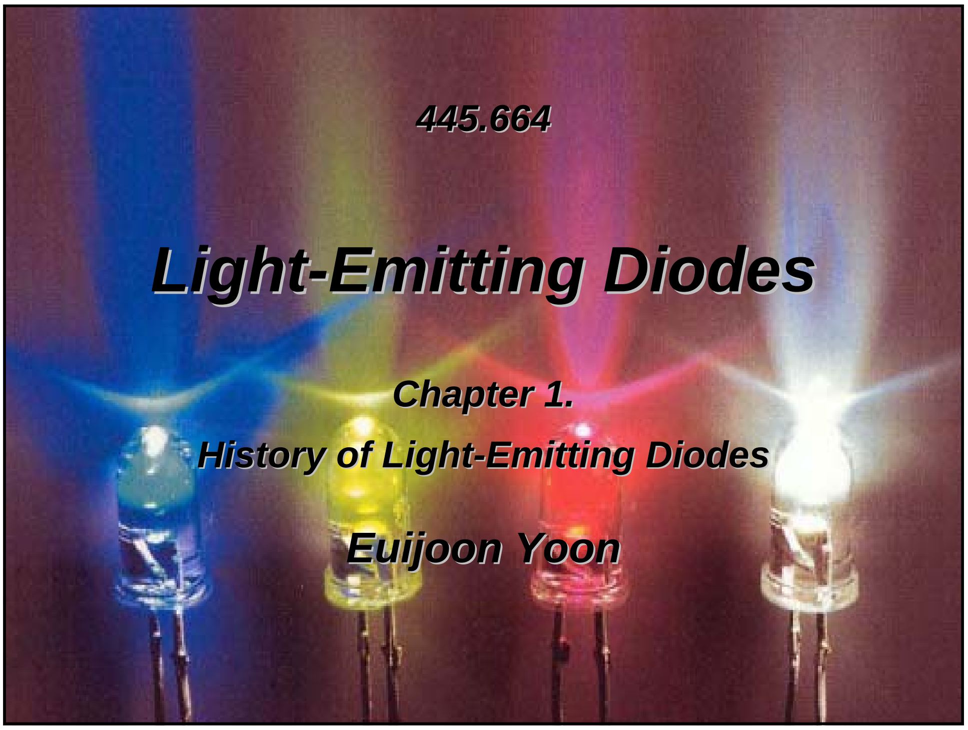


445.664

Light-Emitting Diodes

Chapter 1.
History of Light-Emitting Diodes

Euijoon Yoon

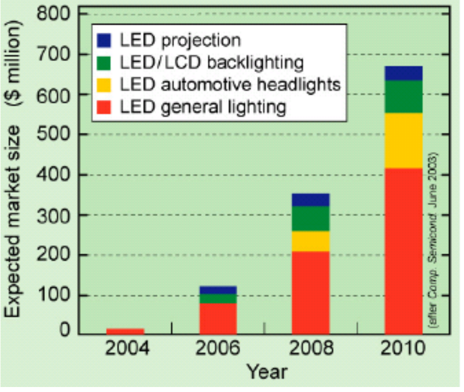
Light Emitting Diodes (LEDs)

There are two major technologies :
- All-semiconductor-based illumination devices
- Semiconductor/phosphor devices

- LED-based lighting
  - more efficient than
    incandescent (20 times)
    fluorescent lamp (5 times)
  - Electrical power savings
    ~ 1.50 PWh (Peta = 10^{15})

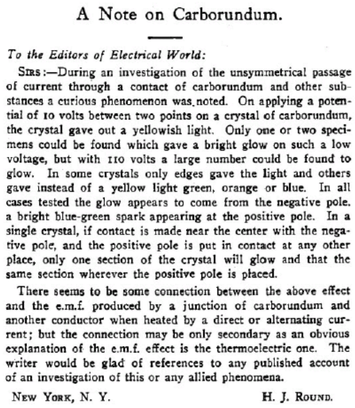
- Environmentally benign technology
  - Reduction of waste & hazardous waste (Hg)

Predicted expansion of market



Compound Semiconductor, June, 2003

History of LEDs


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.

Fig. 1.1. Publication reporting on a "curious phenomenon", namely the first observation of electroluminescence from a SiC (carborundum) light-emitting diode. The article indicates that the first LED was a Schottky diode rather than a pn-junction diode (after H. J. Round, *Electrical World* Vol. **49**, p. 309, 1907)

- **First report on electroluminescence in 1907 by Henry Joseph Round. (First LED)**
- **Active materials was SiC crystallites (highly impure) as used for sandpaper abrasive.**
- **Essentially all colors were demonstrated.**

Light Emission in First LED

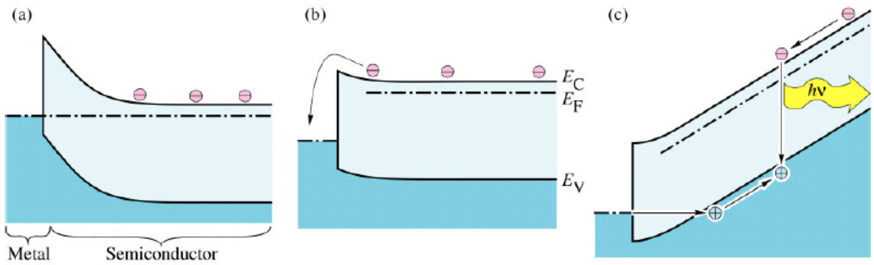


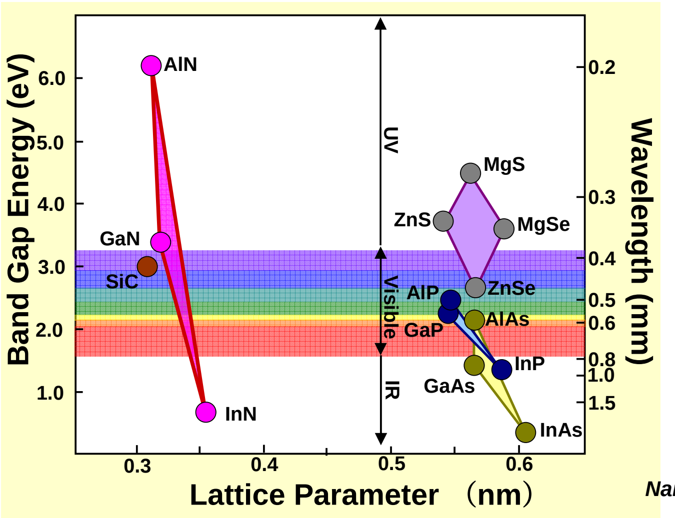
Fig. 1.2. Band diagram of Schottky diode under (a) equilibrium conditions, (b) forward bias, and (c) strong forward bias. Under strong forward bias, minority carrier injection occurs making possible near-bandgap light emission.

- **First LED did not have pn junction. (Schottky contact)**
- **Under strong forward-bias, (H. J. Round, 10 ~ 110 V)**

  minority carrier injection into n-type semiconductor by tunneling effect

  ➔ Light is emitted upon recombination of the minority carriers with the n-type majority carriers.

The Era of III-V Compound Semiconductor



Nanishi et al.

- The era of III-V compound semiconductors started in the early 1950s. ➔ optically very active

Enhancement of Luminous Performance

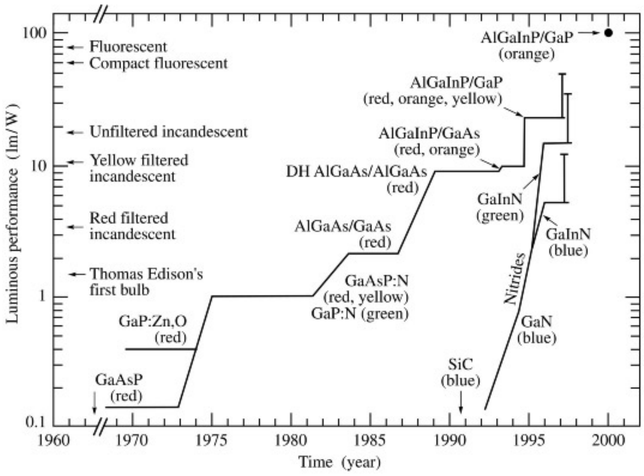
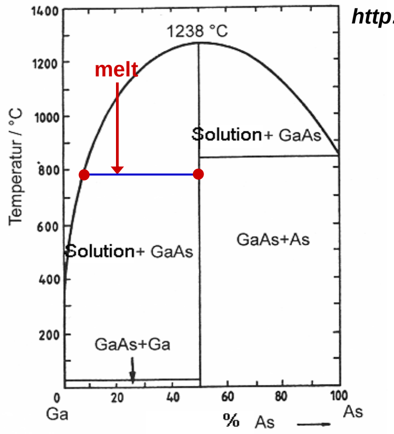


Fig. 8.13. Luminous performance of visible LEDs versus time. Also shown is the luminous performance to other light sources (adopted from Craford, 1997, 1999, updated 2000).

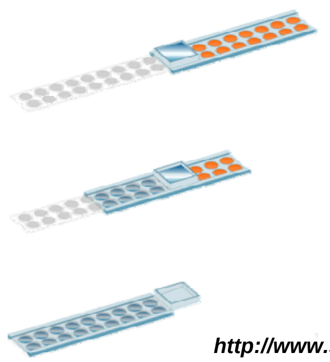
- Strong progress of visible LEDs over past decades

Liquid Phase Epitaxy (LPE)

- In the mid-1950s, III-V semiconductor films were epitaxially grown on sliced GaAs wafers by liquid phase epitaxy (LPE).



http://www.tf.uni-kiel.de/matwis/amat/semi_en/

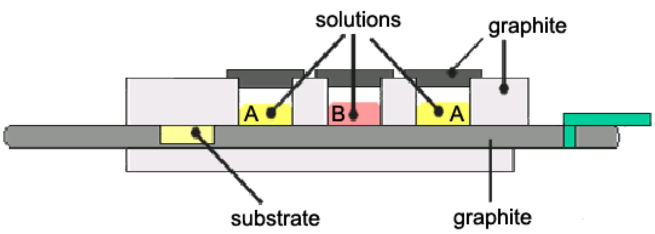


http://www.sof-e.com

Ga melt containing As (High T)

➔ GaAs (s) + Ga melt containing As (Low T)

Heterostructures by Liquid Phase Epitaxy (LPE)



http://www.microelectronique.univ-rennes1.fr

- Growth of heterostructure (A / B / A) by LPE
  ex) AlGaAs / GaAs / AlGaAs / substrate
- Each film was grown with a separate melt.
- Limitations of LPE growth
  - poor thickness uniformity
  - rough surface morphology particularly in thin layers

➔ The CVD and MBE techniques are distinctly superior to LPE

One of the First Application of GaAsP LEDs

Fig. 1.4. This classic 1964 main-frame computer IBM System 360 used high-voltage gas-discharge lamps to indicate the status of the arithmetic unit. In later models, the lamps were replaced by LEDs. The cabinet-sized 360 had a performance comparable to a current low-end laptop computer.

- **The classic IBM System 360 mainframe computer (1964) with high voltage gas-discharge lamps indicating the status and proper function of the circuit board**

  ➔ These lamps were replaced by GaAsP LEDs (red) in later models.

GaAsP LEDs in Calculators

Fig. 1.8. Programmable pocket calculators Model SR-56 of the Texas Instruments Corporation and Model HP-67 of the Hewlett-Packard Corporation both manufactured starting in 1976. Seven-segment numeric characters composed of GaAsP LEDs were used in the display. The SR-56 came with a "huge" program memory of 100 steps. The HP-67 came with a magnetic card reader and had several freely programmable keys.

- **GaAsP LEDs were used in 7-segment numeric display in first generation of calculators of the mid 1970s.**

  Problems - Displayed numbers could not be seen in daylight.
  - LEDs consumed so much power.

➔ LCDs totally replaced LED displays in calculators by the beginning of the 1980s.

GaP Red and Green LEDs

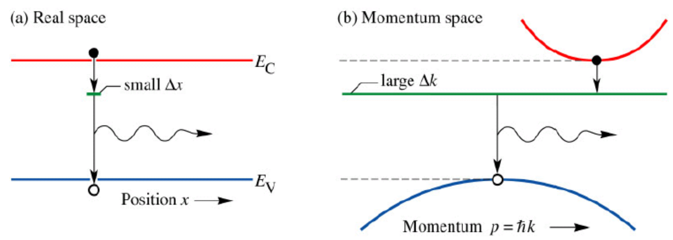


Fig. 1.5. (a) real-space and (b) momentum-space illustration of optical transitions in GaP doped with an optically active impurity level such as O or N, emitting in the red and green, respectively. GaP LEDs employ the *uncertainty principle* ($\Delta x \; \Delta p \geq \hbar$) which predicts that an electron wave function localized in real space is delocalized in momentum space thereby making possible momentum-conserving (vertical) transitions.

- **GaP (indirect bandgap) does not emit significant amounts of light. (requirement of momentum conservation)**
- **Impurity doping in GaP enable light emission.**
- **Strongly localized wavefunction of impurity in real-space (small Δx)**
  ➔ Delocalized level in momentum space (large Δk)
  (*Heisenberg uncertainty principle*)

Red GaP p-n Juction LEDs

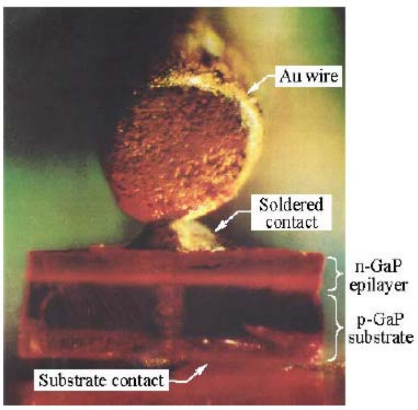


Fig. 1.6. GaP light-emitting diode grown by liquid-phase epitaxy emitting "brilliant red light" from the Zn- and O-doped p-n junction region (courtesy of Pilkuhn, 2000).

- **GaP p-n homojuction LED structure with top-bottom contacts (n-GaP epilayer on p-GaP substrate)**

n-GaP epilayers ➔ Te, S, or Se doning
p-GaP epilayers ➔ N isoelectronic doping (green)
Zn-O co-doping (red)

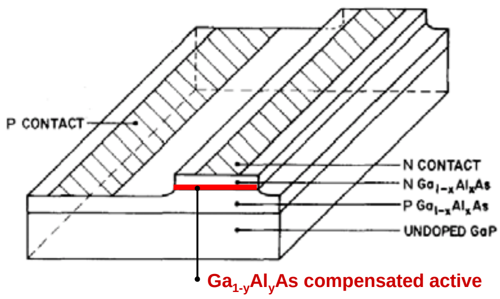
Application for GaP:N Green LEDs

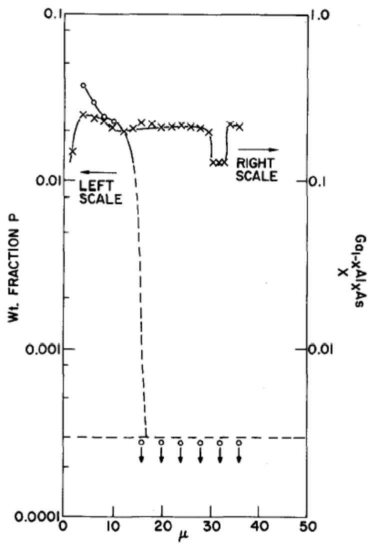
Fig. 1.7. AT&T telephone set ("Trimline" model) with the dial pad illuminated by two green N-doped GaP LEDs. The illuminated dial pad was one of the first applications of green GaP:N LEDs.

- **Many phone models were equipped with an illuminated dial pad.**
- **Telephone designers (AT&T) decided that green was better color than red.**

  ➔ GaP:N Green LEDs for dial pad illumination (1990 version)

Structure of AlGaAs LED





p-type $Al_xGa_{1-x}As$
melt 1 0.0034 g Al & Zn

$Al_yGa_{1-y}As$ active
melt 2 0.0016 g Al & Zn

n-type $Al_xGa_{1-x}As$
melt 3 0.0033 g Al & Te

J. M. Woodall, R. M. Potemski, and S. E. Blum
Appl. Phys. Lett. 20, 375 (1972)

AlGaAs Infrared (IR) and Red LEDs

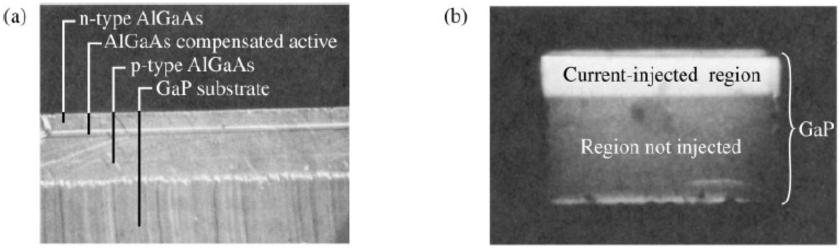


Fig. 1.3. (a) Cross section micrograph of a an AlGaAs LED grown on a transparent GaP substrate. (b) Electroluminescence originating from a current-injected region located under a stripe-shaped contact viewed through the transparent GaP substrate (after Woodall *et al.*, 1972).

- **AlGaAs p-n junction diode structure**
  ➔ Infrared (IR) and red emission
- **AlGaAs LEDs / GaAs substrate ➔ light absorption problem**

  GaAs → GaP substrate : light-transparent
  ➔ high LED efficiency

AlGaInP Material System

- **The AlGaInP material system was first developed in Japan for visible lasers (1985)**
  ➔ AlGaInP / $Ga_{0.5}In_{0.5}P$ lattice-matched double-heterostructure

  $Ga_{0.5}In_{0.5}P$: active material (650 nm)
  lattice-matched to GaAs substrate

  650 nm (Red) : suitable for visible lasers
  (laser pointer, laser unit in DVD player)

- **Addition of Al to the GaInP active region**
  ➔ Red (625 nm) → Orange (610 nm) → Yellow (590 nm)

- **High-brightness AlGaInP LEDs**
  1. **Current-spreading layers for lighting from entire p-n junction plane of LED chip**
  2. **Multiple quantum well (MQW) active regions for high emission efficiency**
  3. **Distributed Bragg reflectors for high extraction of light**
  4. **GaP substrate technology for transparency**

High Brightness AlGaInP LEDs

Fig. 1.12. Example of red and amber AlGaInP / GaAs LEDs used in signage applications.

- **$(Al_xGa_{1-x})_{0.5}In_{0.5}P$**
  x < 0.53 : direct bandgap bright red ~ yellow LEDs
  x > 0.53 : indirect bandgap very low radiative efficiency
- **AlGaInP is not suited for high-efficiency emission at wavelength below 570 nm ➔ *GaN-based semiconductor***

GaN Blue Light Emitters

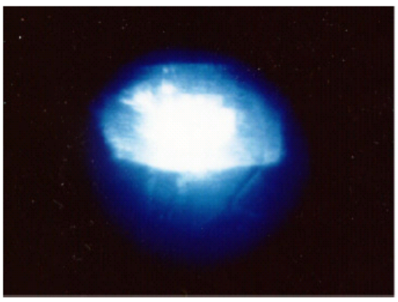
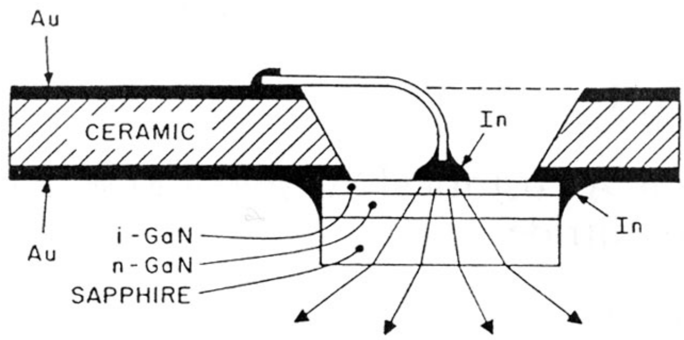


Fig. 1.9. Blue light emission found in 1972 caused by recombining electron-hole pairs created in a highly resistive GaN structure doped with Si and Mg (courtesy of Dr. Paul Maruska, 2000)

- **Full color flat-panel display applications to replace CRTs**
  Red – GaAsP Green – GaP:N Blue – ?
- **The first electroluminescence in 1971**
  from insulating GaN:Zn → 475 nm (blue)
- **Mg-doped GaN in 1972 (figure)→ 430 nm (blue-violet)**
  ➔ Mg is p-type dopant, but it did not exhibit p-type conductivity.

First GaN M-i-n Diode



"Gallium Nitride (GaN) I" Semiconductors and Semimetals Vol. 50, page 2,
- edited by J. I. Pankove and T. D. Moustakas. (Academic Press 1998)

The first current-injected GaN light emitter in 1972
from In contact (M) / GaN:Zn (i) / n-GaN (n) diode

Blue, Green, and White InGaN LEDs

- **The first true p-type GaN by Akasaki *et al.*, 1989**
  - ➔ **Activation of Mg acceptor by electron-beam irradiation**
- **GaN p-n-homojunction LED by Akasaki et al., 1992**
  - **- Ultraviolet (UV) and blue spectral range**
  - **- Efficiency of LED : ~ 1 %**
    - ➔ **surprisingly high value for the highly dislocated GaN material grown on the mismatched sapphire substrate**
- **p-type GaN by Nakamura et al., 1994**
  - ➔ **Easy activation of Mg acceptor by high-temperature post-growth annealing**
- **The first viable blue and green InGaN double-heterostructure LEDs, 1994**
  - **- Efficiency of LED : ~ 10 %**

Commercial Blue InGaN LEDs by the Nichia Co.

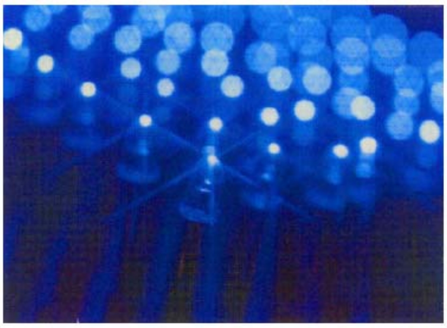


Fig. 1.10. Array of GaInN / GaN blue LEDs manufactured by Nichia Corporation (after Nakamura and Fasol, 1997).

- **Commercial Blue LEDs made by the Nichia Corporation in Japan**
- **Dr. Shuji Nakamura was leader of development in Nichia Corporation.**

Applications of Green LEDs

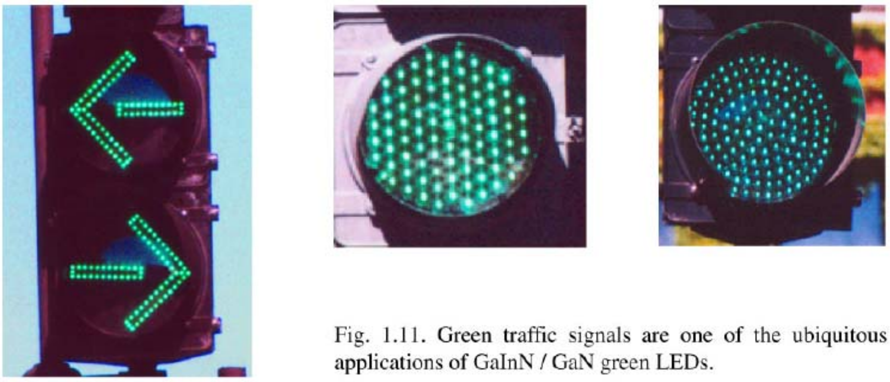


Fig. 1.11. Green traffic signals are one of the ubiquitous applications of GaInN / GaN green LEDs.

- **Common application of high-brightness InGaN green LEDs is traffic signals.**
- **Earlier mentioned GaP:N green LEDs are not suited for this application due to their much lower brightness.**

Luminous Performance vs. Peak Wavelength

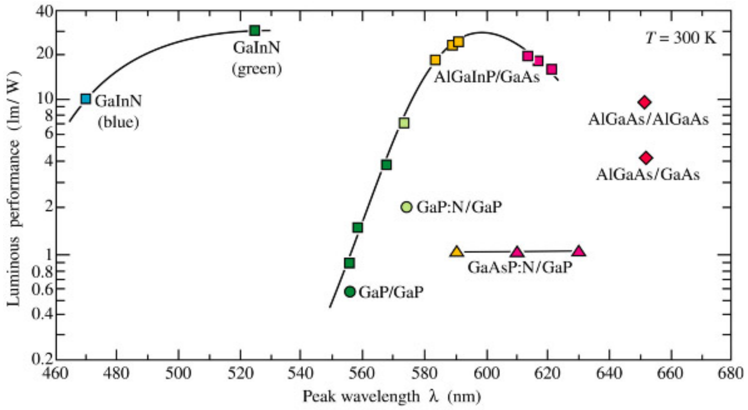


Fig. 8.14. Overview of luminous performance of visible LEDs made from the phosphide, arsenide, and nitride material system (adopted from United Epitaxy Corporation, 1999; updated 2000).

- **Lack of efficient LEDs at 550 nm is sometimes referred to as the "green gap".**

White LEDs and Applications

- **The InGaN material system is also suited for white LEDs.**
- **Two different approaches to white LEDs**
  - phosphor wavelength conversion & RGB LEDs integration
- **Higher luminous efficiency of white LEDs, > 300 lm/W (expected)**
  (conventional incandescent and fluorescent lamp, 15 ~ 100 lm/W)