Low-refractive-index materials:  
A new class of optical thin-film materials for solid-state lighting

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(NUSOD)

University of Delaware, September 24 – 28 (2007)
A Note on Carborundum.

To the Editors of Electrical World:

Sirs:—During an investigation of the unsymmetrical passage of current through a contact of carborundum and other substances a curious phenomenon was noted. On applying a potential of 10 volts between two points on a crystal of carborundum, the crystal gave out a yellowish light. Only one or two specimens could be found which gave a bright glow on such a low voltage, but with 110 volts a large number could be found to glow. In some crystals only edges gave the light and others gave instead of a yellow light green, orange or blue. In all cases tested the glow appears to come from the negative pole, a bright blue-green spark appearing at the positive pole. In a single crystal, if contact is made near the center with the negative pole, and the positive pole is put in contact at any other place, only one section of the crystal will glow and that the same section wherever the positive pole is placed.

There seems to be some connection between the above effect and the e.m.f. produced by a junction of carborundum and another conductor when heated by a direct or alternating current; but the connection may be only secondary as an obvious explanation of the e.m.f. effect is the thermoelectric one. The writer would be glad of references to any published account of an investigation of this or any allied phenomena.

Light-Emitting Diodes – 1923 – SiC – Oleg Lossev

- First detailed study of electroluminescence in SiC by Oleg Lossev
- Brilliant scientist who published first paper at the age of 20 years
- Lessov concluded that luminescence is no heat glow (incandescence)
- Lessov noted similarity to vacuum gas discharge

SiC (carborundum)

First photograph of light emitted by SiC LED (after Lossev, 1924)

SiC crystal

Photograph of Lossev’s LED

Lossev’s I-V characteristic

Re-enactment of 1907 experiment

Oleg V. Lessov, 1928
First correct interpretation of electroluminescence in p-n junctions

Injection of minority carriers

First correct explanation of light emission from LEDs
Demonstration of high-performance emitters emitting at red, orange, and yellow wavelengths

AlGaInP LEDs

Krames et al., 1999

Sugawara et al., 1991
- GaInN – the first viable short-wavelength material
- First blue LED
- Basis for white LEDs and solid-state lighting

- First white LED
- Suitable for illumination applications
- Transition from *information* to *illumination* applications

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Nakamura and Fasol, 1997

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Nakamura, 2004

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Nakamura and Fasol, 1997
Let’s keep the lights on – and strongly reduce power

It is feasible to reduce energy consumption for lighting by 50% – and keep the lights on!
Traditional applications for LEDs and OLEDs

Texas Inst.  Pulsar  AT&T  Kodak
Recent applications

China

Germany

Taiwan

Japan

United States
Solid-state lighting

- **Inorganic devices:**
  - Semiconductor plus phosphor illumination devices
  - All-semiconductor-based illumination devices

- **Organic devices:**
  - Remarkable successes in low-power devices (Active matrix OLED monitors, thin-film transistors, etc.)
  - Substantial effort is underway to demonstrate high-power devices
  - Anticipated manufacturing cost and luminance of organic devices are *orders of magnitude* different from inorganic devices
OLEDs are area sources
They do do not blind
Suitable for large-area sources

LEDs are point sources
They are blindingly bright
Suitable for imaging-optics applications

- Luminance of OLEDs: $10^2 - 10^4 \text{ cd/m}^2$
- Luminance of LEDs: $10^6 - 10^7 \text{ cd/m}^2$
- Luminance of OLEDs is about 4 orders of magnitude lower
- OLED manufacturing cost per unit area must be $10^4 \times$ lower

OLEDs
- Low-cost reel-to-reel manufacturing

LEDs
- Expensive epitaxial growth
Nobel Laureate Richard Smalley: “Energy is the single most important problem facing humanity today” and “conservation efforts will help the worldwide energy situation”.

Testimony to US Senate Committee on Energy and Natural Resources, April 27, 2004

- Solid-state lighting is singular opportunity for conservation of energy
Quantification of solid-state lighting benefits

- **Energy benefits**
  - 22% of electricity used for lighting
  - LED-based lighting can be $20 \times$ more efficient than incandescent and $5 \times$ more efficient than fluorescent lighting

- **Financial benefits**
  - Electrical energy cost reduction, but also savings resulting from less pollution, global warming

- **Environmental and economic benefits**
  - Reduction of CO$_2$ emissions, a global warming gas
  - Reduction of SO$_2$ emissions, acid rain
  - Reduction of Hg emissions by coal-burning power plants
  - Reduction of hazardous Hg in homes
Quantification of benefits

Global benefits enabled by solid-state lighting technology over period of 10 years. First numeric value in each box represents annual US value.

US uses about ¼ of world’s energy.

<table>
<thead>
<tr>
<th></th>
<th>Savings under “5.5% scenario”</th>
<th>Savings under “11% scenario”</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction in total energy consumption</td>
<td>$43.01 \times 10^{18} \text{J} \times 5.5% \times 4 \times 10 = 94.62 \times 10^{18} \text{J}$</td>
<td>$43.01 \times 10^{18} \text{J} \times 11% \times 4 \times 10 = 189.2 \times 10^{18} \text{J}$</td>
</tr>
<tr>
<td>Reduction in electrical energy consumption</td>
<td>$228.9 \text{TWh} \times 4 \times 10 = 9,156 \text{TWh} = 32.96 \times 10^{18} \text{J}$</td>
<td>$457.8 \text{TWh} \times 4 \times 10 = 18,310 \text{TWh} = 65.92 \times 10^{18} \text{J}$</td>
</tr>
<tr>
<td>Financial savings</td>
<td>$22.89 \times 10^9 \text{$} \times 4 \times 10 = 915.6 \times 10^9 \text{$}$</td>
<td>$45.78 \times 10^9 \text{$} \times 4 \times 10 = 1,831 \times 10^9 \text{$}$</td>
</tr>
<tr>
<td>Reduction in CO$_2$ emission</td>
<td>$133.5 \text{Mt} \times 4 \times 10 = 5.340 \text{Gt}$</td>
<td>$267.0 \text{Mt} \times 4 \times 10 = 10.68 \text{Gt}$</td>
</tr>
<tr>
<td>Reduction of crude-oil consumption (1 barrel = 159 liters)</td>
<td>$12.03 \times 10^6 \text{barrels} \times 4 \times 10 = 481.2 \times 10^6 \text{barrels}$</td>
<td>$24.07 \times 10^6 \text{barrels} \times 4 \times 10 = 962.4 \times 10^6 \text{barrels}$</td>
</tr>
<tr>
<td>Number of power plants not needed</td>
<td>$35 \times 4 = 140$</td>
<td>$70 \times 4 = 280$</td>
</tr>
</tbody>
</table>

(*) 1.0 PWh = 1000 TWh = 11.05 PBTu = 11.05 quadrillion Btu “=” 0.1731 Pg of C = 173.1 Mtons of C
1 kg of C “=” [(12 amu + 2 × 16 amu) / 12 amu] kg of CO$_2$ = 3.667 kg of CO$_2$
Quantitative data based on Schubert et al., Reports on Progress in Physics, invited review, to be published (2006)

Fundamental innovations

- **Innovation in materials, devices, and systems**
  - Omnidirectional reflectors
  - New materials with unprecedented low refractive index
  - New materials with very high refractive index

- **The future**
  - Future smart lighting systems
  - New functionalities
Light-emitting diodes with reflectors

To avoid optical losses, ideal device structures possess either:

*Perfect Transparency or Perfect Reflectivity*

Example of **reflective** structure:

![Diagram of reflective structure](after Osram Corporation)

Example of **transparent** structure:

![Diagram of transparent structure](after Lumileds Corporation)
Omni-directional reflector (ODR)

Search for the “perfect reflector”: $R = 100\%$ for all $\Theta$, all $\lambda$, and TE and TM

- Omni-directional reflection characteristics
- High reflectivity (> 99 %)
- Electrical conductivity
- Broad spectral width
**AlGaInP LED**

$\lambda = 650$ nm, MQW active region

AlGaAs window layer

GaAs substrate removed, Si submount

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**GaInN LED**

$\lambda = 460$ nm, MQW active region

Sapphire substrate

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![Image of AlGaInP LED with ODR](attachment:image1.png)

![Image of GaInN LED with ODR](attachment:image2.png)

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**Graph:**

- **AlGaInP LEDs $T = 300$ K**
  - TS-LED $\lambda = 650$ nm $A_l=0.25\text{mm}^2$
  - ODR-LED $\lambda = 650$ nm $A_l=0.09\text{mm}^2$
  - DBR-LED $\lambda = 630$ nm $A_l=0.25\text{mm}^2$
  - TS-LED $\lambda = 595$ nm $A_l=0.05\text{mm}^2$

**Reflectivity $R$ (%)**

- **GaN/RuO$_2$/SiO$_2$/Ag**
- **GaN/SiO$_2$/Ag**
- **GaN/Ag**
- **GaN/Ni/Au**

**Wavelength (nm):**

- 300 to 600
Figure of merit for DBR: Index contrast $\Delta n$

- Fresnel reflectance of interface
  \[ r = \frac{n_h - n_1}{n_h + n_1} = \frac{\Delta n}{n_h + n_1} \]

- DBR reflectance
  \[ R_{DBR} = \left| r_{DBR} \right|^2 = \left[ \frac{1 - (n_1 / n_h)^{2m}}{1 + (n_1 / n_h)^{2m}} \right]^2 \]

- Spectral width of stop band
  \[ \Delta \lambda_{\text{stop}} = \frac{2 \lambda_{\text{Bragg}} \Delta n}{n_{\text{eff}}} \]

- Penetration depth
  \[ L_{\text{pen}} \approx \frac{L_1 + L_2}{4r} = \frac{L_1 + L_2}{4} \frac{n_1 + n_2}{\Delta n} \]

- Critical angle (max. angle for high reflectivity)
  \[ \theta_c \approx \frac{n_1}{n_0} \sqrt{\frac{2}{n_0} \frac{2\Delta n}{n_1 + n_2}} \]

By increasing index contrast $\Delta n$, figures of merit improve
New materials are required
From total internal reflection ... to waveguiding

(1) Johannes Kepler (1571-1630)
Discovered and described total internal reflection in book entitled *Dioptrice* (1611)

(2) Willebrord Snellius (1591-1626)
Discovered sin-law of refraction

(3) Isaac Newton (1642-1727)
Discovered optical density (now called refractive index)

(4) Augustin Fresnel (1788-1827)
Quantitatively described reflection

(5) Daniel Colladon (1802-1893)
Developed first wave guiding apparatus

E. F. Schubert
New class of materials: Low-\(n\) materials

- Dense materials \(n \approx 1.4\): SiO\(_2\) (\(n = 1.45\)); MgF\(_2\) (\(n = 1.39\))
- Low-\(n\): refractive index \(n < 1.25\)
- Low-\(n\) optical films by oblique-angle evaporation
Unprecedented low refractive index of $n \approx 1.05$: World record!

- Pore sizes $<< \lambda$ (Rayleigh scattering)
- Pore sizes 2 – 8 nm achieved
- Maxwell’s equations: $n^2 = \varepsilon_r \mu_r (= k)$
- Low-$k$ material in Si VLSI (field dielectric)
- Low-$n$ films are new class of materials with distinct properties
Playing with refractive index of materials

- **Controllability** of refractive index of a film by varying deposition angle
- $1.46 < n_{\text{SiO}_2} < 1.05; \ 2.19 < n_{\text{ITO}} < 1.17$
- Design freedom in optical components afforded by oblique angle deposition
- Select materials based on materials properties other than refractive index, and tune the refractive index to desired value
GRIN AR coating demonstrated by oblique-angle deposition of TiO2 and SiO2 with various deposition angles

Reflectivity as low as $R \approx 0.1\%$ due to virtual elimination of Fresnel reflection
Extremely low reflectivity

- Low reflectivity with broad spectral width ($R < 0.5\%$ at $570 \text{ nm} < \lambda < 1000 \text{ nm}$)
- Omni-directionality
- Measured lowest reflectivity: $R = 0.10\%$
- A near-perfect anti-reflection coating
- Applications: Solar cells, LEDs, etc.

J. Q. et al., Nature Photonics 2007
Application of low-\(n\) materials: AR coating for LEDs

- **Indium-tin oxide (ITO)**: transparent-conducting-oxide ⇒ suitable for *transparent-antireflection contact for GaInN LEDs*
- Graded-index (GRIN) ITO anti-reflection (AR) coating shows a low reflectivity and broadband characteristics

*Jong Kyu Kim et al., 2007*
Fabrication of GaInN LEDs with GRIN ITO

(1) GaInN LED on sapphire (~ 474 nm)

(2) AgCu (2 nm)/GRIN ITO
- oblique angle deposition
- 6 layers (0, –45, 60, –75, 80, –85)
- oxidation annealing

(3) Mesa etching by CAIBE
- Ar + Cl2

(4) N-metal & Bonding metal
- Ti/Al/Ni/Au deposition
- annealing at 750°C, 1 min.
- Ti/Au deposition
GaInN LEDs with GRIN ITO

- **Conductive** graded-index anti-reflection coating made of a single material, ITO, fabricated on a GaInN blue LED
- Enhanced light output by > 45% by using ITO graded-index anti-reflection due to reduced Fresnel reflection
- Fresnel reflection is strongest for III-V phosphides (AlGaN, $R \approx 30\%$) due to high refractive index ($n = 3.0 – 3.5$).
Single material optical component: select ITO due to its transparency & conductivity, tune its refractive index to desired value

*Conductive* distributed Bragg reflector (DBR) composed of a *single* material, ITO, fabricated by oblique angle deposition
- DBRs with several periods demonstrated
- Experimental reflection spectrum agrees well with theory
- New opportunities using dielectric materials
Solid-state lighting technologies and figures of merit

Lighting technologies

Figures of merit of new lighting technologies

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Desirable value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Luminous source efficiency</td>
<td>150 lm/W</td>
</tr>
<tr>
<td>Luminous flux</td>
<td>1000 lm</td>
</tr>
<tr>
<td>Color rendition capability (CRI)</td>
<td>&gt; 75</td>
</tr>
<tr>
<td>Color temperature</td>
<td>3000 – 6000 K</td>
</tr>
<tr>
<td>Lifetime</td>
<td>100 000 hrs</td>
</tr>
<tr>
<td>Cost</td>
<td>&lt; $ 10 per lamp</td>
</tr>
</tbody>
</table>
### Different technical approaches
- Blue LED plus yellow phosphor
- UV LED plus RGB phosphor
- Phosphor has excellent color stability
- Multiple LEDs
- Which one is best?

### Efficiencies
- Incandescent light bulb: 17 lm/W
- Monochromatic green: 680 lm/W
- Di-chromatic white source: 420 lm/W
- Trichromatic white source: 300 lm/W
- Color rendering: CRI > 90
- Demonstrated SSL sources: > 100 lm/W

### What is the optimum spatial distribution of phosphors?
- Proximate and remote distributions
Innovation in white LEDs – Phosphor distribution

- Novel phosphor distributions promise higher efficiency

Proximate distribution (after Goetz et al., 2003)

Remote distribution (after Kim et al., 2005)

Innovation in white LEDs – Phosphor distribution

- Remote phosphor distributions reduce absorption of phosphorescence by semiconductor chip
- Improvement of phosphorescence efficiency:
  - 15.4 % for blue-pumped yellow phosphor
  - 27.0 % for UV-pumped blue phosphor
Novel loss mechanisms in white lamps with remote phosphor

- Whispering Gallery Mode
- Trapped optical mode
- Solution:
  - Non-deterministic element that breaks symmetry
  - Suppression of trapped whispering-gallery modes

Lord Rayleigh (1842–1919)

“Especially remarkable is the narrowness of the obstacle, held close to the concave surface, which is competent to intercept most of the effect” (1912)
Remote phosphors with diffuse and specular reflector cups

- Reflectance versus angle
- Surface texture by bead blasting
- Diffuse reflectance increased by two orders of magnitude
Efficiency of III-V nitride LEDs is very high, despite high density of dislocations
Efficiency decreases with increasing injection current
Severe obstacle for lasers and high-power solid-state lighting devices
Green LEDs have largest efficiency droop
Not caused by device heating
Challenges: Dislocations

- Dislocations in III-V nitrides affect:
  - LED Efficiency
  - LED efficiency droop

In collaboration with Sandia National Labs’ Drs. Mary H. Crawford, Dan D. Koleske, and Art J. Fischer
Challenges: Green LEDs

- Power efficiency of III-V nitride green LEDs much lower than that of blue LEDs
A light source has color rendering capability.
This is the capability to render the true colors of an object.

Example: False color rendering
- What is the color of a yellow banana when illuminated with a red LED?
- What is the color of a green banana when illuminated with a yellow LED?
Examples of Different Color Renditions

Franz Marc “Blue Horse” (1911)

High CRI illumination source

Low CRI illumination source

Solid-state lighting is crosscutting technology that will enable brilliant displays with the most vivid colors ever seen.
As temperature increases, hot objects sequentially glow in the red, orange, yellow, white, and bluish white.

- Hot physical objects exhibit heat glow (incandescence) and a color.
- Planckian radiator = Black, physical object with temperature $T$.
- Color temperature = Temperature of planckian radiator with same location in chromaticity diagram.
Demonstration of Trichromatic Source

- Color rendering index (CRI) depends strongly on alloy broadening
- 64 lm/W demonstrated at this time (CRI = 84) for trichromatic sources
- For some applications CRI is irrelevant
  - For such applications, 680 lm/W would be possible with perfect SSL device
2017 and Beyond: Smart Sources

Smart light sources can be controlled and tuned to adapt to different requirements and environments

\[ \lambda \ E_{\perp \parallel} \ T_C \ \tau \ (x,y,z) \]
2017 and Beyond: Smart Sources

Smart light sources will enable a wealth benefits and new functionalities

- **Example:** Communicating automotive lights and room lights

- **Example:** Circadian lights

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**Example:** Communicating automotive lights and room lights

Shade, blue sky

<table>
<thead>
<tr>
<th>Shade</th>
<th>Blue sky</th>
<th>Overcast sky</th>
<th>Direct sunlight</th>
<th>Evening</th>
<th>Sunset</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_C = 20,000$ K</td>
<td>$T_C = 6500$ K</td>
<td>$T_C = 5500$ K</td>
<td>$T_C = 3500$ K</td>
<td>$T_C = 2000$ K</td>
<td></td>
</tr>
</tbody>
</table>

**Example:** Circadian lights

- Scotopic vision $P(\lambda)$ CIE 1931
- Circadian efficacy $\Gamma(\lambda)$, Berson *et al.*, 2002
- Photopic vision $P(\lambda)$ CIE 1978

![Graph showing daylight, blue sky, and red sunset wavelengths](image)

![Graph showing vision and circadian efficiency](image)

![Diagram showing ganglion cell (circadian receptor)](image)
2017 and Beyond: Future Transportation Systems

- seat belts … air bags … anti-lock brake … electronic stability control …

and

… communicative traffic lights …
Conclusions

- 100 years have passed since demonstration of first LED

- Solid-state lighting is revolutionary technology that enables
  - Huge energy savings
  - Less global-warming gas and acid-rain-causing gas emissions
  - Reduced dependency on oil

- Fundamental innovation required to satisfy needs. Examples:
  - New low-$n$ materials $n = 1.05$
  - Omnidirectional reflectors with $100 \times$ lower mirror losses than metal reflectors
  - Role of dislocations
  - High-refractive index encapsulants
  - Remote phosphor distributions enhance luminous performance

- The future
  - Smart sources
  - New functionalities
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  - Sandia National Laboratories
  - National Science Foundation
  - Department of Energy
  - New York State, NYSTAR
  - Crystal IS
  - Samsung Advanced Institute of Technology
  - Applied Materials
  - Troy Research Corporation
Innovation in high-refractive index encapsulation materials

- **Fundamental problem of light extraction**
  - Index mismatch between semiconductor and surrounding air
  - Fresnel reflection and total internal reflection

- Encapsulation materials with high refractive index would solve light-extraction problem
- **Titania nanoparticles in**
  - Silicone
  - Epoxy
  - PMMA

- **Titania, TiO$_2$, $n = 2.68$**
- **Polymer: $n \approx 1.6$**
- ➔ **Mixture $n > 2.0$**


Frank Mont et al. 2007
High-refractive index encapsulation materials

- Optical scattering in film with poissonian distribution of nano-particles?
- Ordered distributions feasible?