckian locus at coordinates of that blackbody temperature, as indicated in Figure A-4b.

The terms "warm white" and "cool white" are often used in lighting discussions. "Warm white" is similar to light from an incandescent bulb and is somewhat yellow or red in appearance, whereas "cool white" has more of a pure white (or even blue) tone. Interestingly, "warm white" actually has a lower correlated color temperature (in the range of 2,700 K) than does "cool white" (with a CCT in the range of 4,100 K).

A powerful feature of the chromaticity diagram is that light produced by mixing output from two sources having different chromaticity coordinates will fall on the line connecting the coordinates of the sources alone; the position along the line is determined by the weighted average of the brightness of each source. Similarly, the chromaticity coordinate of light produced by mixing three light sources will fall within the triangle formed by the chromaticity coordinates of the three sources as the vertices. It is important to note that any color falling outside this triangle cannot be produced by mixing the three sources. The complete subset of colors that can be produced by mixing *n* light sources is referred to as the *color gamut*.

The definition of *luminous efficacy* depends upon whether one is referring to properties of (1) *radiation* (in which it is often more precise to use the term "luminous efficacy of radiation," LER) or of (2) a *source* that emits radiation. Both usages are expressed in lm/W. In the first case, Watts refers to the radiant power content of the radiation; in the second case, it refers to the amount of electrical power input to the radiation source. The second usage is directly related to the effectiveness of a device in converting input electrical power into visible light. Unless stated otherwise, the second usage is meant when discussing SSL and efficacy targets.

Luminous Efficacy of Radiation is a measure of the amount of radiant power (radiant flux in W) that can be observed by the eye as luminance (luminous flux in lm). The LER is determined by the sensitivity of the eye to different wavelengths of light, (i.e., the photopic luminous efficiency function, $V(\lambda)$) and the spectral power distribution (SPD, or $P(\lambda)$) of the radiation. For monochromatic light of wavelength λ, the LER is simply $K_{rad}(\lambda) = K_m \cdot V(\lambda)$, where K_m is a conversion factor relating radiant power (W) to luminous flux (lm) at the single wavelength (555 nm) at which $V(\lambda)=1$; this factor is 683 lm/W. Thus, the maximum possible luminous efficacy of radiation is, for monochromatic light at 555 nm (green), at the peak of the eye's responsiveness, 683 lm/W. For radiation with a distribution of wavelengths, the LER K_{rad} is found by integrating the product of the radiation's SPD, $P(\lambda)$, and the photopic luminous efficiency function, $V(\lambda)$, over all wavelengths, and normalizing by the total amount of radiant power:

$$K_{rad} = K_m \frac{\int P(\lambda)V(\lambda)d\lambda}{\int P(\lambda)d\lambda}. \tag{2}$$

The *Luminous Efficacy of a Source* is a measure of the amount of radiant power emitted by a source that can be observed by the eye as luminous flux divided by the electrical power that is input into the source (W_{in}), normalized by the same constant K_m used above. Thus, the luminous efficacy of a source, such as an LED or OLED, is given by

$$K = K_m \frac{\int P(\lambda)V(\lambda)d\lambda}{W_{in}}. \tag{3}$$

Manipulating the two formulas above, it is easy to see that the luminous efficacy of a source K is just the LER multiplied by the "wall-plug efficiency" (WPE), where

$$\text{WPE} = \frac{\int P(\lambda)d\lambda}{W_{in}}. \tag{4}$$

The *Color Rendering Index* (CRI) is a metric for color quality. It takes a subjective measure and attempts to quantify it. The CRI gauges how colors of certain standard reference objects appear when illuminated by a test light source, compared to the colors observed under illumination by a reference light source of the same correlated color temperature; if there were no difference between the colors rendered by the reference and test light sources, the test source would have a CRI of 100. Light from a standard incandescent light bulb has a CRI near 100. CRI is calculated from the SPD of the test light source. To evaluate the CRI of real light sources, the SPD must be measured, although mathematical models exist to simulate the SPDs of various white LEDs [Ohno 2004].

Recently, there has been some discussion about the adequacy of the current CRI scale. One problem is that it is based on an obsolete color space (the 1964 W*U*V* color space), which is no longer recommended for use. Another problem is that it is based on eight reference samples of low-to-moderate color saturation. On the one hand, this causes some Red Green Blue (RGB) LEDs to have high CRI scores even though they render some poorly saturated colors. On the other hand, RGB white LEDs tend to enhance color contrast, which is generally preferred and can be an important feature of SSL, but is currently penalized by the present CRI system [Ohno 2004]. To solve these problems, new metrics are being proposed (e.g., see Davis and Ohno 2005). Since color quality is very important for acceptance of SSL products in the marketplace, these problems need to be studied further with visual experiments. The CIE Technical Committee 1-62 "Colour Rendering of White LED Light Sources" is investigating problems with the CRI scale, with a plan for developing a new metric.

Cost of Light: Capital and Operating Cost Breakout

The Cost of Light (COL) is the total cost of ownership for an SSL LED, that is, the sum of the purchase, maintenance, and operating costs over its entire lifetime. The commonly accepted formula for calculating the COL is [IESNA 2000; Navigant 2006]:

$$CostofLight = \left(\frac{1}{LampLumens}\right)\left(\frac{LampCost + LaborCost}{Lifetime} + EnergyUse \times EnergyCost\right), \tag{5}$$

where *CostofLight* is the total cost of the light over its operational lifetime (in \$/10^6 lmh); *LampLumens* is the light output of the lamp (in 1,000 lumens); *LampCost* is the initial cost of the lamp (in \$); *LaborCost* is the labor cost to replace the lamp (in \$); *Lifetime* is the useful life of the lamp (in 1,000 h); *EnergyUse* is the power consumption of the lamp (in W); and *EnergyCost* is the cost of electricity (in \$/kWh). For SSL, the useful lifetime of the lamp is often measured at 70% lumen maintenance; the labor cost is typically taken to be \$1 for a 1 klm lamp, which is used in our analysis.

In the formula above, the first term in the second set of parentheses determines the Capital Cost, and the second term determines the Operating Cost; the sum of the two determines the Cost of Light.

The COL for different white-lighting technologies is displayed in Figure A-5; cost is plotted in units of dollars per million lumen hours. The three solid curves represent contours of constant COL. In Figure A-5, the triangle, square, and diamond symbols represent the highest market-value incandescent, fluorescent, and high-intensity discharge (HID) lamps, respectively.[5] Of the three traditional lighting technologies, incandescent has the highest COL, because of low luminous efficacy (high operating cost).

Three representative SSL white lights are shown in Figure A-5. The point labeled "High CRI LED 2006" is a Lumileds LXHL-BW03 "Warm White" emitter. The two points labeled "Low CRI LED 2006" represent Lumileds K2 series emitters driven at 0.35 A and 1.0 A (note that, as can be seen in Table A-1 at the end of this appendix, these two LEDs have similar COL. Driving the LED "harder" produces more lumens, so the capital cost of the lamp decreases; but the luminous efficacy decreases, so operating cost increases).[6] The point labeled "WOLED" (for "white OLED") is taken from the 2002 OLED Roadmap [OIDA 2002], although no WOLEDs are being manufactured for lighting, rendering this point very speculative.
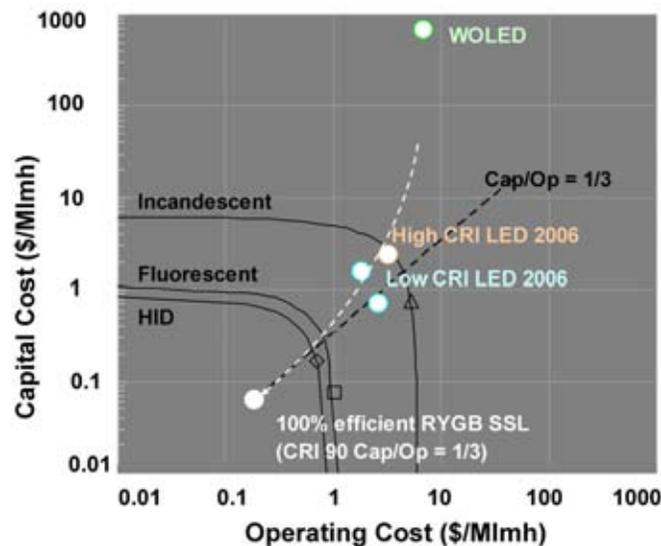
Figure A-5 Factors contributing to SSL total cost of light. The SSL data in this and subsequent figures are gathered in Table A-1.

The 100% efficient SSL point corresponds to the maximum possible luminous efficacy of 376.4 lm/W, calculated using a spreadsheet simulator developed by Ohno [2002], of a red, yellow, green, blue (RYGB) source with a CRI of 90, a CCT of 4,000 K, and full-width-half-maximum (FWHM) spectral linewidths of 20/20/30/20 nm, respectively. The center wavelengths of the RYGB sources, which the spreadsheet determines as it maximizes luminous efficacy, were found to be 612/572/531/459 nm, respectively. Given this luminous efficacy, the operating cost can then be calculated, assuming an electricity cost of $0.07/kWh, to be ($0.07/kWh)/(376.4 lm/W) = $0.186/Mlmh. Finally, to estimate a capital cost, we assume a capital to operating cost ratio of 1/3 — somewhat higher than those of common incandescent (1/5.8), fluorescent (1/8.0), and HID (1/6.3), but low enough for the capital cost to be a small fraction (1/4) of the overall cost of light.

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[5] Based on published market analysis [Navigant 2002].
[6] All luminous efficacies are "typical" as quoted on the published specification sheets.

Cost of Light: Luminous Efficacy and Power Delivery Breakout

Another way of characterizing white lighting technologies is displayed in Figure A-6, in which the abscissa and ordinate correspond more directly to quantities the technologist can impact.

The first of these quantities is the "power delivery cost," which is the capital cost to make a lamp that can be driven at a certain power ($/kW$_{in}$). It reflects the fact that the more power one can supply to a lamp, the greater the light output, but at a higher manufacturing cost (heat sinking the device being one important driver). The second of these quantities is luminous efficacy (lm/W$_{in}$).

Note that these two quantities, together with the lamp lifetime, are sufficient to determine the various components of the COL introduced earlier in Equation 5. *EnergyUse/LampLumens* is just the reciprocal of luminous efficacy; *LampCost* / (*LampLumens* x *Lifetime*) is just power delivery cost over luminous efficacy, divided by the lamp lifetime.

Figure A-6 Relationship between luminous efficacy and power delivery cost for different lighting technologies.

The solid curves are contours of fixed COL. The meanings of the symbols are the same as in Figure A-5. The 100% efficient SSL point corresponds to the maximum possible luminous efficacy of 376.4 lm/W for an RYGB source with CRI 90 and CCT 4,000 K. The high-CRI commercial device from Figure A-4 is also plotted, to give a sense for the very large (22.4x) gap in COL that separates current SSL technology from its potential. The low-CRI data points from Figure A-4 are not plotted, so as not to convey a false sense of this gap: by sacrificing color-rendering quality it is possible to decrease COL (either by increasing luminous efficacy or decreasing power delivery cost), but at the expense of not being able to satisfy many white-lighting applications. A hypothetical "trajectory" for improving SSL is perpendicular to the contours of constant COL, shown schematically as the dashed white curve.

This trajectory will require a much larger (17.3x) increase in luminous efficacy than it will a smaller (3.2x) decrease in power delivery cost. The current luminous efficacy of 21.7 lm/W is only 5.8% of the ideal luminous efficacy of 376.4 lm/W.

Luminous Efficacy

Luminous efficacy and wall-plug efficiency of LEDs are strong functions of emission wavelength, as illustrated in the top and middle portions of Figure A-7, respectively. For several of the lamps, the luminous efficacy and the electrical-to-optical power-conversion efficiency are plotted for output at more than one drive current and voltage.[7]

Note that for LED devices, wall-plug efficiency drops significantly as emission approaches the deep green and yellow regions. Efficiency in the nitride materials goes down because of the difficulty of attaining high indium composition (which shifts emission to longer wavelength) while still maintaining good material quality. (Generally, achieving high-In content requires low growth-temperatures, resulting in poor quality material with greatly increased defect densities.) Phosphide LED emission drops sharply as the Al content x increases, where the alloy composition is $(Al_xGa_{1-x})_{0.5}In_{0.5}P$; increasing Al fraction pushes emission to shorter wavelengths. In this alloy system, the drop in emission with increasing x is because the X-valley drops in energy relative to the Γ-valley, leading to an increasing number of electrons involved in indirect transitions, which are not radiative. The bandgap crosses over from direct to indirect near x=0.5, leading to a nearly complete suppression of light emission.

Although the wall-plug efficiency of these visible-light LEDs has a minimum in the region near 550 nm, the luminous efficacy of this series of LEDs is highest in this range (upper portion of Figure A-7). This is simply because the human eye response to light (also plotted in the top part of Figure A-7) is most sensitive at 555 nm.

High CRI is best achieved by a broad spectral distribution of light covering the entire visible range. Mixing a small number of different wavelengths of light (e.g., three or four) to approximate natural white light decreases the CRI (<100), but improves the luminous efficacy by concentrating the light output to subsets of the spectrum. Thus, there is a fundamental trade-off between CRI and luminous efficacy for any light source.

For a given CRI, one can calculate the combination of RGB or RYGB wavelengths that would give the maximum luminous efficacy. These wavelength combinations are given in the bottom portion of Figure A-7. This plot was generated using a white LED simulator [Ohno 2004]. (The calculations assume that the source full-width at half maximum power is 20 nm for the red, yellow, and blue sources and 30 nm for the green, and CCT = 4,000 K.) The black dotted line in this plot represents the approximate upper limit of CRI that can be obtained using the three-color (RGB) approach.

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[7] The blue and beige lines correspond to the Lumileds Low CRI and High CRI white LEDs, respectively. For the nitride-based LEDs (colored symbols in the range 455 to 530 nm), the data correspond to: 0.35 A, 1.2 W (higher luminous efficacy points), and 1.0 A, 3.7 W.
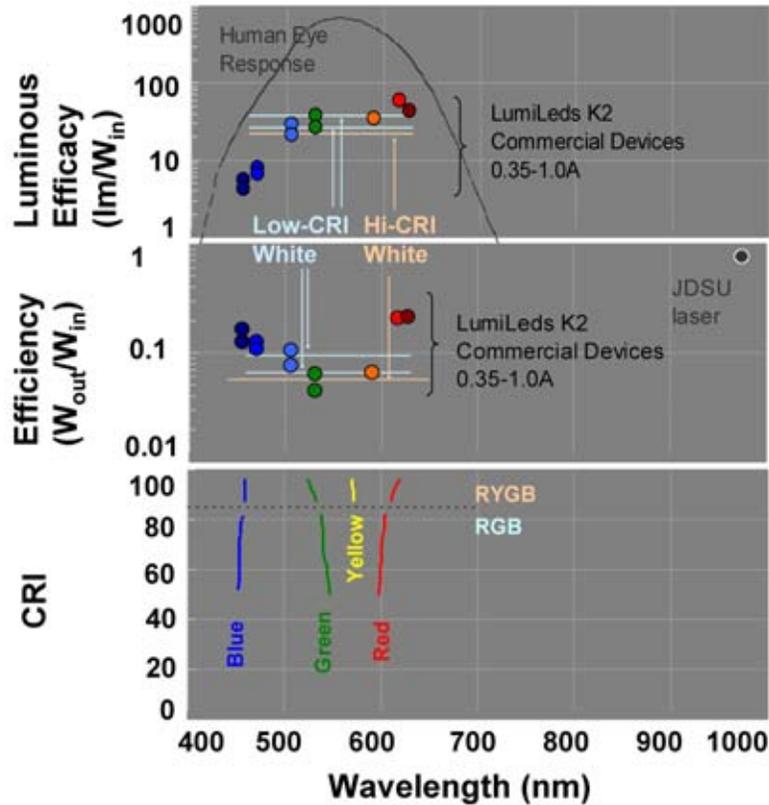
Figure A-7 (Top) Luminous efficacy as a function of wavelength of commercially available LEDs. (Middle) External energy conversion efficiency as a function of wavelength of commercially available LEDs, and a high-efficiency (76%) research laser from JDS Uniphase [Peters 2006]. (Bottom) LED wavelengths that give the best luminous efficacy for a specified CRI.

The CRI vs. luminous efficacy for current light sources is shown in Figure A-8. The two steep, solid (blue and beige) curves near the right of Figure A-8 represent the maximum theoretical luminous efficacy that could be obtained from either an RGB or RYGB color combination scheme. For example, for a CRI of 50, the maximum luminous efficacy that can be achieved is 421 lm/W; for a CRI of 70, the maximum luminous efficacy is 404 lm/W; for a CRI of 85, the maximum luminous efficacy is 386 lm/W; for a CRI of 90, the maximum luminous efficacy is 376.4 lm/W (values at CCT = 4,000 K).

CRI and luminous efficacy are shown for several different incandescent (triangle symbols), fluorescent (squares), and high-intensity discharge (diamonds) lamps; the areas of these symbols are proportional to usage in Tlmh/yr (Teralumen hours per year). Of the three traditional white lighting sources, incandescent lamps have the highest CRI, but the lowest luminous efficacy. Fluorescent lamps and high-intensity discharge lamps provide lower CRI, but much higher luminous efficacy. Also plotted are data from two current commercial LEDs (the high-CRI and low-CRI devices from Lumileds discussed in previous plots). The dashed white and blue curves in Figure A-8 are hypothetical technology evolution curves that would eventually achieve both a high CRI and the maximum possible luminous efficacy.
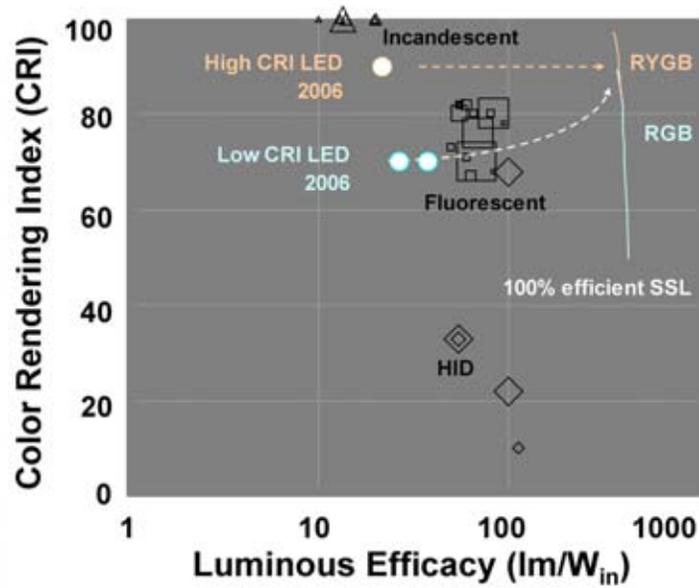
Figure A-8 Map of Color Rendering Index vs. Luminous Efficacy for different white-lighting technologies.

Power Delivery Cost

The power delivery cost can be further broken down into the ratio of the maximum input power density to the device (W_{in}/cm^2) and the capital cost of making the LED normalized to its chip area ($\$/cm^2$), illustrated in Figure A-9. As the figure illustrates, different approaches can achieve the same ratio.

WOLEDs, for example, have very low lamp cost per chip area, but also very low chip power density. High-power lasers have high lamp cost per chip area, but also high chip power density. Conventional low-power LEDs have medium lamp cost per unit chip area, and medium chip power density.

In 2006, the high-CRI device lies between the low-power LEDs and the high-power lasers, and one can ask the question whether there is more "room" for the technology to improve by lowering its lamp cost per chip area or by increasing its chip power density. Normally these quantities are strongly coupled (i.e., increasing chip power density usually means increasing lamp cost per chip area). A technology "breakthrough" or "shift" would be needed that allows one either to lower lamp cost per chip area without decreasing chip power density, or to increase chip power density without raising lamp cost per chip area.

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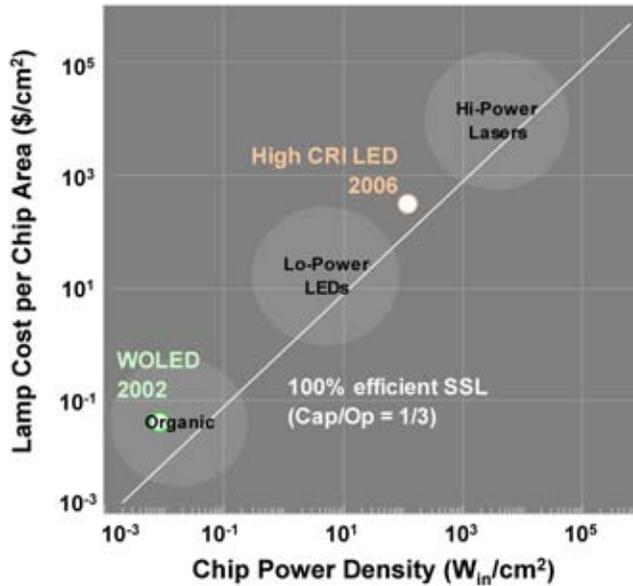
Figure A-9 Trade-off between LED lamp cost and maximum power input.

INORGANIC LIGHT-EMITTING DIODES

SSL technologies based on inorganic LEDs start with inorganic direct bandgap semiconductors that emit in the visible spectrum. There are two inorganic LED-based architectures in use for white lighting, as discussed below.

White-Light Creation Architectures

The entire spectral range of visible light can be produced by III-V semiconductor LEDs. AlGaInP LEDs can cover the spectral range from red to amber, and their commercial production is relatively mature. AlGaInN LEDs are the prime candidates for producing wavelengths from blue to yellow. Two main approaches for producing white light are being pursued:

Color Mixing. This approach mixes output from three (or possibly four) different colors of LEDs. First, it has the potential for higher luminous efficacy, provided that efficient LEDs of the constituent colors can be developed; there is no Stokes loss from energy down-conversion, as in the blue + phosphor or photon-recycling approaches. Color rendering index will be highest by blending output from at least three different wavelengths. However, substantial problems still exist with this approach. A major limitation is that *efficient green and yellow LEDs are still not currently available*. A second problem is that LEDs of different colors tend to age and degrade at different rates. Over time, the color balance and color rendering quality of a multi-LED white light may decay significantly; electronic solutions exist, but at a cost. Third, uniform color mixing can be a problem; color variation in the far-field pattern depends on architecture. Fourth, even in the blue, overall efficiencies are far from 100%, and they decrease significantly when driven at high currents.

Wavelength Down-Conversion. By using light from a blue LED to excite fluorescence from a yellow phosphor, the combination of blue and yellow produces white light. Because of the early development of blue LEDs and ready availability of yellow phosphors, the first white LED products, for example flashlights, have used this scheme. The current state-of-the-art uses an InGaN LED emitting at about 460 nm to excite a cerium-doped yttrium aluminum garnet (YAG) phosphor, which is ground into a powder

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and dispersed in an epoxy cap on the device. There is an unavoidable Stokes energy-loss in converting a blue photon to a lower-energy yellow photon. The color quality in this approach can be enhanced, making it closer to that of incandescent lamps, by adding a red phosphor to improve CRI.

Ultraviolet (UV) LED pumping of RGB phosphors is another possible down-conversion approach. This scheme would potentially be simple to manufacture; it is similar to a television or fluorescent lamp, with electron excitation replaced by a UV LED. Excellent color rendering would be possible, but with fundamental limitations on efficiency because of phosphor conversion efficiency and Stokes loss. In addition, LED packaging material would degrade more quickly from exposure to high-energy near-UV photons.

Wavelength Conversion Materials

Rare-Earth Phosphors. Inorganic phosphors doped with rare-earth metals are used for a variety of applications. A wide array of these phosphors has been developed for use with fluorescent lamps. The first SSL white LEDs have used an yttrium aluminum garnet doped with trivalent cerium (YAG:Ce^{+3}) to convert output from a blue LED into very broad-band yellow light. The sum of the two emissions appears white. For efficient white lighting with good color rendering, quantum efficiencies >85% (for phosphors absorbing in the near-UV) at operating temperatures >155 ^{o}C (for phosphors in intimate contact with the LED) will be needed.

A red-emitting phosphor centered near 610 nm with narrow band emission (required because of the steep drop-off in human eye sensitivity at longer wavelength) and absorption in the near-UV or blue region has been difficult to achieve. Broader-band emission is acceptable in the green region because of the eye's sensitivity to a wider range of wavelengths in this region. Phosphors based on divalent europium (Eu^{+2}) are available in the green and even into the blue emission region.

Photon Recycling Semiconductors. This approach is a photon down-conversion scheme similar to using yellow phosphors, in which an AlGaInP photoluminescent quantum well (QW) or active layer is laminated to a GaN LED. Some of the blue emission from the GaN chip is absorbed in the phosphide layer, which emits complementary yellow light. The combined blue and yellow emission produces white light.

Semiconductor Nanoparticles. White light can be produced using semiconductor nanoparticles. For example, the band-gap of CdS nanoparticles can be tuned over the entire visible spectrum by the changing their size (because of quantum confinement effects) and surface characteristics (e.g., coating the nanoparticles with ZnS, or changing the nature of chemical groups bonded to the nanoparticle surface).

Light-Creation Materials

Different families of inorganic semiconductor materials can contribute to solid-state white lighting. The primary chemical systems used for LEDs are Group-III nitrides and Group-III phosphides. It is, however, possible that breakthroughs in a different material system, for example ZnO, will be important.

AlGaInN Materials. LEDs based on gallium nitride (GaN) and ternary alloys with indium (InGaN) and aluminum (AlGaN), as well as quaternary alloys (AlGaInN) can span the entire visible spectrum. The current applications for SSL utilize InGaN structures to produce high brightness blue and green light; longer wavelength light can be efficiently generated by AlGaInP LEDs. UV light from AlGaN LEDs could also be used to pump RGB phosphors, as mentioned above. A schematic of a current nitride LED is shown in Figure A-10.
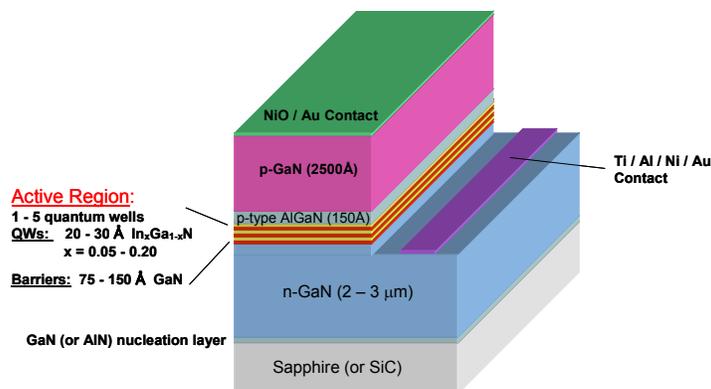
Figure A-10 Schematic of a nitride LED.

Nitride materials are usually grown by Metal Organic Vapor Phase Epitaxy (MOVPE)—also referred to as Metal Organic Chemical Vapor Deposition (MOCVD)—from organometallic sources (e.g., trimethyl-gallium, -indium, or -aluminum) and an excess of ammonia. A major difficulty is the lack of low-cost, single-crystal GaN to use as a growth substrate. Group-III nitrides are normally grown on poorly matched sapphire (lattice mismatch +16%, thermal expansion mismatch +39%) or more expensive silicon carbide (lattice mismatch -3.5%, thermal expansion mismatch -3.2%) substrates. As a result, the films have a great number ($>10^8$/cm^2) of dislocations and other structural defects, resulting in defect-mediated nonradiative recombination of electron-hole pairs and reduced mobility because of carrier scattering from charged defect centers. An intermediate buffer (or nucleation) layer is normally grown at reduced temperature between the substrate and the n-GaN layer (a GaN nucleation layer on sapphire substrates, or AlN on SiC). This low temperature buffer reduces defect densities from up to 10^{12} to 10^9/cm^2. Further defect reduction (by roughly two orders of magnitude) can be achieved by substrate patterning techniques such as Epitaxial Lateral Overgrowth, Pendeo Epitaxy, or Cantilever Epitaxy; these approaches rely on spatial "filtering," terminating, and/or turning of threading dislocations, so they do not reach the device active region.

GaN is readily n-doped with Si (usually using a silane source). However, p-type doping with Mg (usually using the metal organic precursor bis-cyclopentadienyl magnesium, Cp$_2$Mg) is much more difficult, because of passivation by hydrogen during growth, and the magnitude of the hole ionization potential associated with Mg. Depassivation of the Mg acceptors is achieved by thermal annealing or low-energy electron beam irradiation.

Indium incorporation pushes emissions to longer wavelengths; indium fractions greater than 20% are required for green LEDs. This represents a significant challenge in material growth. Low temperatures are required for In incorporation because of lower thermal stability, leading to poorer material. As In composition increases, lattice-mismatch strain also increases, leading to a variety of strain-induced defects (e.g., point-defects, v-defects, and carbon and oxygen impurities) and lower optical efficiencies.

AlGaInP Materials. The $(Al_xGa_{1-x})_{0.5}In_{0.5}P$ alloys are nearly lattice matched to GaAs, and production of LEDs emitting from 555 nm (yellow-green) to 650 nm (deep red) is a relatively mature technology. The availability of single crystal GaAs substrates enables growth of high-quality phosphide material by MOVPE. But the bandgap of GaAs is 1.42 eV (870 nm) at room temperature, so this substrate absorbs emitted light below this wavelength, greatly lowering the LED efficiency. Two solutions to this problem are illustrated in Figure A-11.

One way to prevent absorption of emitted light by the substrate is to insert a reflective structure between the LED active region and substrate, illustrated in the left portion of Figure A-11. The mirror structure is a Distributed Bragg Reflector (DBR), consisting of many (e.g., 5 to 50) alternating high-refractive index and lower-refractive index layers. Because of the differences in refractive indices, a portion of the downwardly directed light is reflected upward (and out of the device) at each layer interface. The mirror stack thicknesses are adjusted so that all of the reflected waves are in constructive interference. The DBR is highly effective for light incident normal to the DBR plane; glancing incident light, however, is only partially reflected by the DBR.
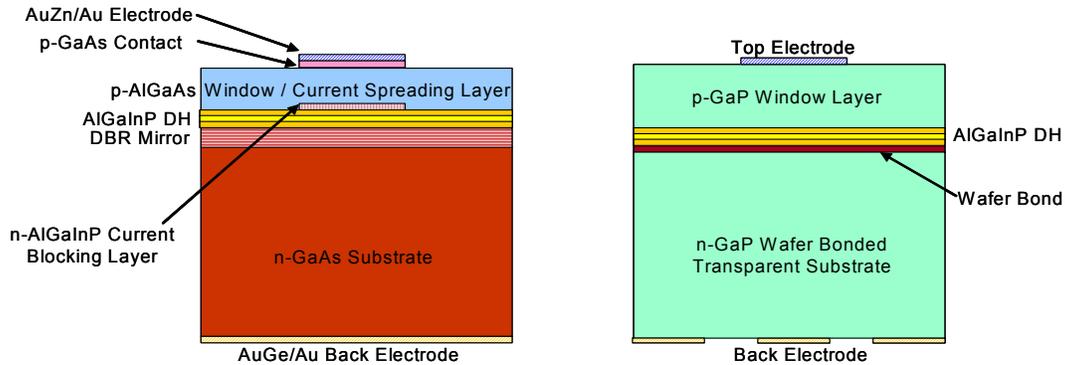
Figure A-11 (Left) AlGaInP LED with DBR mirror for improved light extraction. (Right) AlGaInP LED wafer-bonded to transparent GaP substrate.

Another approach is to remove the GaAs substrate after the epitaxial layers have been grown, and then to bond the remaining structure to a transparent GaP substrate. The resulting structure of a wafer-bonded LED is shown in the right half of Figure A-11. Total light extraction from the wafer-bonded AlGaInP LED can be more than a factor of two greater than the LED + DBR design.

For low Al fraction, the internal quantum efficiency approaches 100%. $(Al_xGa_{1-x})_{0.5}In_{0.5}P$ is a direct bandgap semiconductor for $x < 0.5$; above that composition, it is an indirect-gap material. The crossover occurs at bandgap energy of about 2.23 eV (555 nm). Thus, the AlGaInP LED quantum efficiency drops precipitously (Figure A-7) at shorter wavelengths because of the approach of the direct-indirect bandgap crossover. That is, as the indirect-gap X-band becomes more populated, the radiative lifetime increases, allowing other nonradiative processes to become more dominant. Efficiency also drops at higher drive currents and operating temperatures because of poor carrier confinement in heterostructures as the direct-indirect-gap crossover is approached.

ZnO Materials. ZnO-based alloys are another possibility for generation of light from the visible to the near-UV. ZnO has a number of physical properties that make it a good potential candidate for SSL. However, progress toward making it a practical material is still at an early stage.

The material is a wide-bandgap semiconductor (3.4 eV, comparable to the 3.5 eV of GaN) with a wurtzite crystal structure. Single-crystal ZnO can now be produced, and commercial 2 inch wafers are available, offering the possibility of homoepitaxy. The material can be etched by wet chemical means, making it relatively easy to process. Because ZnO has a high exciton binding energy (60 meV, compared to less than 30 meV for GaN), higher operating temperatures are possible.

ZnO has a high intrinsic n-type conductivity, the source of which is not known. It has been difficult to obtain p-doping; although there has been good recent progress, consistency is still hard to achieve. Growth of high-quality ZnO films and heterostructures is still being developed. It may be possible to tune the bandgap of ZnO by alloying with MgO (7.9 eV bandgap) or CdO (2.3 eV). However, these two oxides have cubic crystal structures, so it may be difficult to add large fractions to ZnO without introducing dislocations. Further, the use of the heavy metal Cd in commercial LED structures may not prove acceptable because of long-term safety and environmental issues.

Light-Extraction Approaches

In principle, 100% of the light could be extracted from an LED, but the current state-of-the-art light-extraction efficiency is about 50%. Limitations in light extraction include internal reflection at interfaces and light absorption within the device or in the packaging. Figure A-12 shows some light-extraction methods.
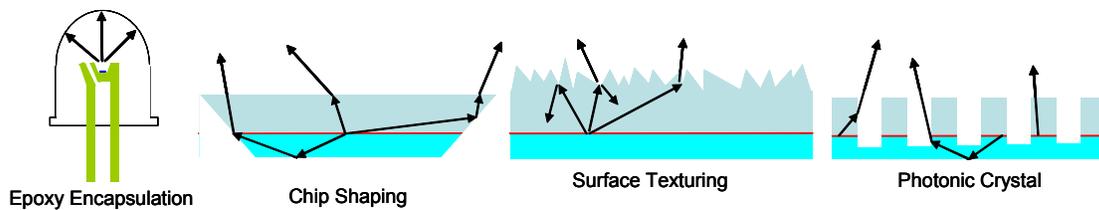
Figure A-12 Some LED light extraction schemes.

Encapsulation can reduce the index step between the semiconductor and air, creating a favorable geometry. High-index encapsulants are desirable. Limitations of this approach include transparency and degradation of epoxy encapsulants from exposure to high temperatures and intense radiation. For this reason, silicone encapsulants are replacing epoxy.

Chip shaping has been used to increase light extraction from LEDs. Lumileds used an inverted pyramid shape to boost light output from a red (AlGaInP) LED to achieve wall-plug efficiency as high as 50%. Cree has also used chip shaping to increase efficiencies in their commercial blue and green LEDs.

Surface texturing produces random scattering at the surface, increasing the likelihood that light will encounter a surface within its escape cone, thus increasing light extraction.

Photonic crystals can be used in multiple ways to increase light extraction. Two-dimensional photonic crystals can be used to scatter waveguided modes out of the active layer region. Another approach is to use 2D photonic crystals to change the photonic density of states in the active layer so that no in-plane modes are permitted. This would cause all emitted light from the quantum wells to be normal to the LED surface so that it would lie within the escape cone and not be reflected. A third possibility is to increase the internal quantum efficiency by enhancing the photonic density of states at the LED emission wavelength. Finally, 3D photonic crystals could be utilized as highly reflective mirrors for resonant cavity LEDs and laser diodes, which are described below.

Resonant cavity LEDs or *lasers* pumping phosphors have the potential to be efficient white-light sources. Resonant cavity LEDs and lasers have the highest energy conversion efficiency of all optoelectronic devices (76% reported for a laser in the infrared). Despite inherent energy loss because of photon down-conversion from exciting phosphors, the net luminous efficacy of this scheme could be very high.

However, capital costs to manufacture these complex devices may make them too expensive to be practical.

Thermal Management

Junction temperature of an LED affects luminous efficacy, color, and reliability. As high brightness LEDs are driven harder, managing the heat from the semiconductor will be increasingly important.

Epoxy encapsulants quickly degrade if the temperature exceeds the epoxy glass transition temperature. This can lead to device failure modes.

An increase of 75 ^{o}C can reduce luminous flux in AlGaInP LEDs to one-half the room temperature value; however, a similar increase in temperature reduces emission intensity of a 470 nm GaInN/GaN LED by only about 5% [Schubert 2003]. The dominant emission wavelength of a phosphide-based LED shifts to longer wavelength with increasing junction temperature, about one nanometer for every 10 ^{o}C [Lumileds 2002]; the shift in emission wavelength of a 400 nm nitride LED is about a factor of three smaller [Cho et al. 2000]. (To put these wavelength shifts into perspective, the human eye can detect wavelength shifts as small as 2 nm to 4 nm, depending upon the color; this is the wavelength discrimination function.)

Removing excess heat from the lamp consists of two or more components of thermal resistance in a serial configuration. As part of the packaging, the LED die is attached to a metal slug (e.g., aluminum or copper) to conduct heat away from the lamp. Depending on the end use, the lamp might be connected to a printed circuit board or other electrical mounting system. In any case, thermal management of heat flow from the lamp package through the mounting and then to the surrounding ambient must be an engineering consideration for any application.

ORGANIC LIGHT-EMITTING DIODES

Organic light-emitting diodes (OLEDs) are based on small molecules [Tang and Van Slyke 1987], dendrimers [Halim et al. 1999], or polymers [Burroughes et al. 1990]. OLEDs have significant potential for low-cost manufacturing and enable novel lighting architectures such as curved light-emitting surfaces. Issues of particular relevance to OLEDs include carrier injection and transport, exciton formation, utilization, and conversion to light, operating lifetime, encapsulation, and light extraction.

White-Light Creation Architectures

The two dominant material sets for white-light OLEDs are small molecule (discrete molecular units with relatively weak inter-molecular bonding) and polymer (covalently bonded repeat units where addition or subtraction of one repeat unit does not significantly affect the properties of the molecule). While OLEDs typically have broad emission spectra, they are not sufficiently broad for white light (the exception is emission from excimers or exciplexes, which is usually relatively inefficient). General lighting, therefore, requires, as with inorganic LEDs, mixing the light from at least two sources by either pumping a down-conversion phosphor, combining two or three electroluminescent devices on a substrate using lateral patterning, co-doping a single layer with spatially separated multiple chromophores, or stacking multiple devices using transparent intervening electrodes to generate coaxial color mixing. Compared to inorganic LEDs, organic devices offer more potential for stacked geometries because lattice matching and strain are essentially irrelevant. However, patterning is more of a challenge since organic semiconductors are typically damaged by photolithography chemicals such as resists, etchants, and solvents. OLEDs are fundamentally broad-area emitters requiring relatively large-area substrates to generate the lumen output required for general lighting; however, the lower operating current density makes heat dissipation less of

a limiting issue. The large-area, low-brightness characteristic also potentially eliminates the need for a luminaire, since there is no dazzle from such a distributed source. This not only saves capital cost, but also increases their *effective* efficiency, since the reflector and diffuser enclosure required for a point source reduces the lighting system efficiency by 30% to 50%.

Small-Molecule OLEDs (SM-OLEDs). The most efficient OLEDs are currently based on "small molecule" materials (referred to as SM-OLEDs); a schematic of a SM-OLED is shown in Figure A-13. SM-OLEDs consist of many layers in a structure such as:

1. Substrate, which is usually transparent. However, it is possible to make either or both electrodes of an OLED transparent [Burrows et al. 2000], so in some cases opaque substrates such as metal foil can be used.

2. A transparent anode through which light is usually emitted; indium tin oxide (ITO) was originally used, but more complex compounds such as zinc indium tin oxide with more optimal work function properties are now common in the displays industry.

3. A hole-injection layer (HIL) such as Poly(3,4-ethylenedioxythiophene)-Polystyrene (PEDOT-PSS) or copper phthalocyanine

4. A hole-transport layer (HTL), such as N,N'-bis-(1-naphthyl)-N,N'-biphenyl-4,4'-diamine (NPD)

5. An emissive layer (EML) containing fluorescent and/or phosphorescent dyes usually doped into a host matrix, discussed separately below

6. An electron transport layer (ETL), e.g., tris(8-hydroxyquinolinato) aluminum (Alq_3); perhaps with an additional hole-blocking molecule, e.g., bathocuproine (BCP), either added to this layer or as a separate exciton and hole-blocking layer (HBL) between the EML and ETL layers to minimize carrier leakage and exciton quenching at the cathode

7. A cathode consisting of a thin layer of LiF capped with aluminum. In top-emitting architectures, the cathode is transparent, permitting the use of extremely low-cost substrate materials, such as metal foil.

SM-OLED organic layers are usually grown by vacuum deposition (also known as vacuum thermal sublimation) in which organic source molecules are heated to sublimation within a vacuum chamber (base pressure around 10^{-6} Torr), for deposition on a substrate that is usually close to room temperature. (Active cooling is typically not required because of the relatively low temperature of the source materials.) The vacuum equipment required represents a high capital cost but is capable of coating large areas and achieving high product throughput, since lattice-matching constraints are absent for this materials system. Another growth technique that has been applied recently is organic vapor phase deposition (OVPD), in which a carrier gas transports organic molecules within a hot-walled, low-pressure (0.1–1 Torr) growth chamber onto a cooled substrate [Baldo et al. 1998]. This method yields higher deposition efficiency than vacuum deposition, since only the substrate is coated while the reactor walls remain clean; this may also reduce downtime for cleaning and allow for an extra degree of control over thin film morphology. However, this, and the related technique [Sun, Shtein, and Forrest 2005] of organic vapor jet printing (OVJP), are very new, and the limits on deposition rate over large areas, throughput, and therefore cost are still unclear.
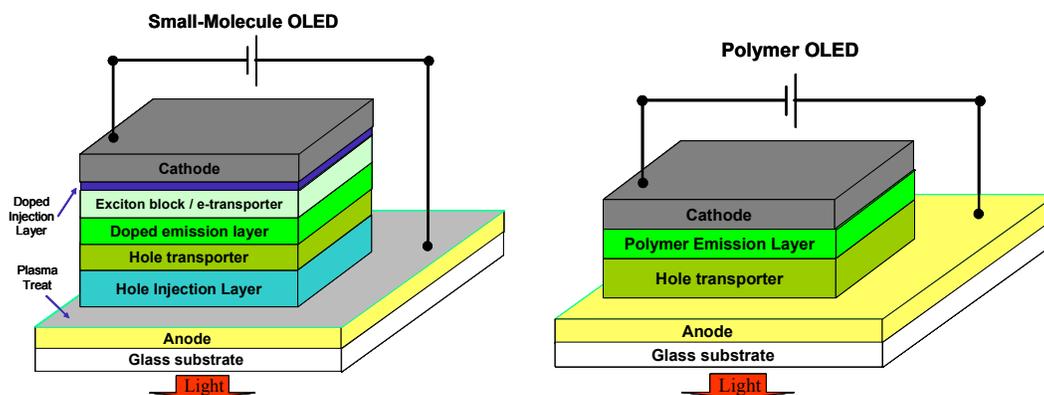
Figure A-13 Schematic diagram of a small-molecule OLED (SM-OLED) and a polymer OLED (PLED).

Solution-based processing for small molecule materials is now also being developed. Branched molecules known as dendrimers have generated particular recent interest for this processing method and are claimed to combine the best features of small molecule and polymeric materials.

The operating lifetime of OLEDs is inversely proportional to the operating current density, which may be of concern for high-brightness lighting applications. Recent results on single-color OLEDs, however, show promise. For example, Universal Display Corporation (UDC) has developed a sky blue (CIE 0.16,0.37) OLED with 100,000 hour lifetime at 200 cd/m^2 and luminous efficacy of 20 cd/A, and a deeper blue (CIE 0.16,0.29) device with a 17,500 hour lifetime at 200 cd/m^2 and 21 cd/A luminous efficacy. In early 2006, Thompson (U. So. Cal.), Forrest (U. Michigan), and UDC announced white OLEDs using (a) side-by-side RGB stripes or (b) mixed phosphors within the same EML, each with luminous efficacy of 20 lm/W at 800 cd/m^2.

Polymer OLEDs (PLEDs). An alternate approach is to use a single polymer-containing emission layer between two electrodes to produce a PLED (polymeric LED), shown schematically in Figure A-13. Polymers can be deposited over broad areas with relatively simple solution-based approaches such as spin casting or doctor-blading, which are less capital-intensive than vacuum deposition. The need to pattern more than one color of device on a single substrate has led to the further development of ink-jet printing techniques.

The limits to the manufacturing cost of such techniques over the large areas required for lighting is unknown. A further challenge of the solution process is the difficulty of making multilayer heterostructure devices, which can give higher efficiency but require either polymers with orthogonal solvent systems or polymers that can be cross-linked by thermal treatment. Currently, PLEDs are less power efficient than small-molecule devices. This is primarily because of the lack of very high quantum efficiency eletrophosphorescence in polymeric systems, which is not fully offset by the lower operating voltage of PLEDs compared to SM-OLEDS. Conjugated polymers such as poly(phenylene)vinylene and polyfluorene polymers have been used for OLEDs in the past for fluorescent devices. However, these polymer systems appear to quench phosphorescence emission, and nonconjugated polymers are now being used for higher-efficiency phosphorescent devices. Nevertheless, 4 square-foot lighting panels have been demonstrated by General Electric [Duggal et al. 2005].

White light can be produced by mixing polymer hosts with RGB-emitting chromophores within a single EML, or in a multilayer structure in which different layers emit different colors of light to produce white.

In addition, polymers with different dopants can be applied using commercial inkjet technology to apply RGB patterning (e.g., pixels or stripes of three colors) to produce white light or for pixelation in full-color displays.

Some recent benchmark PLED results indicate the current state of the art in PLED technology. As for single-color devices, in late 2005 Cambridge Display Technology announced a blue PLED with 37,500 hour lifetime at 200 cd/m^2 and 10 cd/A luminous efficacy, and a red PLED with 125,000 hour lifetime at 200 cd/m^2 and 7 cd/A luminous efficacy.

Concerning white OLEDs (WOLEDs), at the 2005 Fall MRS Meeting, Yang (UCLA) reported a white PLED with 14 lm/W. In early 2006, Franky So's group (U. Florida) also reported a WOLED with 25 lm/W using a blue organic phosphorescent dye (FIrpic) and wavelength down-conversion employing a nitridosilicate phosphor [Krummacher et al. 2006].

Carrier Injection and Transport

General features of carrier injection and transport are schematically shown in Figure A-14; for simplicity, a single organic layer structure is used for illustration, with some details near the interfaces such as band bending and defect states omitted. Many features of injection and transport are common to both PLEDs and SM-OLEDs, although the details differ because of stronger carrier localization in the latter class of materials. Indium tin oxide (ITO) is illustrated here as the hole-injecting anode, and the medium for carrier transport is a conjugated organic material, such as polyphenylene vinylene or tris (8-hydroxyquinoline) aluminum. Delocalized π-bonding orbitals form the equivalent of the valance band, and anti-bonding π^* orbitals form the organic equivalent of the conduction band. The energy of the highest occupied molecular orbital (HOMO) corresponds to the top of the valence band, and the lowest unoccupied molecular orbital (LUMO) energy corresponds to the bottom of the conduction band. (Although the LUMO and HOMO appear similar to conduction and valence bands in semiconductors, charge carriers are much more localized in organics, and they are also more strongly coupled to phonon modes. Where bands exist in any meaningful sense, they are very narrow and background carrier densities are very low relative to conventional semiconductors.)

Figure A-14 OLED energy level diagram of illustrating carrier injection.

In the case where the interaction between adjacent materials is weak and the interface dipole is negligible, the difference between the ionization potential of the organic HTL and the work function of the anode (Φ_a) is the barrier for hole injection (ΔE_h). The energy levels of ITO and PPV are well aligned to give a relatively low barrier of 0.2 eV for hole injection (Brown et al. 1992). In many cases, however, interfacial dipoles or surface chemistry act to change these idealized barriers.

The cathode is a metal film deposited on top of the final organic layer via thermal evaporation. The difference in energy between the cathode work function (Φ_m) and the electron affinity of the LUMO (E_A) is the barrier for electron injection (ΔE_e). As drawn in Figure A-14, a lower cathode work function gives a lower electron injection barrier. For this reason, low work function metals (e.g., barium or calcium) are typically used as OLED cathodes. Because of the reactivity of these metals, the cathode is capped with a

layer of aluminum. Again, however, almost all effective OLED cathodes react with the ETL forming dipoles and defect states which enhance electron injection. In essentially oxygen-free environments, covalent bonds can form between the initially deposited metal atoms and the organic, modifying the electronic structure of the system. The metal-organic interfacial region is on the order of 20 Å to 30 Å, comparable to the electron tunneling distance [Salaneck and Bredas 1996]. The presence of even low amounts of oxygen can cause formation of an insulating oxide layer, which degrades performance. Interface-modification layers such as LiF are often used between the organic layer and the cathode to improve this interface.

When a charged carrier is injected onto a conjugated molecule, it distorts the molecular geometry, which relaxes around the extra charge creating a polaron [Holstein 1959] (often referred to as a self-trapped state). The mechanism of carrier transport through organics is often "polaron hopping" from one molecule to a neighbor. Disorder in the largely amorphous organic films disrupts charge transport and plays a dominant role in determining the charge carrier mobility.

Exciton Dynamics and Light Creation

Electrons and holes within the emission layer combine to form a neutral exciton, which can then diffuse. If normal Langevin statistics prevail, singlet and triplet excitons are formed in a 1:3 ratio. A crucial step towards making very efficient OLEDs is to convert *all* the singlet and triplet excitons into light output. The first generations of OLEDs were based on fluorescent dyes. In fluorescence, quantum mechanical spin is conserved when a singlet excited state (exciton) emits a photon and drops to the singlet ground state. However, because a triplet-to-singlet transition via light emission does not conserve spin, it is a "forbidden transition;" the energy of the triplet excitons is wasted as dissipated heat. Thus, OLEDs utilizing fluorescence alone were fundamentally limited to an internal quantum efficiency of 25%. There is ongoing debate as to the exact singlet-triplet ratio in organics, and there is evidence for a material dependence, with measurements suggesting well over 25% singlets in some PLEDs [Reufer et al. 2005]. There is some practical significance to this debate because the ability to engineer materials for very high singlet exciton generation could potentially recover the exchange energy that is currently lost in phosphorescent devices, yielding even higher efficiencies. Such a device, however, has yet to be demonstrated.

Another approach is a phosphorescent OLED (PhOLED), in which the presence of a heavy metal atom (e.g., Pt, Pd, Ir, Au) within a phosphor provides spin-orbit coupling and mixing of the singlet and triplet states. The goal is conversion of all excitons to the triplet state, followed by rapid phosphorescence; phosphorescent materials can relax from a mixed spin metal ligand charge transfer excited state to the ground state by emission of a photon, and the spin statistics of exciton creation are therefore irrelevant. Examples of such organometallics phosphors are platinum octaethylporphine (PtOEP) and iridium tris(phenylpyridine) (Ir(ppy)$_3$), with triplet excited state lifetimes of ~100 μs for the former and <1 μs for the latter. There is still an inherent energy loss (known as the exchange energy) when a singlet exciton is converted by this process to a lower-energy triplet exciton. A recent approach is to combine fluorescent and phosphorescent dyes to utilize the singlets for blue light and the triplets for lower-energy green and red light (Sun et al. 2006). The relatively long excited-state lifetime of triplet excitons also creates exciton-exciton and exciton-polaron quenching effects at high drive currents, which result in efficiency loss at high brightness [Baldo, Adachi, and Forrest 2000].

Encapsulation

Low-cost packaging and encapsulation approaches are needed to limit degradation of OLEDs. Low work-function metals such as Ca are used as cathodes in OLEDs and must be protected from reactions with

oxygen and water. These ambient vapors will particularly degrade the metal-organic interface, limiting device lifetime. Excited-state organic molecules in the OLED EML are also very susceptible to oxidation (photo-oxidation), and must be protected from contact with air. Ingress of water vapor likely leads to electrochemical reactions near the electrodes and is particularly deleterious.

Currently, OLEDs are encapsulated by attaching a glass or metal lid above the cathode using a bead of epoxy. Desiccant is incorporated in the package to absorb residual moisture released from, and permeating through, the epoxy seal. This approach is limited to rigid and small-area devices. For the envisioned flexible and large-area OLEDs required for lighting, new encapsulation methods will be needed unless air-stable materials can be developed. High-barrier coatings can be used to provide low-cost thin-film encapsulation. These barriers must be pin-hole free, robust, and tolerant to high temperatures that will occur when devices are driven for high brightness. These barriers need to transmit $<10^{-6}$ g/m^2/day of water and $<10^{-5}$ cc/m^2/day of oxygen to ensure adequate OLED lifetimes [Burrows et al. 2001]. Furthermore, these targets will have to be met at low cost over large areas and in a manufacturing environment. Achieving this may require new breakthroughs in both the science and engineering of encapsulation.

Light Extraction

As much as 80% of the light produced in an OLED can be lost to internal reflections and waveguiding within the device or substrate layers (Figure A-15). A number of different approaches to improving the light extraction coefficient, R_e, have been employed. Because of the difference in refractive indices of air (1.0) and the glass substrate and organic layers (both on the order of 1.5 to 1.8), only light incident on the interface within a certain escape cone will pass through. Techniques for improving light extraction efficiency primarily try to increase the effective light cone. Light extraction is even more of a problem for inorganic LEDs, where the solid indices of refraction are much larger, on the order of 2.5. While the same fundamental physics likely applies to both cases, the economics of light extraction from large area OLEDs, rather than a small inorganic semiconductor die, likely creates new challenges.
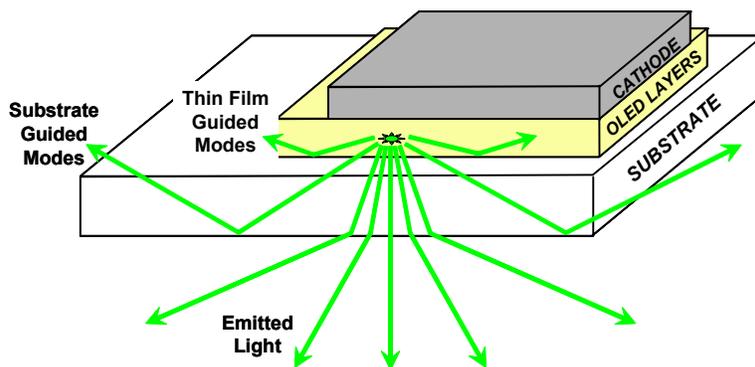
Figure A-15 This simplified schematic cross section of an OLED shows the fate of photons generated from an isotropic source in an organic thin film. Less than a quarter of the photons are emitted from a simple planar structure. The rest undergo total internal reflection at interfaces and waveguiding in either the substrate or the device layers. The substrate modes are relatively easy to recover using shaping or roughening techniques. The thin-film guided modes are rapidly absorbed. For solid-state lighting applications, all modes must be extracted over large areas at low cost.

Many approaches for improved light extraction are being pursued including roughening or texturing the outside surface of the glass substrate; corrugating the surface to increase Bragg scattering in the forward direction; using a two-dimensional photonic crystal structure to improve light output coupling; attaching an ordered array of micro lenses to the glass substrate; shaping the device into a mesa structure, and including reflective surfaces within the device.

Improvements in light extraction efficiency by factors of two to three have been reported for most of the techniques listed above. Other issues that must be considered include manufacturing cost and avoiding undesirable changes in the radiation pattern or an angular-dependent emission spectrum. A single standard approach to light extraction for OLEDs has yet to be established, and this is an important area for development.

Table A-1 Cost and Performance Characteristics for Some Solid-State Lighting Technologies[1]

Product or Technology	I (A)	V (V)	Die Size mm²	Output (lm)	lm/W	Wout/Win	Life (khr)	CRI	CCT (K)	$/lamp	λ/Δλ (nm/nm)
Low CRI Power White Luxeon® LEDs											
K2 LXK2-PW12-R00	0.35	3.42	1.00	45.00	37.6	0.093	50[2]	70	6500	3.45[3]	440/20 + 560/130
K2 LXK2-PW14-U00	1.00	3.72	1.00	100.00	26.9	0.067	50[2]	70	6500	3.45[3]	560/130
High CRI Power Warm White Luxeon® LEDs											
LXHL-BW03	0.35	3.42	1.00	26.00	21.7	0.058	50[4]	90	3200	2.99[3]	450/20 + 560/100 + 640/90
Power Color Luxeon® LEDs											
K2 Royal Blue LXK2-PR12-L00	0.35	3.42	1.00	200 mW[5]	n/a	0.167	50[6]	n/a	n/a	2.86[3]	455/20
K2 Royal Blue LXK2-PR14-Q00	1.00	3.72	1.00	475 mW[5]	n/a	0.128	50[6]	n/a	n/a	2.86[3]	455/20
K2 Blue LXK2-PB12-K00	0.35	3.42	1.00	9.50	7.9	0.128	50[6]	n/a	n/a	2.86[3]	470/25
K2 Blue LXK2-PB14-N00	1.00	3.72	1.00	25.00	6.7	0.108	50[6]	n/a	n/a	2.86[3]	470/25
K2 Cyan LXK2-PE12-Q00	0.35	3.42	1.00	35.00	29.2	0.105	50[6]	n/a	n/a	2.86[3]	505/30
K2 Cyan LXK2-PE14-T00	1.00	3.72	1.00	80.00	21.5	0.077	50[6]	n/a	n/a	2.86[3]	505/30
K2 Green LXK2-PM12-R00	0.35	3.42	1.00	45.00	37.6	0.064	50[6]	n/a	n/a	2.86[3]	530/35
K2 Green LXK2-PM14-U00	1.00	3.72	1.00	100.00	26.9	0.046	50[6]	n/a	n/a	2.86[3]	530/35
K2 Amber LXK2-PL12-Q00	0.35	2.95	0.65	35.00	33.9	0.066	50[7]	n/a	n/a	2.57[3]	590/14
K2 Red-Orange LXK2-PH12-S00	0.35	2.95	0.65	60.00	58.1	0.207	50[7]	n/a	n/a	2.57[3]	617/20
K2 Red LXK2-PD12-R00	0.35	2.95	0.65	45.00	43.6	0.218	50[7]	n/a	n/a	2.57[3]	627/20
OLED											
SSL 2002 EERE/OIDA Roadmap			11,764.70	10.00	10.0	0.025	0.3			2.00	
High Power IR Laser											
JDSU Diode Laser [Peters 2006]						0.760					915/5
100%-efficient hypothetical high CRI SSL											
100% Efficient RYGB SSL with CRI = 90 and cap/op = 1/3				1,500	376.4	1.000	50	90	4000	3.15	459/20 + 531/30 + 572/20 + 612/20

Notes:
1. Data compiled in May 2006.
2. Lifetime for White Luxeon K2 is projected as 70% lumen maintenance at 50,000 hours at 1000 mA operation, Tj maintained at or below 120 °C.
3. Price listed is for volumes up to 10K units. Higher volume pricing is negotiated depending on customer and application specific requirements.
4. Lifetime for White Luxeon is projected as 70% lumen maintenance at 50,000 hours at 350 mA operation, Tj maintained at or below 90 °C.
5. Royal Blue product is tested and binned for radiometric power rather than photometric flux.
6. Lifetime for Royal Blue, Blue, Green and Cyan Luxeon K2 is projected as 70% lumen maintenance at 50,000 hours (1000 mA operation, Tj ≤ 150 °C).
7. Lifetime for Red, Red-Orange, and Amber Luxeon K2 is projected as 70% lumen maintenance at 50,000 hours at 350 mA operation, Tj ≤ 120 °C).

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APPENDIX 2. WORKSHOP PARTICIPANTS

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APPENDIX 3. WORKSHOP PROGRAM

Workshop on Basic Research Needs for Solid-State Lighting
May 22–24, 2006
Bethesda Marriott 5151 Pooks Hill Road, Bethesda, Maryland 20814

Agenda for Plenary Sessions

Plenary Opening Session — Monday, May 22, 2006	
Salons A-C	
Moderator: Julie Phillips, Sandia National Laboratories	
7:30 am - 8:30 am	Registration and Continental Breakfast	
8:30 am - 8:45 am	Welcome and Workshop Charter BES Energy Security Plan	Pat Dehmer, Director, Office of Basic Energy Sciences
8:45 am - 9:00 am	DOE-EERE SSL Technologies Program Overview	Jim Brodrick, Lighting R&D Manager Office of Energy Efficiency and Renewable Energy
9:00 am - 9:30 am	Solid-State Lighting – Opportunities for Fundamental Innovation	Fred Schubert, Professor, Rensselaer Polytechnic U
9:30 am - 10:00 am	Perspectives on Light Emitting Diodes	George Craford, CTO, Philips Lumileds
10:00 am - 10:30 am	Break	
10:30 am - 11:00 am	OLEDs for Solid State Lighting: The Opportunity and the Challenge	Alan Heeger, Professor, UC Santa Barbara
11:00 am - 11:15 am	Workshop Format and Goals	Paul Burrows, Workshop Co-Chair, Pacific Northwest National Lab
11:15 am - 11:30 am	LED Science Panel Overview	Bob Davis, Professor, Carnegie Mellon University Jerry Simmons, Sandia National Laboratories
11:30 am- 11:45 am	OLED Science Panel Overview	George Malliaras, Professor, Cornell University Franky So, Professor, University of Florida
11:45 am - 12 noon	Cross-Cutting and Novel Materials Science/ Optical Physics Panel Overview	Jim Misewich, Brookhaven National Laboratory Arto Nurmikko, Professor, Brown University Darryl Smith, Los Alamos National Laboratory
12 noon - 1:00 pm	Lunch (Congressional Ballroom)	
12:30 pm - 1:00 pm	Light Extraction from LEDs vs. Light Absorption into Solar Cells (Lunch Presentation)	Eli Yablonovitch, Professor, UC at Los Angeles

<u>Plenary Closing Session</u> — Wednesday, May 24, 2006		
Salons A-C		
Moderator: Paul Burrows, Pacific Northwest National Laboratory		
10:00 am - 10:25 am	Grand Challenges	Julie Phillips, Workshop Chair, Sandia National Laboratories
10:25 am - 10:50 am	LED Science Panel Survey and Priority Research Directions	Bob Davis, Professor, Carnegie Mellon University Jerry Simmons, Sandia National Laboratories
10:50 am - 11:15 am	OLED Science Panel Survey and Priority Research Directions	George Malliaras, Professor, Cornell University Franky So, Professor, University of Florida
11:15 am - 11:40 am	Cross-Cutting and Novel Materials Science / Optical Physics Panel Survey and Priority Research Directions	Jim Misewich, Brookhaven National Laboratory Arto Nurmikko, Professor, Brown University Darryl Smith, Los Alamos National Laboratory
11:40 am - 11:50 am	Workshop Concluding Remarks	Julie Phillips, Workshop Chair, Sandia National Laboratories
11:50 am - 12:00 pm	Final Closing Remarks	Pat Dehmer, Director, Office of Basic Energy Sciences
12:00 pm	Workshop Adjourns (Box Lunches Provided)	

Agenda for Breakout Sessions

DOE-SC Basic Energy Sciences Solid-State Lighting Workshop: Breakout Session Detail

	LED Science	OLED Science	Cross-Cutting and Novel Materials Science / Optical Physics
Panel	LED Science	OLED Science	Cross-Cutting and Novel Materials Science / Optical Physics
Chairs	Bob Davis (Carnegie Mellon U) and Jerry Simmons (SNL)	George Malliaras (Cornell U), Franky So (U Florida)	Jim Misewich (BNL), Arto Nurmikko (Brown), Darryl Smith (LANL)
Moderator	As indicated	Same as primary speaker	Panel chairs
Topic	Primary Speaker • 10-15m • Reviews state-of-the-art of topic • Identifies "must do" future research / Additional Contributing Speakers • 1-2 VGs each / Moderator • Guides generation of ideas and potential PRDs/GCs	Primary Speaker • 15m • Reviews state-of-the-art of topic • Identifies "must do" future research	Primary Speaker • 20m • Reviews state-of-the-art of topic • Identifies "must do" future research

7:30a-8:30a — Badge and Workshop Package Pickup / Continental Breakfast

8:30a-12:00p — Plenary Opening Session Salons A-C

12:00p-1:00p — Lunch Congressional Ballroom

Monday, May 22, 2006

Location:
LED Science — Salon D (Montrose available for overflow discussions)
OLED Science — Bethesda/Potomac (Salon E available for overflow discussions)
Cross-Cutting — Rockville/Chevy Chase (Kentwood available for overflow discussions)

Time	LED Science (Salon D)	OLED Science (Bethesda/Potomac)	Cross-Cutting & Novel Materials Science / Optical Physics (Rockville/Chevy Chase)
1:00p	Panel Directives — Moderator: Davis/Simmons	Panel Directives — Malliaras/So	Panel Directives — Misewich/Nurmikko/Smith
1:15p	Break	Break	Break
1:30p			
1:45p	Photon manipulation and extraction — Krames; Additional: Yablonovitch, Lin, All Panelists; Moderator: Speck	Science of small molecule devices — Forrest	Hybrid light emitters — Achermann
2:00p			
2:15p			
2:30p	In situ epi characterization — Streiffer; Additional: All Panelists; Moderator: Dapkus	Science of polymer devices — Crone	Nanowire optoelectronics — Leonard
2:45p			
3:00p	Break	Break	
3:15p			Break
3:30p	Nitride materials and synthesis — Speck; Additional: Davis; Moderator: Crawford	Amorphous Molecular Materials — Tang	Nanowire arrays for SSL — Yang
3:45p			
4:00p	Defects and Recombination Processes in GaN-Based Materials — Hangleiter; Additional: Krames, Dapkus, Amano, Speck, All panelists; Moderator: Cheetham	Conjugated polymers — Galvin	Adaptive quantum design for photon creation and manipulation — Levi
4:15p			
4:30p			
4:45p			
5:00p			
5:15p	Break	Break	Break
5:30p-7:00p	Working Dinner Salons A-C		

Location (evening):
LED Science — Salon D (Montrose available for overflow discussions)
OLED Science — Bethesda/Potomac (Salon E available for overflow discussions)
Cross-Cutting — Rockville/Chevy Chase (Kentwood available for overflow discussions)

Time	LED Science (Salon D)	OLED Science (Bethesda/Potomac)	Cross-Cutting & Novel Materials Science / Optical Physics (Rockville/Chevy Chase)
7:00p	Break	Break	Break
7:15p			
7:30p	Polarization and Piezo-optoelectronic Phenomena — Wetzel; Additional: Hangleiter, All panelists; Moderator: Norton	Phosphorescent Emitters — Thompson	Electronic theory for nano-composite materials — Littlewood
7:45p			
8:00p			
8:15p	Recap of Day 1 • PRD Nominations • GC Suggestions; Additional: All panelists; Moderator: Davis/Simmons	Recap of Day 1 • PRD Nominations • GC Suggestions — Malliaras/So; Davis/Simmons	Recap of Day 1 • PRD Nominations • GC Suggestions — Misewich/Nurmikko/Smith
8:30p			
8:45p			
9:00p	Adjourn for evening		

Continental Breakfast (7:15a – 7:45a)

Salon D (Montrose available for overflow discussions)

Time	Topic	Speaker	Panelists
8:00a	InN and In-rich InGaN	Haller	Wetzel, Hangleiter, Krames
8:30a	Influence of In on InGaN Materials Synthesis and Properties	Crawford	All panelists
9:30a	Break		
10:00a	Alternative Inorganic Semiconductor Materials	Norton	All panelists
10:45a	Doping and Charge Transport in Wide Bandgap Semiconductors	Singh	Haller, All panelists
11:30a	Break		

Bethesda/Potomac (Salon E available for overflow discussions)

Time	Topic	Speaker	Chair
8:00a	Purity Issues	Shi	Craford
8:45a	Energetics	Soos	
9:30a	Break		
10:00a	Interfaces, Doping	Kafafi	
10:45a	Spin Statistics	Shinar	
11:30a	Break		

Rockville/Chevy Chase (Kentwood available for overflow discussions)

Time	Topic	Speaker
8:00a	Enhancing light emission with optical antennas	Novotny
8:45a	Efficient white light sources with colloidal quantum dot lumophores	Bulovic
9:30a	Break	
10:00a	Photon manipulation	Zia
10:45a	Scalable photonic bandgap structures	Lin
11:30a	Break	

Working Lunch — Congressional Ballroom (12:00p – 12:45p)
Workshop/Panel Chairs meet separately to discuss emerging PRDs/GCs (Salon D)

Salon D (Montrose available for overflow discussions)

Time	Topic	Speaker	Panelists
1:00p	Break		
1:30p	Novel Device Physics and Architectures	Dapkus	Crawford, All panelists
2:15p	Photon and Exciton Conversion Materials	Cheetham	Achermann, All panelists
3:00p	Break		
3:30p	Low-Dimensional Light-Emitting Structures	Amano	Singh, Dapkus, Norton, Wetzel, Hangleiter
4:45p	Recap of Day 1 • PRD Nominations • GC Suggestions	Davis/Simmons	All panelists

Bethesda/Potomac (Salon E available for overflow discussions)

Time	Topic	Speaker	Chair
1:00p	Break		
1:30p	Exciton Dynamics	Vardeny	Singh
2:15p	Energy Transfer	Barbara	Wetzel
3:00p	Break		
3:15p	Charge Injection	Bradley	
3:45p	Charge Transport	Smith	Krames
4:45p	Recap of Day 1 • PRD Nominations • GC Suggestions	Malliaras/So	Davis/Simmons

Rockville/Chevy Chase (Kentwood available for overflow discussions)

Time	Topic	Speaker
1:00p	Break	
1:30p	Optics in a new light; inspired by nature, enabled by chemistry	Buckley
2:15p	Resonant organic-inorganic nanostructures for optoelectronics	Agronovich
3:00p	Break	
3:30p	Organic-inorganic hybrids	Rumbles
4:15p		Misewich/Nurmikko/Smith
4:45p	Recap of Day 1 • PRD Nominations • GC Suggestions	
5:15p	Break	

Non-Working Dinner (6:00p – 6:45p)
Workshop/Panel Chairs meet separately to discuss emerging PRDs/GCs (Salon D)

Salon D (Montrose available for overflow discussions)

Time	Topic	Speaker
7:30p	Outline PRDs/GCs Assign VG/writing duties	Davis/Simmons
8:15p	Viewgraph preparation	All panelists

Bethesda/Potomac (Salon E available for overflow discussions)

Time	Topic	Speaker
7:30p	Outline PRDs/GCs Assign VG/writing duties	Malliaras/So
8:15p	Viewgraph preparation	All panelists

Rockville/Chevy Chase (Kentwood available for overflow discussions)

Time	Topic	Speaker
7:30p	Outline PRDs/GCs Assign VG/writing duties	Misewich/Nurmikko/Smith
8:15p	Viewgraph preparation	All panelists

Adjourn for evening (9:00p)

Wednesday, May 24, 2006

	Location	Salon D (Montrose available for overflow discussions)	Bethesda/Potomac (Salon E available for overflow discussions)	Rockville/Chevy Chase (Kentwood available for overflow discussions)
7:15a				
7:30a		Continental Breakfast		
7:45a				
8:00a				
8:15a		VG preparation and report writing	VG preparation and report writing	VG preparation and report writing
8:30a				
8:45a			All panelists	All panelists
8:45a		All panelists		
9:00a				
9:15a				
9:30a		Break	Break	Break
9:45a				
10:00a–12:00p		Plenary Closing Session Salons A-C		
12:00p		Workshop Adjourns (Box Lunches Provided)		
12:00p–12:30p		Break		
12:30p–1:30p		Writers' Working Lunch		
1:30p–5:00p		Writing Session (Salon D, Bethesda / Potomac, Rockville / Chevy Chase)		
5:00p–5:30p		Break		
5:30p–7:00p		Writers' Non-Working Dinner		
7:00p–7:30p		Break		
7:30p–9:00p		Writing Session (Salon D, Bethesda / Potomac, Rockville / Chevy Chase)		
9:00p		Adjourn for evening		

Thursday, May 25, 2006

7:15a	
7:30a	Continental Breakfast
7:45a	
8:00a–11:30a	Writing Session (Salons D-E)
11:30a	Adjourn (box lunches provided)

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APPENDIX 4. ADDITIONAL READING

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APPENDIX 5. PRE-WORKSHOP "BIG SCIENCE" QUESTIONS

The following are science questions generated before the workshop by the panel chairs and panelists to guide the selection of topic areas to be discussed at the workshop.

Panel	Topic Area	Important Question
LED Science	Photon Mode Manipulation and Extraction	Can 100% photon extraction efficiency be achieved? How does photon extraction scale with lateral area?
	In situ Characterization of Epitaxial Growth Growth of Nitride Films and Heterostructures	What are the fundamental relationships between microscopic growth mechanisms and defect densities in GaN-based materials?
	Defects and Recombination Processes in GaN-Based Materials	What are the microscopic mechanisms by which extended and point defects alter spontaneous and stimulated emission in GaN-based materials and heterostructures? How are these mechanisms altered in low-dimensional structures? What is the minimum tolerable dislocation density for near-100%radiative efficiency devices?
	Polarization and Piezo-optoelectronic Phenomena	How do polarization and piezoelectric effects alter growth mechanisms of SiC, GaN and ZnO? How do they alter light emission in strained heterostructures?
	Influence of In on InGaN Materials and Physics	What are the microscopic mechanisms by which In (at low and high concentrations) alters radiative efficiency in GaN-based materials and heterostructures?
	Alternative Inorganic Semiconductor Materials	Can we "design" complex inorganic materials for electroluminescence (e.g., LaCuOSe oxychalcogenides)?
	Doping and Charge Transport in Wide Bandgap Semiconductors	What are the fundamental limits to doping (especially p-type) in wide-bandgap semiconductors and heterostructures? What is the origin of shallow donor states in wide-bandgap materials (e.g., nominally undoped ZnO)? Can we predict nonequilibrium, metastable defect structures and their doping behavior? What limits minority carrier injection in ZnO? What are the fundamental limits to carrier transport in wide-bandgap semiconductors and heterostructures? How does lateral transport influence nonradiative recombination?
	Novel Device Physics and Architectures	How do ultra-high-carrier-densities affect spontaneous and stimulated emission rates? How might resonant-cavity and micro-cavity devices alter carrier/photon interactions and light extraction efficiencies? Can we go beyond the one electron = one photon limit? Can quantum efficiencies exceed 100%? Can continuous spectrum white light be generated by direct electronic excitation in an LED?

Panel	Topic Area	Important Question
	Photon and Exciton Conversion Materials	What are the fundamental limits to efficiency of visible-light-emitting narrow-line-width phosphors? How can we tailor and manipulate the transfer of electronic excitations through homogeneous and heterogeneous materials?
	Low-Dimensional Light Emitting Structures	What are the microscopic mechanisms for energy transfer to, and light emission from, individual and arrayed low-dimensional nanostructures? Can low-dimensional systems allow lateral carrier transport towards dislocations? Can self-assembly of dots and wires lead to better LEDs in nitrides? Can photoluminescence be used to predict LED performance?
OLED Science	Spin Statistics	How can we obtain predictive control of S*/T* ratio and exchange energy (singlet-triplet gap) in electrically excited organic semiconductor?
	Energy Transfer and exciton quenching	Why organic phosphors limited to $\tau > 0.5\mu s$?
	Blue Phosphorescence	Fundamental limits on short wavelength organic phosphors and hosts Can we achieve high efficiency white without using phosphorescent blue?
	Assay and Purity	Active and inactive impurities affecting device efficiency and lifetime? How can we assay to the accuracy required to answer such questions?
	Molecular Control of Directionality	Why should a molecule emit isotropically? Could dipole alignment force light into optimal modes for escape?
	Interfacial barriers and Engineering	Do metal/organic and organic/organic interfacial energy alignments follow the Schottky model? What determines the barriers?
	Materials with improved stability	Can we engineer air-stable organics and injecting cathodes? Would presumably need air-stable radical cations/anions. Operation stability. Are air stable cathodes possible? Can plastic substrates be prepared that are sufficiently hermetic for WOLEDs? How can WOLEDs on flexible substrates be packaged? Key may be to minimizing aerobic exposure and not eliminating it. What material and architecture modifications can be made to minimize the affects of differential aging?
	Carrier injection and transport, Charge Mobility and Trapping	What is the limit? How to achieve it? How does it relate to molecular structure? What is an ohmic contact in organic semiconductors?
	Conjugated polymers vs. nonconjugated polymers	Fundamental limitations of conjugated polymers for PHOLEDs, can non-conjugated polymers work?
	Simple device architecture	What are the fewest number of layers that can be used to make high efficiency WOLEDs (i.e., ensure carrier balance at all brightness).

Panel	Topic Area	Important Question
Cross-Cutting and Novel Materials Science / Optical Physics	Photon Manipulation	How do we employ nanophotonic structures (below diffraction limit) as a means to enhance internal and external quantum efficiency? What are the fundamental and practical limitations of subwavelength optics?
	Photon Manipulation	How can collective excitations such as plasmon polaritons in metals advance light extraction (e.g., via near field interactions)?
	Photon Manipulation	What materials or fabrication challenges limit the low-cost mass production of photonic crystal structures?
	Electronic processes	How can low dimensional materials enhance the control of excitonic energy transfer and photon coupling processes for solid-state lighting (e.g., from weak to strong coupling in quantum dots and wires in organic and inorganic semiconductors)?
	Electronic processes	Is the rational design of nanoscale materials for reduced energy dissipation and improved thermal management feasible?
	Electronic processes	What are characteristics of heterojunctions and (quantum) transport in nanocomposite hybrid materials? What determines the interface energetics in metal/inorganic vs. metal organics and organic/organic and organic/organic interfaces?
	Electronic processes	Can we understand and enhance the relatively defect tolerant properties of conjugated small molecule organics, conjugated polymers and nitrides?
	New Materials	What are strategies for the enhancement of optical cross sections and tailoring electronic energy pathways in nanocomposite materials (e.g., hybrid inorganic, organic semiconductors)?
	New Materials	Can we learn strategies from biological materials that would have impact in solid-state lighting? (e.g., collective effects in multiple chromophores; use of biomolecular templates for nanofabrication)
	New Materials	Can we design light extraction structures via bioinspired and biomimicking optics?
	Tools	What are the limitations in determining the electronic properties of nanocomposite materials?
	Tools	What are the promising theoretical approaches to condensed phases of disordered molecular materials? What is the bridge between condensed matter physics and quantum chemistry?
	Tools	What are strategies for the design of defect-tolerant nanophotonic materials (e.g., photonic crystals) for solid-state lighting?
	Tools	How to develop new kinds of optical and electronic microprobes that can locally access nanoscale materials?

Acronyms
O-I: organic-inorganic
S*: excited singlet exciton
T*: excited triplet exciton
PV photovoltaic
τ: intrinsic excited state radiative lifetime

BASIC RESEARCH NEEDS FOR
SOLID-STATE LIGHTING

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