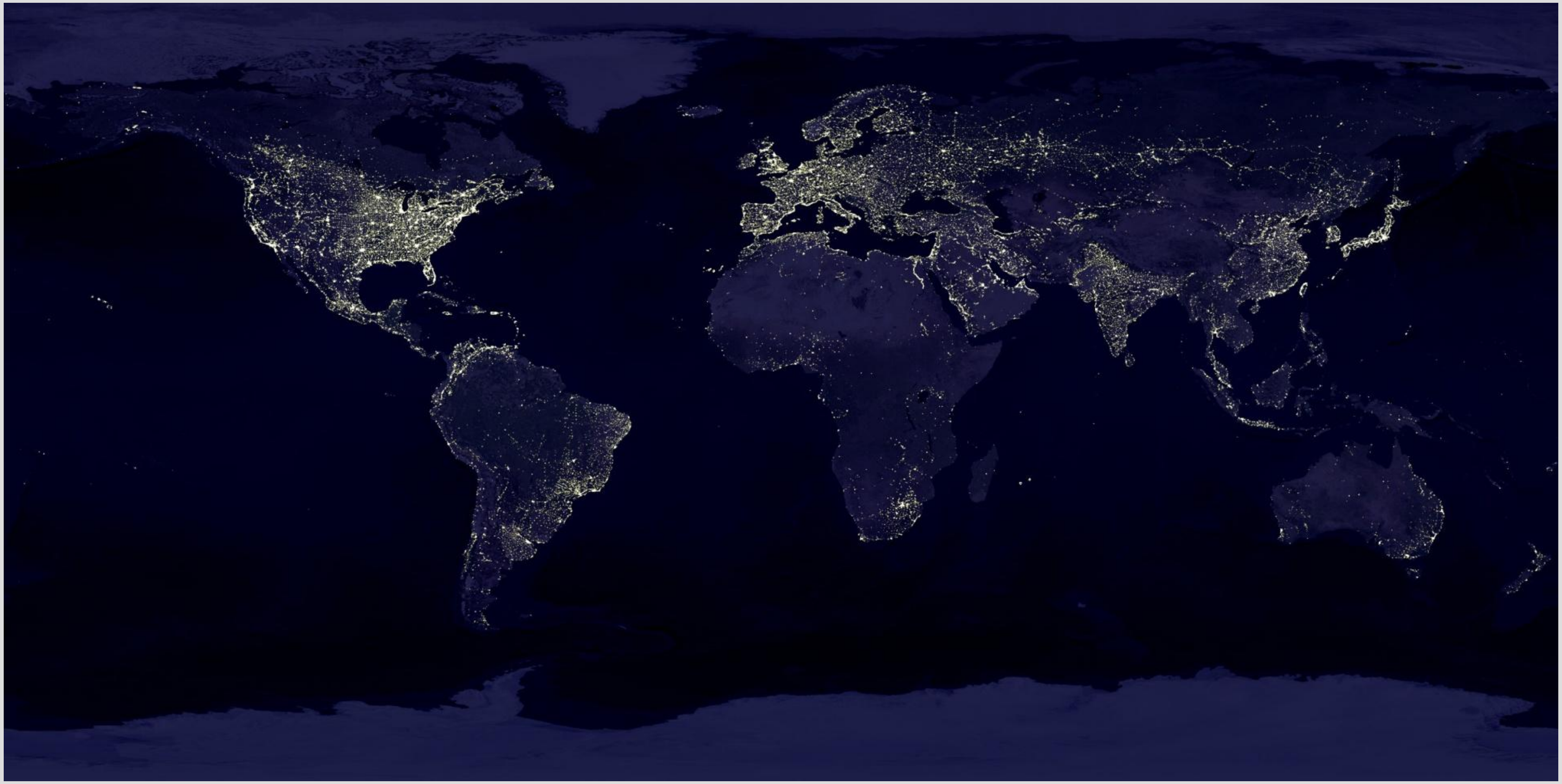
Modré a bílé světlo z GaN

Josef Humlíček, Přírodovědecká fakulta MU Brno & CEITEC MU

USp ČR, 19.1.2016

20 – 30 % spotřeby elektrické energie

<u>osvětlování</u>

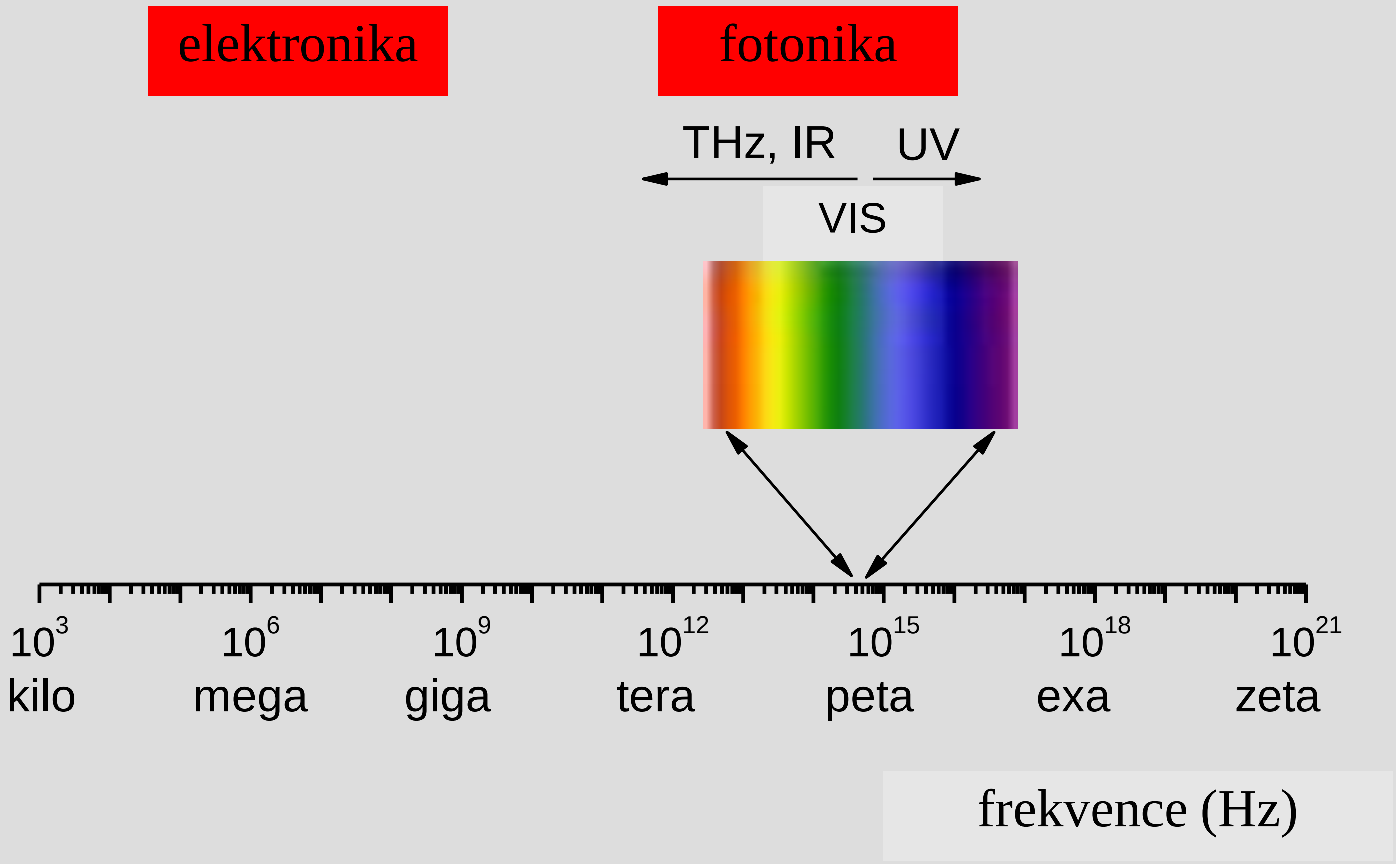


- Generace světla v polovodičích, LED a lasery
- III-V, nitridy
- GaN
- generace modrého světla:

  Nobelova cena za fyziku 2014: Akasaki, Amano, <u>Nakamura</u>
- „bílé“ světlo
- účinnost zdrojů světla

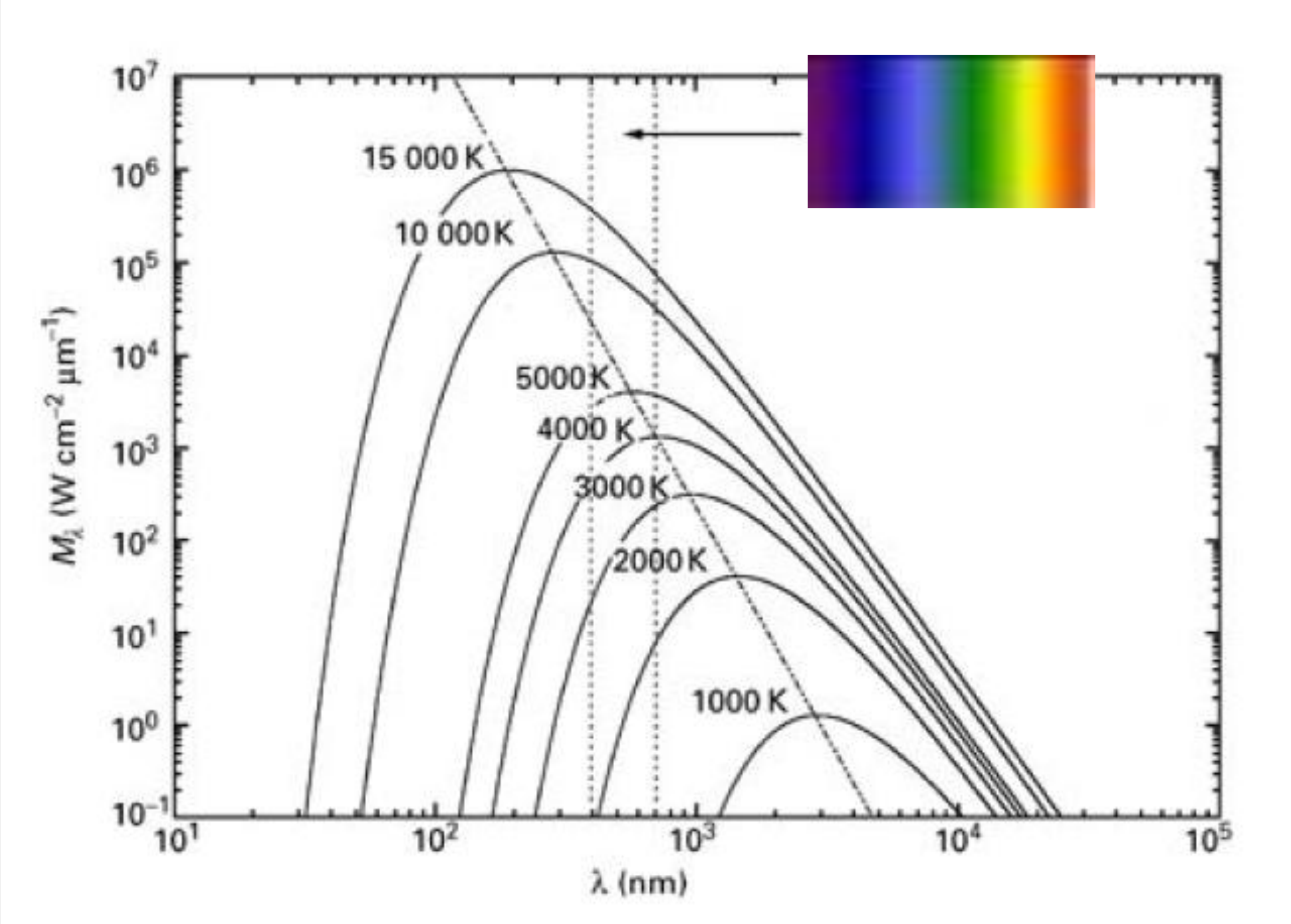
Elektromagnetické spektrum, světlo

1PHz $\propto$ 1 fs $\propto$ 0.3 μm $\propto$ 33000 cm^{-1} $\propto$ 4.1 eV $\propto$ 48000 K



Termální zdroje světla - chaotický pohyb atomových jader a elektronů rozhoduje teplota (povrch Slunce, vlákno žárovky, kosmické mikrovlnné pozadí)

Spektrální hustota záření černého tělesa (Planckův zákon)

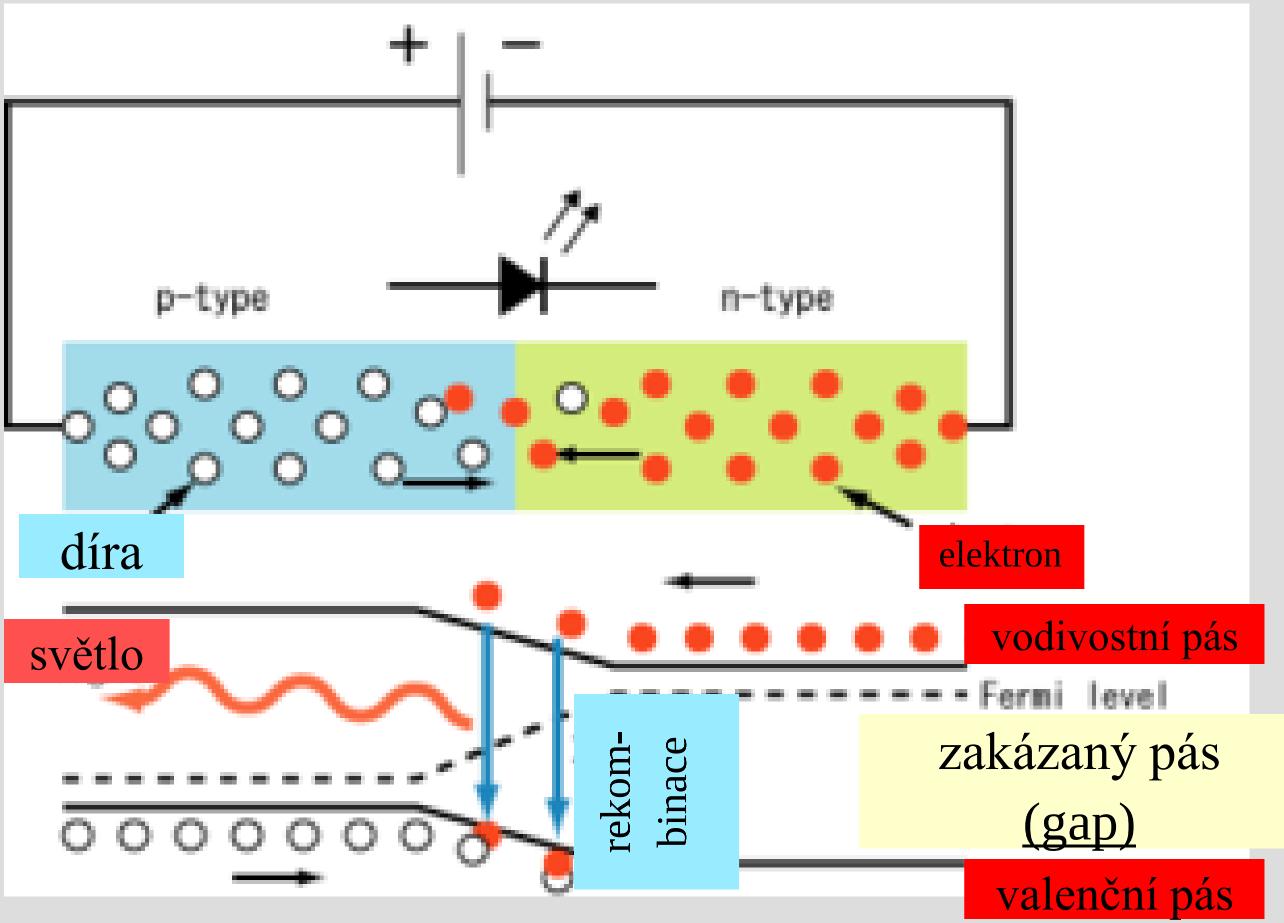


Luminiscenční dioda (LED, Light-Emitting Diode)

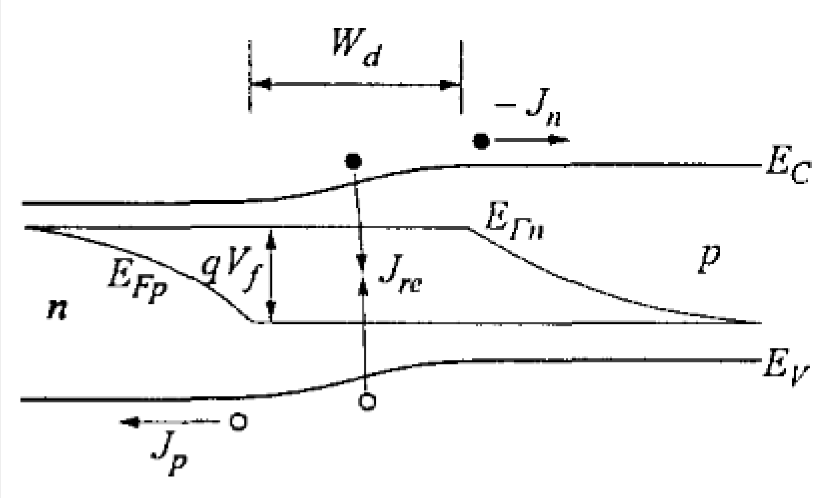
p-n přechod v propustném směru

excitace elektrickým polem, zářivá rekombinace

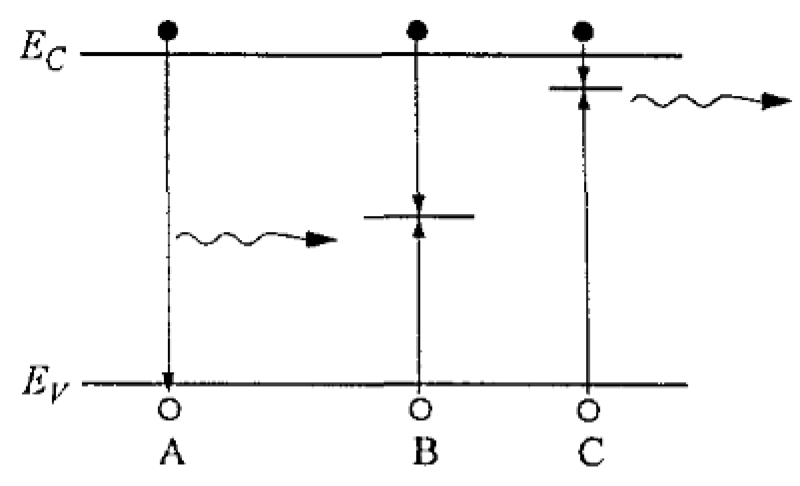
IR emise z GaAs pozorována r.1955 (R. Braunstein, RCA), použitelné diody ve VIS od r. 1962 (N. Holonyak, TI)



p-n přechod polarizovaný v propustném směru, rekombinační proud



rekombinační procesy



Luminiscenční dioda (LED, Light-Emitting Diode)

Energie gapu v oblasti rekombinace excitovaných nosičů („aktivní oblast“) je rozhodující pro emisi
např.

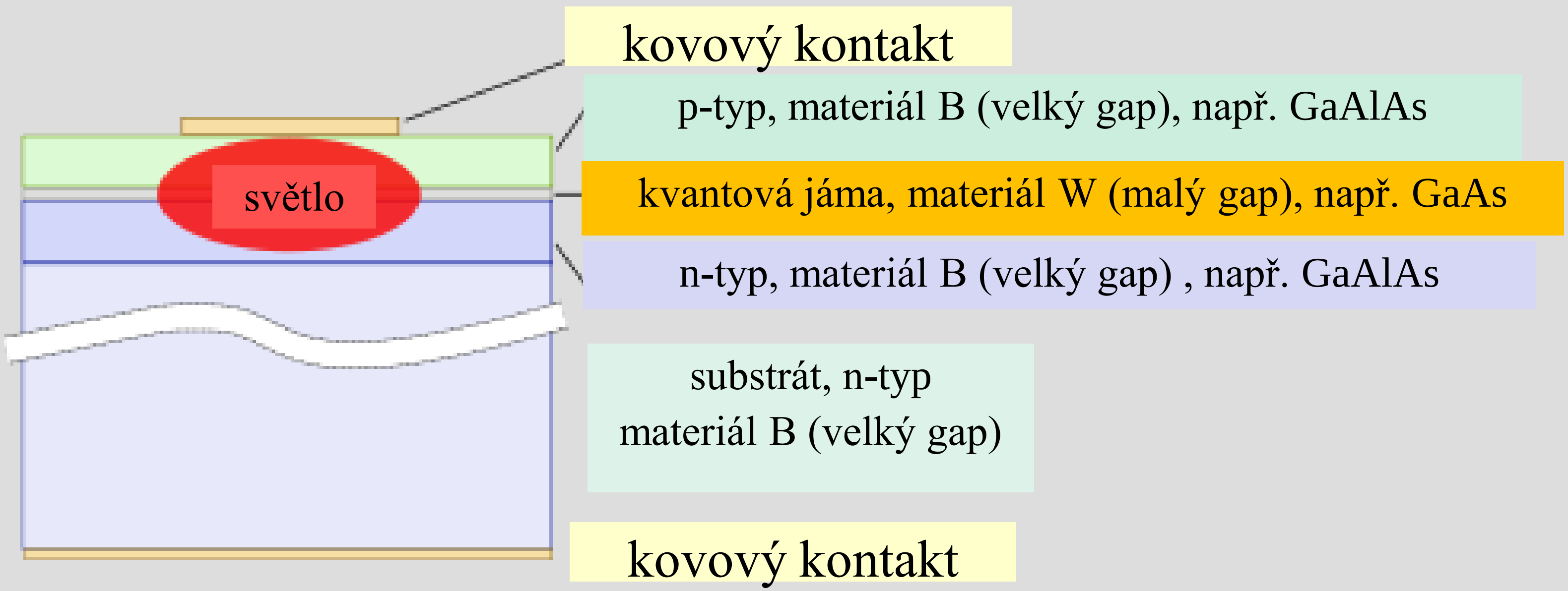
červená	AlGaAs, GaAsP
žlutá	AlGaInP, GaAsP
zelená	GaP, AlGaP
modrá	**InGaN**
UV	AlN, AlGaN, AlGaInN
„bílá“	fialová nebo UV + luminifor

běžně výkony v jednotkách W
životnost desítky let (při malých proudech)

Laserová dioda - aktivní oblast mezi zrcadly rezonátoru

emise koherentního světla, 1962 (R.N. Hall, GE)

schematický řez strukturou



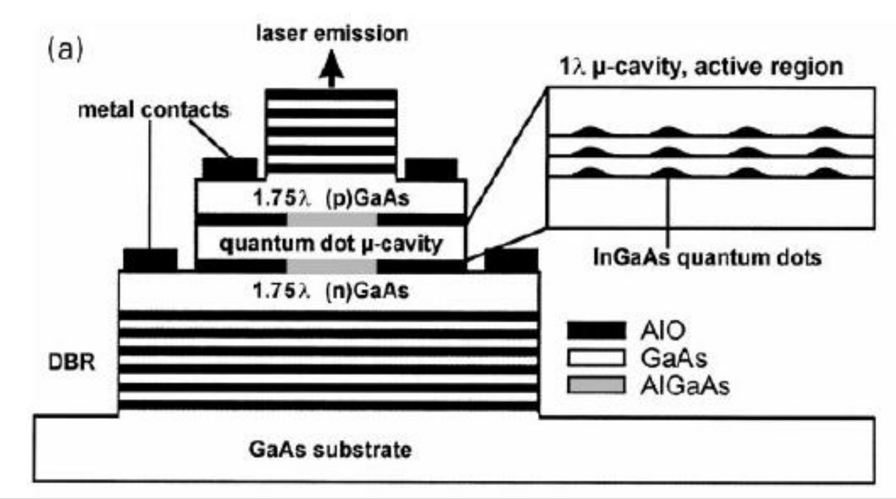
štípané boční plochy jsou rezonátorem

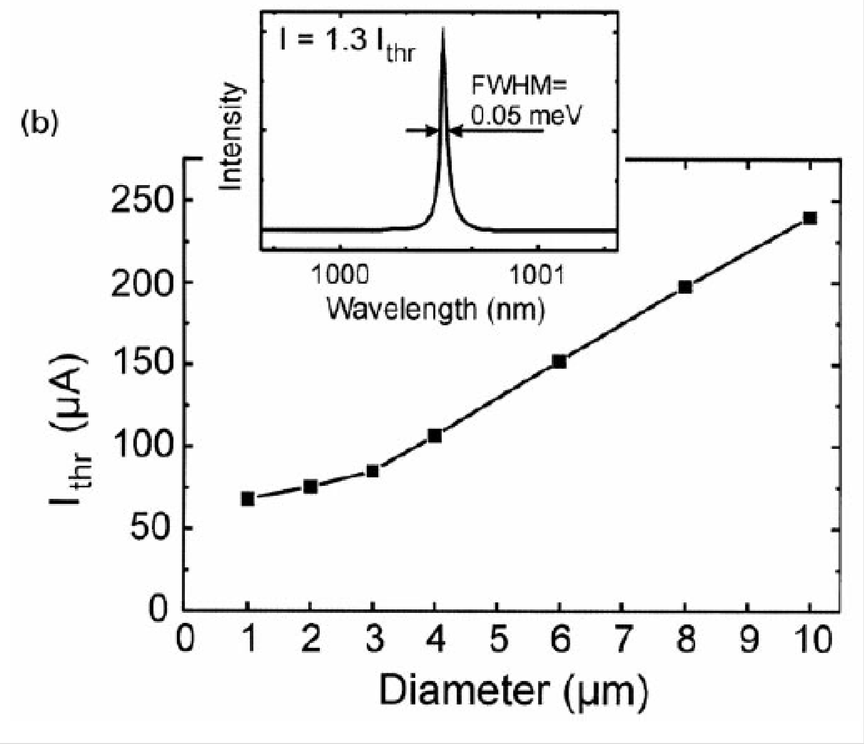
„horizontální kavita“

velká rozbíhavost svazku (10-30^{o}), kolimační čočka

Laserová struktura s kvantovými tečkami

- Aktivní trojitá vrstva v optické kavitě
- Integrovaný rezonátor s Braggovskými zrcadly
- Extrémně malý prahový proud, veliká účinnost





Elektronové stavy v krystalech

doping, přesuny elektronů a děr elektrickým polem

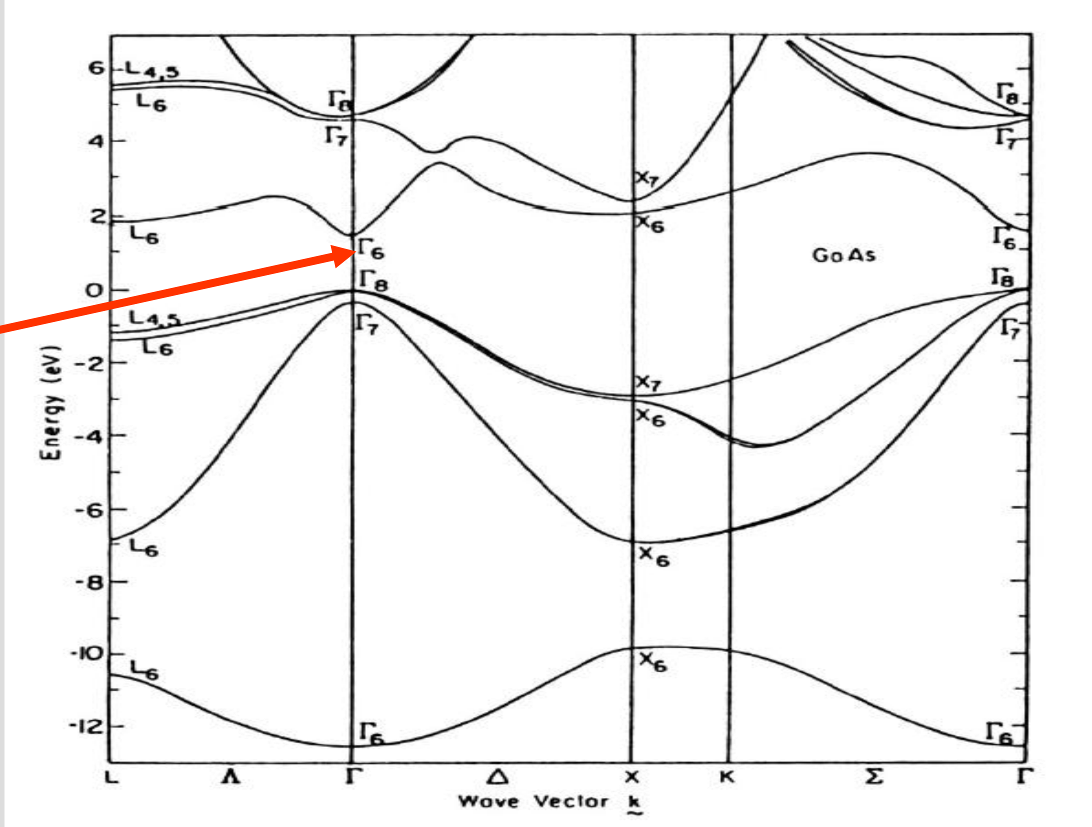
(GaAs)

gap zhruba

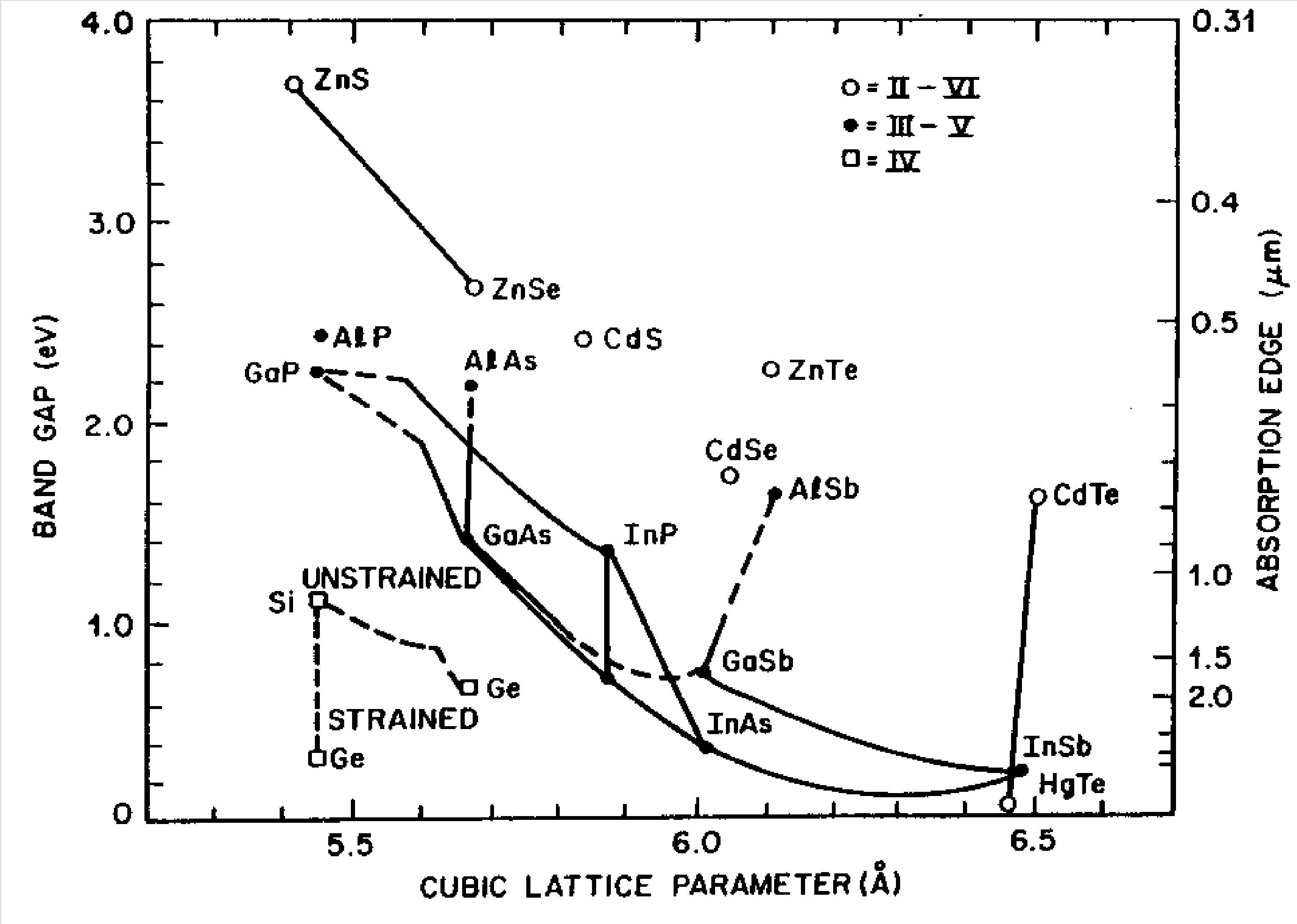
1.5 eV

vlnová délka

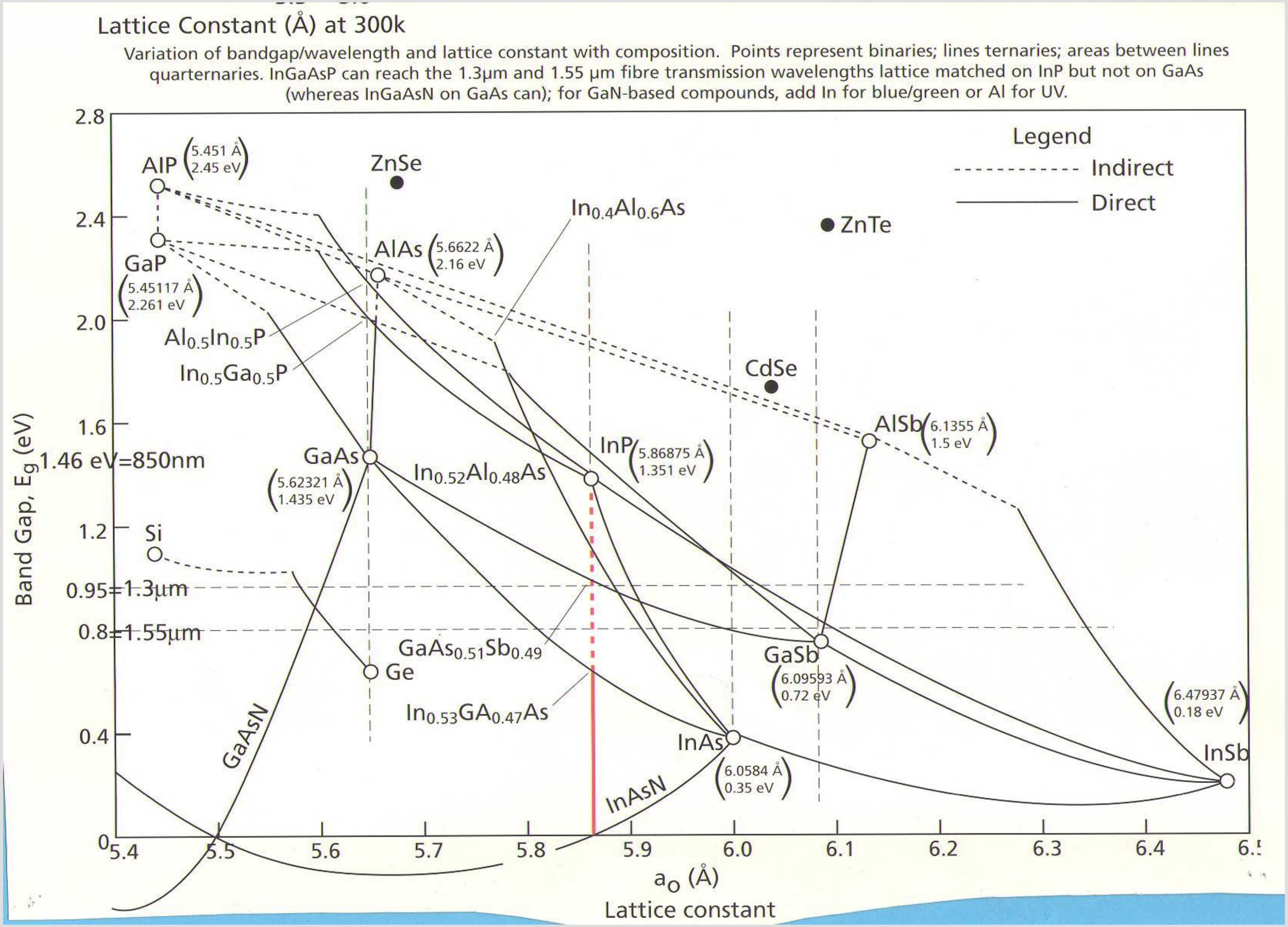
830 nm



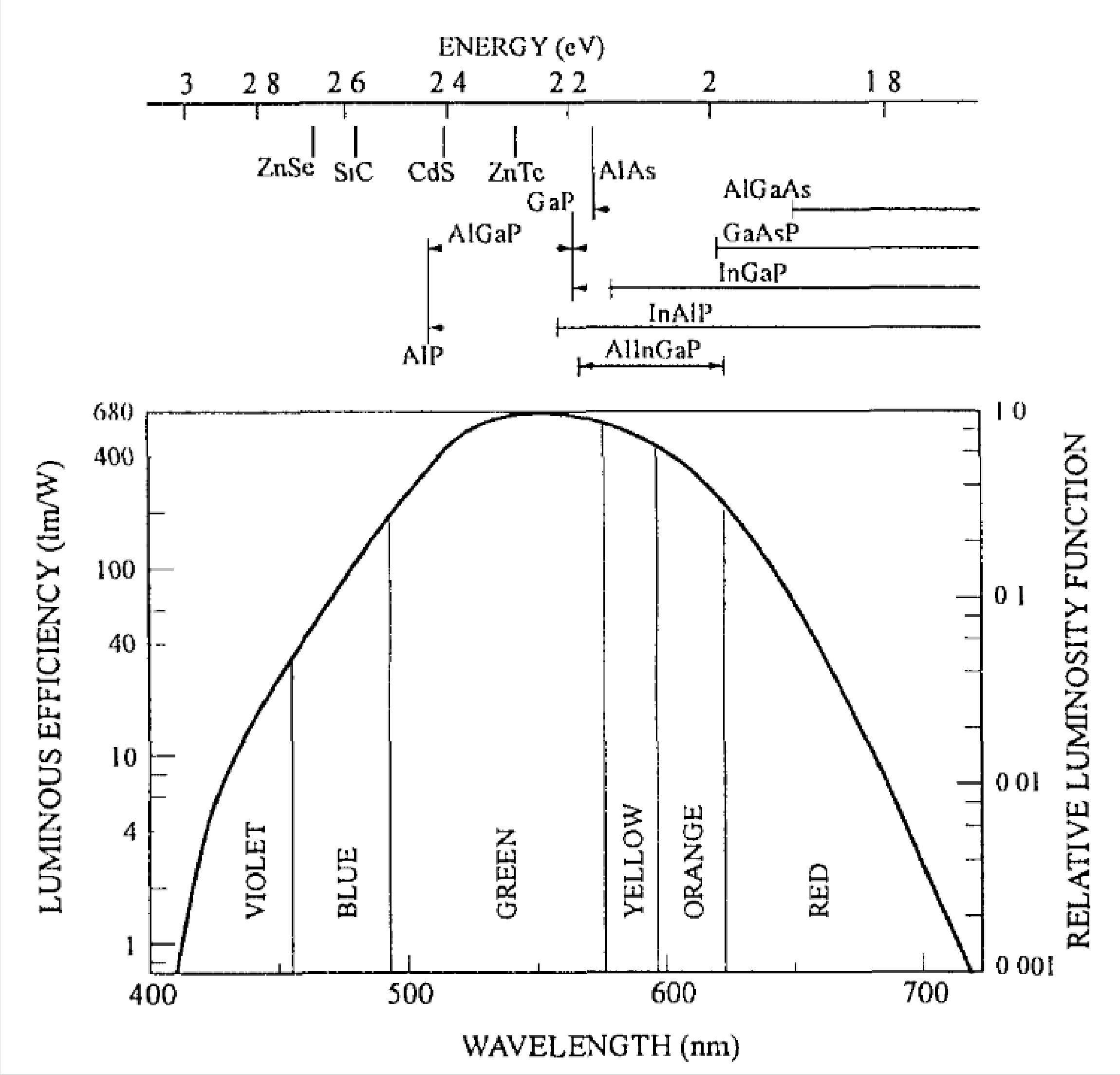
materiály doby přednitridové



přídavek GaAsN a InAsN



materiály doby přednitridové
citlivost lidského oka

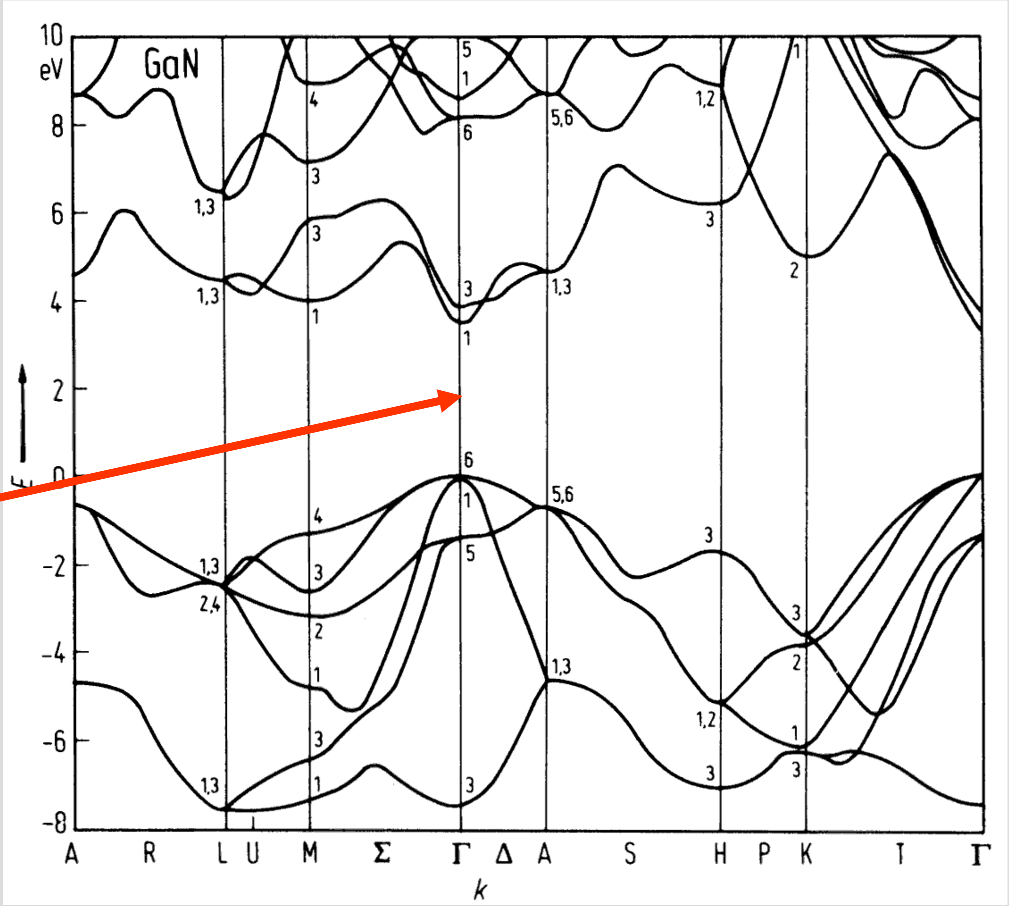


Hexagonální GaN

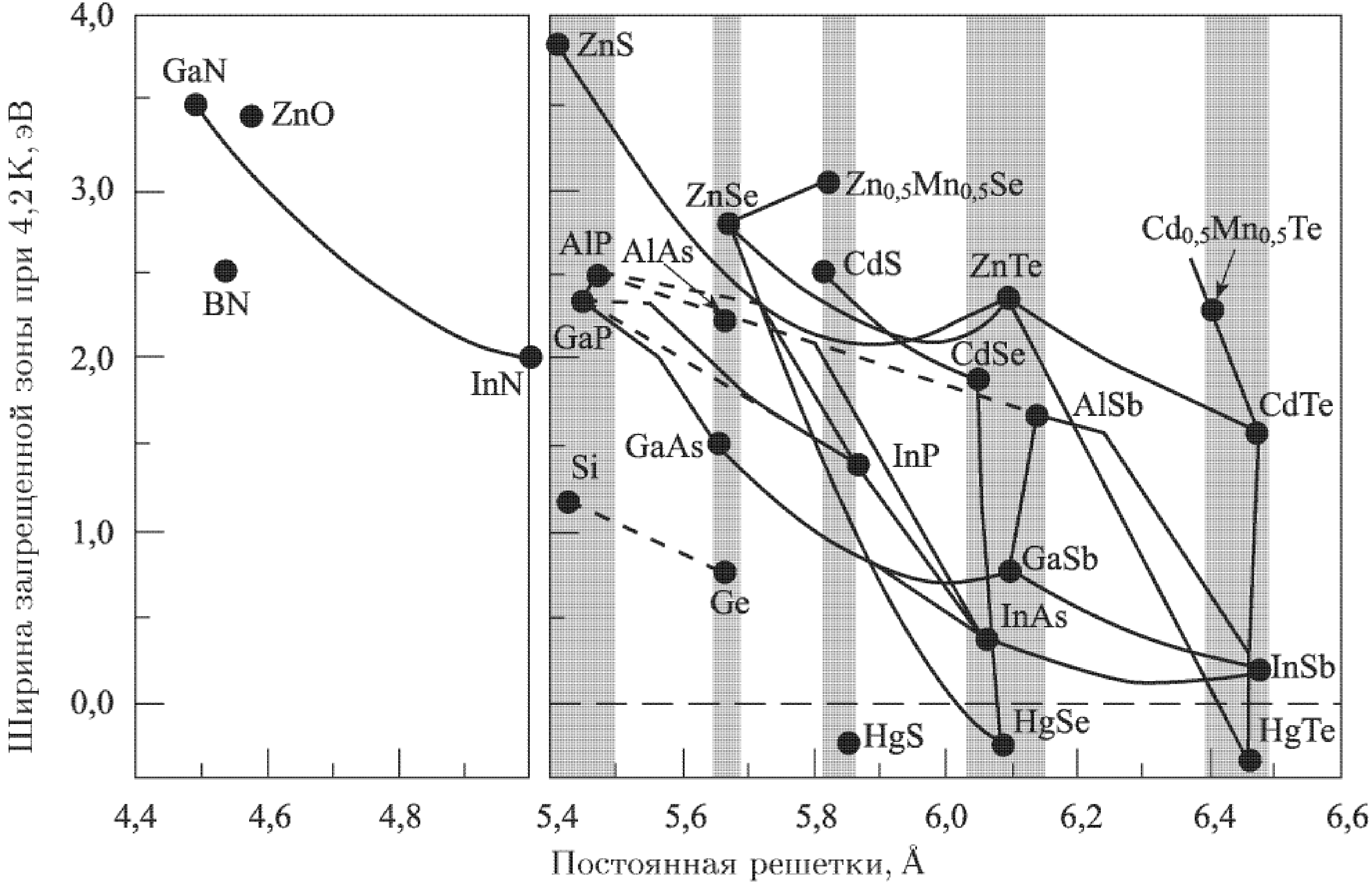
(GaN)

gap zhruba
3.4 eV

vlnová délka
365 nm

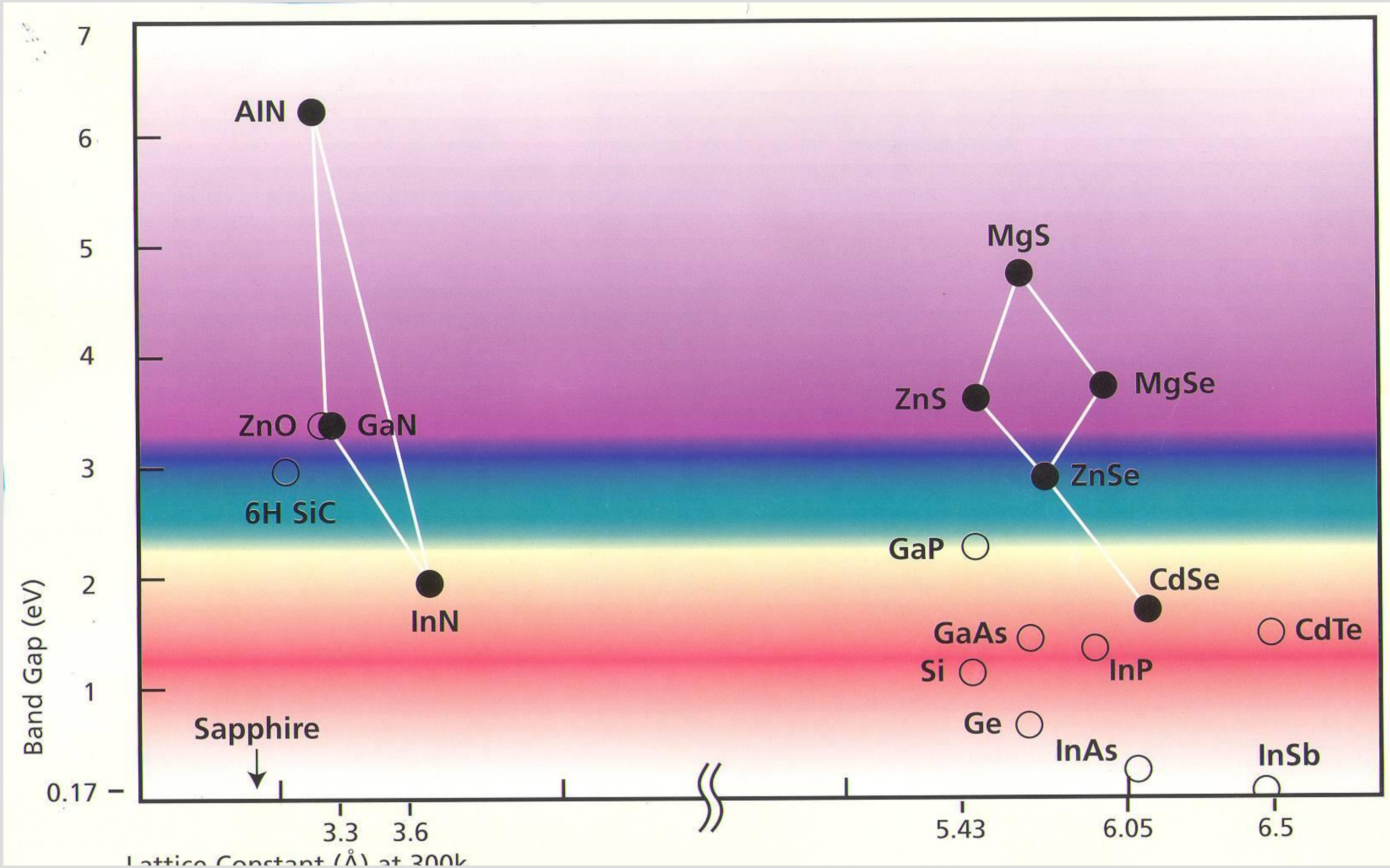


nitridy (+ZnO)



Ширина запрещенной зоны при 4,2 К, эВ
Постоянная решетки, Å
4,0
3,0
2,0
1,0
0,0
4,4
4,6
4,8
5,4
5,6
5,8
6,0
6,2
6,4
6,6
GaN
ZnO
BN
InN
ZnS
ZnSe
$Zn_{0,5}Mn_{0,5}Se$
$Cd_{0,5}Mn_{0,5}Te$
AlP
AlAs
CdS
ZnTe
GaP
CdSe
AlSb
CdTe
GaAs
InP
Si
GaSb
Ge
InAs
InSb
HgSe
HgS
HgTe

nitridy (+ SiC, ZnO)



Blue LEDs – Filling the world with new light

***Isamu Akasaki*, *Hiroshi Amano* and *Shuji Nakamura* are rewarded for inventing a new energy-efficient and environment-friendly light source – the blue light-emitting diode (LED). In the spirit of Alfred Nobel, the Prize awards an invention of greatest benefit to mankind; by using blue LEDs, white light can be created in a new way. With the advent of LED lamps we now have more long-lasting and more efficient alternatives to older light sources.*

KUNGL.
VETENSKAPS-
AKADEMIEN

THE ROYAL SWEDISH ACADEMY OF SCIENCES

7 OCTOBER 2014

Scientific Background on the Nobel Prize in Physics 2014

EFFICIENT BLUE LIGHT-EMITTING DIODES LEADING TO BRIGHT AND ENERGY-SAVING WHITE LIGHT SOURCES

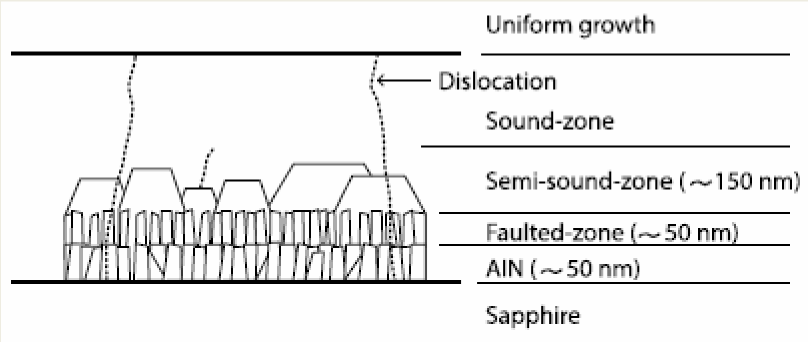
compiled by the Class for Physics of the Royal Swedish Academy of Sciences

Akasaki a Amano 1992:
Kvalitní vrstvy GaN,
silnější emise světla z GaN /AlN / Al_2O_3 v elektronovém mikroskopu

Nakamura 1992:
„nízkoteplotní buffer GaN“ + kvalitní vrstva za vyšších teplot
Vysvětlení efektivního dopingu Mg při ozáření elektrony v mikroskopu (odstranění H), náhrada vhodným žíháním

Gallium Nitride

GaN is a semiconductor of the III-V class, with Wurtzite crystal structure. It can be grown on a substrate of sapphire (Al_2O_3) or SiC, despite the difference in lattice constants. GaN can be doped, *e.g.* with silicon to n-type and with magnesium to p-type. Unfortunately, doping interferes with the growth process so that the GaN becomes fragile. In general, defects in GaN crystals lead to good electron conductivity, *i.e.* the material is naturally of n-type. GaN has a direct bandgap of 3.4 eV, corresponding to a wavelength in the ultraviolet.



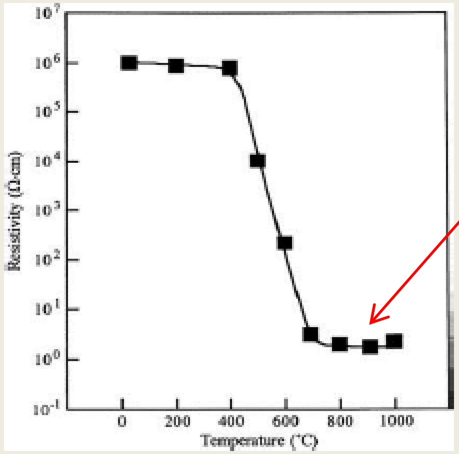


Fig. 2.
a) Growth of GaN on sapphire using an AlN layer [27].

b) Resistivity of Mg doped GaN as a function of annealing temperature [32].

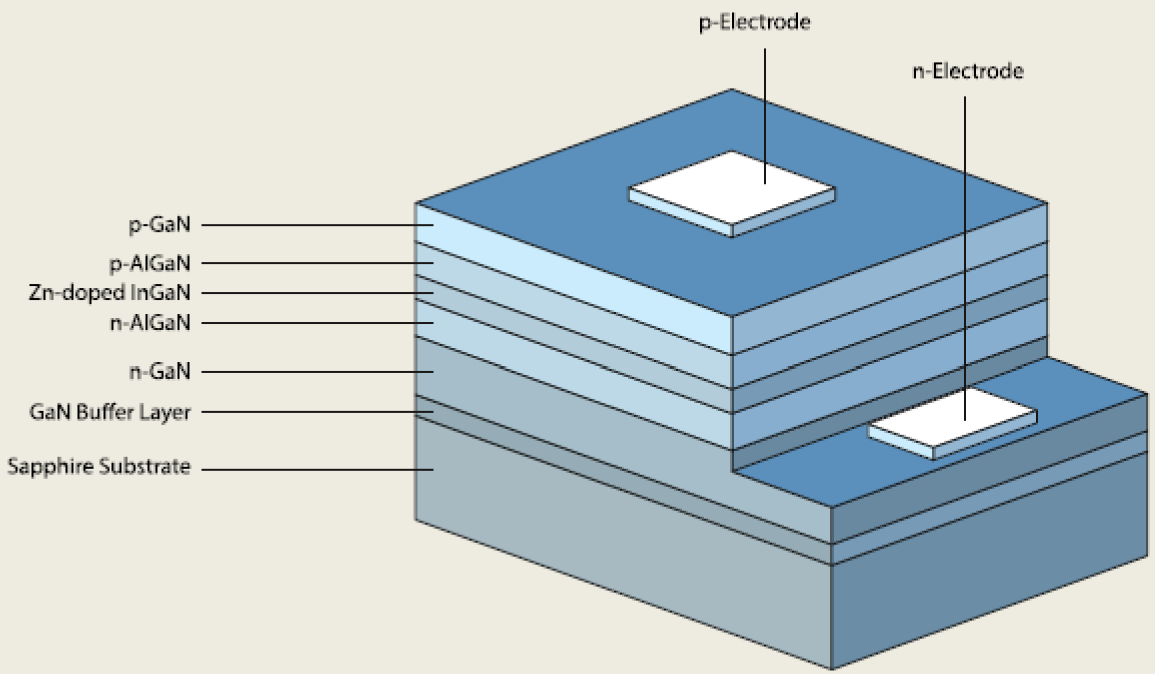
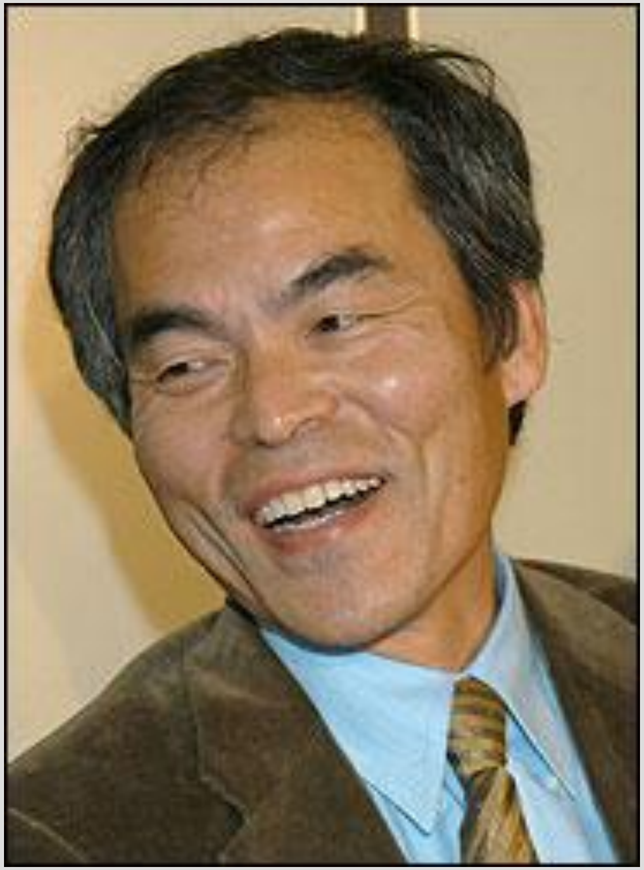


Fig. 3. Structure of a blue LED with a double heterojunction InGaN/AlGaN. From [39]

39. S. Nakamura, T. Mukai & M. Senoh, *Appl. Phys. Lett.* **64**, 1687 (1994).

Shuji Nakamura
nar. 1954
Tokushima Univ.
1979-99 Nichia Chemical Ind., Ltd.
1999- UCSB



S. Nakamura - 1992→ (WoS 2011: asi 500 prací, 18000 citací)

2390 Appl. Phys. Lett. 62 (19), 10 May 1993 0003-6951/93/192390-03$06.00 2390

High-power InGaN/GaN double-heterostructure violet light emitting diodes

Shuji Nakamura, Masayuki Senoh, and Takashi Mukai
Department of Research and Development, Nichia Chemical Industries, Ltd., 491 Oka, Kaminaka, Anan, Tokushima 774, Japan

(Received 2 November 1992; accepted for publication 15 February 1993)

InGaN/GaN double-heterostructure light-emitting diodes were fabricated. The output power was 90 μW and the external quantum efficiency was as high as 0.15% at a forward current of 20 mA at room temperature. The peak wavelengths of the electroluminescence (EL) varied between 411 and 420 nm with changes in the growth temperatures of an InGaN active layer between 820 and 800 °C. The full widths at half maximum of EL were between 22 and 25 nm.

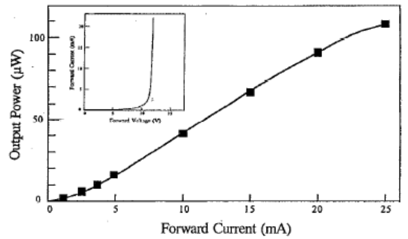


FIG. 3. The output power of the *p*-GaN/*n*-InGaN/*n*-GaN double-heterostructure blue LED as a function of the forward current. The inset shows the typical *I-V* characteristics of the *p*-GaN/*n*-InGaN/*n*-GaN double-heterostructure blue LED.

InGaN films were grown by the two-flow metalorganic chemical vapor deposition (MOCVD) method. Details of the two-flow MOCVD are described in other papers.[15,16] Sapphire with (0001) orientation (C face) was used as a substrate. Trimethylgallium (TMG), trimethylindium (TMI), monosilane (SiH_4), bis-cyclopentadienyl magnesium (Cp_2Mg) and ammonia (NH_3) were used as Ga, In, Si, Mg, and N sources, respectively. First, the substrate was heated to 1050 °C in a stream of hydrogen. Then, the substrate temperature was lowered to 510 °C to grow the GaN buffer layer. The thickness of the GaN buffer layer was approximately 250 Å. Next, the substrate temperature was elevated to 1020 °C to grow GaN films. During the deposition, the flow rates of NH_3, TMG, and SiH_4 (10 ppm SiH_4 in H_2) in the main flow were maintained at 4.0 ℓ/min, 50 μmol/min, and 10 nmol/min, respectively. The flow rates of H_2 and N_2 in the subflow were both maintained at 10 ℓ/min. The Si-doped GaN films were grown for 60 min. The thickness of Si-doped GaN film was approximately 4 μm. After GaN growth, the temperature was decreased to 800 °C, and the Si-doped InGaN film was grown for 8 min. During Si-doped InGaN deposition, the flow rates of NH_3, TMI, TMG, and SiH_4 in the main flow were maintained at 4.0 ℓ/min, 24 μm/min, 1 μmol/min, and 1 nmol/min, respectively. The thickness of the Si-doped InGaN layer was approximately 100 Å. After the Si-doped InGaN growth, the temperature was increased to 1020 °C to grow Mg-doped *p*-type GaN film. Mg-doped *p*-type GaN film was grown for 15 min by introducing Cp_2Mg gas at the flow rate of 3.6 μmol/min. After the growth, electron-beam irradiation was performed to obtain a highly *p*-type GaN layer under the condition that the accelerating voltage of incident electrons was kept at 15 kV. Fabrication of LED chips was accomplished as follows: the surface of the *p*-type GaN layer was partially etched until the *n*-type layer was exposed. Next, an Au/Ni contact was evaporated onto the *p*-type GaN layer and an Al contact onto the *n*-type GaN layer. The wafer was cut into a square shape (0.9 mm×0.9 mm). These chips were set on the lead frame, and then were molded. The characteristics of LEDs were measured under direct current (dc) biased conditions at room temperature.

S. Nakamura

HONORS & AWARDS

1994, 1996	Nikkei BP Engineering Award
1994, 1997	Best Paper Award of Japanese Applied Physics Society
1995	Sakurai Award
1996	Nishina Memorial Award
1996	IEEE Lasers and Electro-Optics Society Engineering Achievement Award
1996	Society for Information Display (SID) Special Recognition Award
1997	Okochi Memorial Award
1997	Materials Research Society (MRS) Medal Award
1998	Innovation in Real Materials (IRM) Award
1998	C&C Award
1998	IEEE Jack A. Morton Award
1998	British Rank Prize
1999	Julius-Springer Prize for Applied Physics
2000	Takayanagi Award
2000	Carl Zeiss Research Award

HONORS & AWARDS (Continued)

2000 Honda Award

2000 Crystal Growth and Crystal Technology Award

2001 Asahi Award

2001 Cree Professor in Solid State Lighting and Display Endowed Chair

2001 OSA Nick Holonyak Award

2001 LEOS Distinguished Lecturer Award

2002 IEEE/LEOS Quantum Electronics Award

2002 Recipient of the Franklin Institute’s 2002 Benjamin Franklin Medal in Engineering

2002 Takeda Award

2002 The Economist Innovation Award 2002 “No Boundaries”

2002 World Technology Award

2003 CompoundSemi Pioneer Award

2003 National Academy of Engineering Member

2003 Blue Spectrum Pioneer Awards

2004 The Society for Information Display Karl Ferdinand Braun Prize

2006 Global Innovation Leader Award, Optical Media Global Industry Awards

2006 Millennium Technology Prize

2007 Santa Barbara Region Chamber of Commerce Innovator of the Year Award

2007 Czochralski Award

2008 Japanese Science of Applied Physics (JSAP) Outstanding Paper Award for the “Demonstration of Nonpolar m-Plane InGaN/GaN Laser Diode”

2008 The Prince of Asturias Award for Technical Scientific Research (The Prince of Asturias Foundation)

2009 Harvey Prize

New York Times:

Japanese Company to Pay Ex-Employee $8.1 Million for Invention

Published: January 12, 2005

TOKYO, Jan. 11 - The inventor of a revolutionary lighting technology has reluctantly agreed to a record settlement from his former employer in a dispute that challenged the idea that the fruits of the labor of Japanese workers belong only to companies.

Shuji Nakamura, now a professor at the University of California, Santa Barbara, will receive 840 million yen ($8.1 million) from his former employer, the Nichia Corporation, for inventing blue-light-emitting diodes. Nichia secured lucrative patents for Mr. Nakamura's invention, which allowed the creation of more vibrant video billboards and traffic signal lights and helped lead to the development of blue lasers, which are used in the latest DVD players. His invention was also useful in creating white-light-emitting diodes, which may someday replace incandescent bulbs as a source of indoor lighting.

Mr. Nakamura sued his former employer four years ago, seeking a share of the royalties from his invention after the company gave him an award of 20,000 yen, or less than $200, for his work.

Komerční úspěch - patentová ochrana

(12) **United States Patent**
Nakamura et al.

(10) **Patent No.: US 6,900,465 B2**
(45) **Date of Patent: *May 31, 2005**

(54) **NITRIDE SEMICONDUCTOR LIGHT-EMITTING DEVICE**

(75) Inventors: **Shuji Nakamura**, Tokushima (JP); **Shinichi Nagahama**, Komatsushima (JP); **Naruhito Iwasa**, Tokushima (JP); **Hiroyuki Kiyoku**, Tokushima-ken (JP)

(73) Assignee: **Nichia Corporation**, Tokushima (JP)

(21) Appl. No.: **09/809,038**

(22) Filed: **Mar. 16, 2001**

(65) **Prior Publication Data**

US 2001/0030318 A1 Oct. 18, 2001

Related U.S. Application Data

(63) Continuation of application No. 09/069,240, filed on Apr. 29, 1998, now abandoned.

U.S. PATENT DOCUMENTS

4,759,024 A	*	7/1988	Hayakawa et al.	....	372/45
4,941,146 A		7/1990	Kobayashi	....	372/45
5,132,750 A		7/1992	Kato et al.		
5,146,465 A		9/1992	Khan et al.		
5,237,581 A		8/1993	Asada et al.		

OTHER PUBLICATIONS

Japan J. Appl. Phys. vol. 34 (1995) pp. L797–L799.

Japan J. Appl. Phys. vol. 34 (1995) pp. L332–L–1335.

Applied Physics Leitt 67 (13) Sep. 1995.

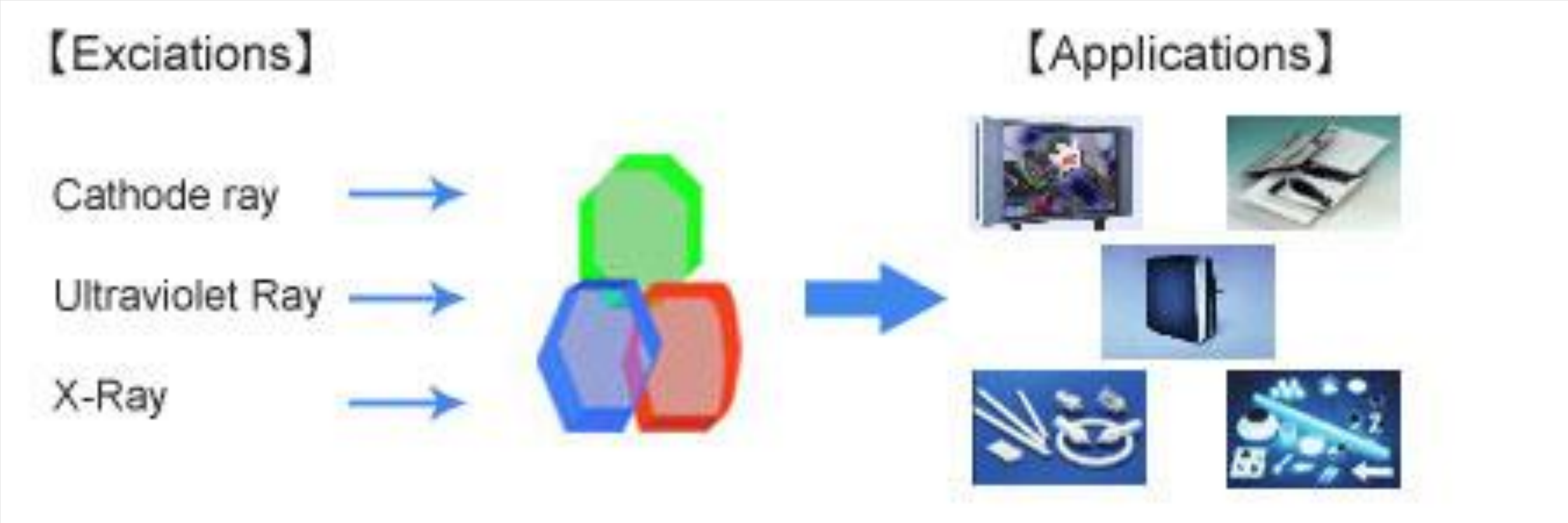
Nakamura et al., 320 Applied Physics Letters 67 (1995) Sep. 25, No. 13 *High–Power InGaN Single Quantum–Well–Structure Blue and Violet Light Emitting Diodes.*

Khan et al., *Reflective Filters Based on Single–Crystal GaN/AlxGal–xN Multilayers Deposited Using Low–Pressure Metalorganic Chemical Vapor Deposition*, Appl. Phys. Lett., vol. 59, No. 12.

Primary Examiner—Long Pham
Assistant Examiner—Wai-Sing Louie
(74) *Attorney, Agent, or Firm*—Nixon & Vanderhye PC

UV + luminifor → bílé světlo

Luminifory („phosphors“) Nichia

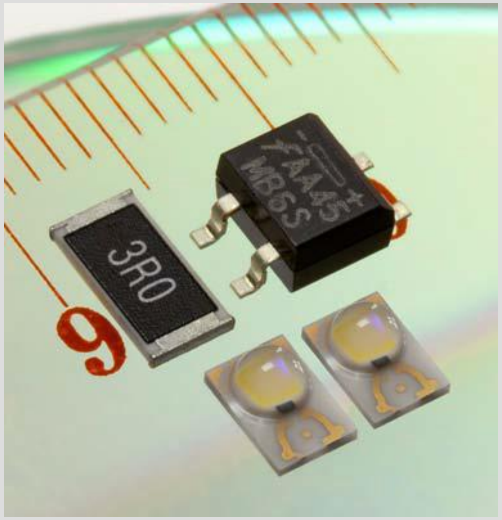


Luminifory („phosphors“) Nichia

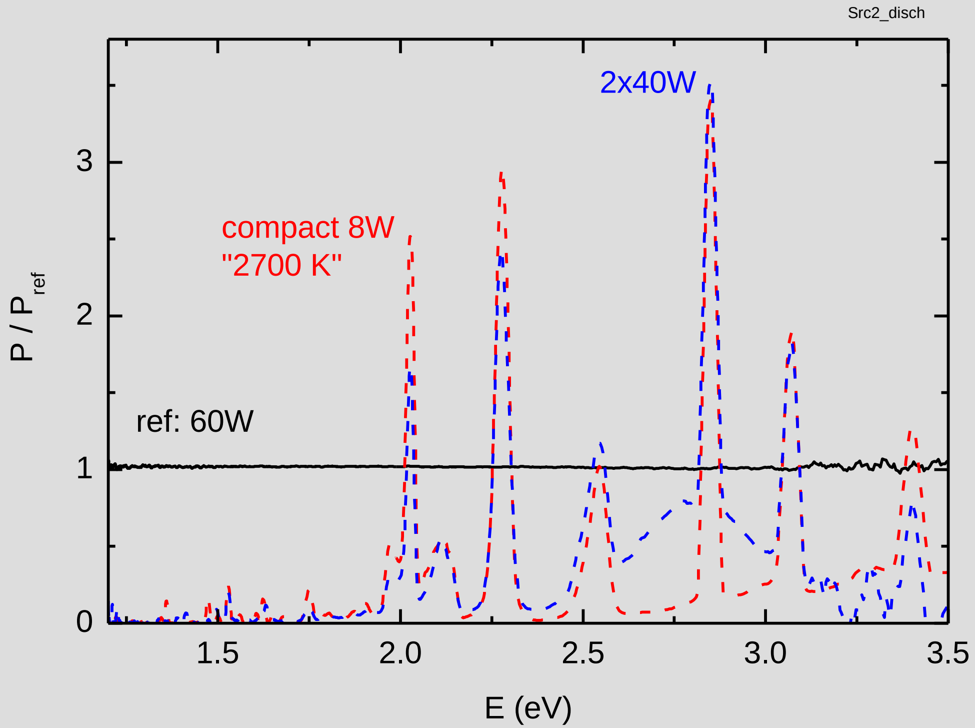
CRT Phosphor	Blue	ZnS:Ag,Al	Cathode Ray Tube	
	Green	ZnS:Cu,Al		
	Red	Y_2O_2S:Eu		
Lamp Phosphor	Blue	$(SrCaBaMg)_5(PO_4)_3Cl$:Eu	Fluorescent Lamp	
	Green	$LaPO_4$:Ce,Tb		
	Red	Y_2O_3:Eu		
	White	$Ca_{10}(PO_4)_6FCl$:Sb,Mn		
PDP Phosphor	Blue	$BaMgAl_{10}O_{17}$:Eu	PDP	
	Green	Zn_2SiO_4:Mn		
	Red	$(Y,Gd)BO_3$:Eu		

Výrobci LED

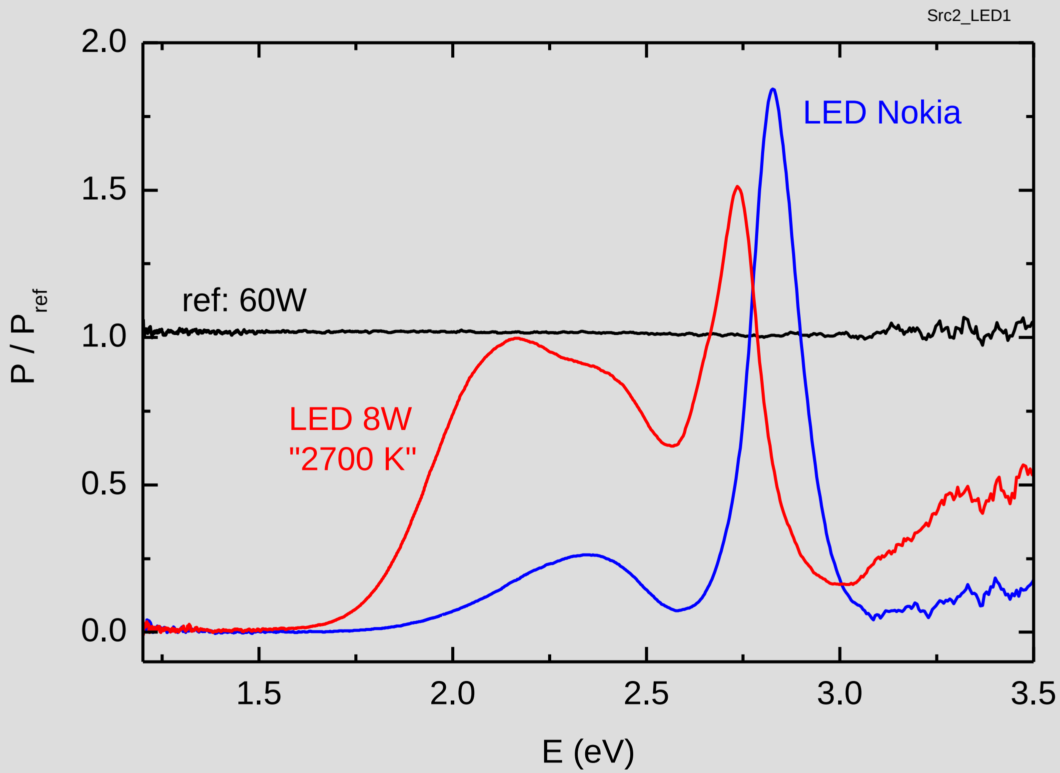
Nichia
Cree
OSRAM Opto
Philips Lumileds
Seoul Semiconductor
Toyoda Gosei



Spektrální charakteristiky „bílého“ světla : zářivky



Spektrální charakteristiky „bílého“ světla : LED



Účinnost LED:

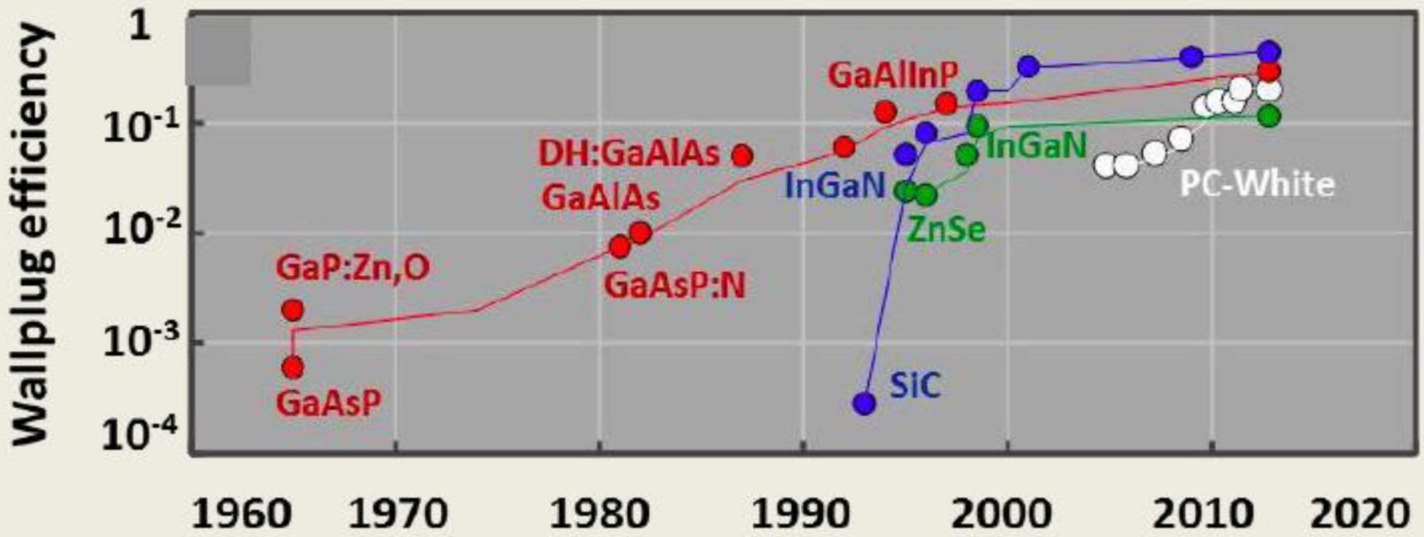
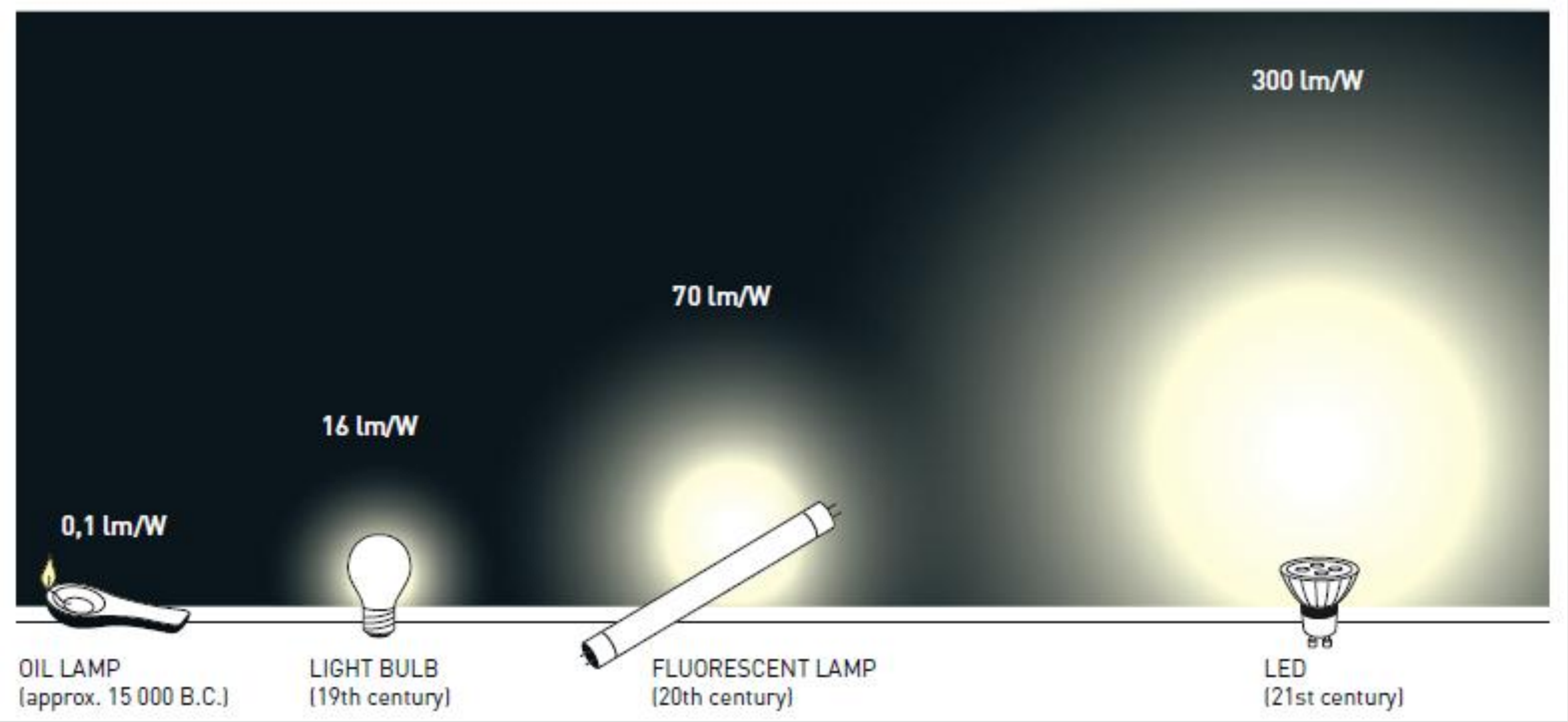


Fig. 4. Historical evolution of commercial LEDs. From [42]. PC-White stands for phosphor converted white light, DH stands for double heterostructure. The wallplug efficiency is the ratio between emitted light power and supplied electrical power.

Účinnost generace „bílého“ světla:



Závěr

Nitridové heterostruktury (AlGaIn)N

čekají

s velkou pravděpodobností

opravdu světlé zítřky