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

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Light-Emitting Diodes – 1907 – SiC – Henry Round

- First observation of electroluminescence
- First SiC LED

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.

NEW YORK, N. Y. H. J. ROUND.

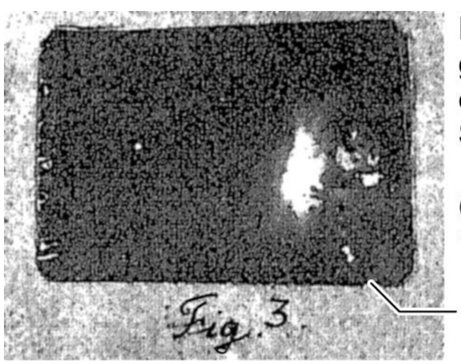
Henry Joseph Round

Henry Joseph Round, 1907

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

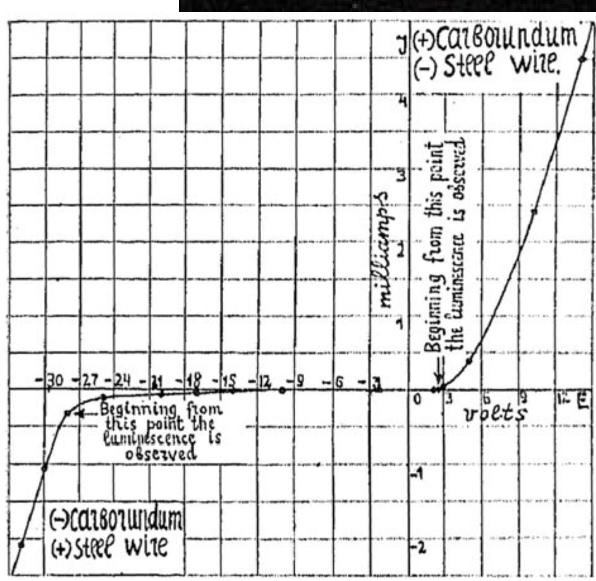


First photograph of light emitted by SiC LED

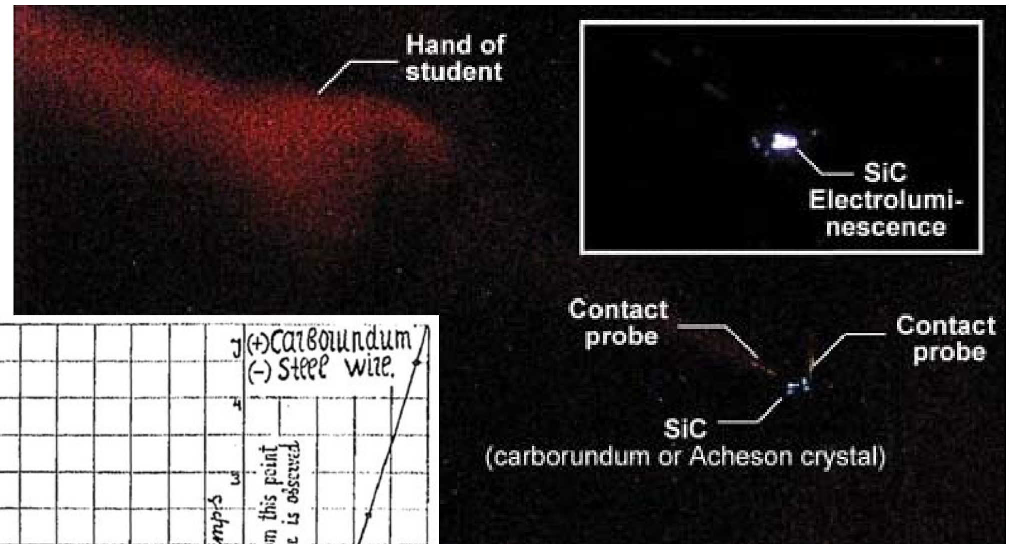
(after Lossev, 1924)

SiC crystal

Photograph of Lossev's LED



Lossev's I-V characteristic

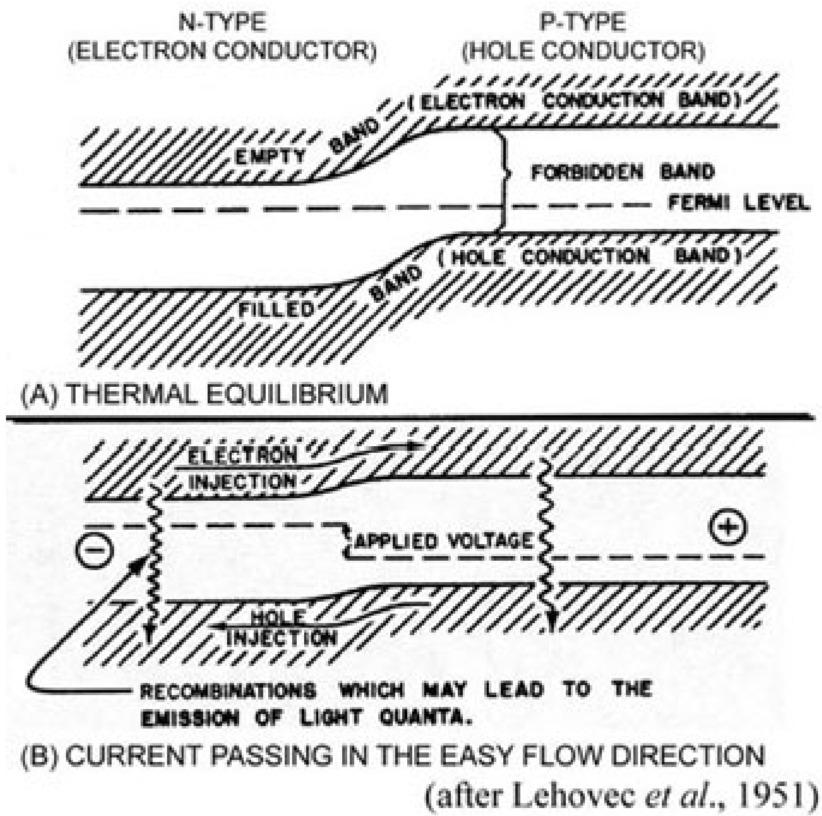


Re-enactment of 1907 experiment

Oleg V. Lessov, 1928

Light-Emitting Diodes – 1951 – SiC – Lehovec *et al*.

- First correct interpretation of electroluminescence in p-n junctions
- Injection of minority carriers

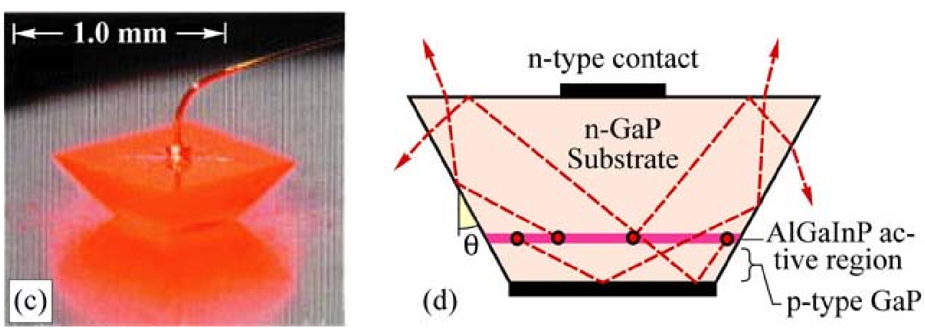


First correct explanation of light emission from LEDs

Lehovec et al., 1951

- Demonstration of high-performance emitters emitting at red, orange, and yellow wavelengths

AlGaInP LEDs



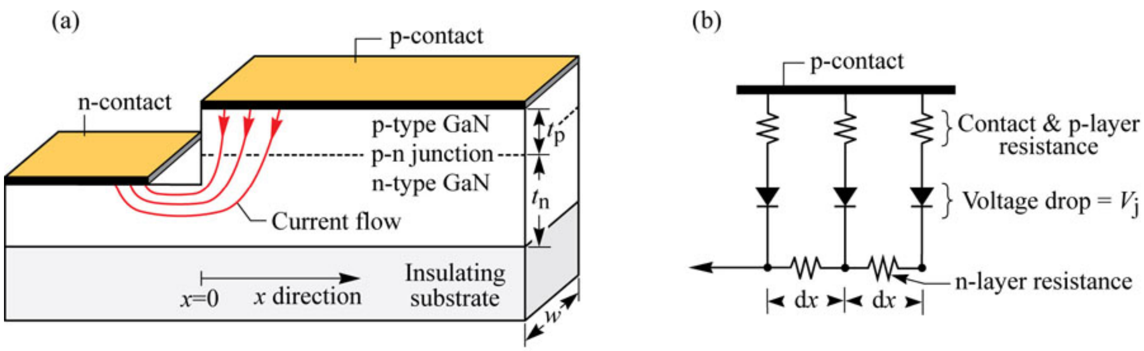
Krames et al., 1999

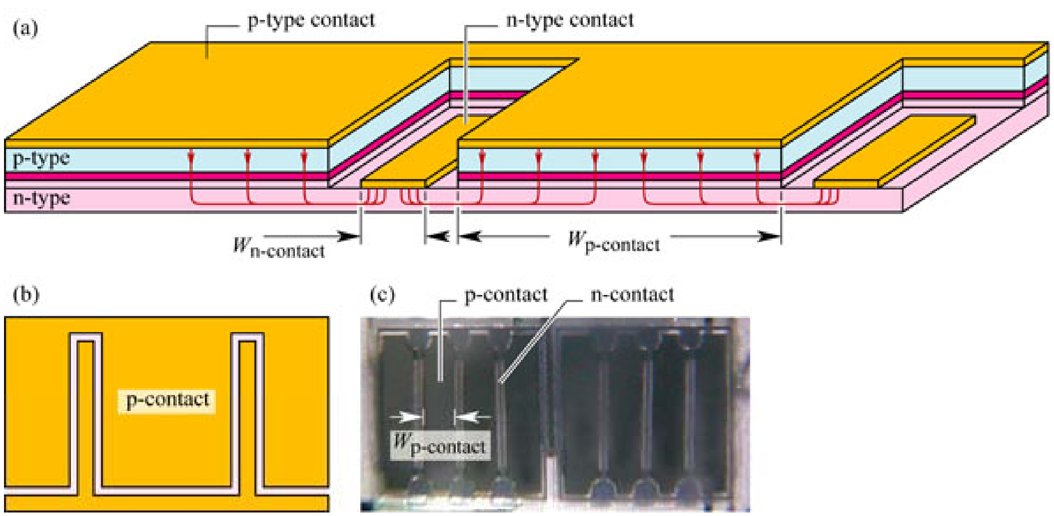
Sugawara et al., 1991

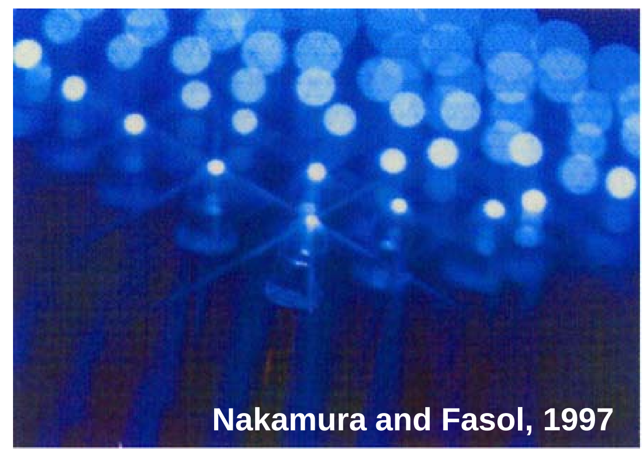
Light-Emitting Diodes – 1991 – GaInN – Nakamura et al.

- GaInN – the first viable short-wavelength material
- First blue LED
- Basis for white LEDs and solid-state lighting

Maruska, 1972





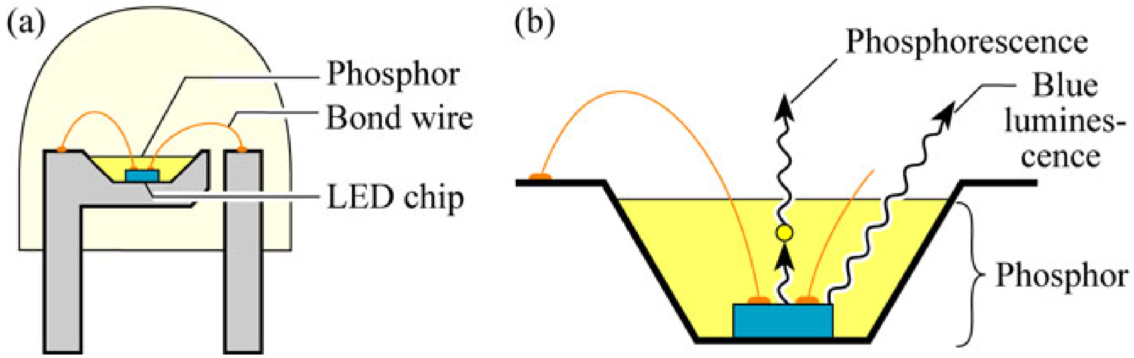


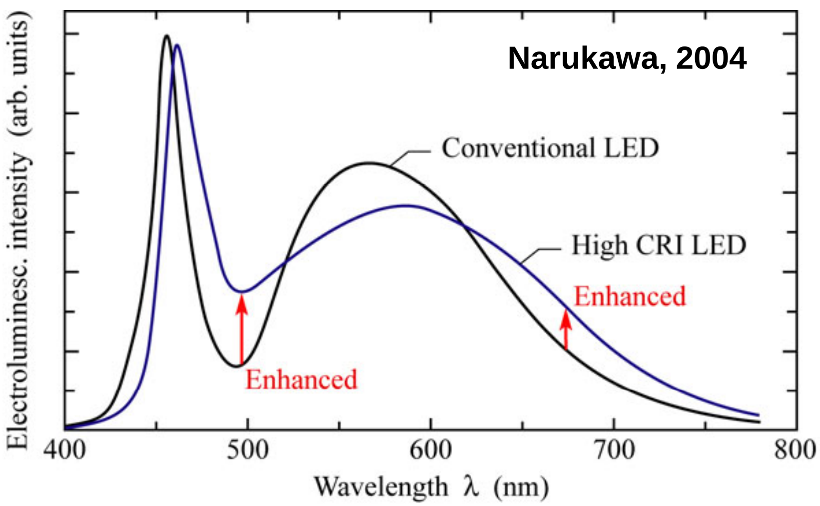
Nakamura and Fasol, 1997

Nakamura et al., 1991

Light-Emitting Diodes – 1997 – White LEDs – Nakamura at al.

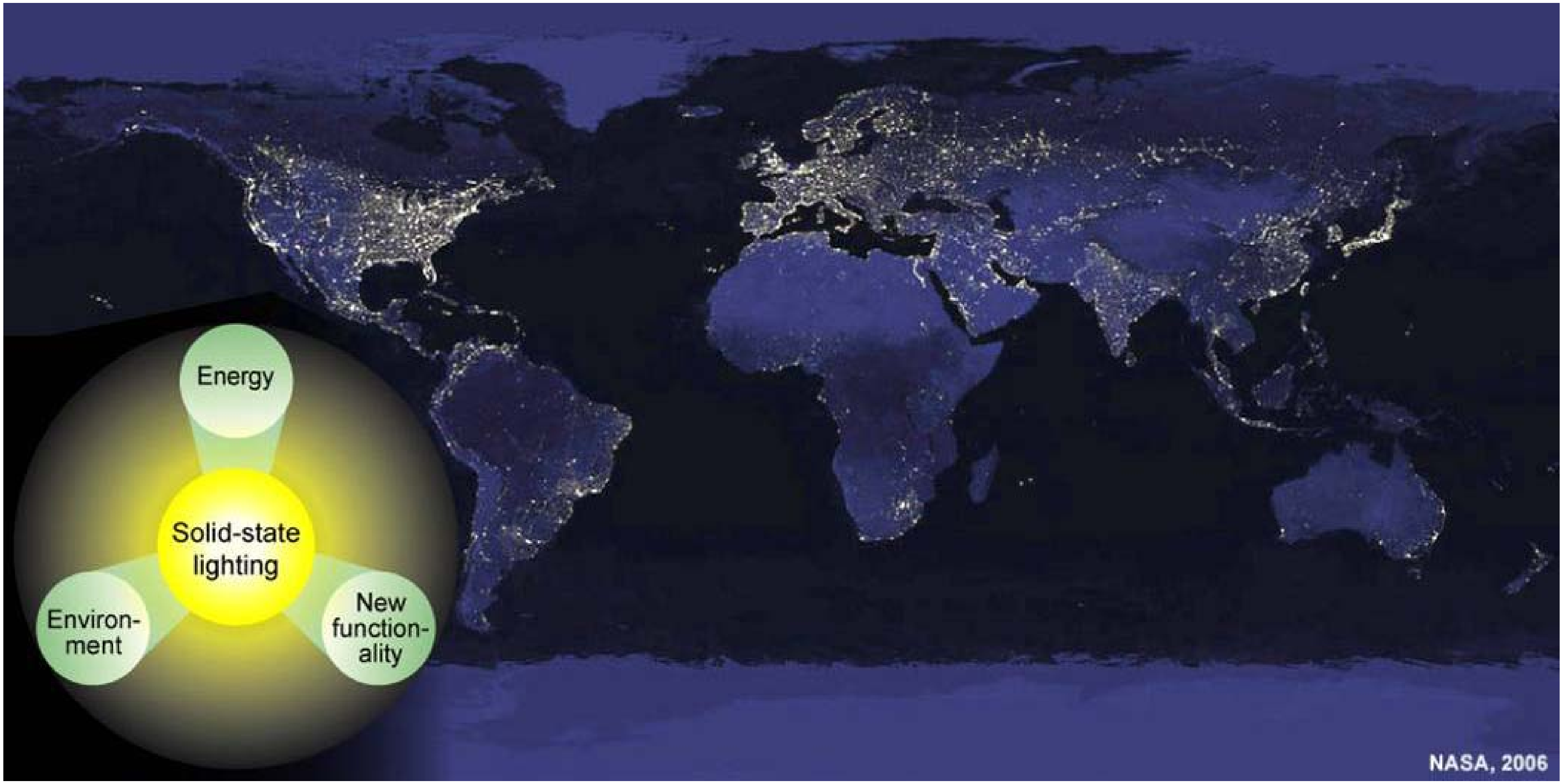
- First white LED
- Suitable for illumination applications
- Transition from ***information*** to ***illumination*** applications





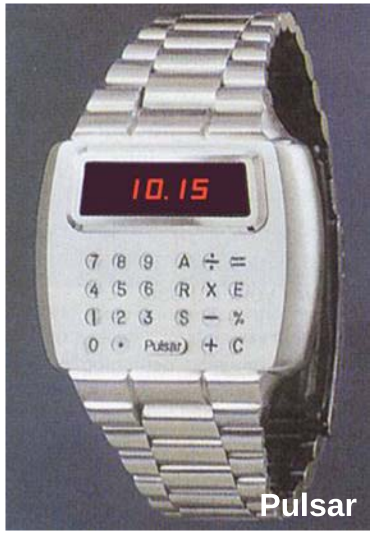
Nakamura and Fasol, 1997

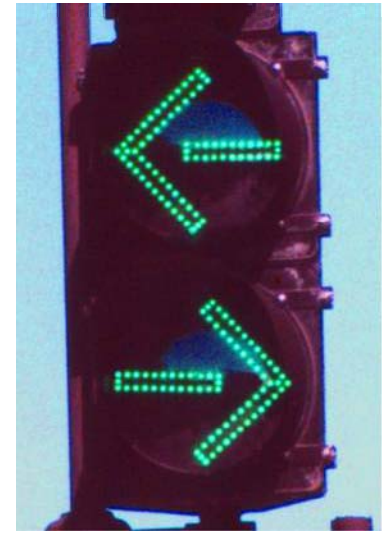
Let's keep the lights on – and strongly reduce power

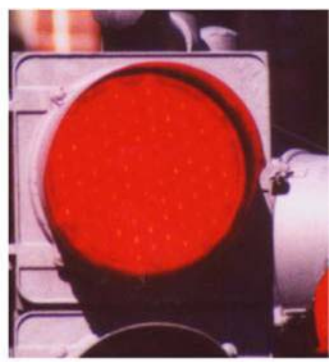


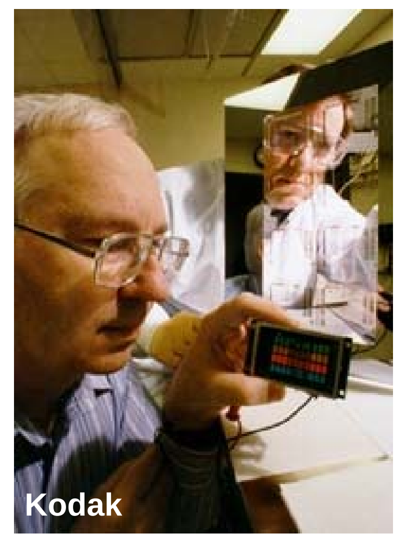
It is feasible to reduce energy consumption for lighting by 50% – and keep the lights on!

Traditional applications for LEDs and OLEDs

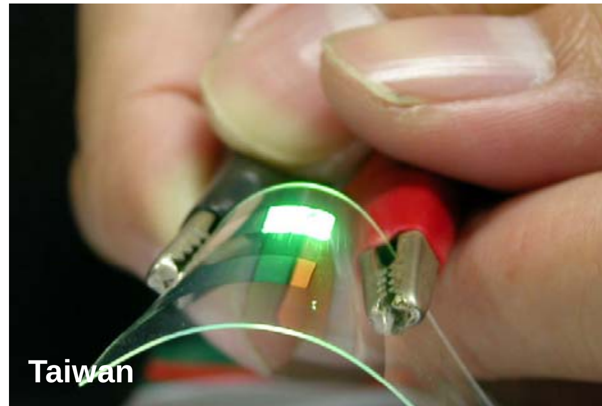








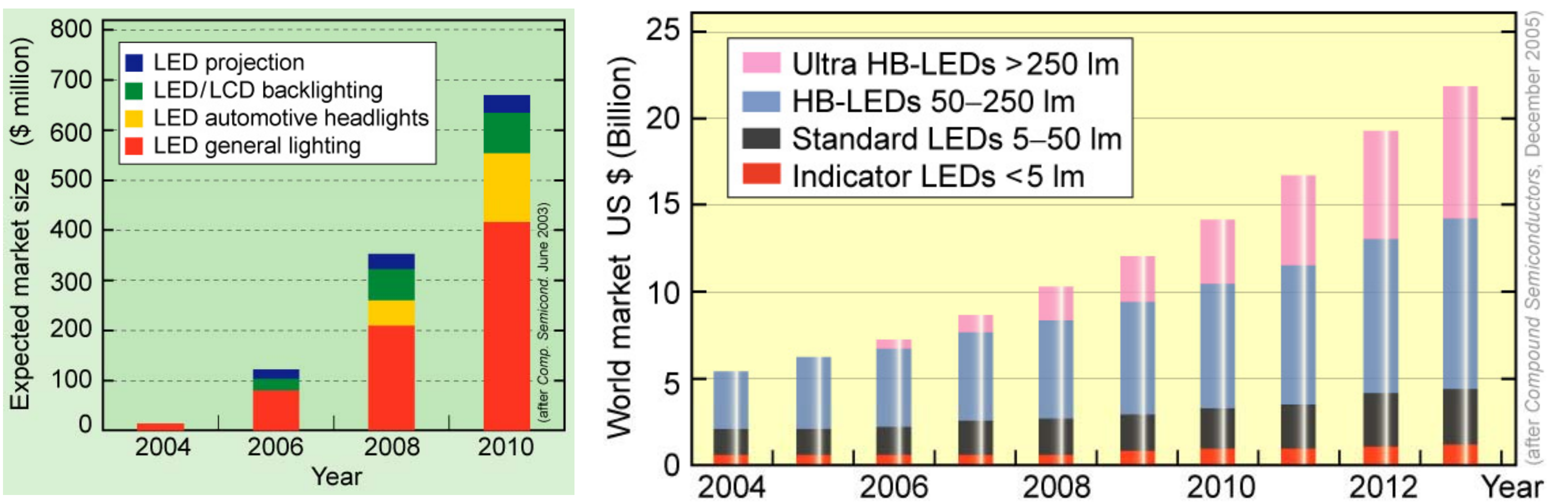
Recent applications



Solid-state lighting

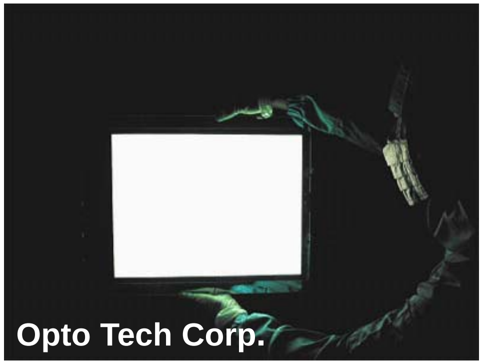
- **Inorganic devices**:
  - Semiconductor plus phosphor illumination devices
  - All-semiconductor-based illumination devices
- **Organic devices**:
  - Remarkable successes in low-power devices
    (Active matrix OLED monitors, thin-film transistors, etc.)
  - Substantial effort is underway to demonstrate high-power devices
  - Anticipated manufacturing cost and luminance of organic devices are *orders of magnitude* different from inorganic devices


Comp. Semiconductors, 2006



Predicted growth of LED market

OLED versus LED



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

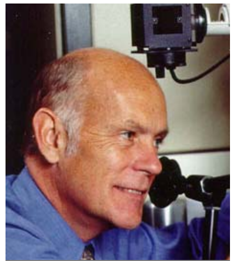
- Luminance of OLEDs: $10^2 – 10^4$ cd/m^2
- Luminance of LEDs: $10^6 – 10^7$ cd/m^2
- Luminance of OLEDs is about 4 orders of magnitude lower
- OLED manufacturing cost per unit area must be $10^4 \times$ lower

OLEDs	**LEDs**
Low-cost reel-to-reel manufacturing	Expensive epitaxial growth

Energy conservation – A singular opportunity

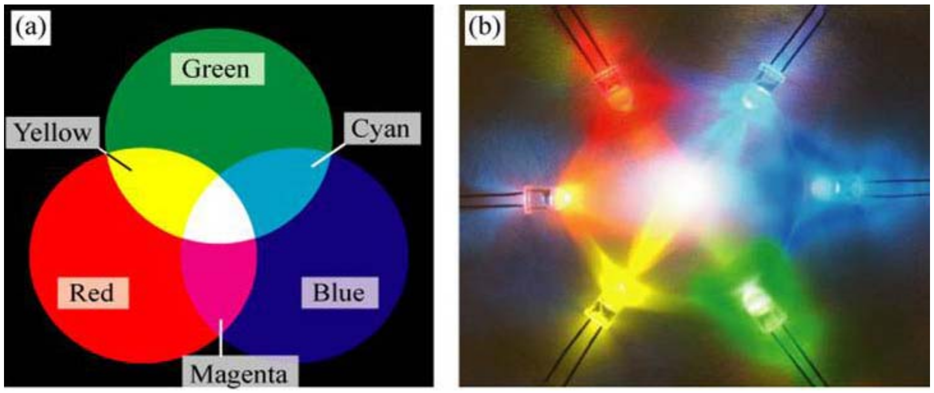
Nobel Laureate Richard Smalley: "Energy is the single most important problem facing humanity today" and "conservation efforts will help the worldwide energy situation".

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

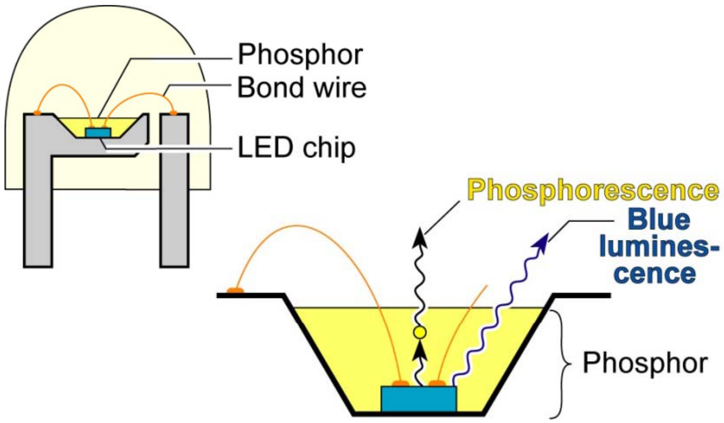


1943 – 2005

- Solid-state lighting is singular opportunity for conservation of energy



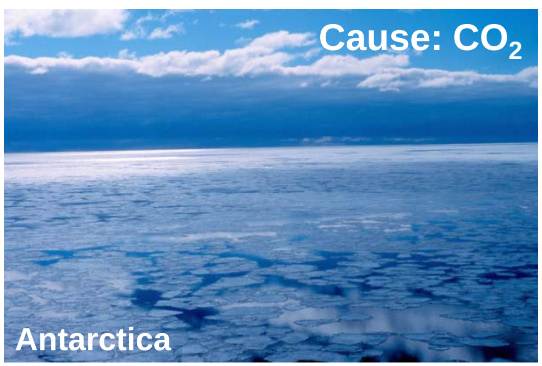
Multiple light-emitting diodes

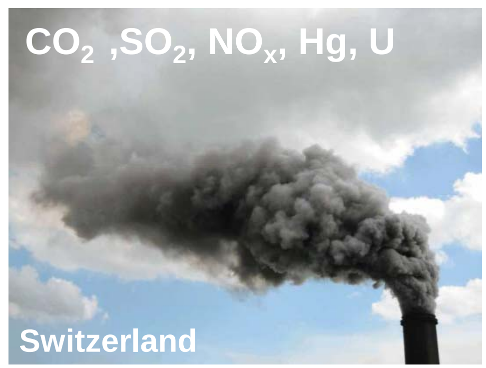


LED with wavelength (λ) converter

Quantification of solid-state lighting benefits

- **Energy benefits**
  - 22 % of electricity used for lighting
  - LED-based lighting can be **20** × more efficient than incandescent and **5** × 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.

	Savings under "5.5% scenario"	**Savings under "11% scenario"**
Reduction in total energy consumption	43.01×10^{18} J $\times$ 5.5% $\times 4 \times 10$ = = 94.62×10^{18} J	43.01×10^{18} J $\times$ 11% $\times 4 \times 10$ = = 189.2×10^{18} J
Reduction in electrical energy consumption	228.9 TWh $\times 4 \times 10$ = = 9,156 TWh = 32.96×10^{18} J	457.8 TWh $\times 4 \times 10$ = = 18,310 TWh = 65.92×10^{18} J
Financial savings	22.89×10^{9} \$ $\times 4 \times 10$ = = 915.6×10^{9} \$	45.78×10^{9} \$ $\times 4 \times 10$ = = $1{,}831 \times 10^{9}$ \$
Reduction in CO_2 emission	133.5 Mt $\times 4 \times 10$ = 5.340 Gt	267.0 Mt $\times 4 \times 10$ = 10.68 Gt
Reduction of crude-oil consumption (1 barrel = 159 liters)	12.03×10^{6} barrels $\times 4 \times 10$ = = 481.2×10^{6} barrels	24.07×10^{6} barrels $\times 4 \times 10$ = = 962.4×10^{6} barrels
Number of power plants not needed	$35 \times 4 = 140$	$70 \times 4 = 280$

(*) 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 $\times$ 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)
see also R. Haitz *et al*. *Adv. in Solid State Physics*, *Physics Today* 2001; see also US DOE (2006)

Schubert *et al*., *Reports on Progress in Physics* (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

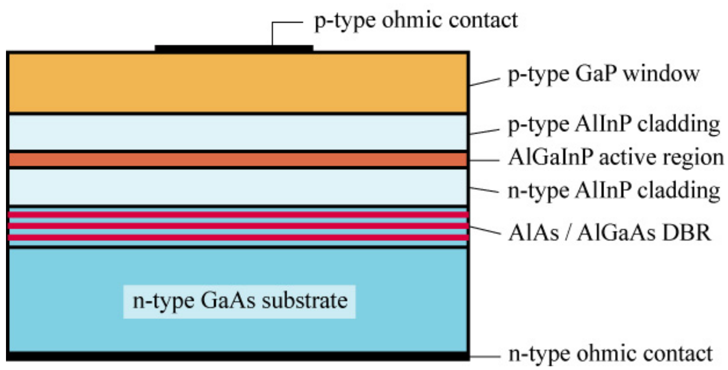
Light-emitting diodes with reflectors

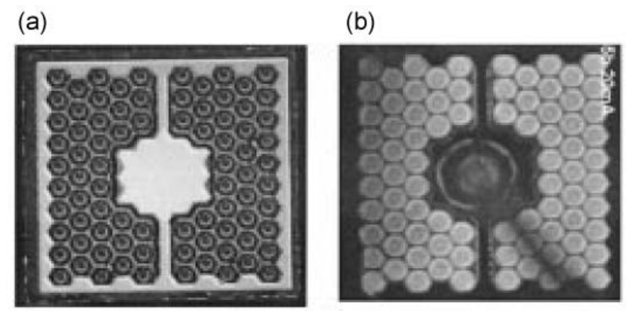
To avoid optical losses, ideal device structures possess either:

Perfect Transparency* or *Perfect Reflectivity

Example of **reflective** structure:

(after Osram Corporation)

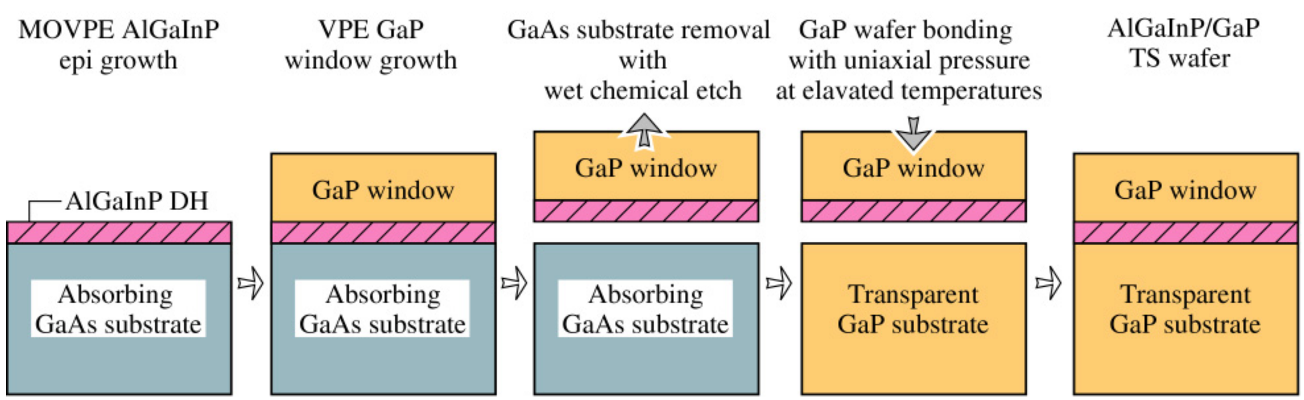




Top view (a) andi llumination pattern (b) of a 615-nm thin-film LED (after Streubel et al., 2002)

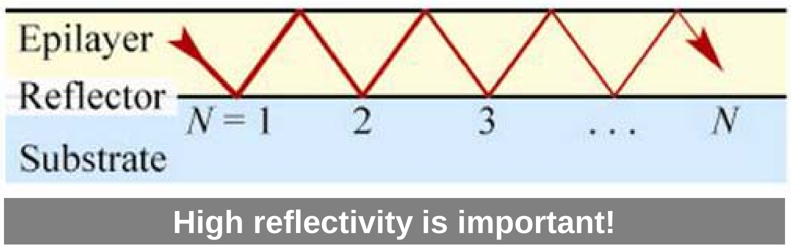
Example of **transparent** structure

(after Lumileds Corporation)

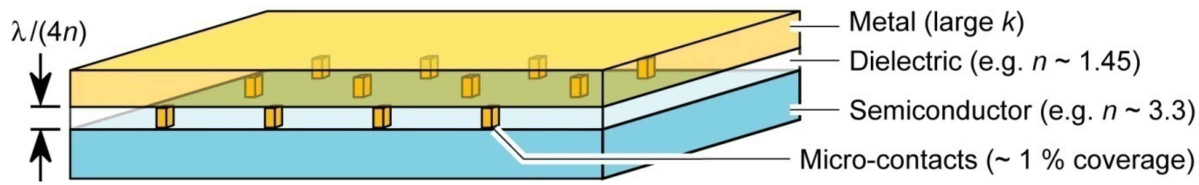


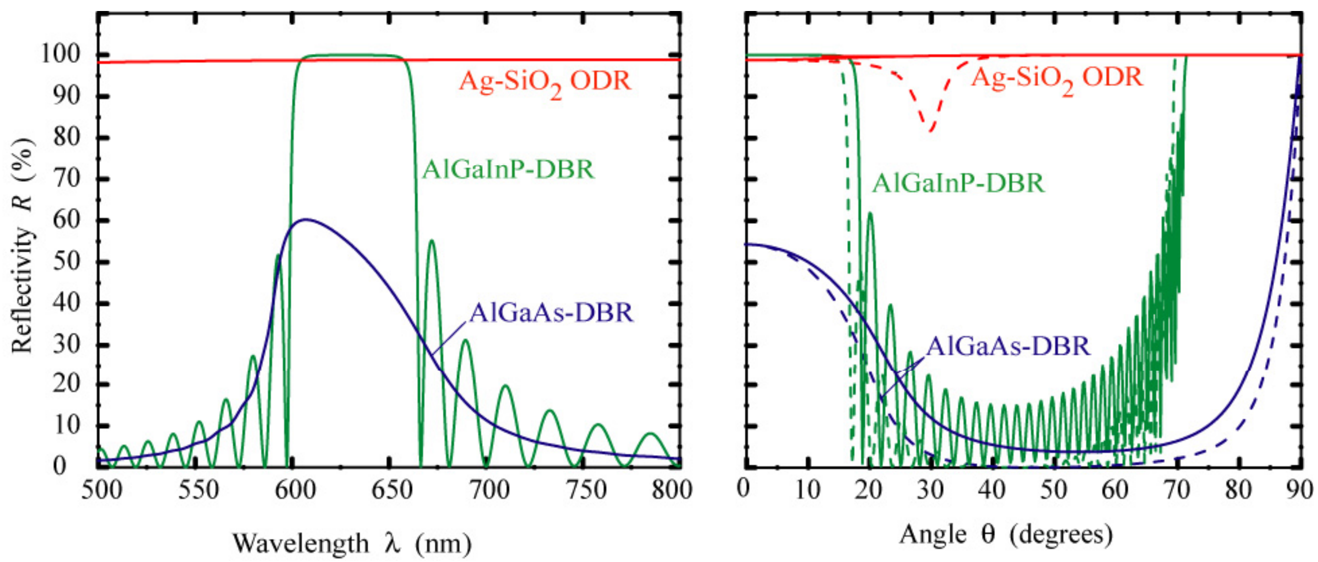
Omni-directional reflector (ODR)

Search for the "perfect reflector": R = 100% for all Θ, all λ, and TE and TM



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

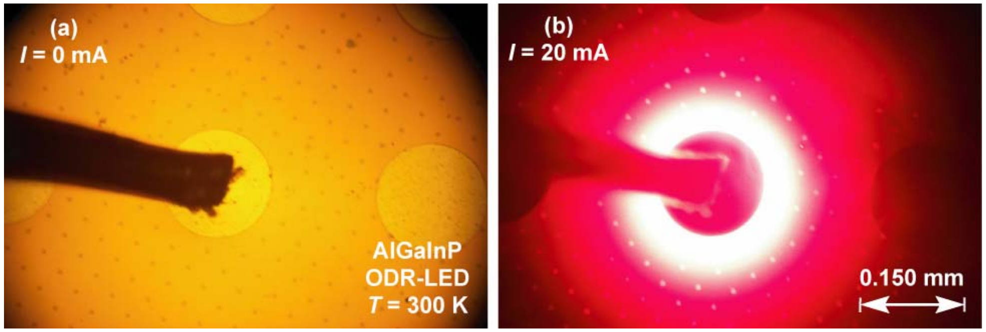


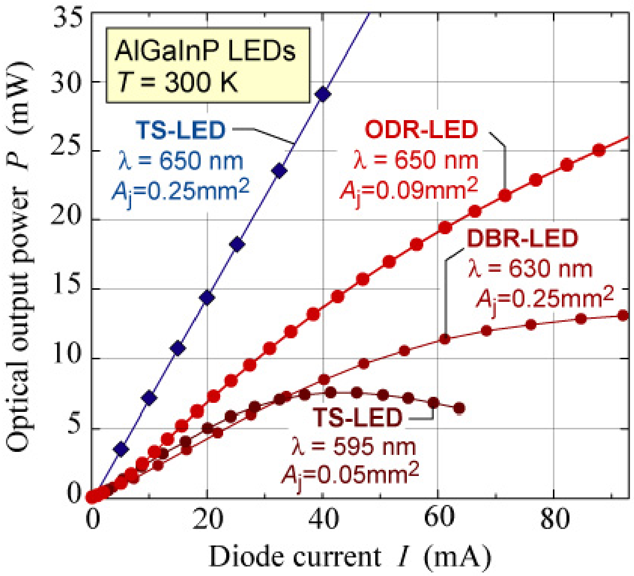


AlGaInP and GaInN LEDs with ODR

AlGaInP LED

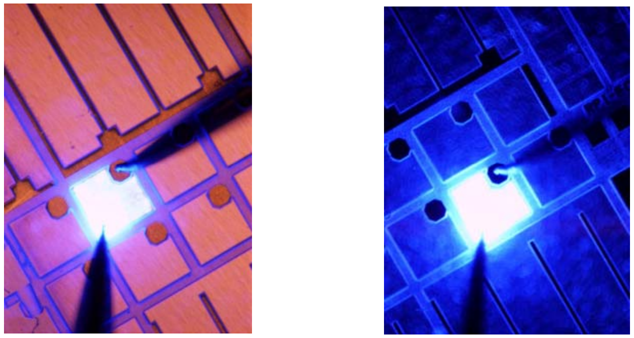
λ = 650 nm, MQW active region
AlGaAs window layer
GaAs substrate removed, Si submount





GaInN LED

λ = 460 nm, MQW active region
Sapphire substrate



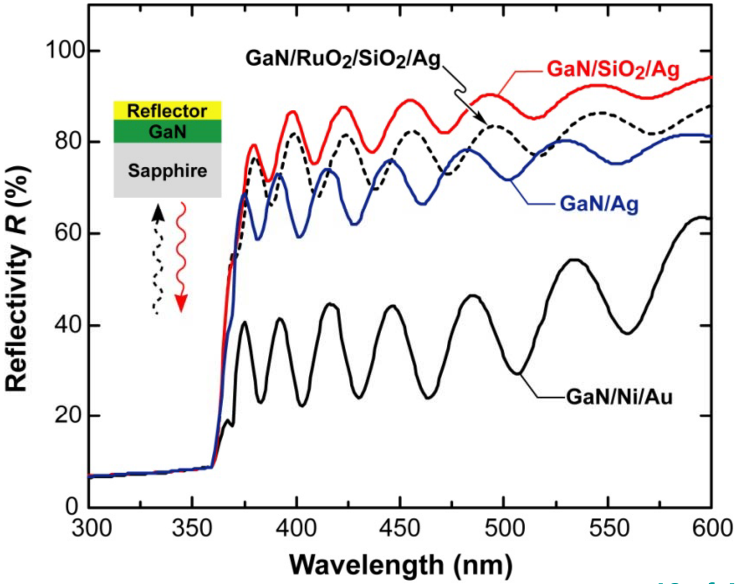


Figure of merit for DBR: Index contrast Δn

- Fresnel reflectance of interface

$$r = \frac{n_h - n_l}{n_h + n_l} = \frac{\Delta n}{n_h + n_l}$$

- DBR reflectance

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

- Spectral width of stop band

$$\Delta\lambda_{stop} = \frac{2\, \lambda_{Bragg}\, \Delta n}{n_{eff}}$$

- Penetration depth

$$L_{pen} \approx \frac{L_1 + L_2}{4\, r} = \frac{L_1 + L_2}{4} \frac{n_1 + n_2}{\Delta n}$$

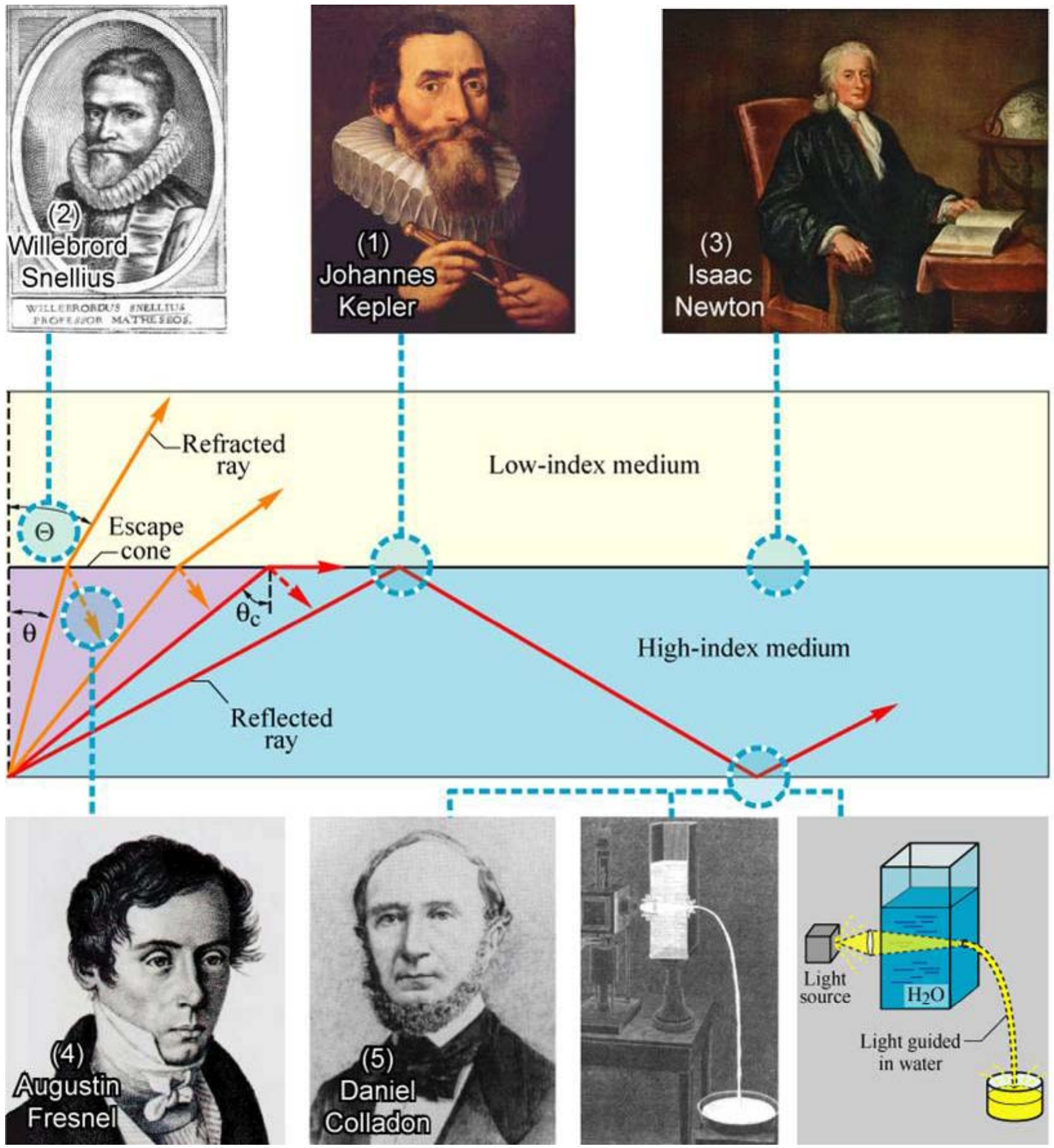
- Critical angle (max. angle for high reflectivity)

$$\theta_c \approx \frac{n_1}{n_0} \sqrt{\frac{2}{n_0} \frac{2\Delta n}{n_1 + n_2}}$$

➔ *By increasing index contrast Δn, 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)

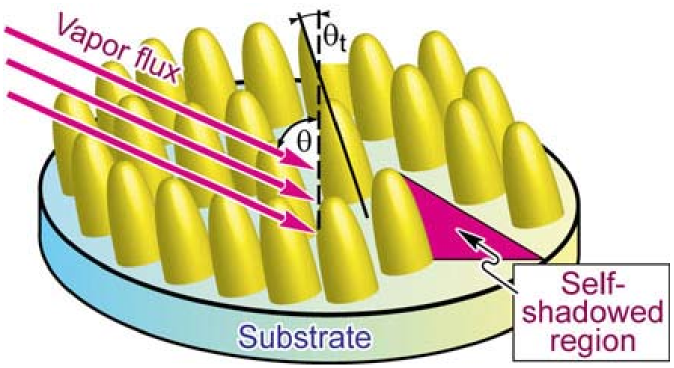
(4) Augustin Fresnel
(1788-1827)
Quantitatively discribed reflection

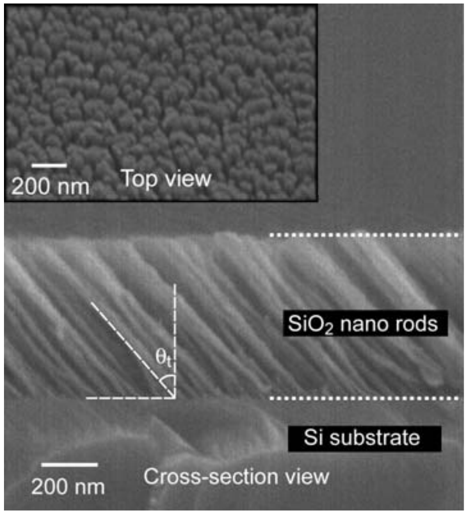
(5) Daniel Colladon
(1802-1893)
Developed first wave guiding apparatus

E. F. Schubert

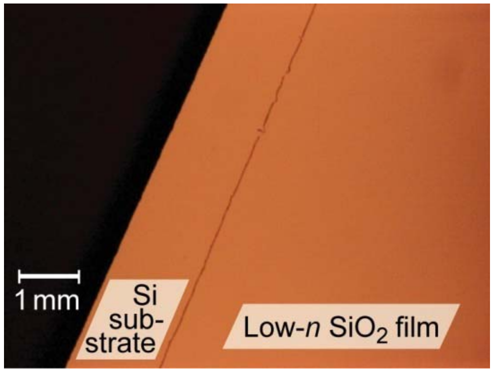
New class of materials: Low-*n* materials

- 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

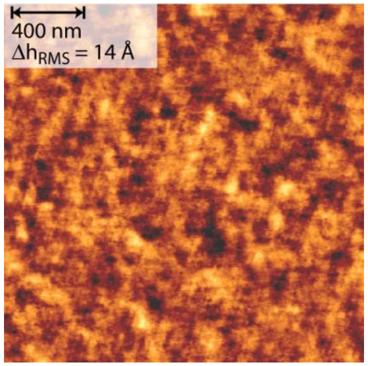




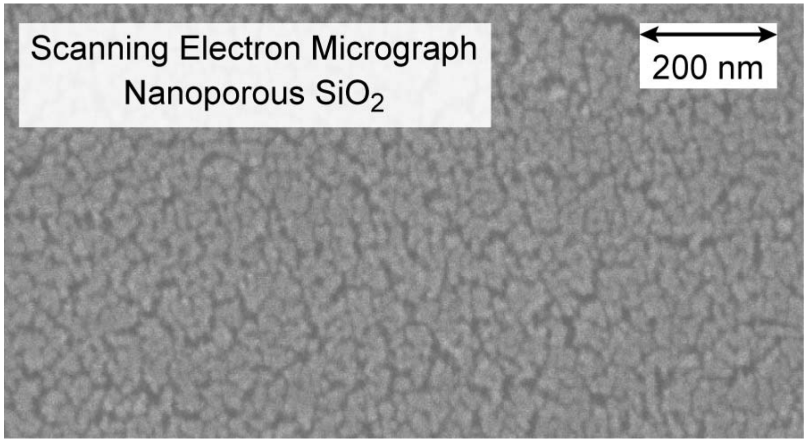
Low-*n* SiO_2



Optical micrograph

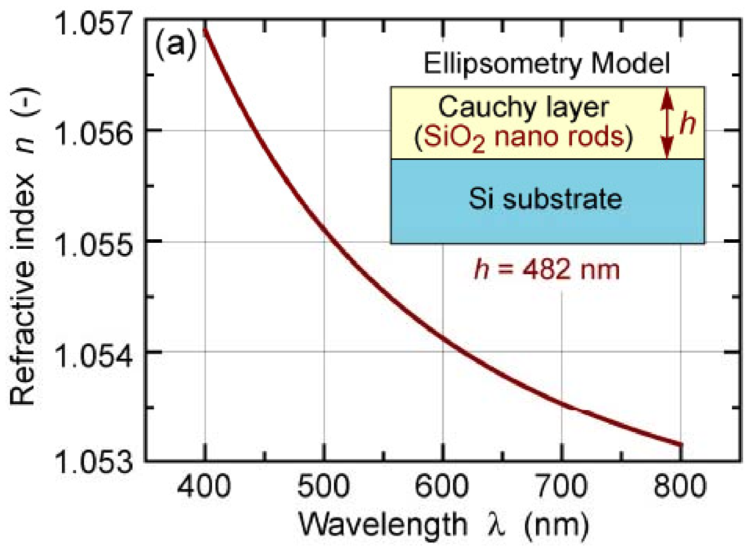


Atomic force micrograph

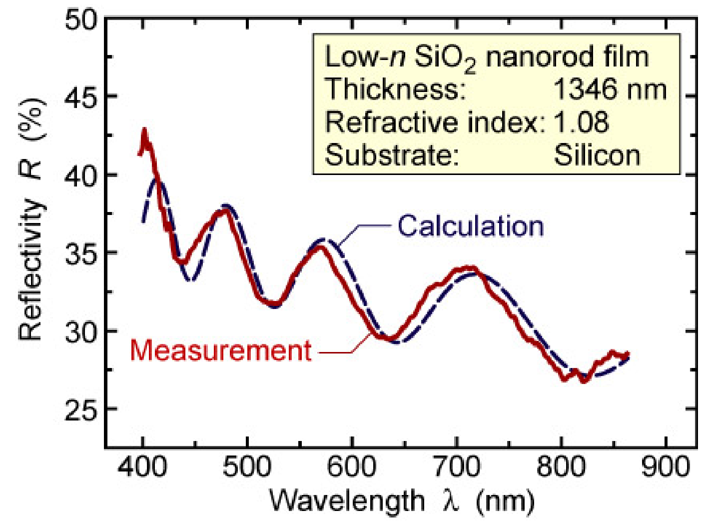


Low-*n* xerogels, after Gill and Plawsky, 2005

Unprecedented low refractive index



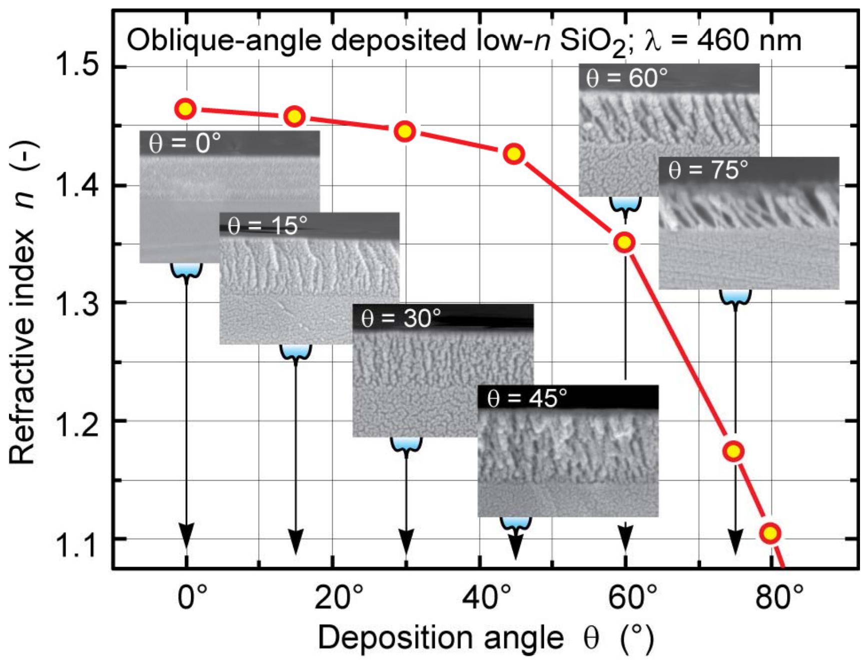
Ellipsometry

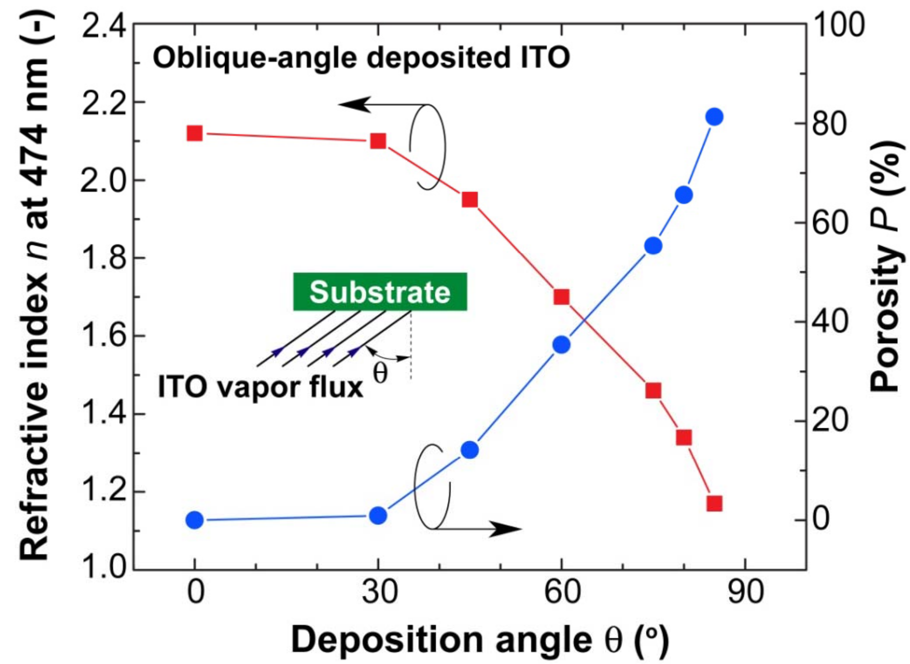


Thin-film interference

- Unprecedented low refractive index of $n \approx 1.05$: World record!
- Pore sizes << λ (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



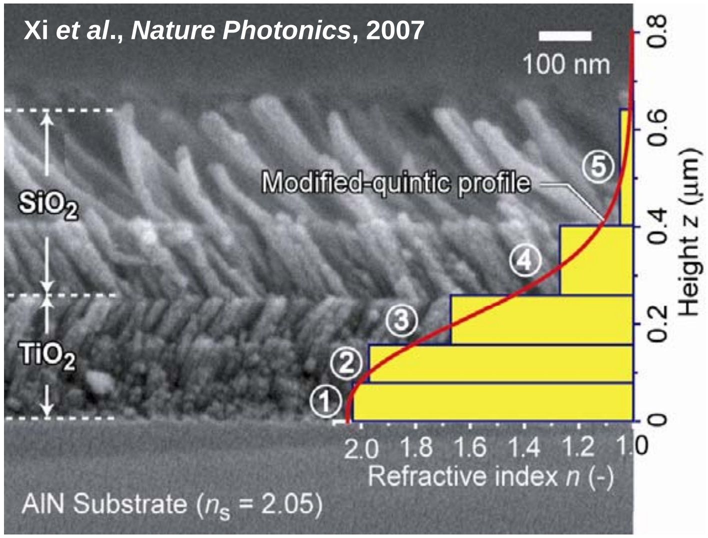


- ***Controllability*** of refractive index of a film by varying deposition angle
- $1.46 < n_{SiO2} <$ **1.05**; $2.19 < n_{ITO} < 1.17$
- Design freedom in optical components afforded by oblique angle deposition
- Select materials based on materials properties other than refractive index, and tune the refractive index to desired value

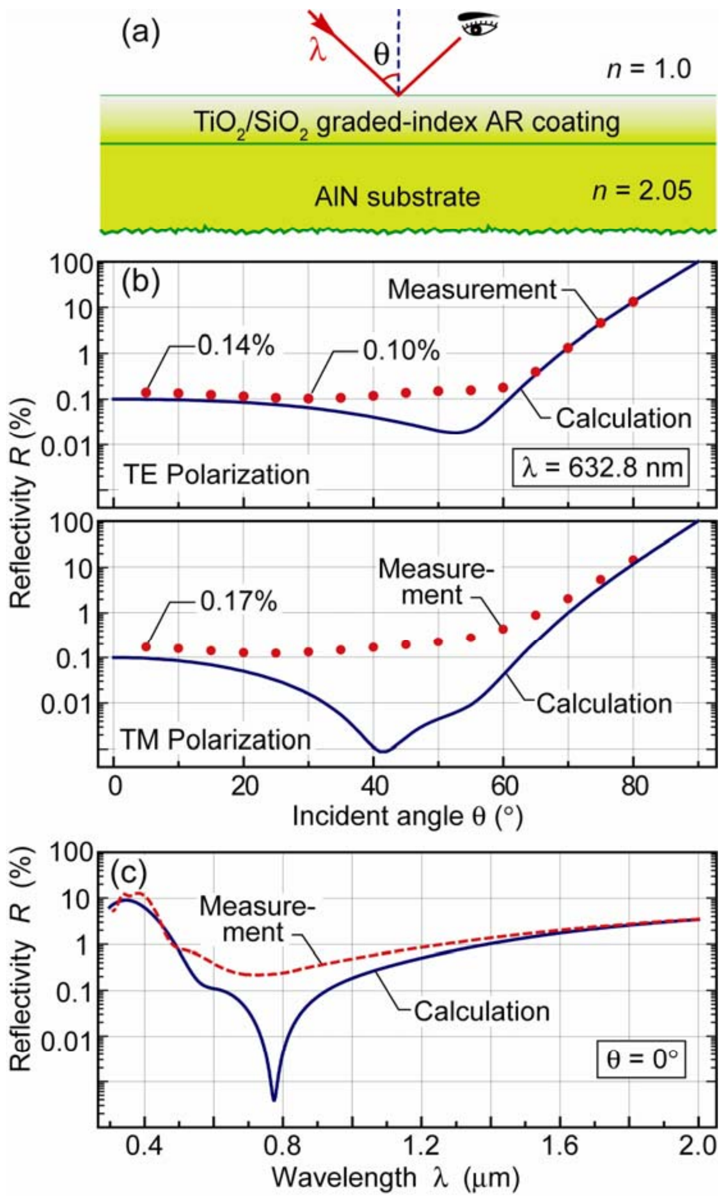
Applications of low-*n* materials – AR coatings

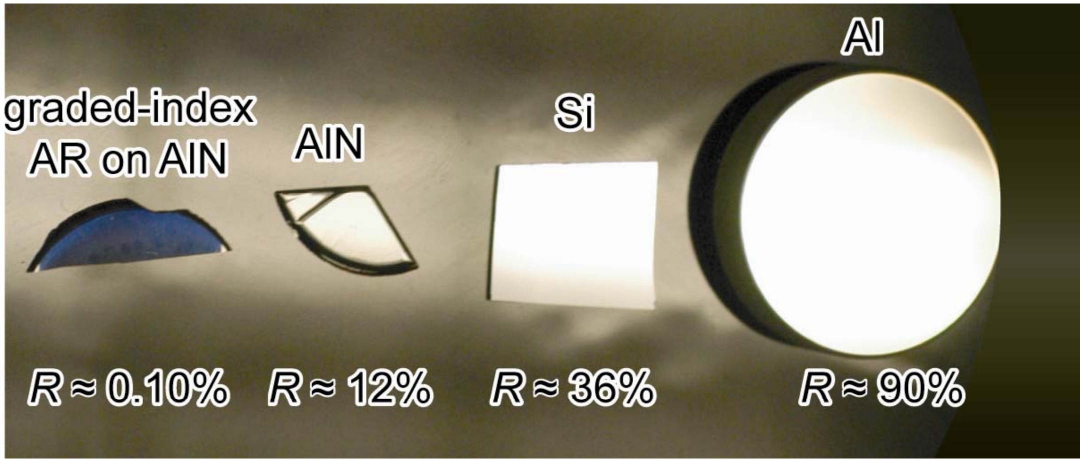
GRIN AR coating demonstrated by oblique-angle deposition of TiO2 and SiO2 with various deposition angles

Reflectivity as low as ***R* ≈ 0.1%** due to virtual elimination of Fresnel reflection



Extremely low reflectivity

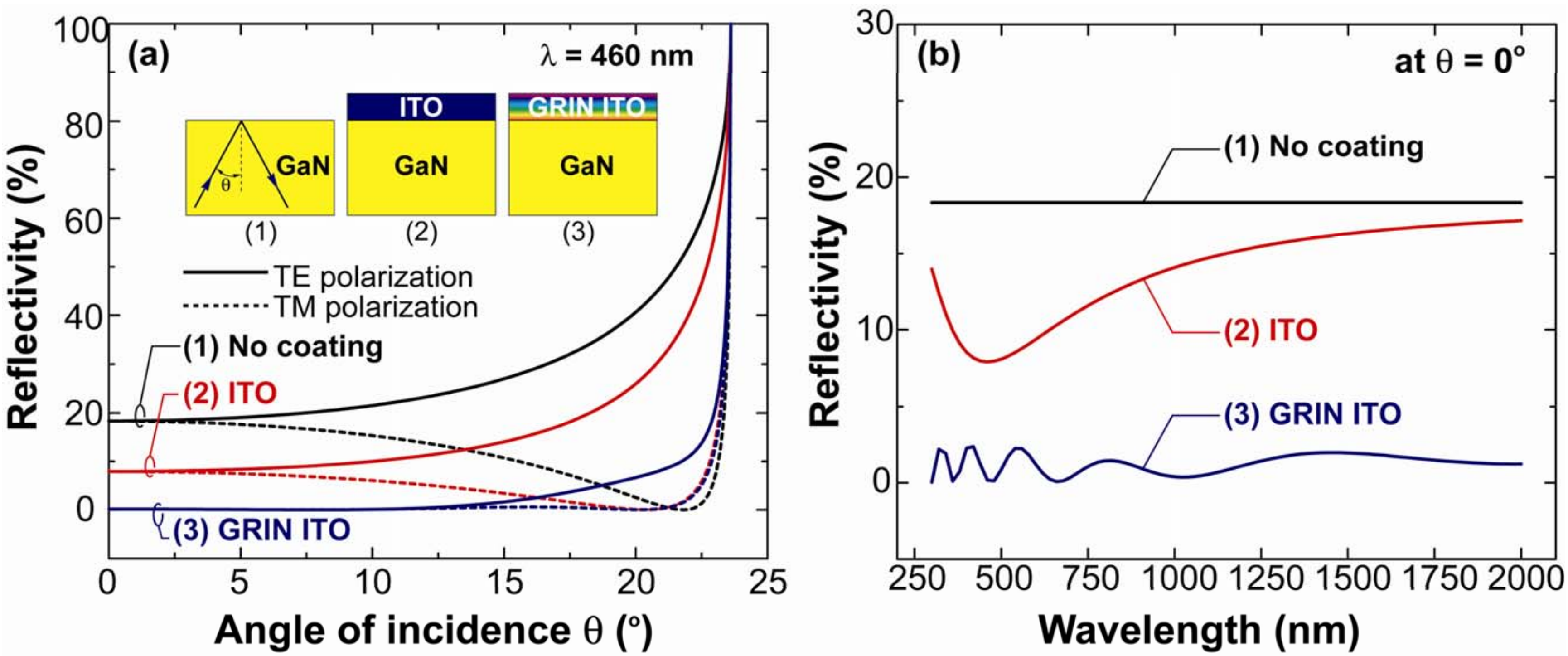




J. Q. *et al.*, Nature Photonics 2007

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

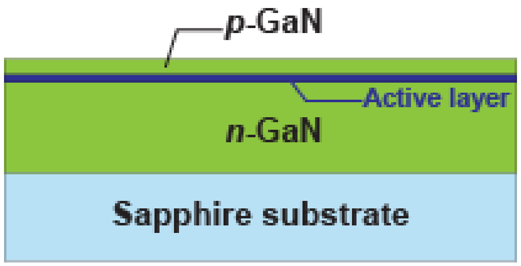
Application of low-*n* materials: AR coating for LEDs



- **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

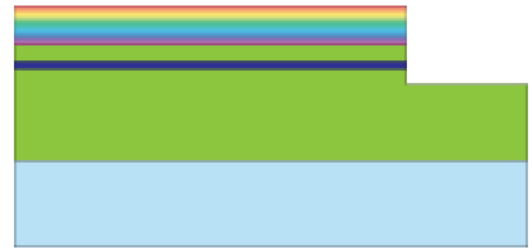
Jong Kyu Kim et al., 2007

Fabrication of GaInN LEDs with GRIN ITO

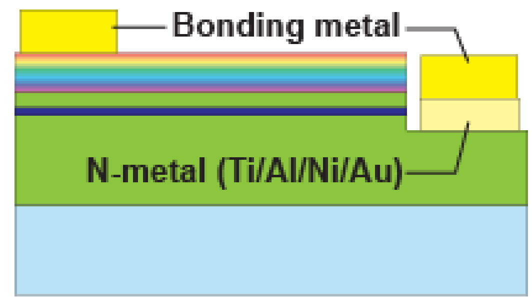


(1) GaInN LED on sapphire
(~ 474 nm)

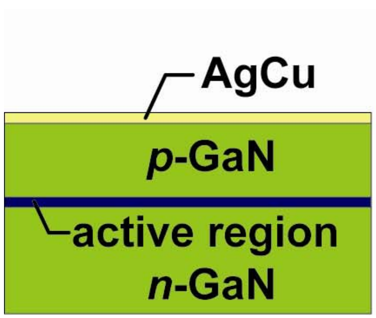
(2) AgCu (2 nm)/GRIN ITO
- oblique angle deposition
- 6 layers (0, –45, 60, –75, 80, –85)
- oxidation annealing



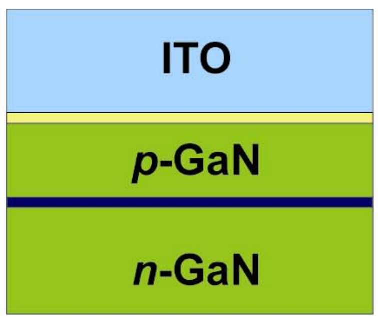
(3) Mesa etching by CAIBE
- Ar + Cl2



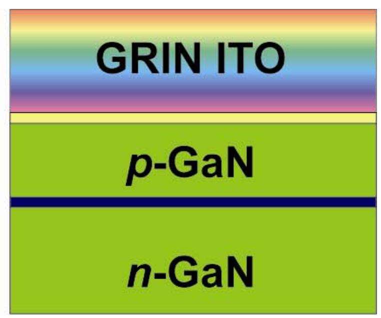
(4) N-metal & Bonding metal
- Ti/Al/Ni/Au deposition
- annealing at 750°C, 1 min.
- Ti/Au deposition



(a) without AR coating

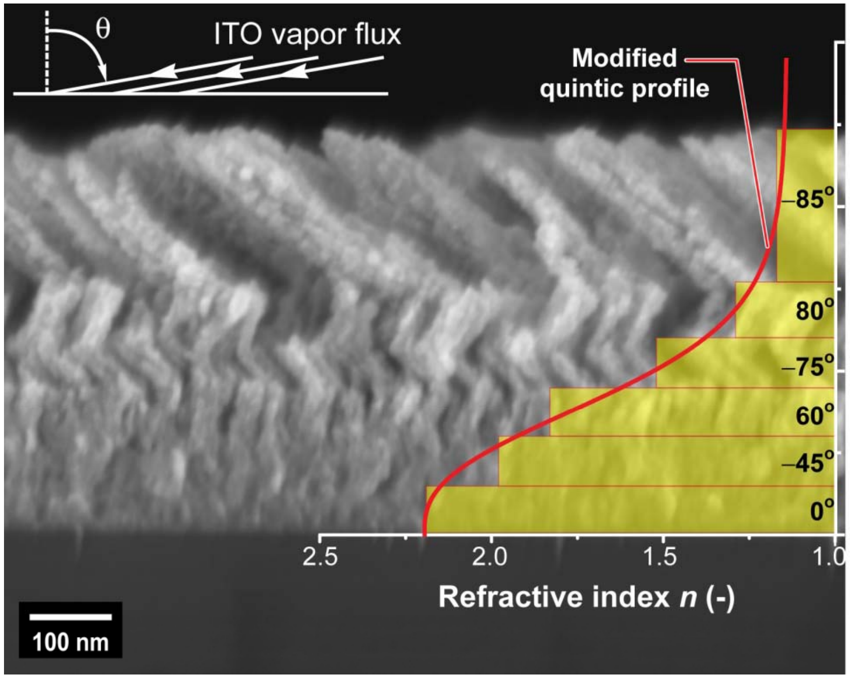


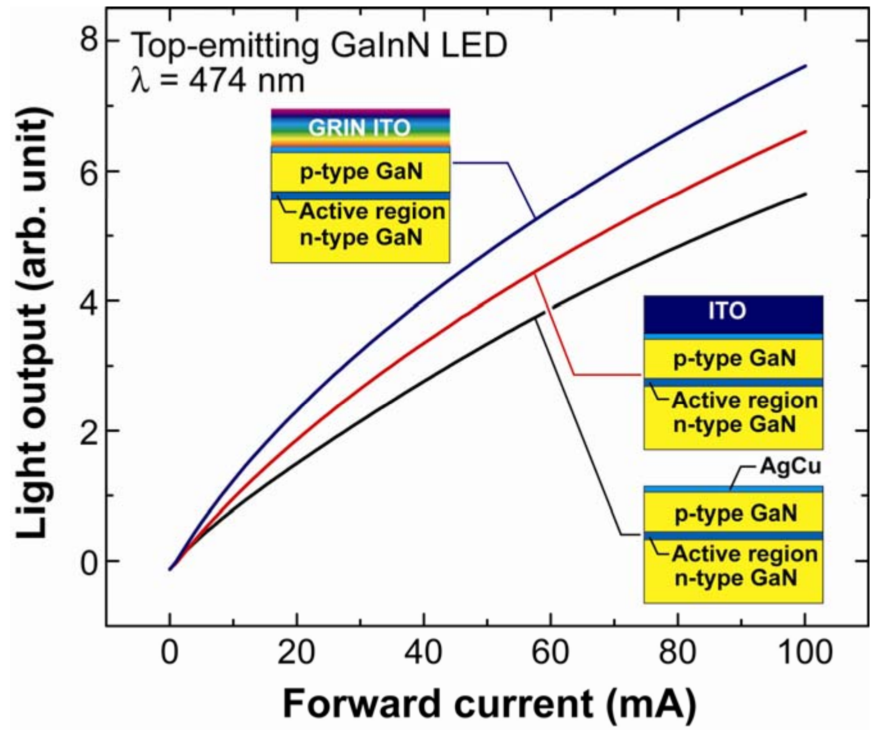
(b) ITO AR coating



(c) GRIN ITO AR coating

GaInN LEDs with GRIN ITO



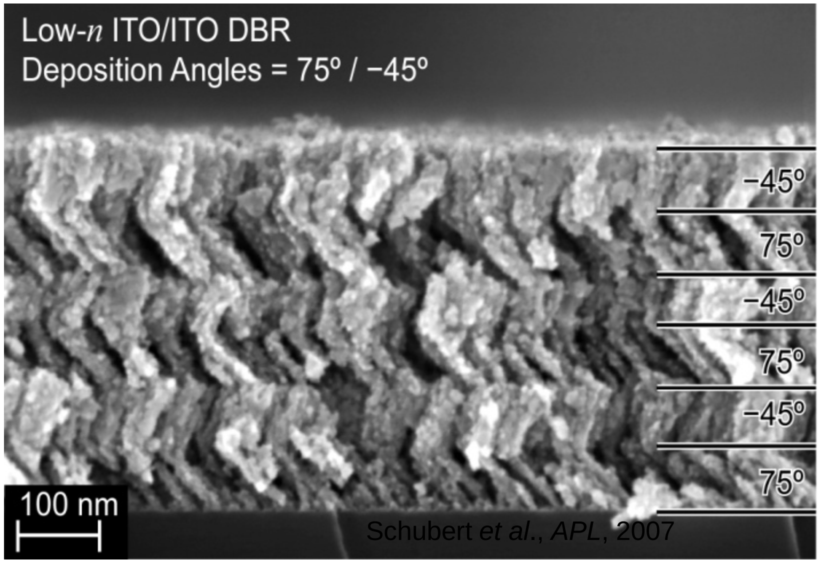


- ***Conductive*** graded-index anti-reflection coating made of a ***single*** material, ITO, fabricated on a GaInN blue LED
- Enhanced light output by **> 45%** by using ITO graded-index anti-reflection due to reduced Fresnel reflection
- Fresnel reflection is strongest for III-V phosphides (AlGaInP, $R \approx 30\%$) due to high refractive index (n = 3.0 – 3.5).

Applications of low-*n* materials – DBRs

Single material optical component: select ITO due to its transparency & conductivity, tune its refractive index to desired value

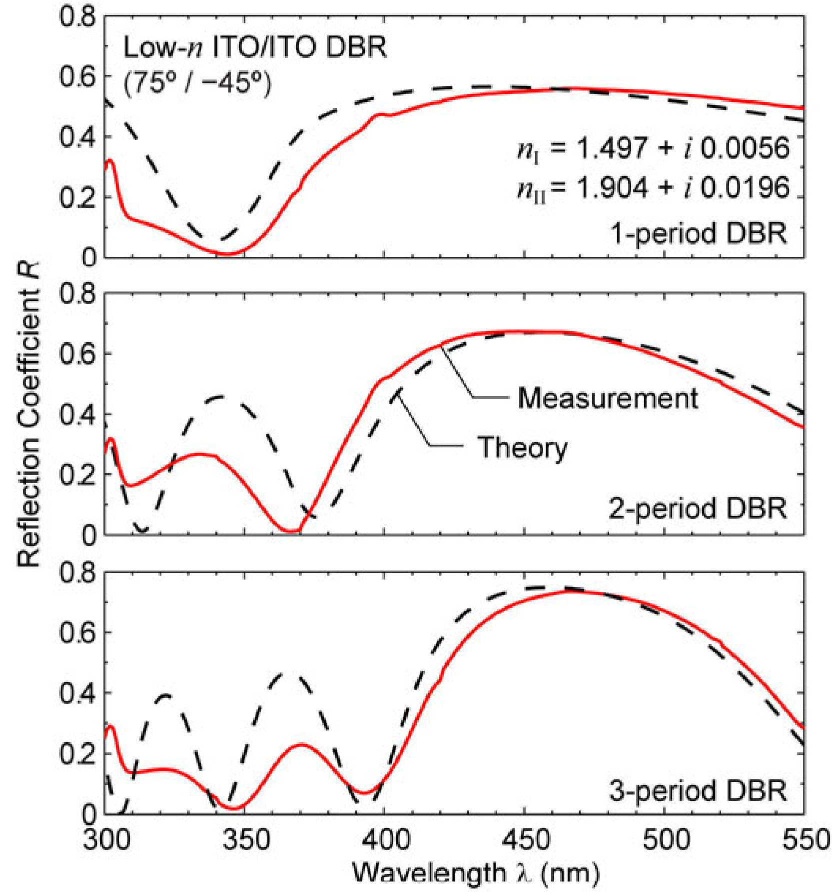
Conductive distributed Bragg reflector (DBR) composed of a ***single*** material, ITO, fabricated by oblique angle deposition

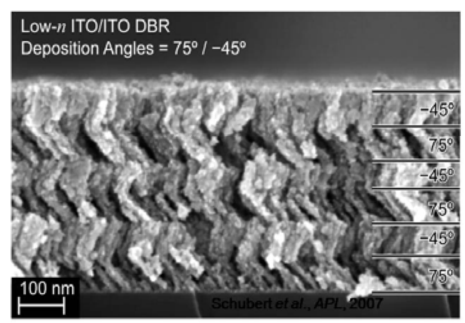


Schubert *et al.*, *APL*, 2007

DBRs

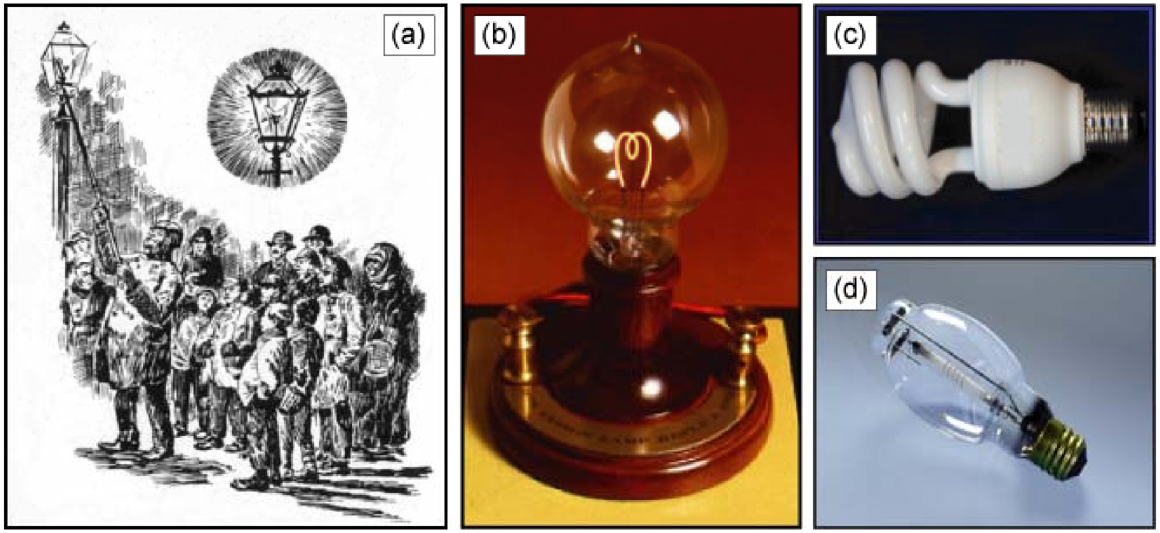
- DBRs with several periods demonstrated
- Experimental reflection spectrum agrees well with theory
- New opportunities using dielectric materials





Solid-state lighting technologies and figures of merit

Lighting technologies

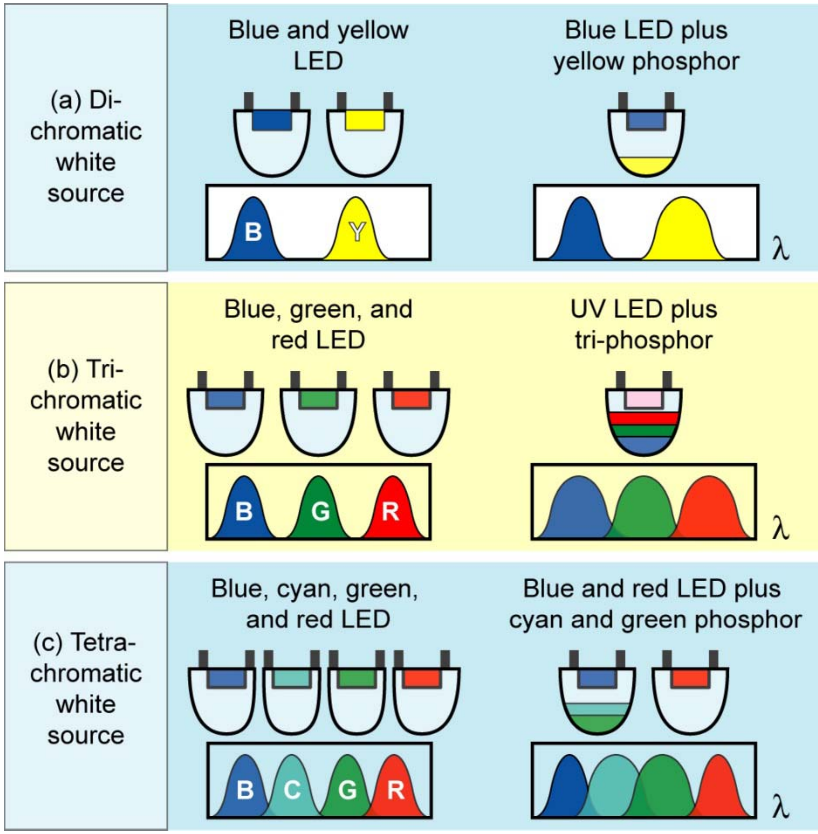


Figures of merit of new lighting technologies

Quantity	Desirable value
Luminous source efficiency	150 lm/W
Luminous flux	1000 lm
Color rendition capability (CRI)	> 75
Color temperature	3000 – 6000 K
Lifetime	100 000 hrs
Cost	< $ 10 per lamp

White solid-state lighting sources

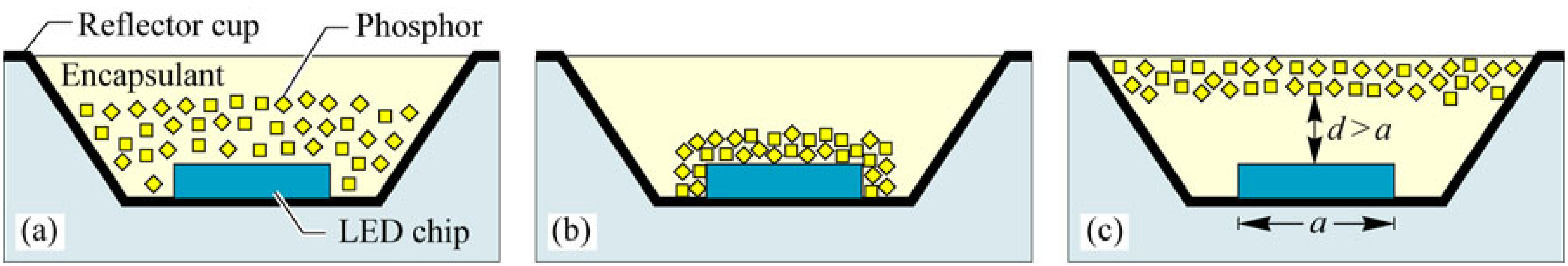
- Different technical approaches
  - Blue LED plus yellow phosphor
  - UV LED plus RGB phosphor
  - Phosphor has excellent color stability
  - Multiple LEDs
  - Which one is best?
- Efficiencies
  - Incandescent light bulb: 17 lm/W
  - Monochromatic green: 680 lm/W
  - Di-chromatic white source: 420 lm/W
  - Trichromatic white source: 300 lm/W
  - Color rendering: CRI > 90
  - Demonstrated SSL sources: > 100 lm/W

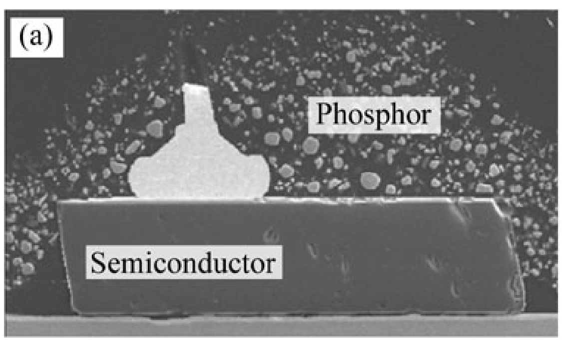


- What is the optimum spatial distribution of phosphors?
  - Proximate and remote distributions

Innovation in white LEDs – Phosphor distribution

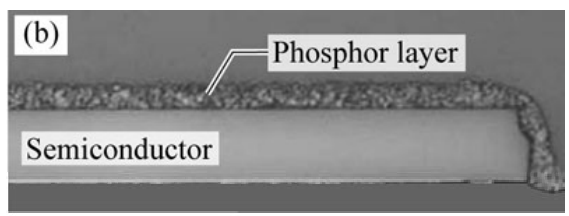
- Novel phosphor distributions promise higher efficiency





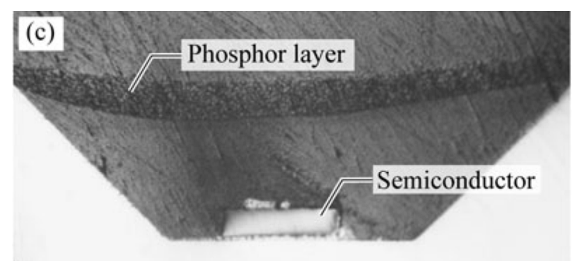
Proximate distribution

(after Goetz *et al.*, 2003)



Proximate distribution

(after Goetz *et al.*, 2003)



Remote distribution

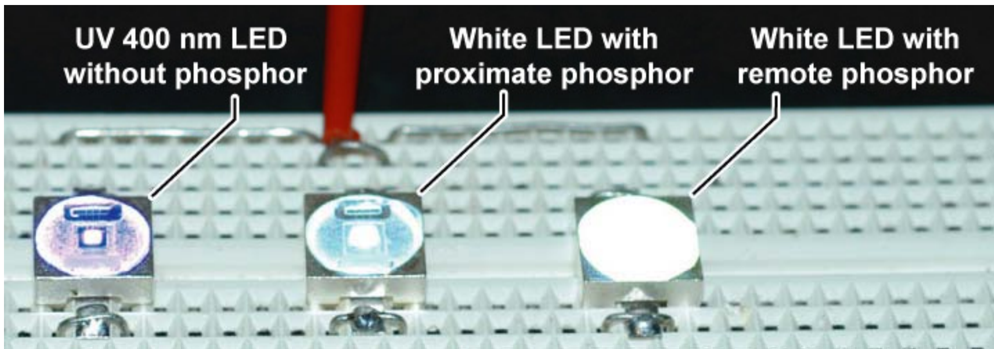
(after Kim *et al.*, 2005)

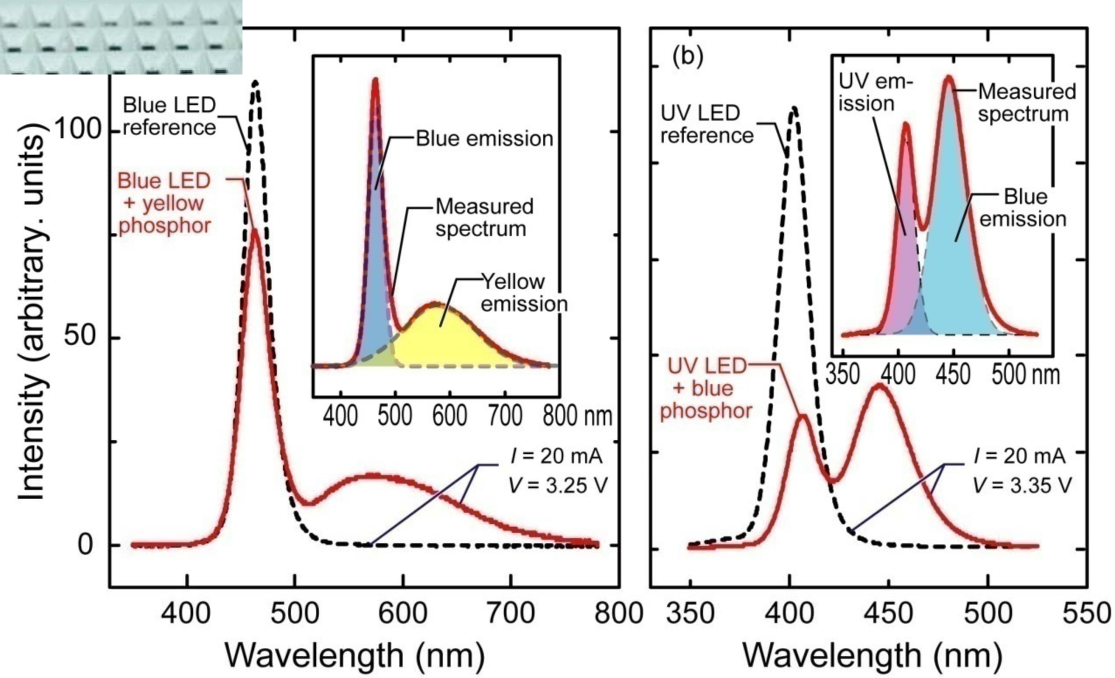
Kim *et al.*, *Jpn. J. Appl. Phys. Exp. Lett.* 44, L649 (2005)

Luo *et al.*, *Appl. Phys. Lett.* 86, 243505 (2005)

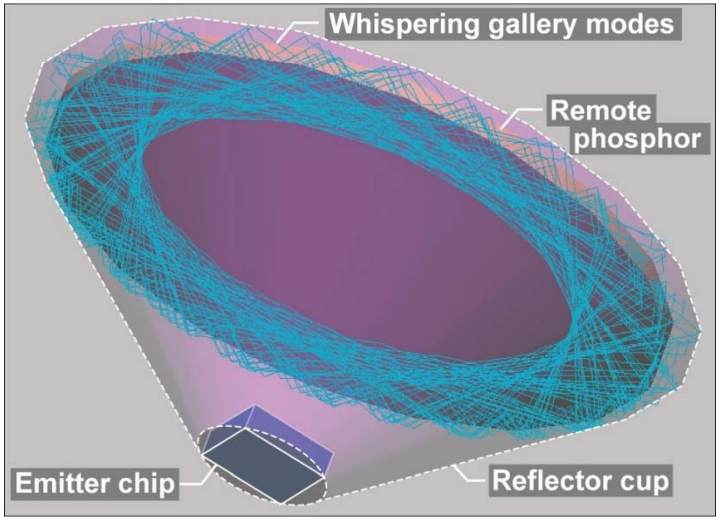
Innovation in white LEDs – Phosphor distribution

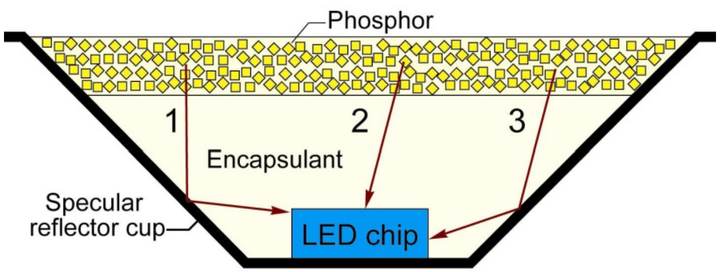
- Remote phosphor distributions reduce absorption of phosphorescence by semiconductor chip
- Improvement of phosphorescence efficiency:
  - 15.4 % for blue-pumped yellow phosphor
  - 27.0 % for UV-pumped blue phosphor



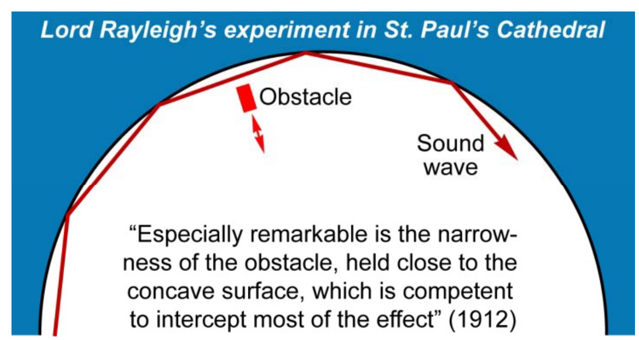


Novel loss mechanisms in white lamps with remote phosphor



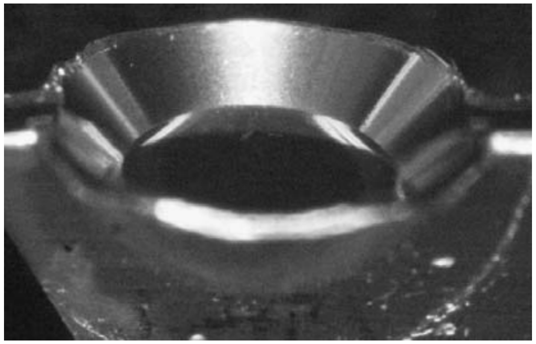


Lord Rayleigh (1842–1919)

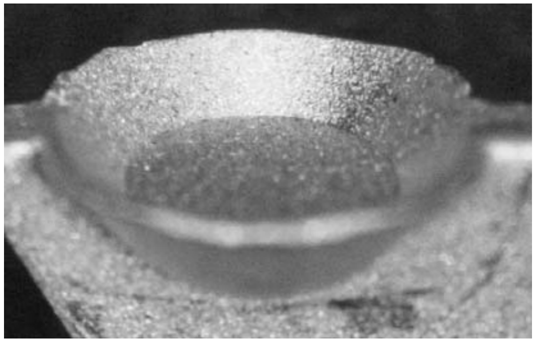


- **Whispering Gallery Mode**
- *Trapped optical mode*
- *Solution:*
  - Non-deterministic element that breaks symmetry
  - Suppression of trapped whispering-gallery modes

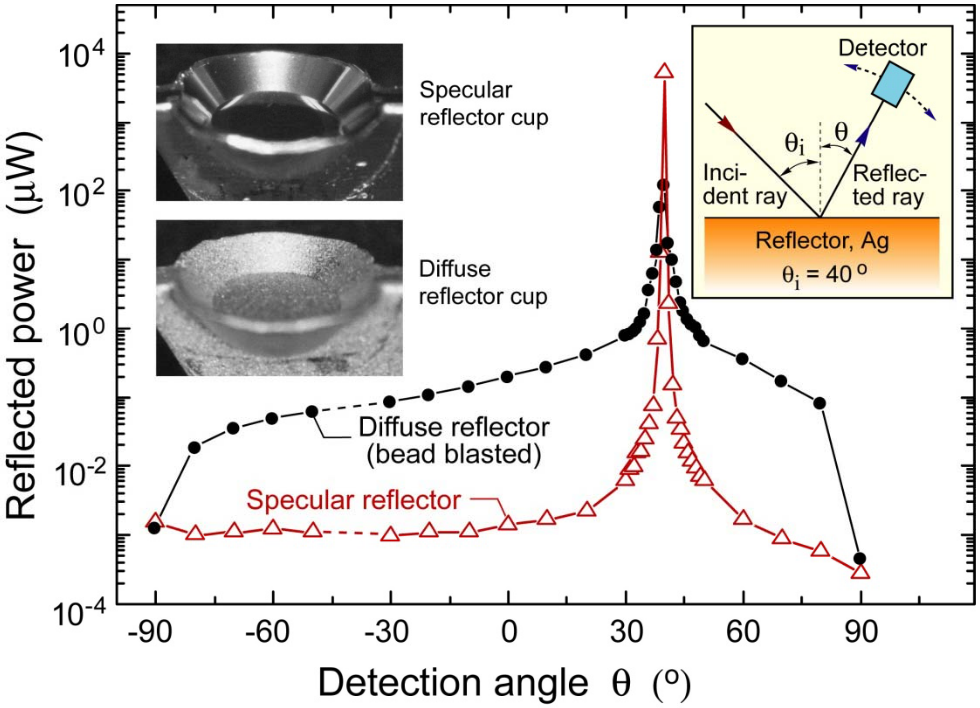
Remote phosphors with diffuse and specular reflector cups



Specular reflector cup

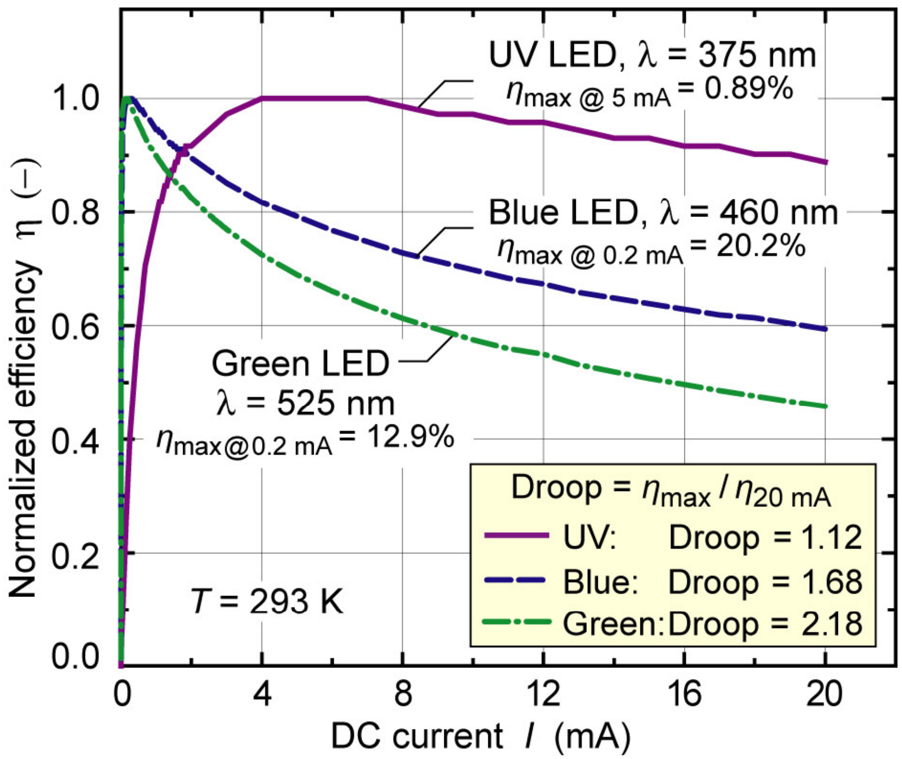


Diffuse reflector cup



- **Reflectance versus angle**
- **Surface texture by bead blasting**
- **Diffuse reflectance increased by two orders of magnitude**

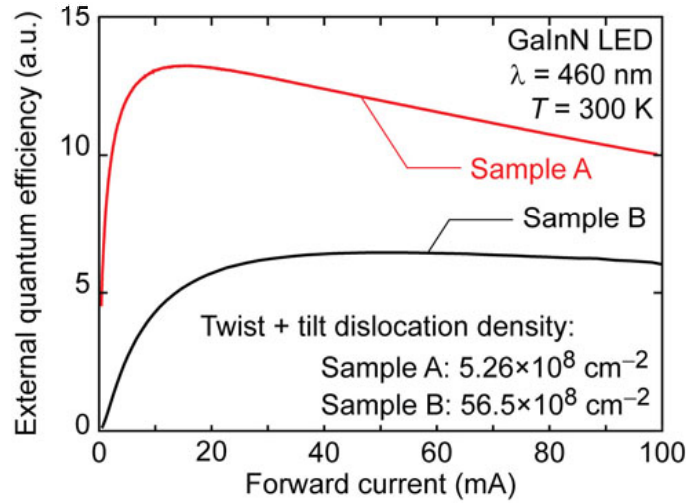
Challenges: Efficiency Droop



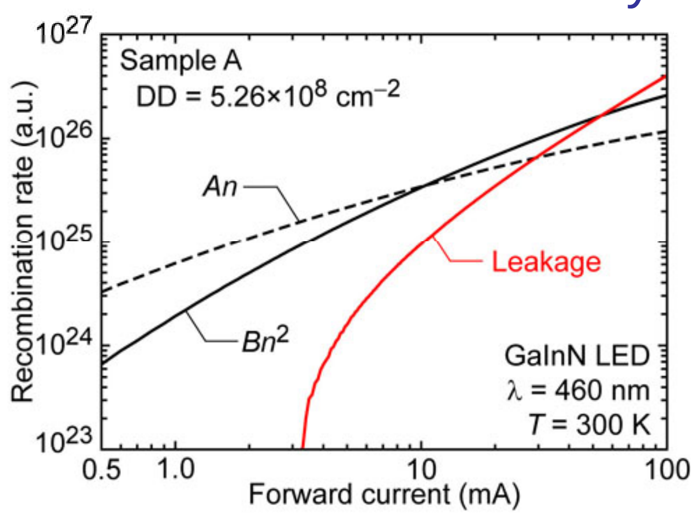
- Efficiency of III-V nitride LEDs is very high, despite high density of dislocations
- Efficiency decreases with increasing injection current
- Severe obstacle for lasers and high-power solid-state lighting devices
- Green LEDs have largest efficiency droop
- ***Not*** caused by device heating

Challenges: Dislocations

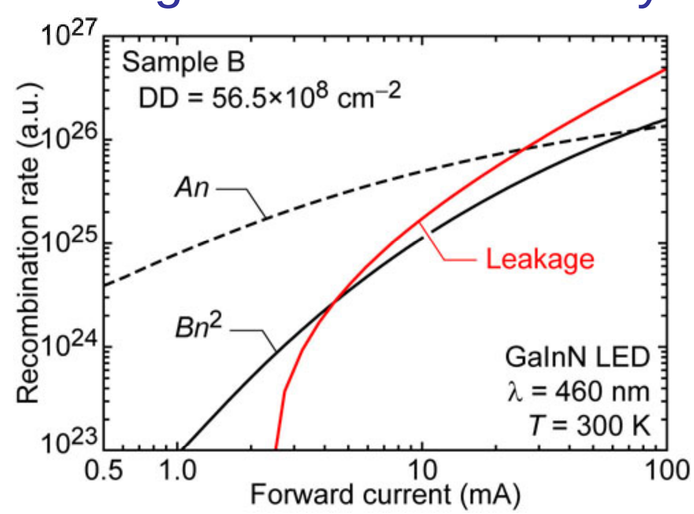
- Dislocations in III-V nitrides affect:
  - LED Efficiency
  - LED efficiency droop



Low dislocation density



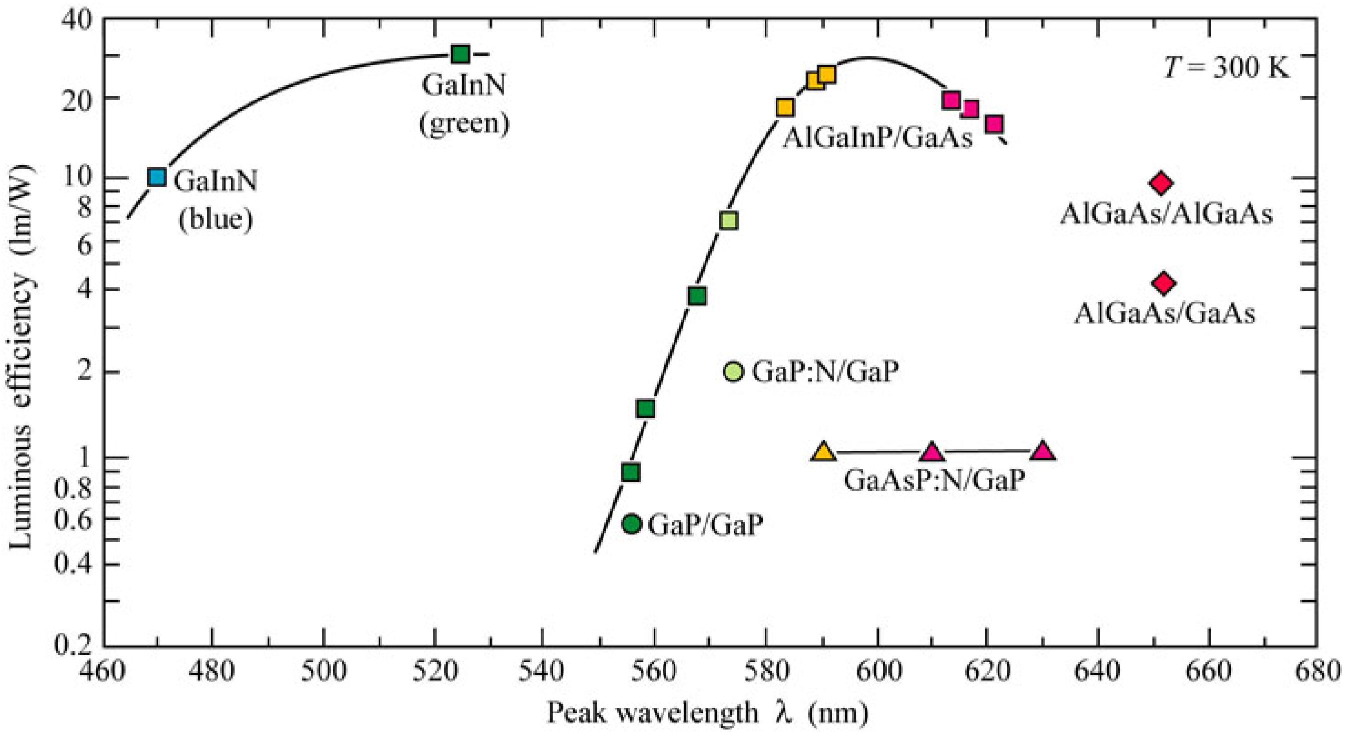
High dislocation density



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

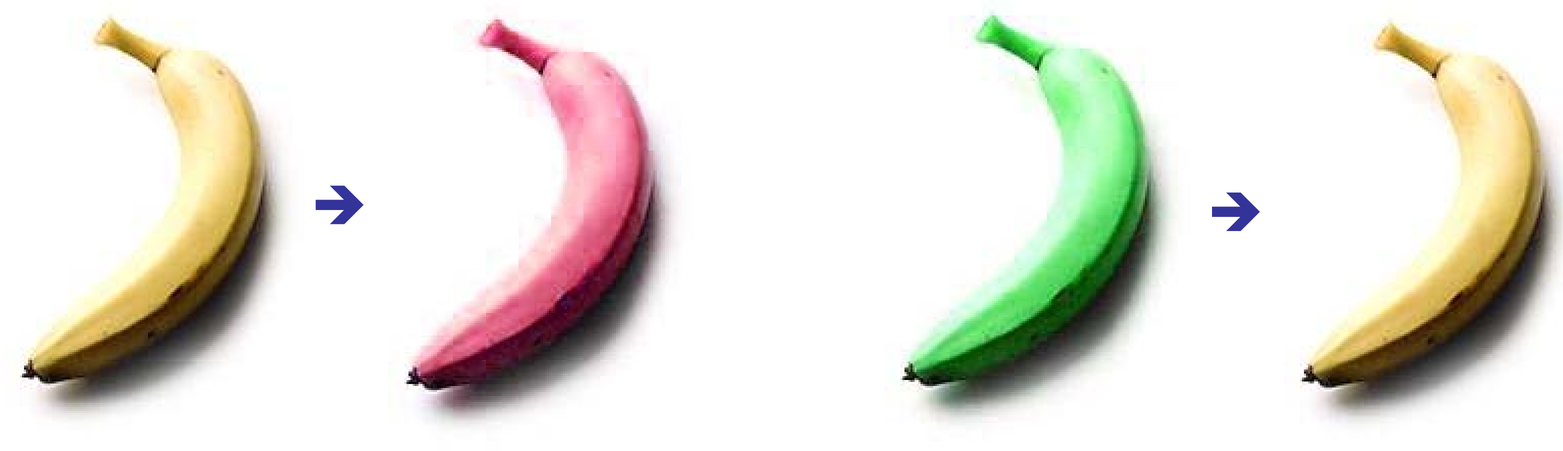


Color Rendition

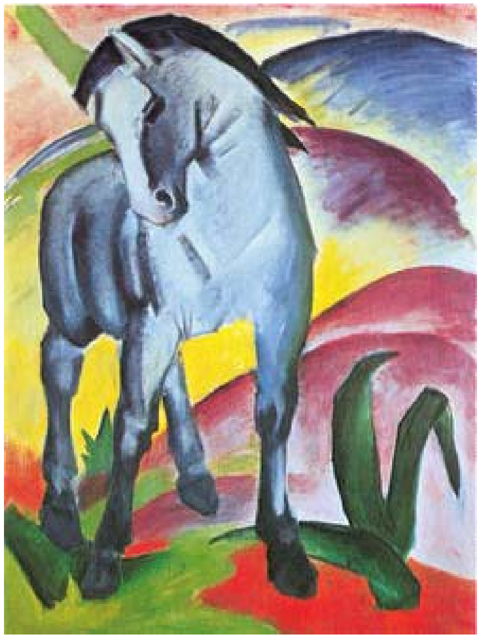
- **A light source has** *color rendering capability*
- **This is the capability to render the true colors of an object**

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



High CRI
illumination source

Low CRI
illumination source

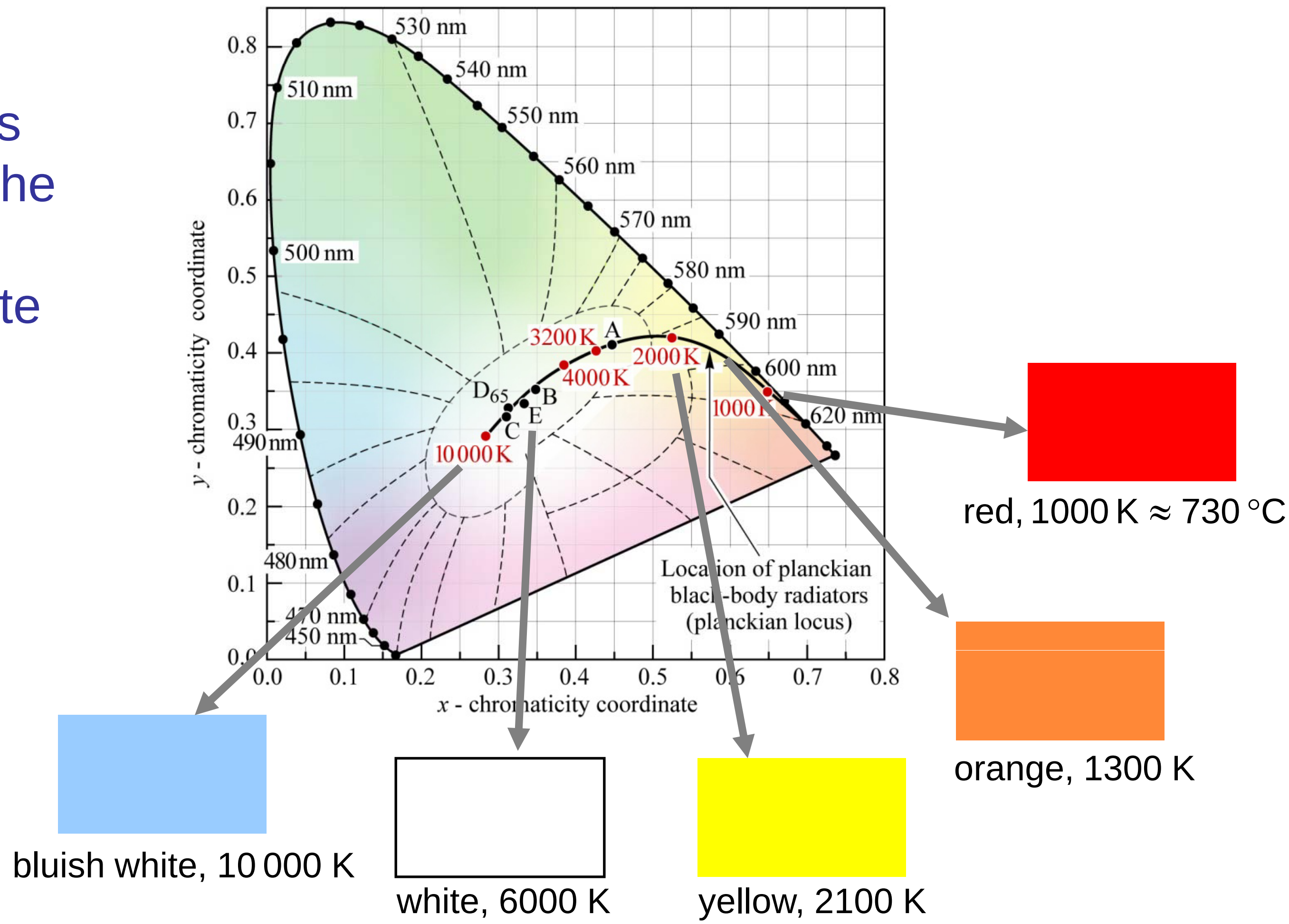
Franz Marc "Blue Horse" (1911)

Solid-state lighting is crosscutting technology that will enable **brilliant displays with the most vivid colors** ever seen

Color Temperature

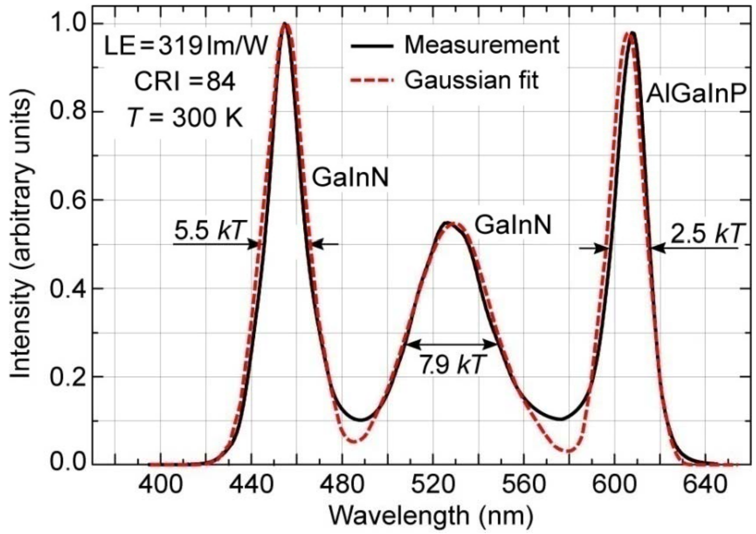
As temperature increases, hot objects sequentially glow in the red, orange, yellow, white, and bluish white

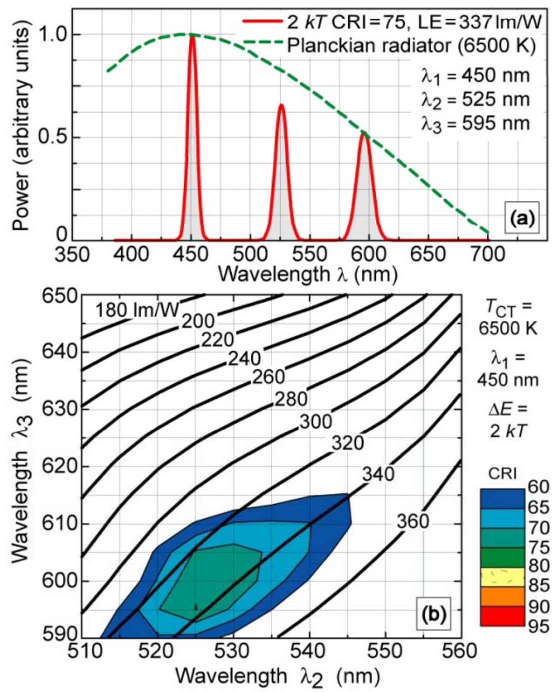
Example: Red-hot horseshoe

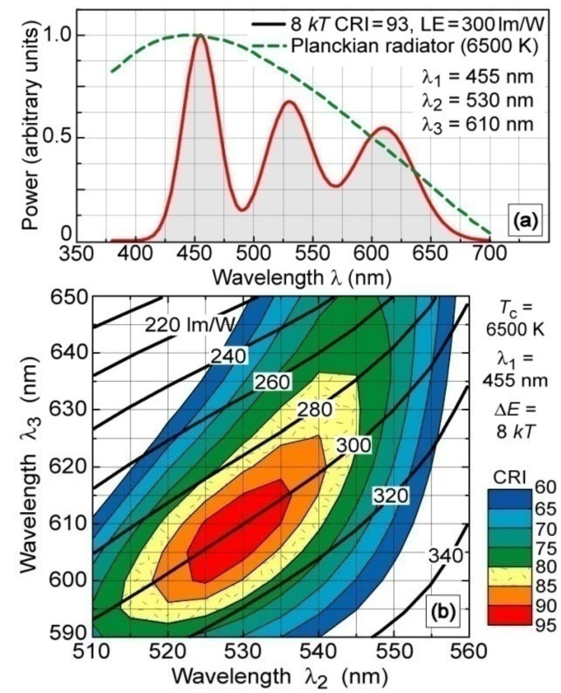


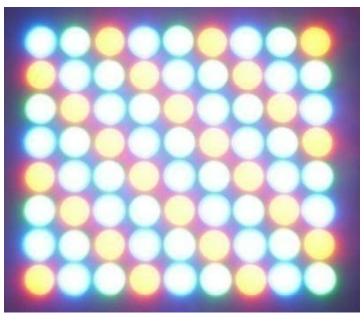
- Hot physical objects exhibit heat glow (incandescence) and a color
- Planckian radiator = Black, physical object with temperature *T*
- Color temperature = Temperature of planckian radiator with same location in chromaticity diagram

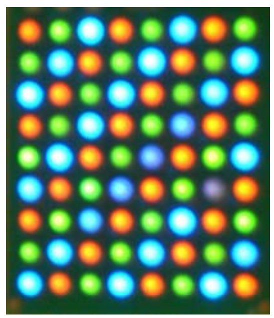
Demonstration of Trichromatic Source





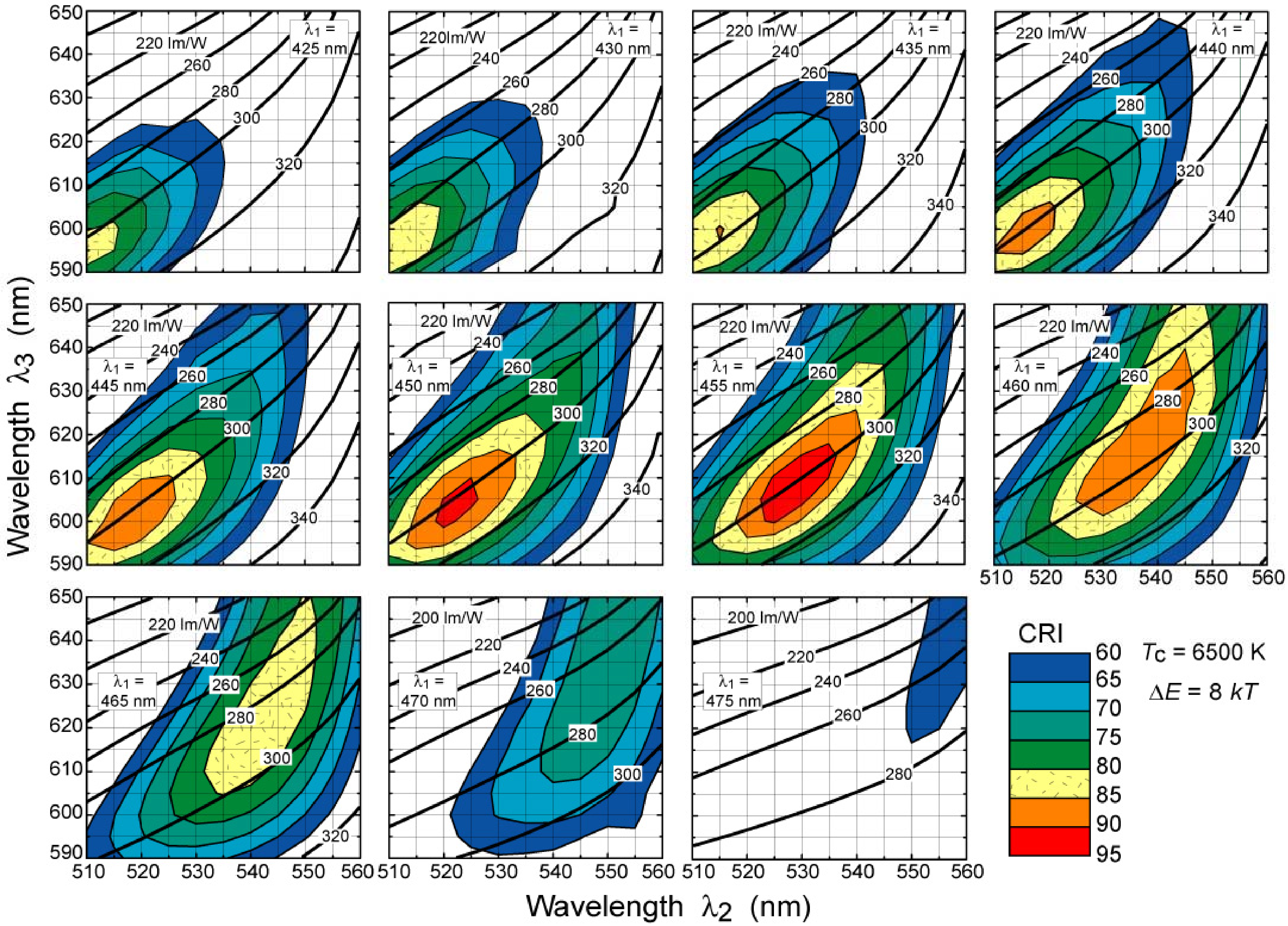






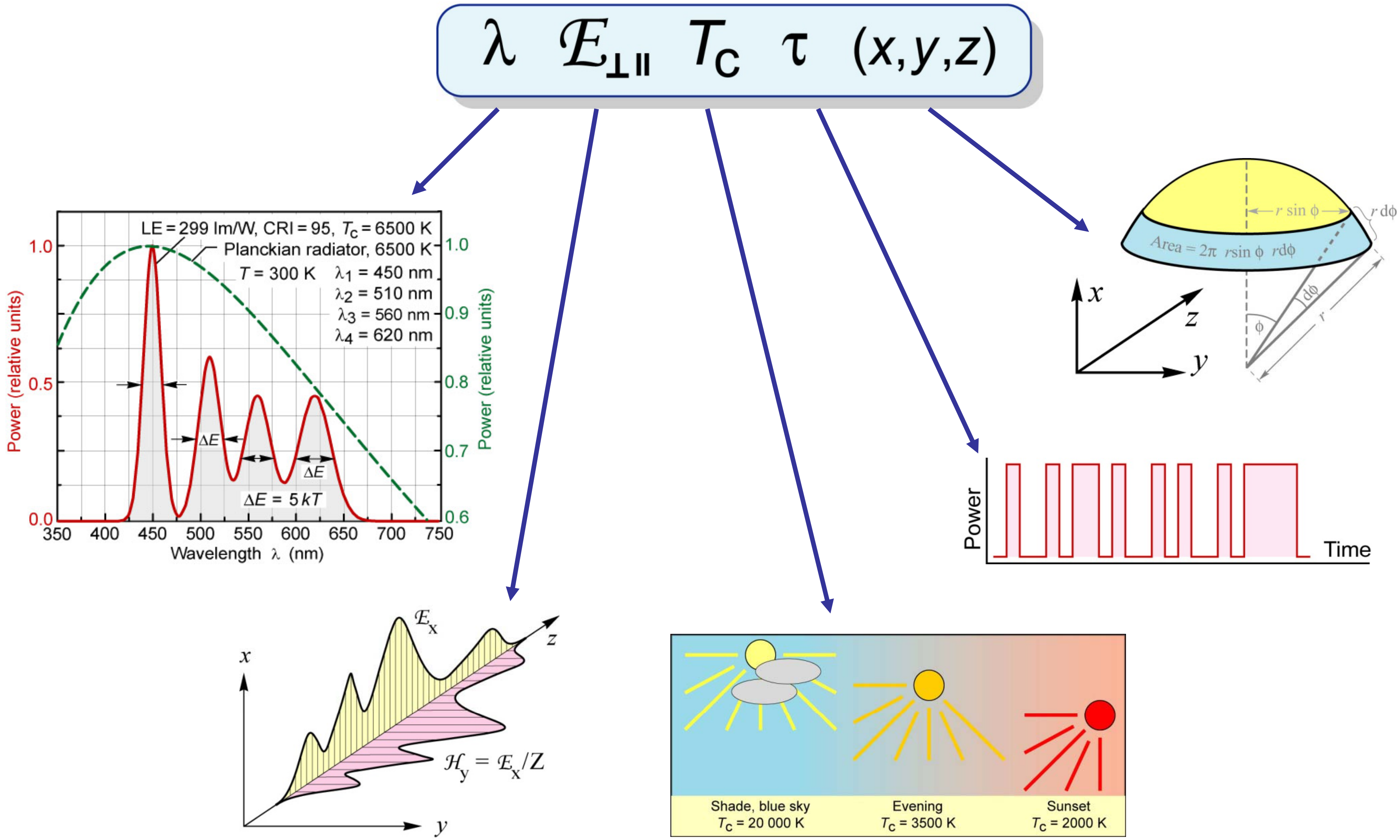
- Color rendering index (CRI) depends strongly on alloy broadening
- 64 lm/W demonstrated at this time (CRI = 84) for trichromatic sources
- For some applications CRI is irrelevant
    - For such applications, 680 lm/W would be possible with perfect SSL device

Luminous Efficacy and CRI for Tri-chromatic Source



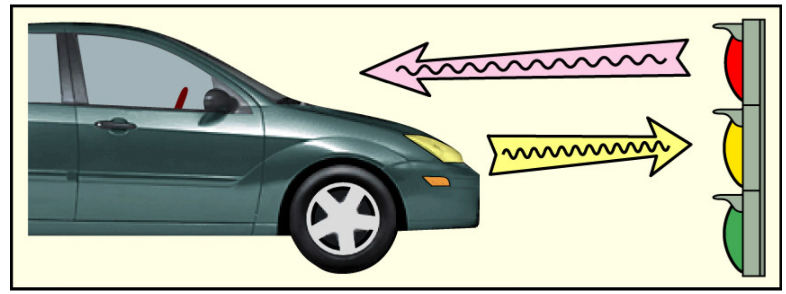
2017 and Beyond: Smart Sources

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

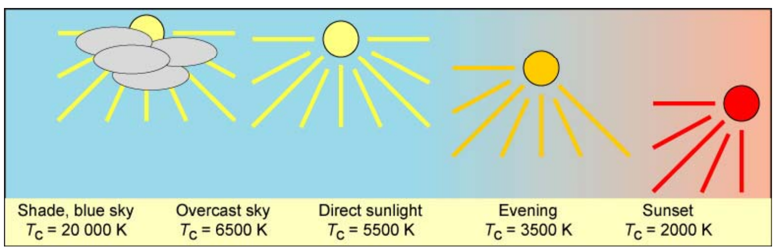


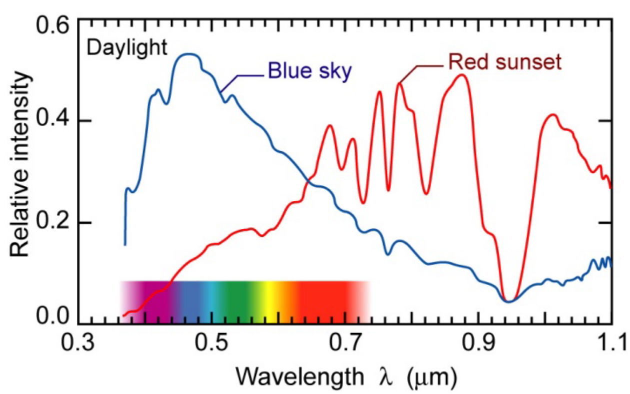
Smart light sources will enable a wealth benefits and new functionalities

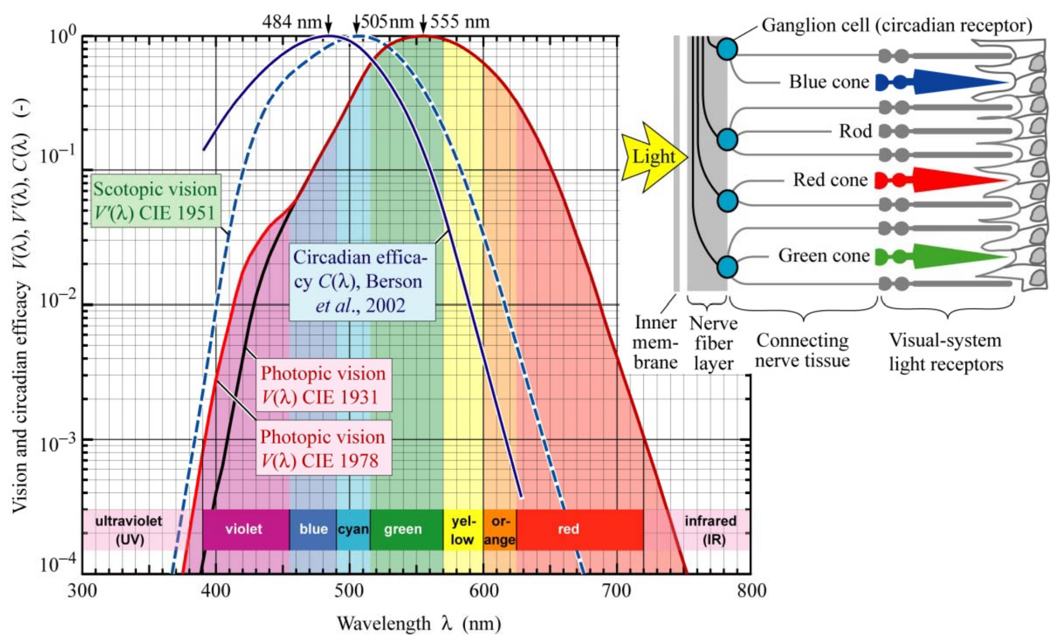
- **Example: Communicating automotive lights and room lights**



- **Example: Circadian lights**

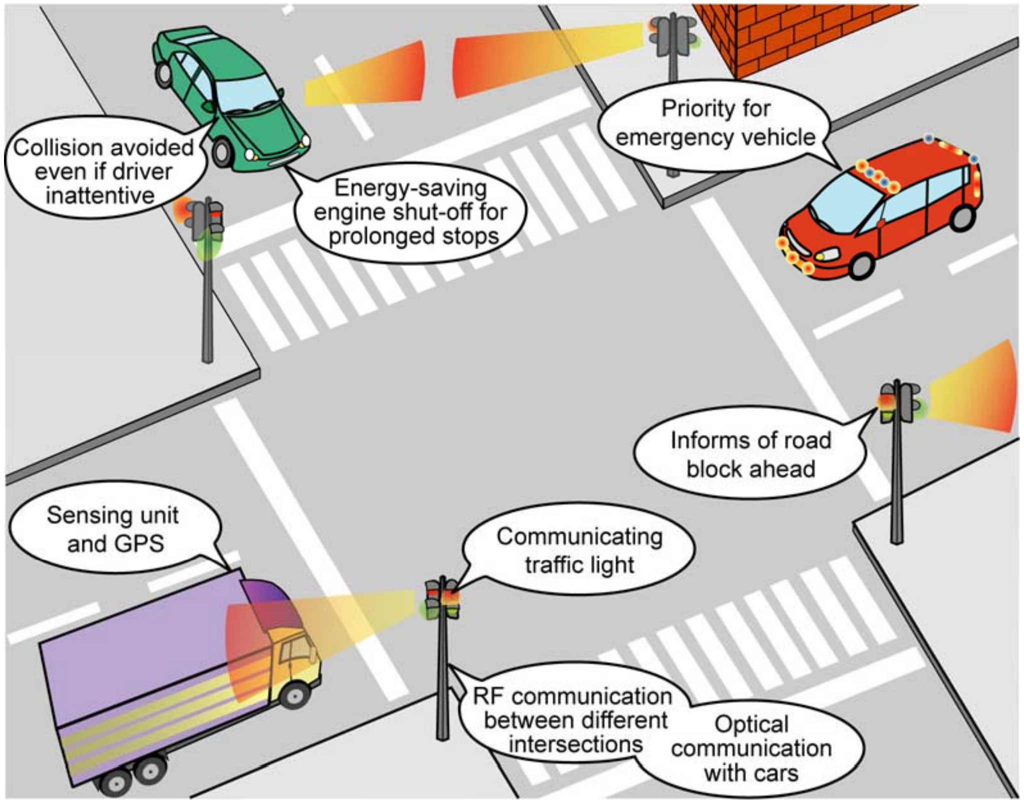






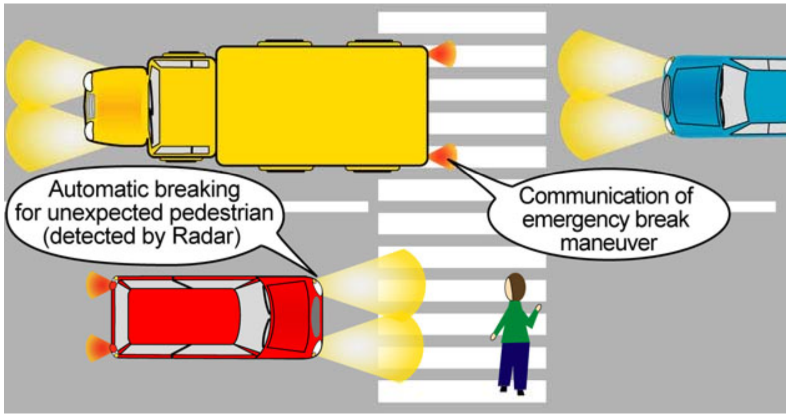
2017 and Beyond: Future Transportation Systems

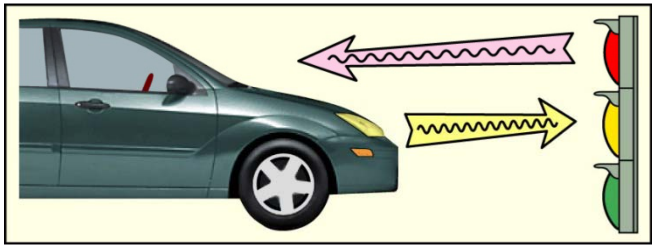
- … seat belts … air bags … anti-lock brake … electronic stability control …

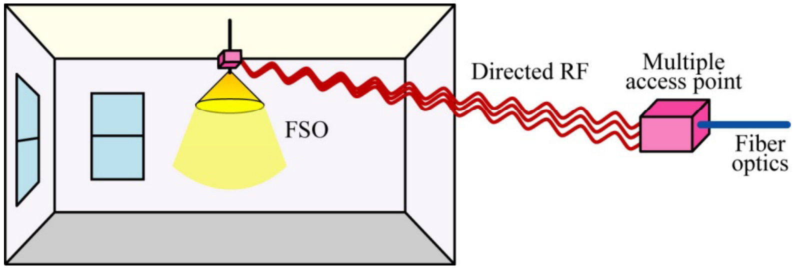


and

… 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

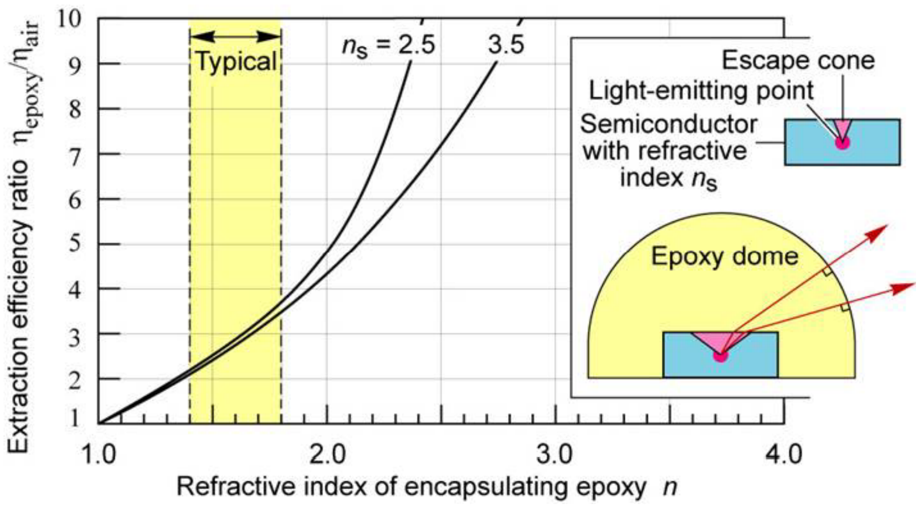
Acknowledgements

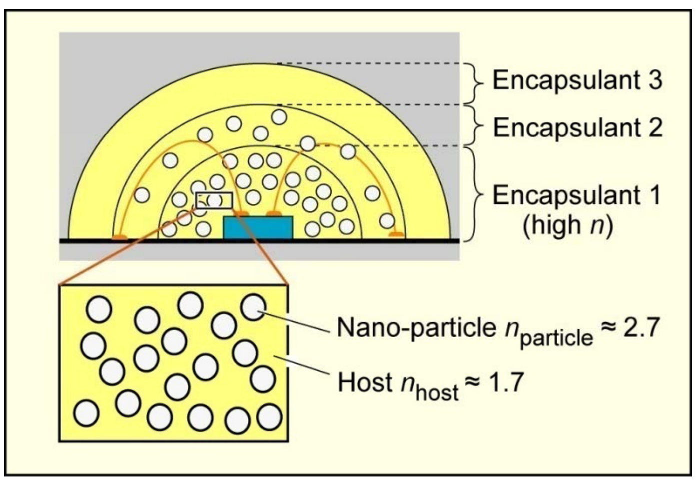
- Profs. Shawn Lin, Christian Wetzel, Jong Kyu Kim, Joel Plawsky, William Gill, Partha Dutta, Richard Siegel, and Thomas Gessmann, Dr. Alex Tran (*RPI*), Drs. Mary Crawford, Art Fischer, Dan Koleske, Andy Allerman *(Sandia)* Drs. Jaehee Cho, Cheolsoo Sone, Yongjo Park, *(Samsung SAIT)* Students: Sameer Chhajed, Charles Li, Pak Leung, Hong Luo, Frank Mont, Alyssa Pasquale, Martin Schubert, Chinten Shah, Jay Shah, JQ Xi, Yangang Andrew Xi (*RPI*)

- Support:
  - 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





Layered approach reduces scattering

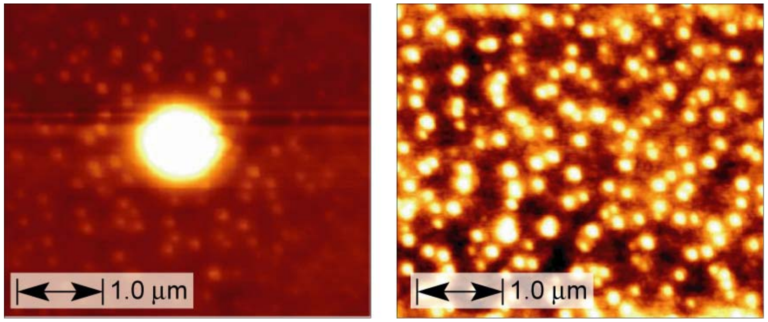
- Encapsulation materials with high refractive index would solve light-extraction problem
- Titania nanoparticles in
  - Silicone
  - Epoxy
  - PMMA
- Titania, TiO_2, n = 2.68
- Polymer: $n \approx 1.6$
- ➔ Mixture $n > 2.0$

Lester *et al*. *US Patent* 5,777,433 (1998)

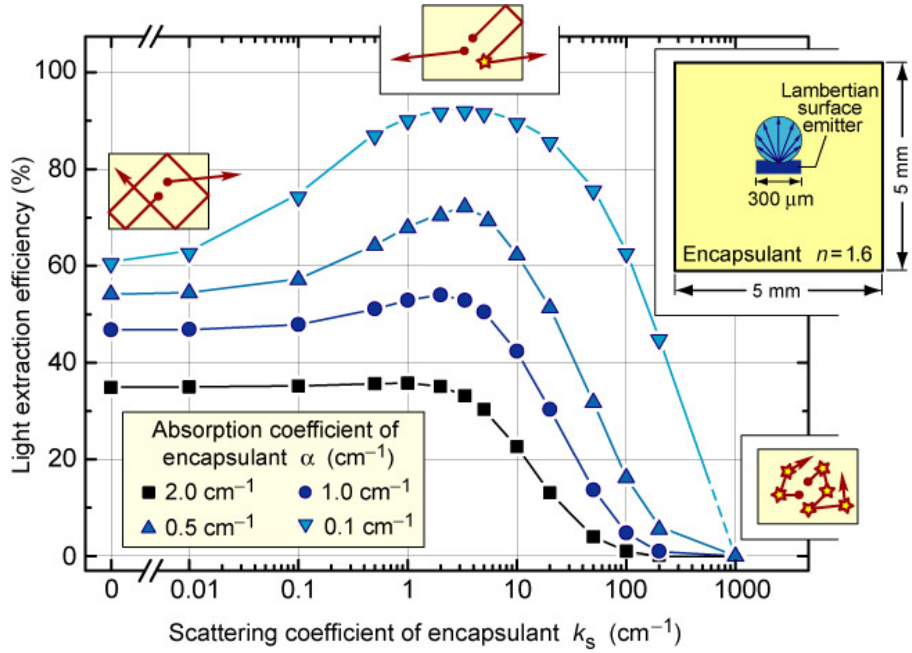
Frank Mont *et al*. *2007*

High-refractive index encapsulation materials

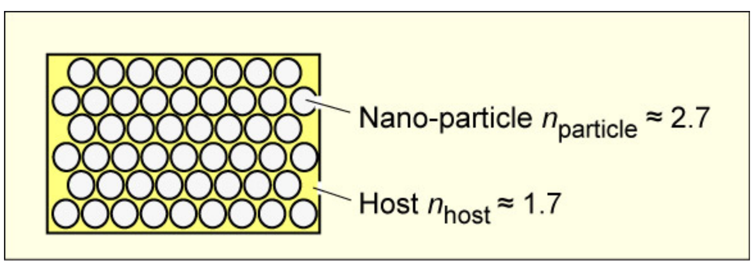
Without surfactant	With surfactant



AFM of TiO_2 nano-particles in epoxy



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



Shiang and Duggal *J. Appl. Phys.* **95**, 2880 (2004)