Širokopásmové polovodiče

<u>GaN / InGaN - ultrafialové a viditelné světlo</u>

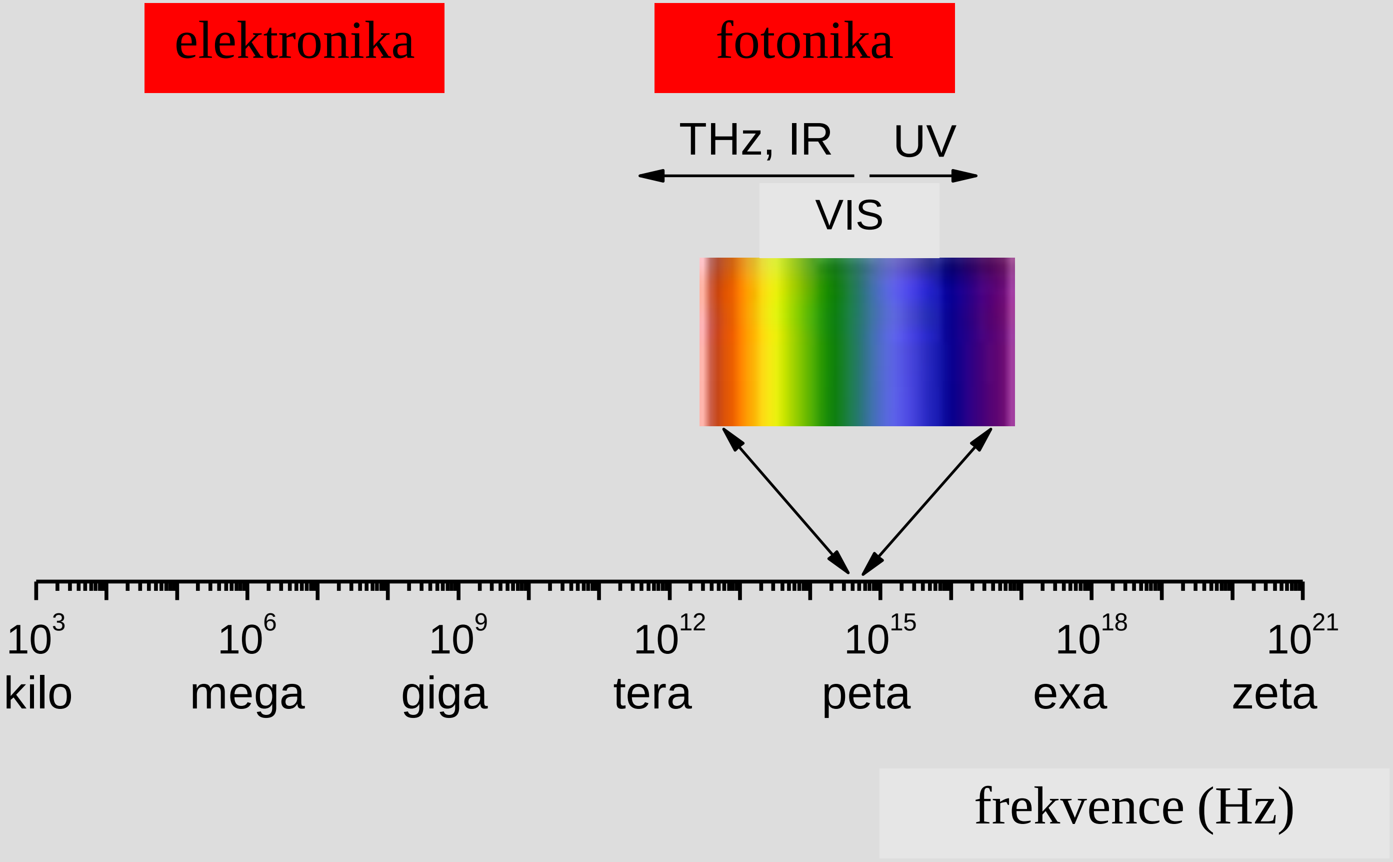
(GaN / AlGaN – výkonové součástky)

Moderní témata FKL, J. Humlíček, 8.12.2020

- Generace světla v polovodičích, LED a lasery
- III-V, nitridy
- GaN
- generace modrého, fialového a UV světla: Shuji Nakamura
- luminifory - „bílé“ světlo
- každodenní život s bílým světlem z GaN

Elektromagnetické spektrum, světlo

$1\,\mathrm{PHz} \propto 1\,\mathrm{fs} \propto 0.3\,\mu\mathrm{m} \propto 33000\,\mathrm{cm}^{-1} \propto 4.1\,\mathrm{eV} \propto 48000\,\mathrm{K}$



elektronika

fotonika

THz, IR

UV

VIS

10^{3} kilo

10^{6} mega

10^{9} giga

10^{12} tera

10^{15} peta

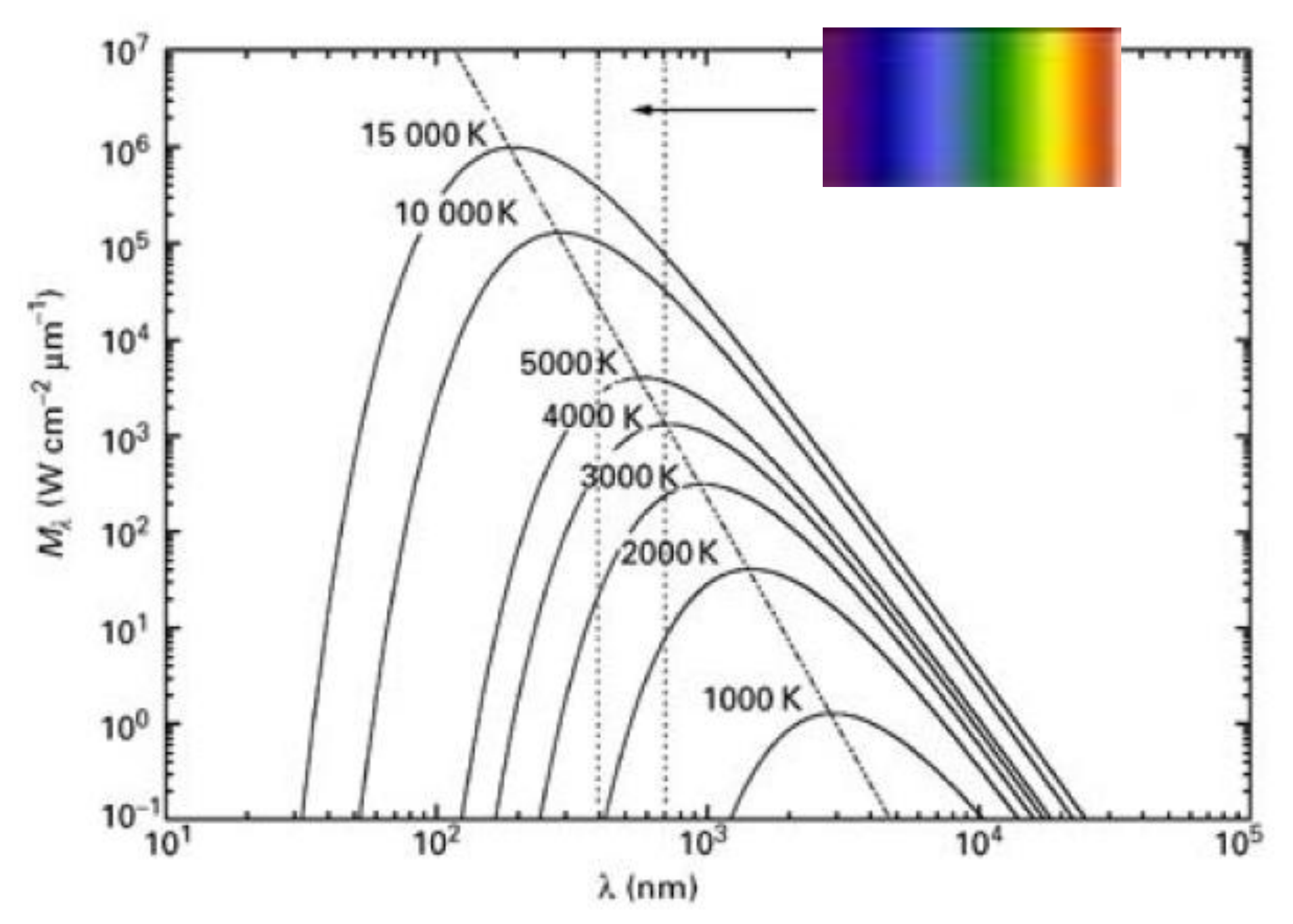
10^{18} exa

10^{21} zeta

frekvence (Hz)

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)

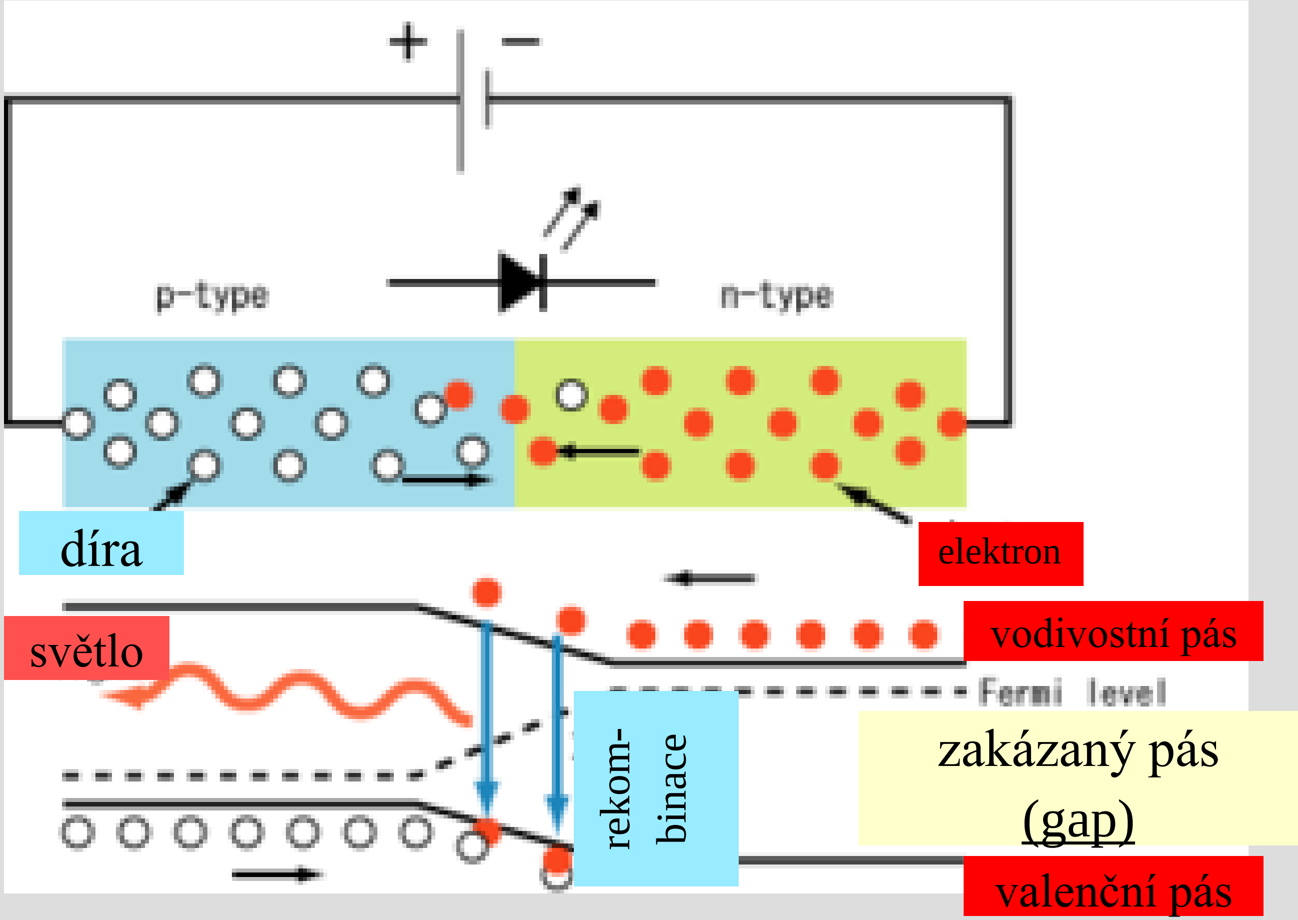


Luminiscenční dioda (LED, Light-Emitting Diode)

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)



díra

elektron

světlo

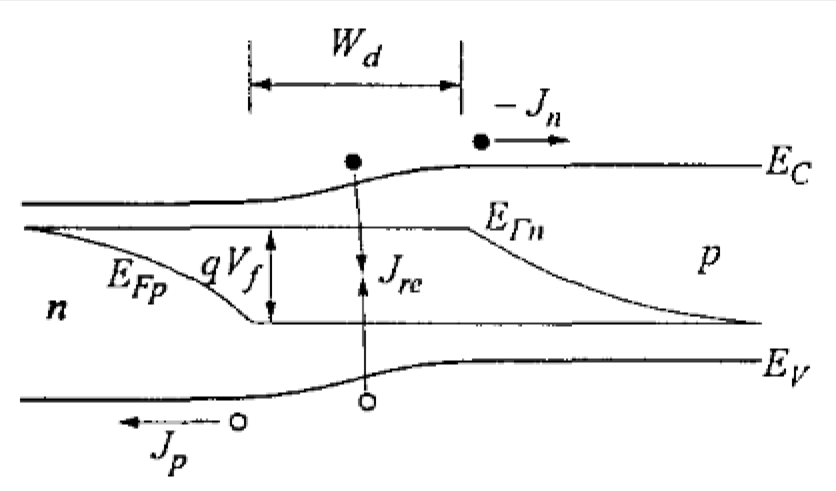
vodivostní pás

rekom-
binace

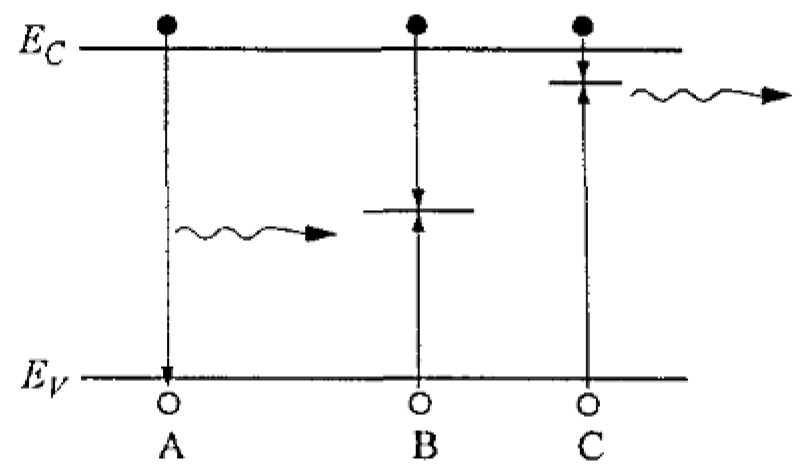
zakázaný pás
(gap)

valenční pás

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

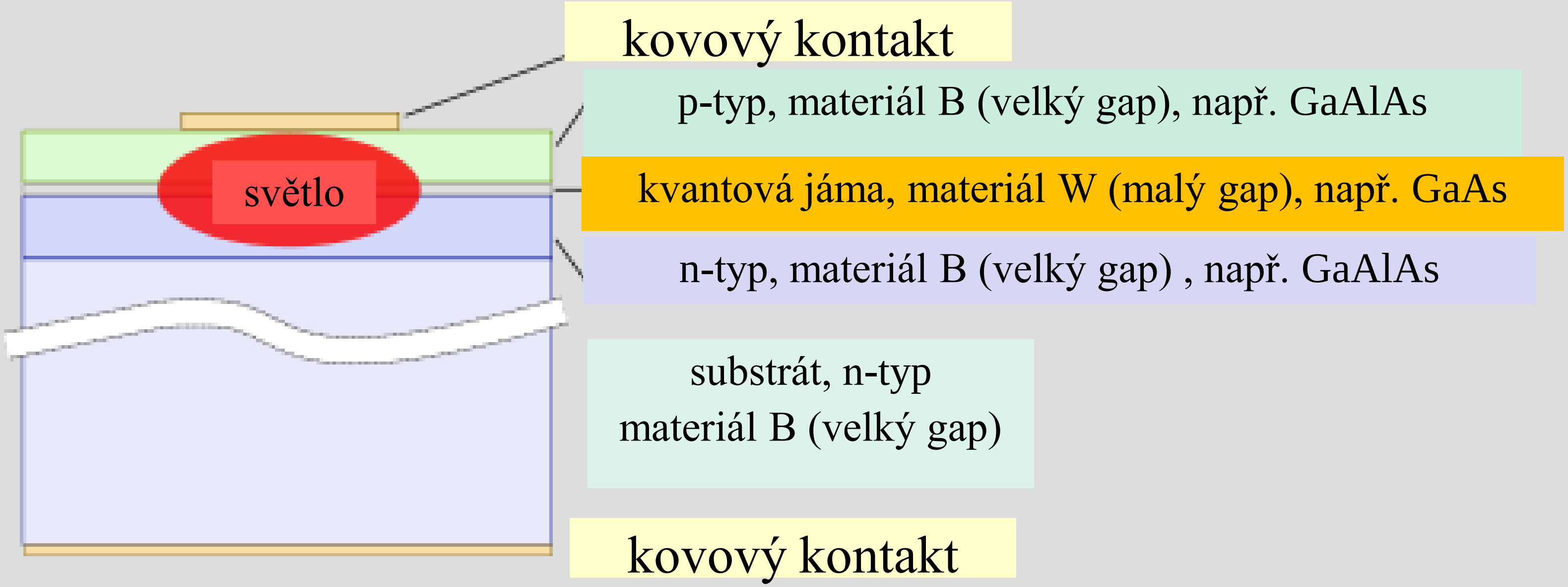
světelná účinnost LED (žárovka ~15 lm/W, zářivka ~100 lm/W)
≥ ~150 lm/W, stále se zlepšuje

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



kovový kontakt

p-typ, materiál B (velký gap), např. GaAlAs

kvantová jáma, materiál W (malý gap), např. GaAs

n-typ, materiál B (velký gap) , např. GaAlAs

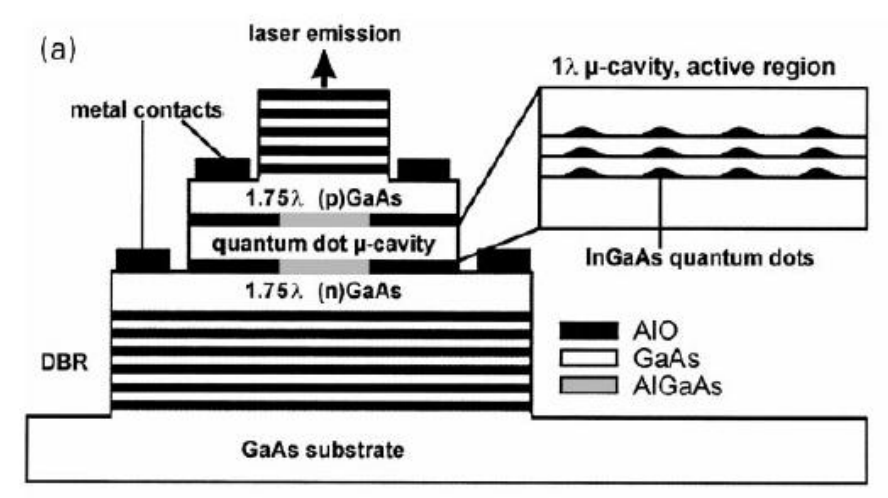
substrát, n-typ
materiál B (velký gap)

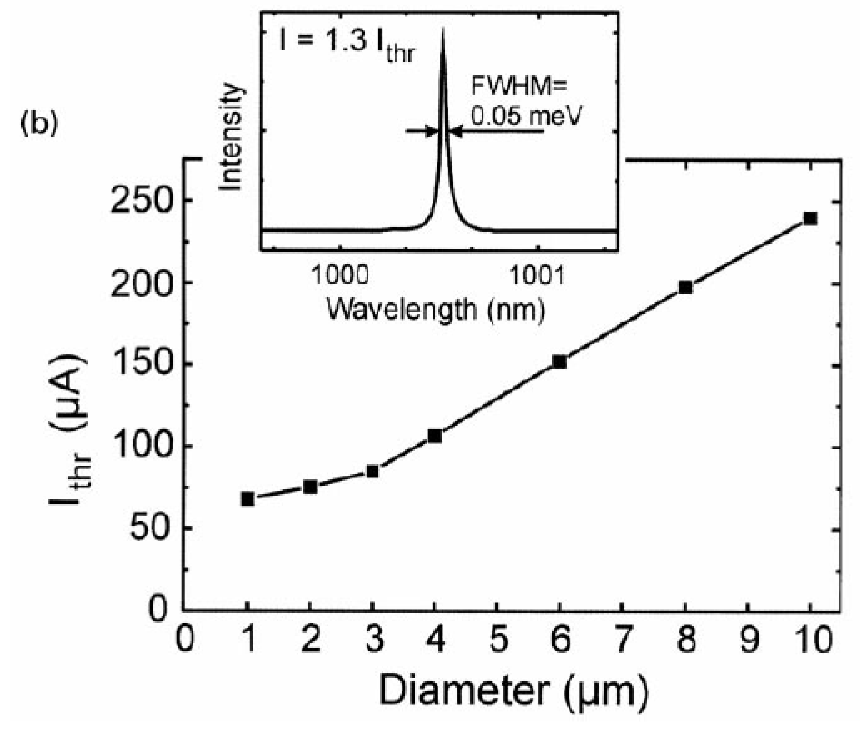
kovový kontakt

štípané boční plochy jsou rezonátorem
„horizontální kavita“
velká rozbíhavost svazku (10-30°), 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

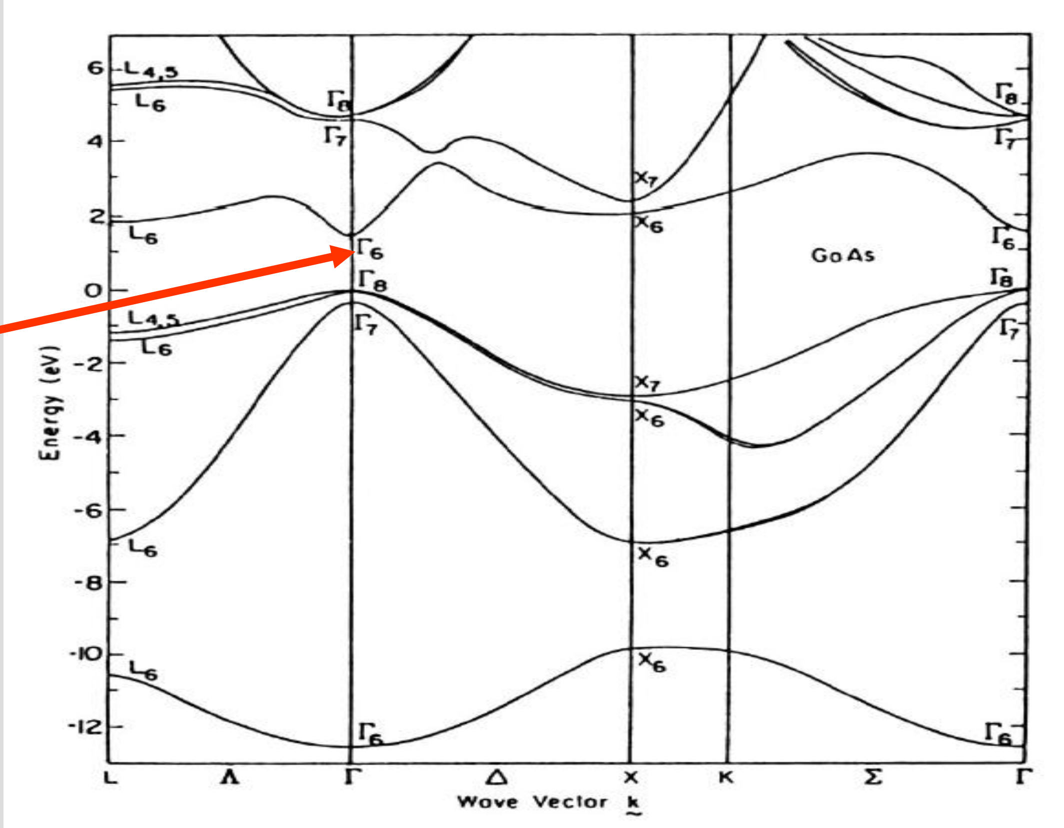
(GaAs)

gap zhruba

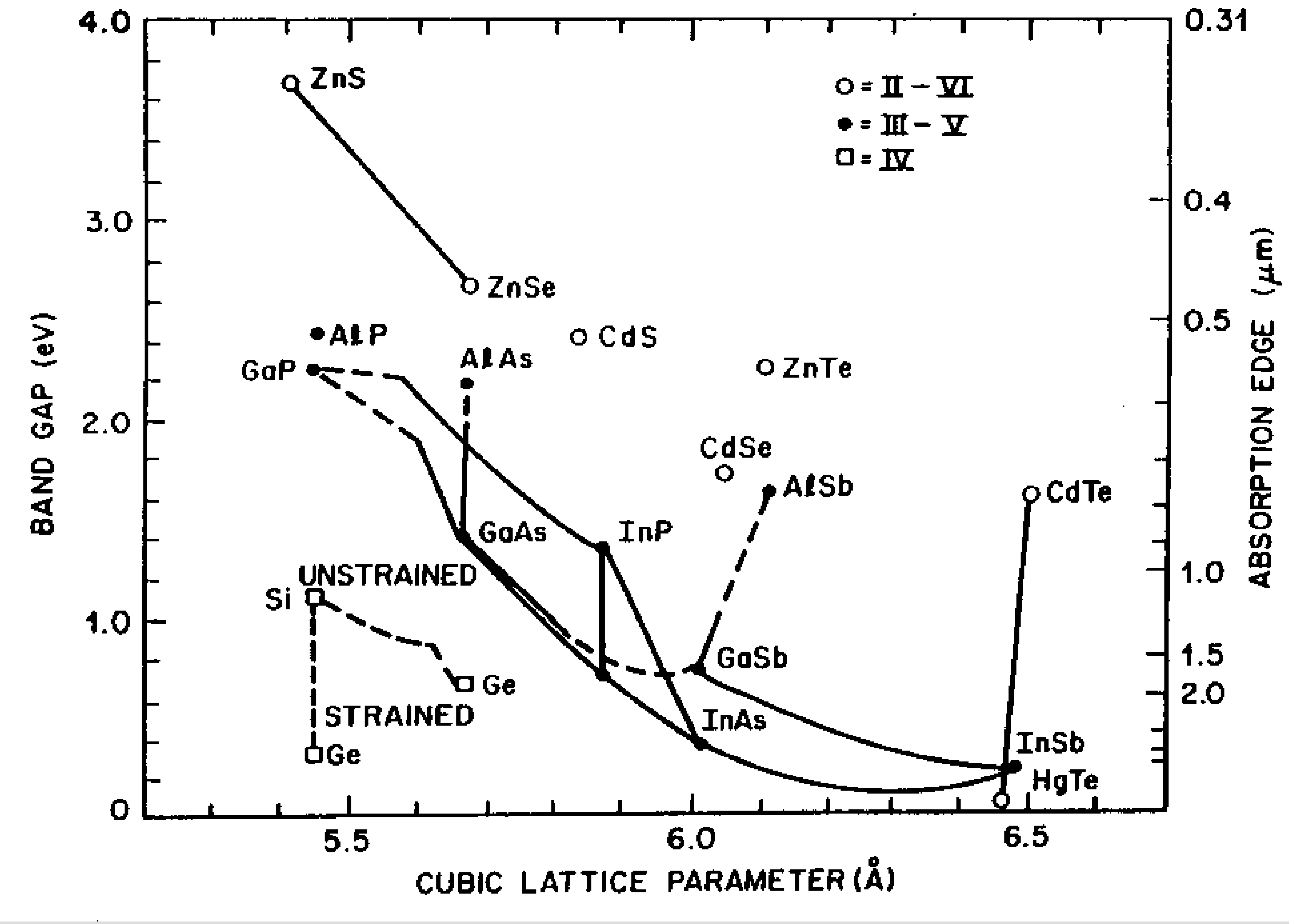
1.5 eV

vlnová délka

830 nm



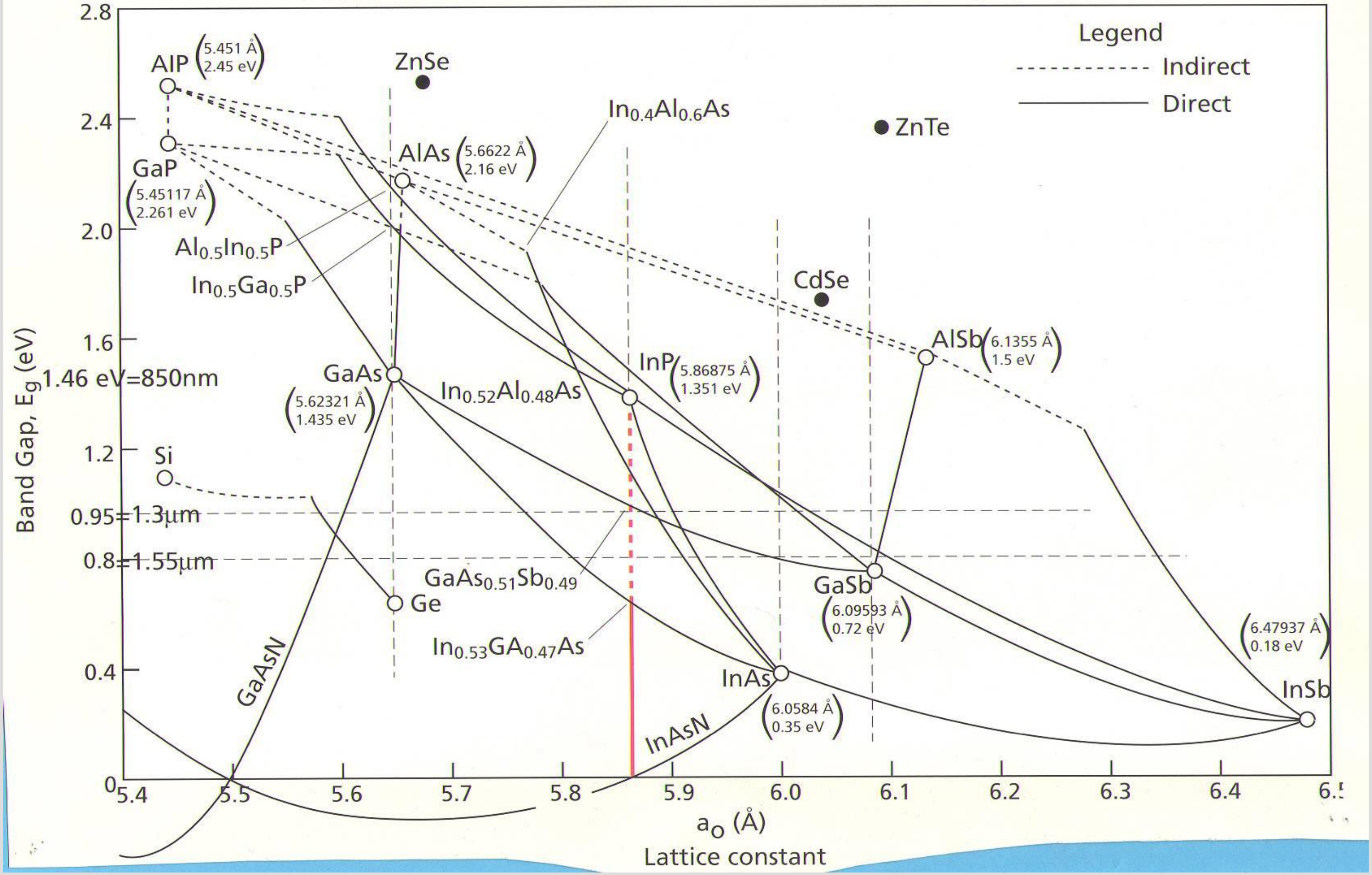
materiály doby přednitridové



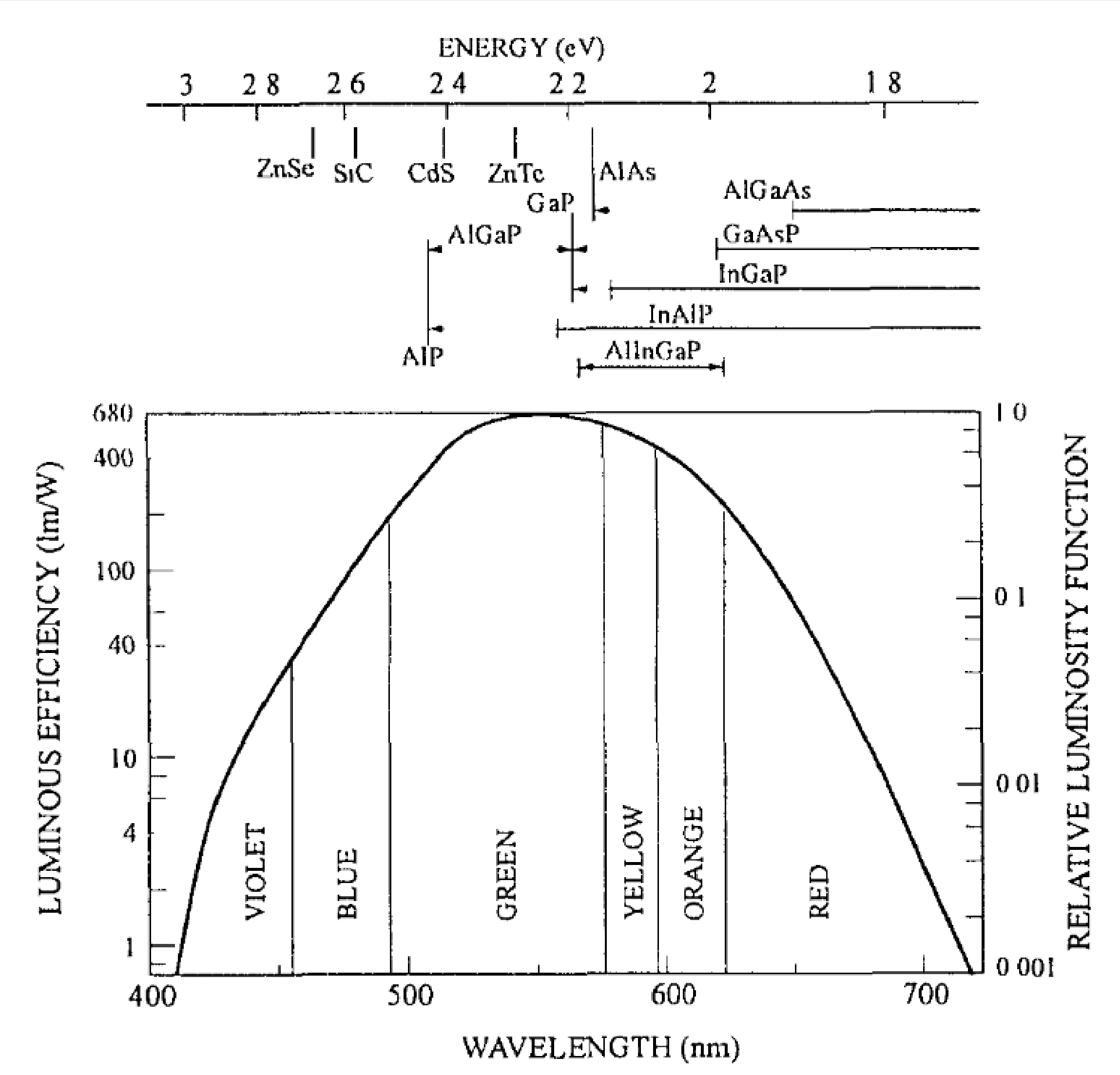
přídavek GaAsN a InAsN

Lattice Constant (Å) at 300k

Variation of bandgap/wavelength and lattice constant with composition. Points represent binaries; lines ternaries; areas between lines quarternaries. InGaAsP can reach the 1.3µm and 1.55 µm fibre transmission wavelengths lattice matched on InP but not on GaAs (whereas InGaAsN on GaAs can); for GaN-based compounds, add In for blue/green or Al for UV.



materiály doby přednitridové
citlivost lidského oka

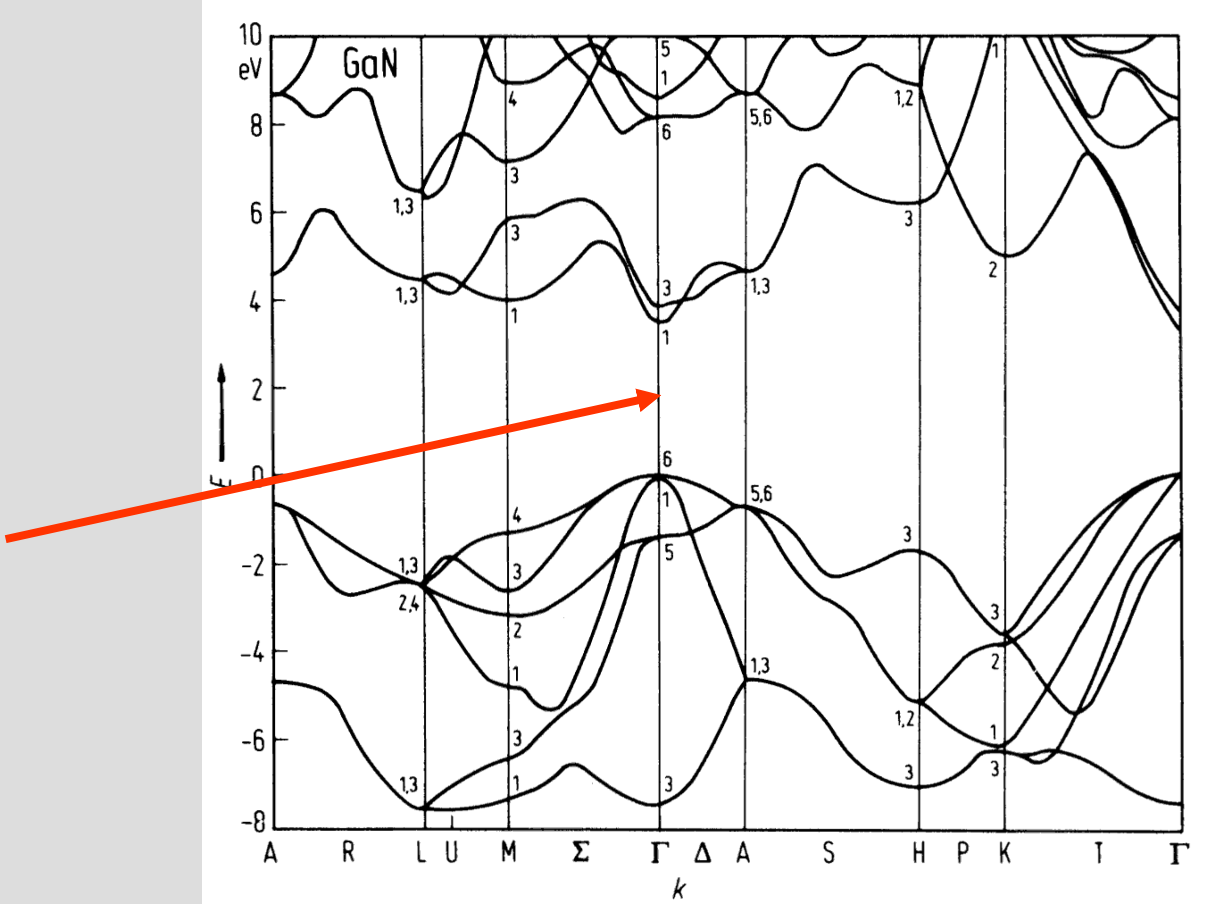


Hexagonální GaN

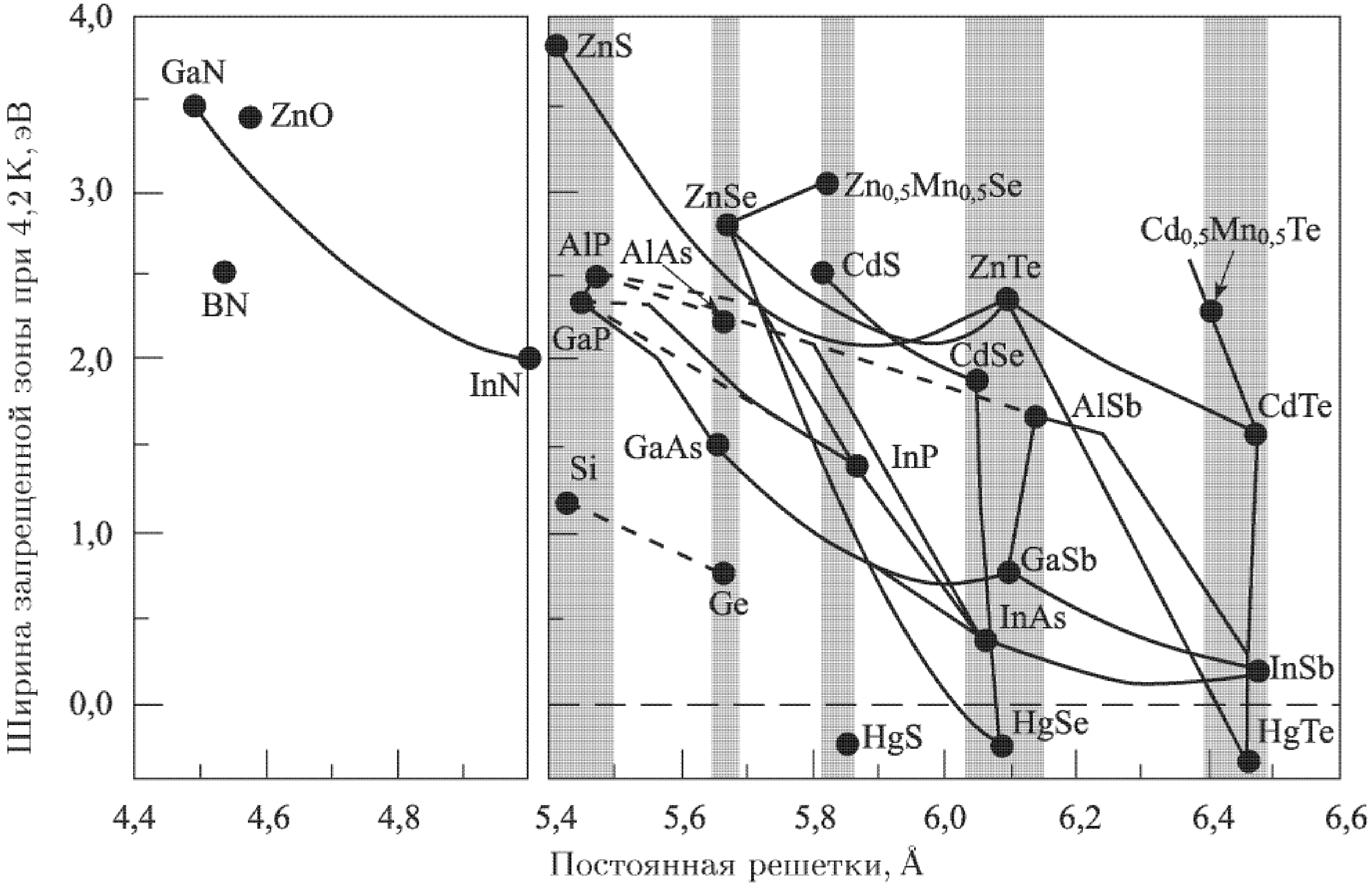
(GaN)

gap zhruba
3.4 eV

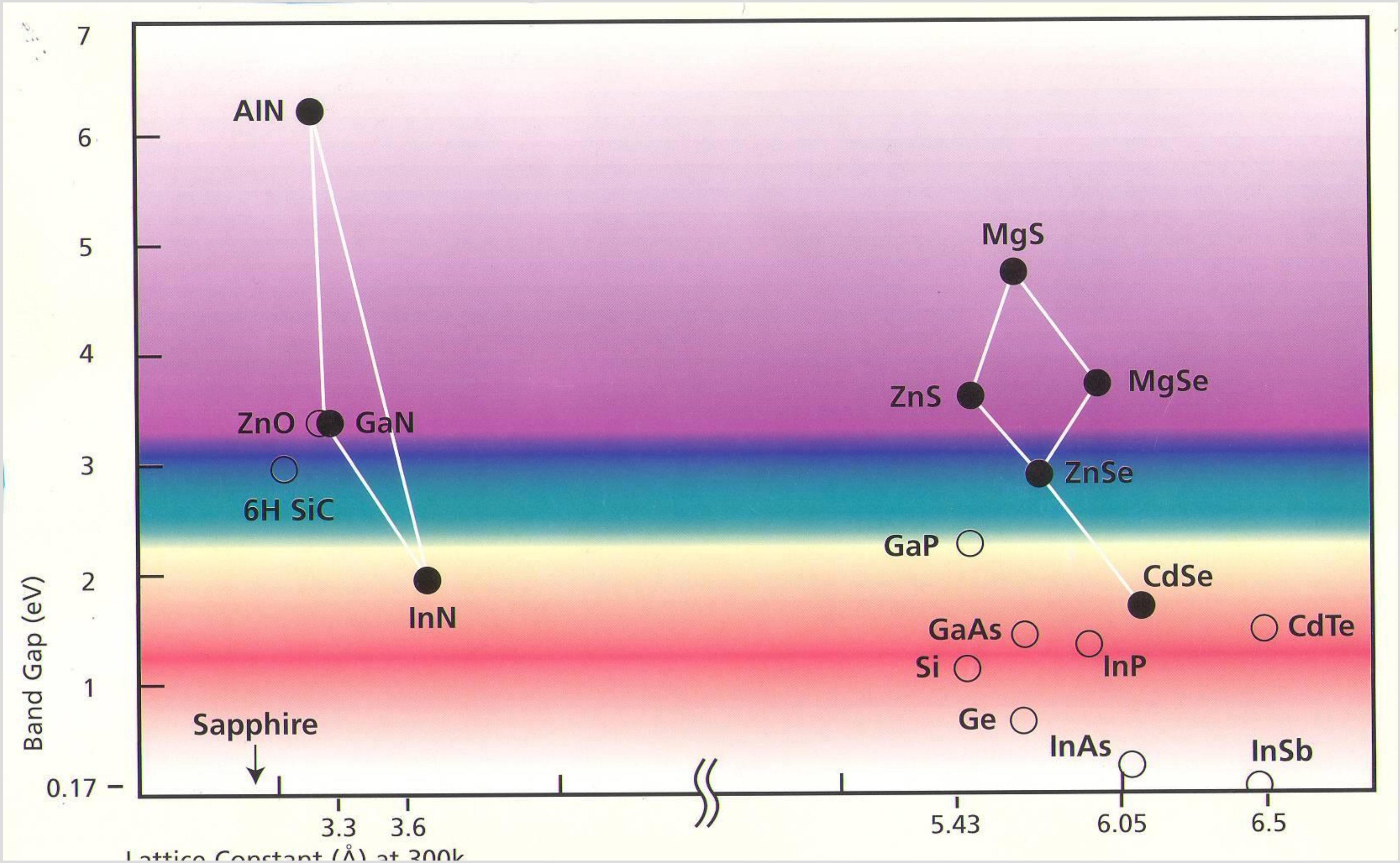
vlnová délka
365 nm



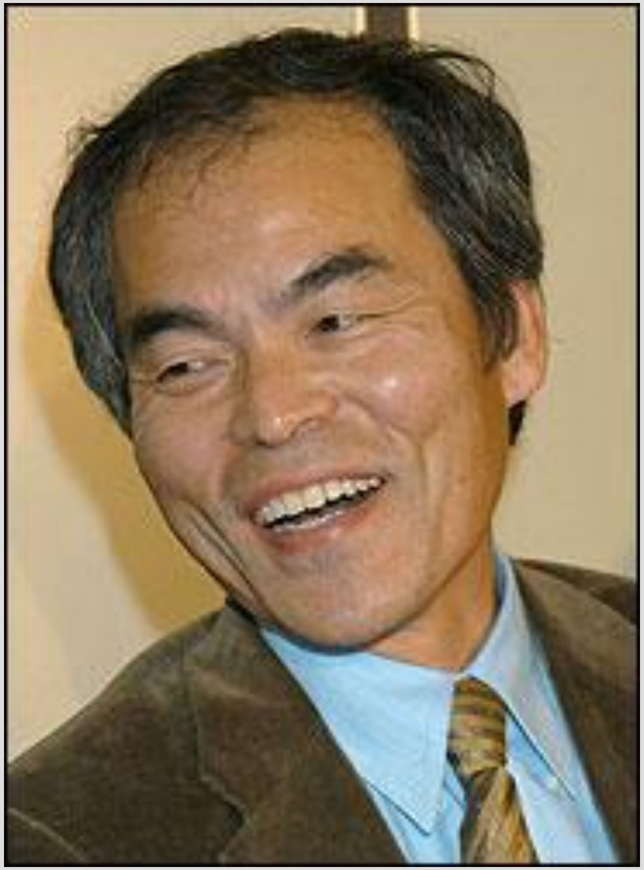
nitridy (+ZnO)


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

nitridy (+ SiC, ZnO)



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



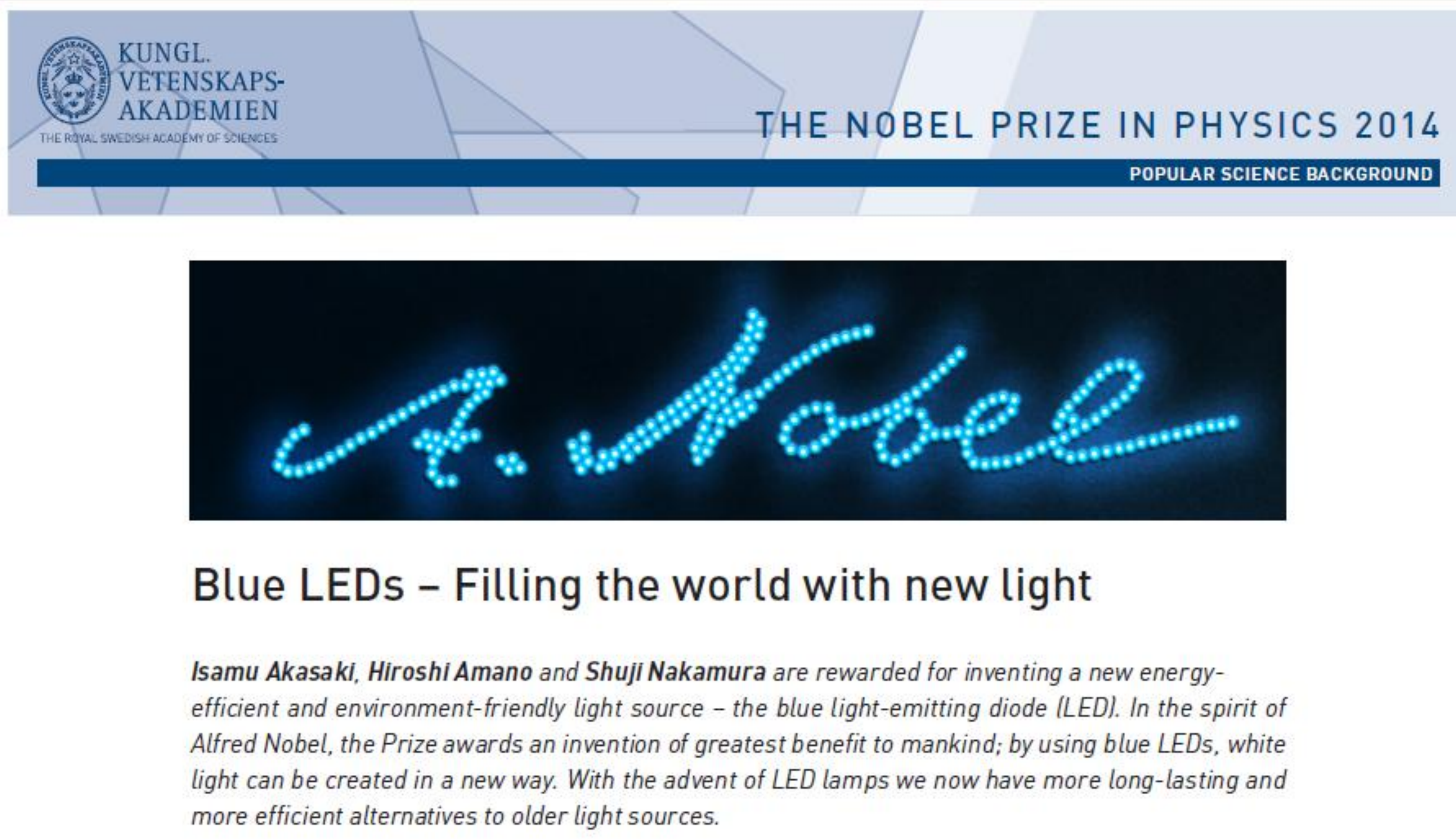
S. Nakamura

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



KUNGL.
VETENSKAPS-
AKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

THE NOBEL PRIZE IN PHYSICS 2014

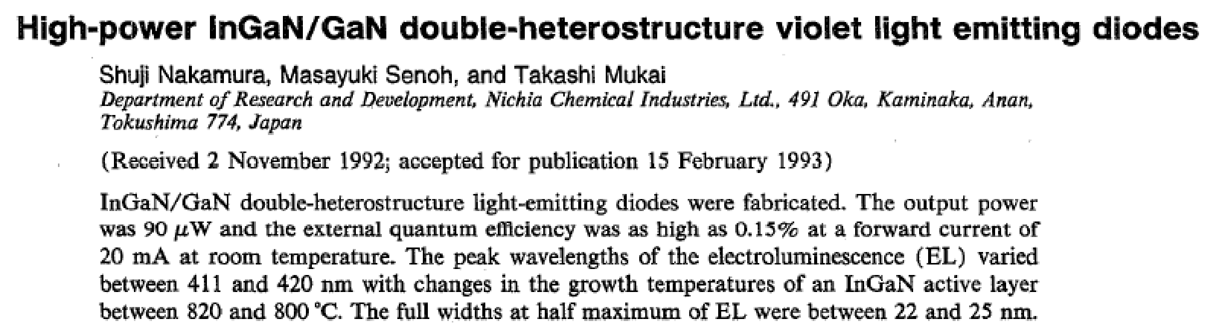
POPULAR SCIENCE BACKGROUND

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.*

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 © 1993 American Institute of Physics 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.

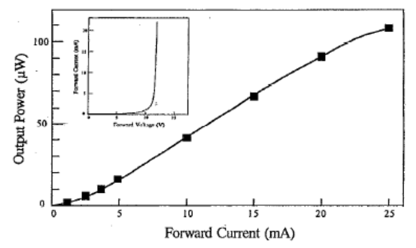
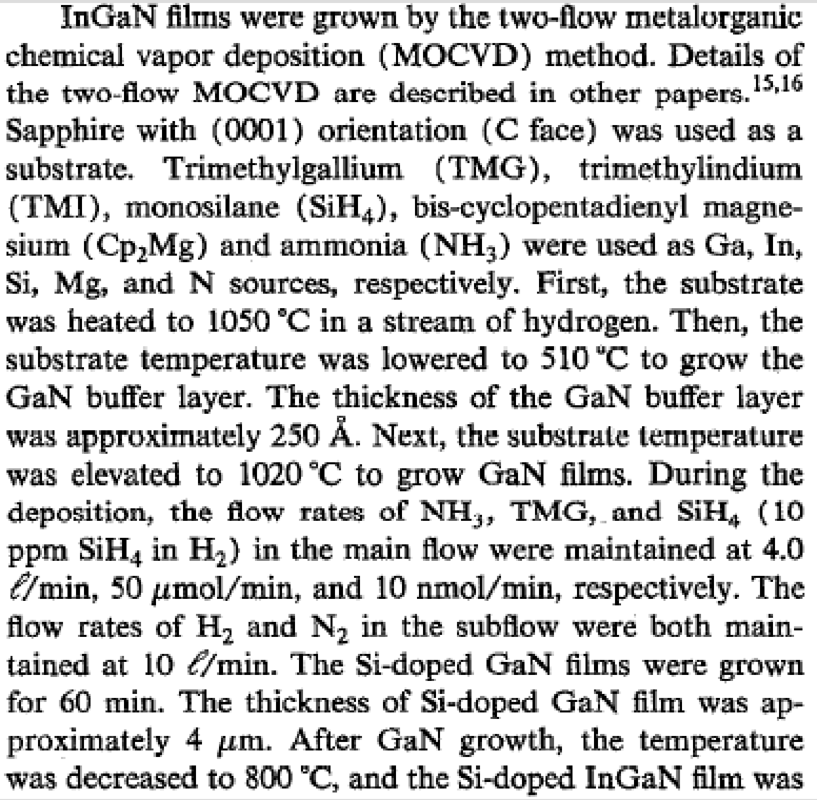
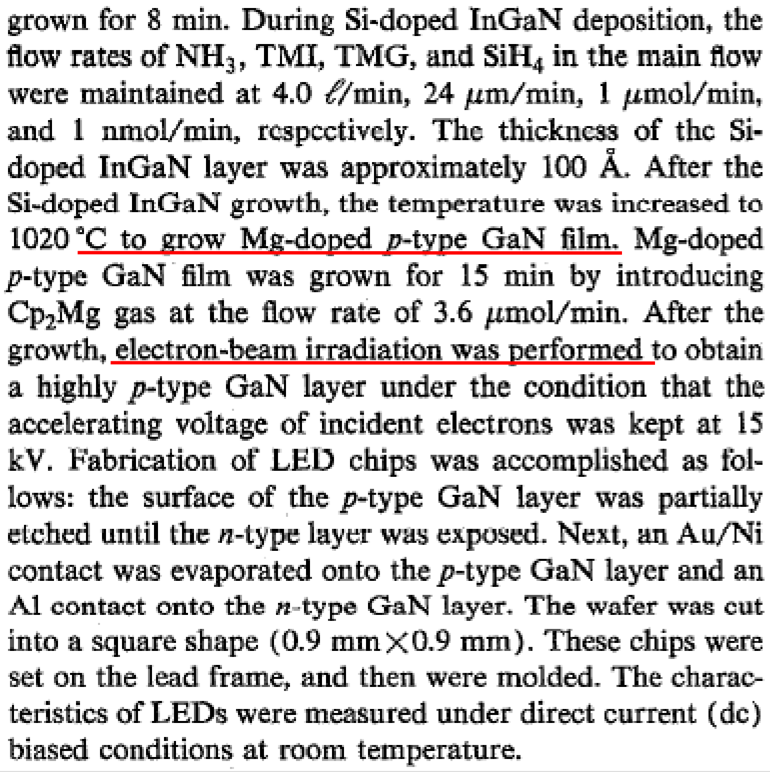


FIG. 3. The output power of the *p*-GaN/*n*-InGaN/*n*-GaN double-heterostructure blue LED as a function of the forward current. The inset shows the typical *I-V* characteristics of the *p*-GaN/*n*-InGaN/*n*-GaN double-heterostructure blue LED.





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.

New York Times:

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

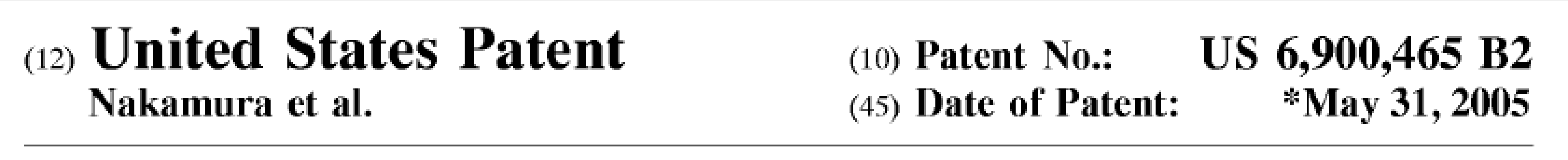
Published: January 12, 2005

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



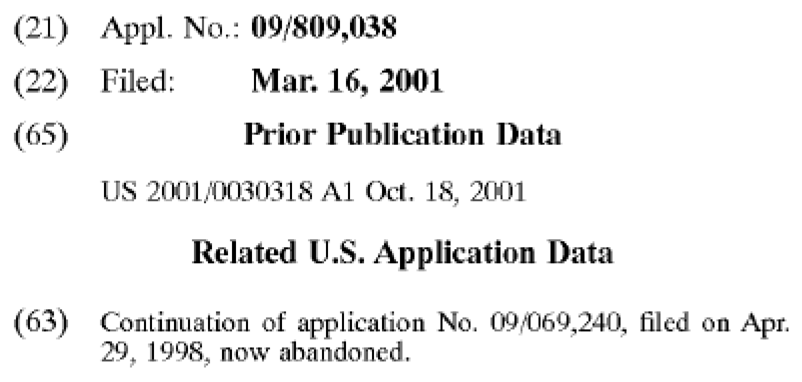
(12) **United States Patent**
Nakamura et al.

(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**

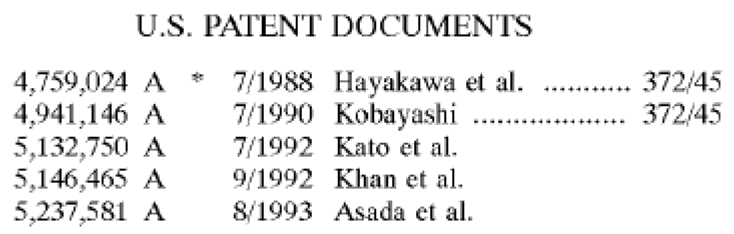
(22) Filed: **Mar. 16, 2001**

(65) **Prior Publication Data**

US 2001/0030318 A1 Oct. 18, 2001

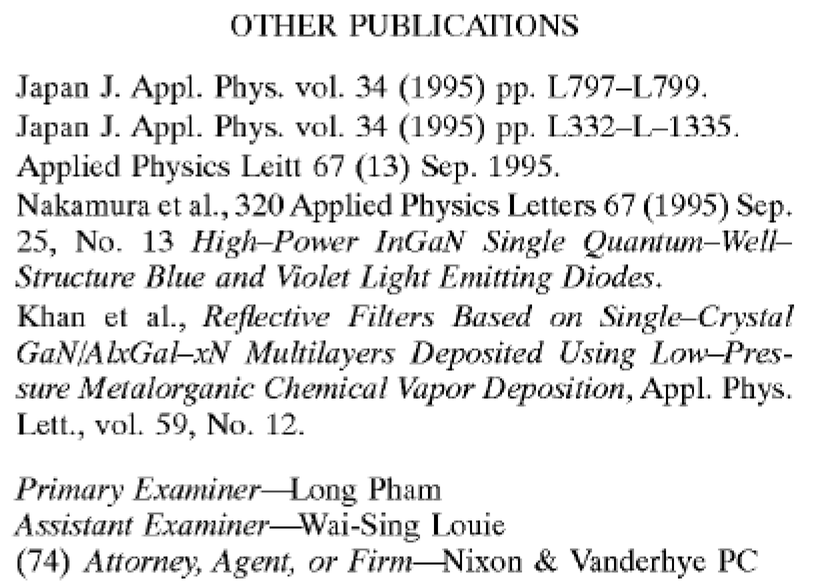
Related U.S. Application Data

(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.

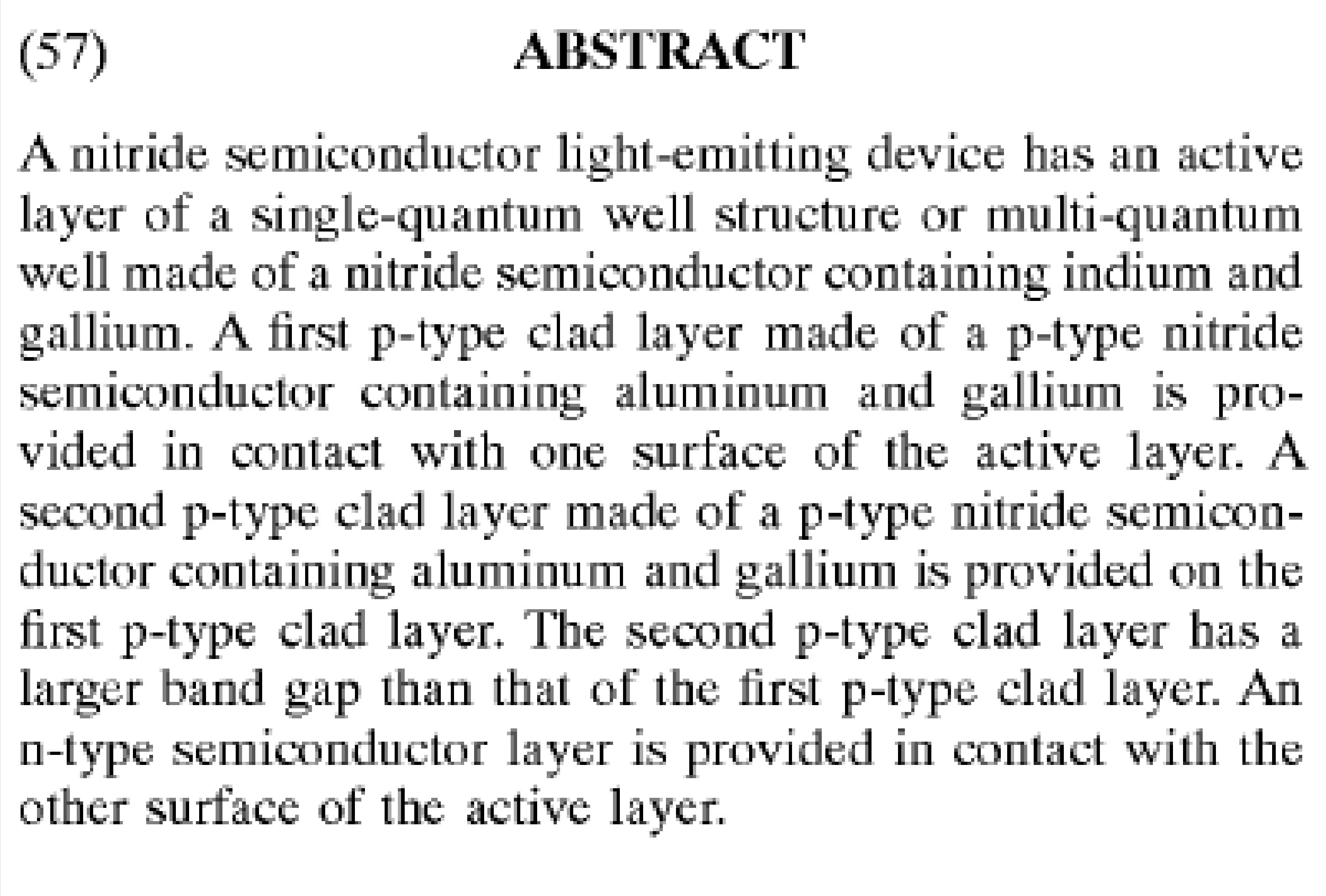
Applied Physics Leitt 67 (13) Sep. 1995.

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

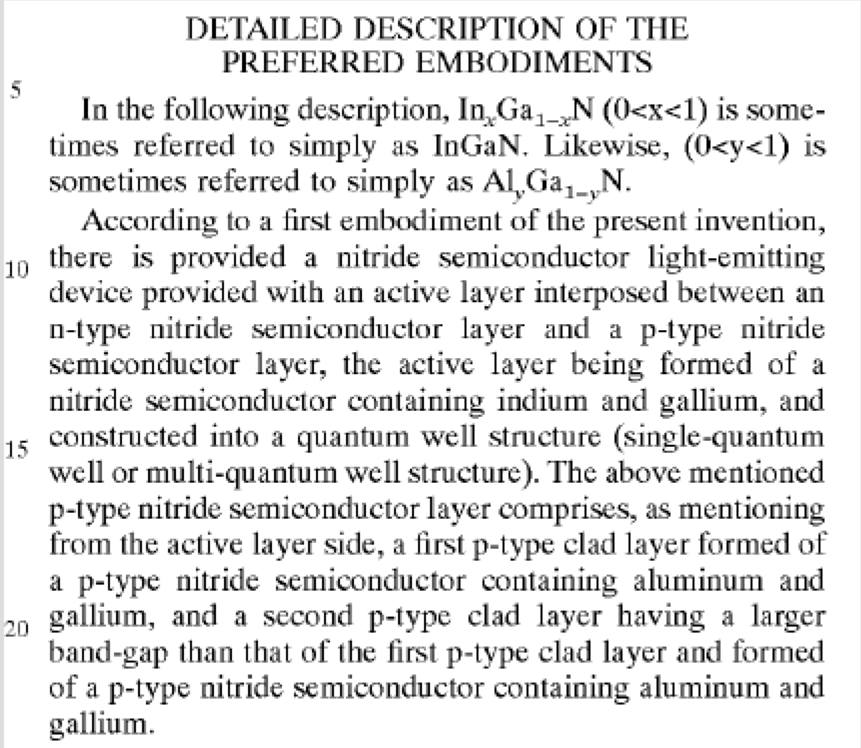
Komerční úspěch - patentová ochrana



(57) **ABSTRACT**

A nitride semiconductor light-emitting device has an active layer of a single-quantum well structure or multi-quantum well made of a nitride semiconductor containing indium and gallium. A first p-type clad layer made of a p-type nitride semiconductor containing aluminum and gallium is provided in contact with one surface of the active layer. A second p-type clad layer made of a p-type nitride semiconductor containing aluminum and gallium is provided on the first p-type clad layer. The second p-type clad layer has a larger band gap than that of the first p-type clad layer. An n-type semiconductor layer is provided in contact with the other surface of the active layer.

Komerční úspěch - patentová ochrana



DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the following description, $In_xGa_{1-x}N$ (0<x<1) is sometimes referred to simply as InGaN. Likewise, (0<y<1) is sometimes referred to simply as $Al_yGa_{1-y}N$.

According to a first embodiment of the present invention, there is provided a nitride semiconductor light-emitting device provided with an active layer interposed between an n-type nitride semiconductor layer and a p-type nitride semiconductor layer, the active layer being formed of a nitride semiconductor containing indium and gallium, and constructed into a quantum well structure (single-quantum well or multi-quantum well structure). The above mentioned p-type nitride semiconductor layer comprises, as mentioning from the active layer side, a first p-type clad layer formed of a p-type nitride semiconductor containing aluminum and gallium, and a second p-type clad layer having a larger band-gap than that of the first p-type clad layer and formed of a p-type nitride semiconductor containing aluminum and gallium.

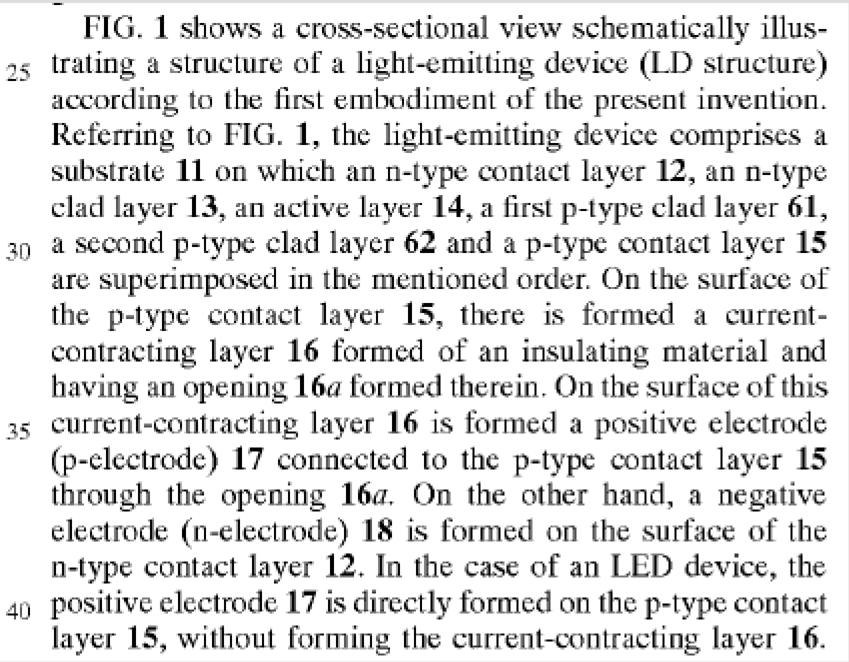
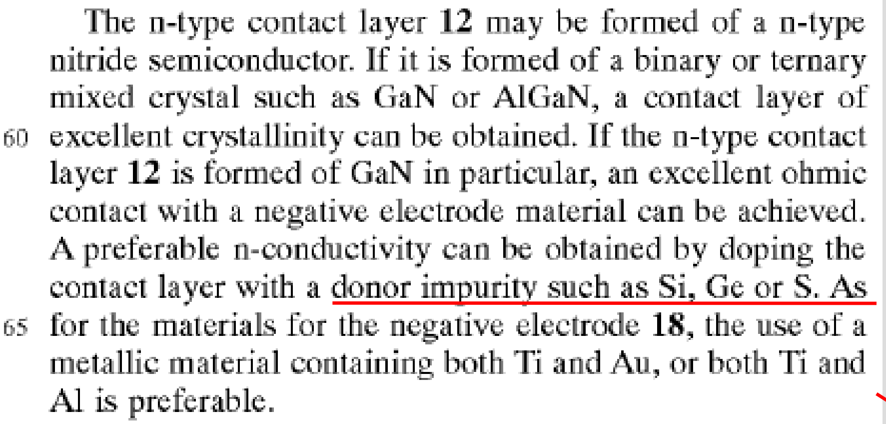
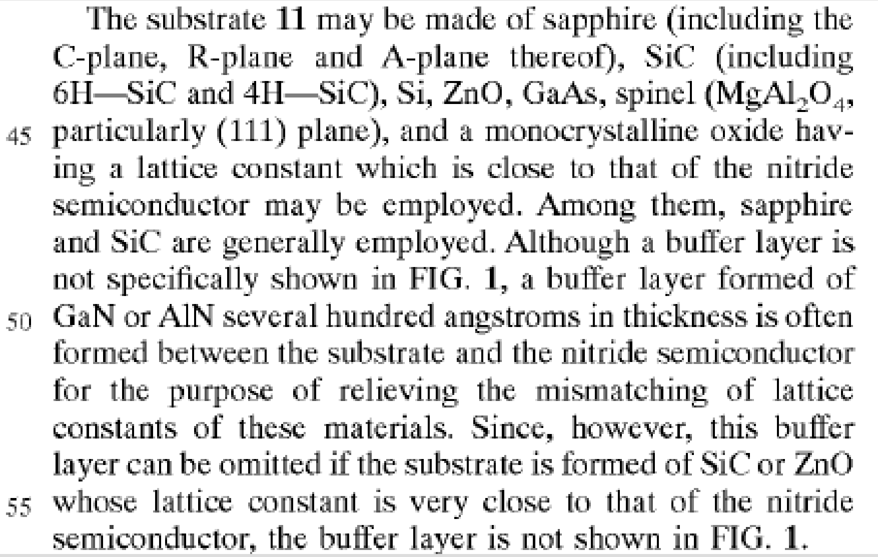


FIG. **1** shows a cross-sectional view schematically illustrating a structure of a light-emitting device (LD structure) according to the first embodiment of the present invention. Referring to FIG. **1**, the light-emitting device comprises a substrate **11** on which an n-type contact layer **12**, an n-type clad layer **13**, an active layer **14**, a first p-type clad layer **61**, a second p-type clad layer **62** and a p-type contact layer **15** are superimposed in the mentioned order. On the surface of the p-type contact layer **15**, there is formed a current-contracting layer **16** formed of an insulating material and having an opening **16***a* formed therein. On the surface of this current-contracting layer **16** is formed a positive electrode (p-electrode) **17** connected to the p-type contact layer **15** through the opening **16***a*. On the other hand, a negative electrode (n-electrode) **18** is formed on the surface of the n-type contact layer **12**. In the case of an LED device, the positive electrode **17** is directly formed on the p-type contact layer **15**, without forming the current-contracting layer **16**.

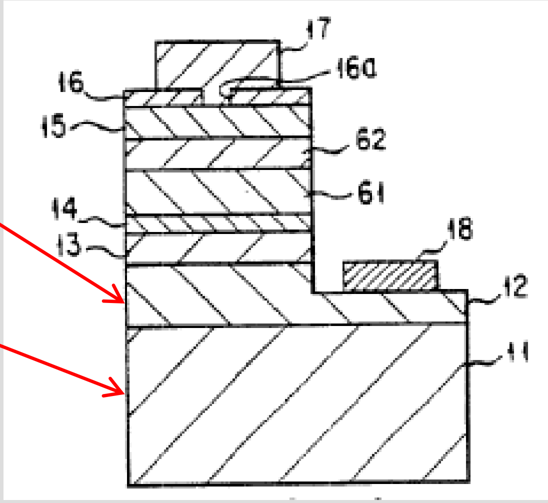
Komerční úspěch - patentová ochrana



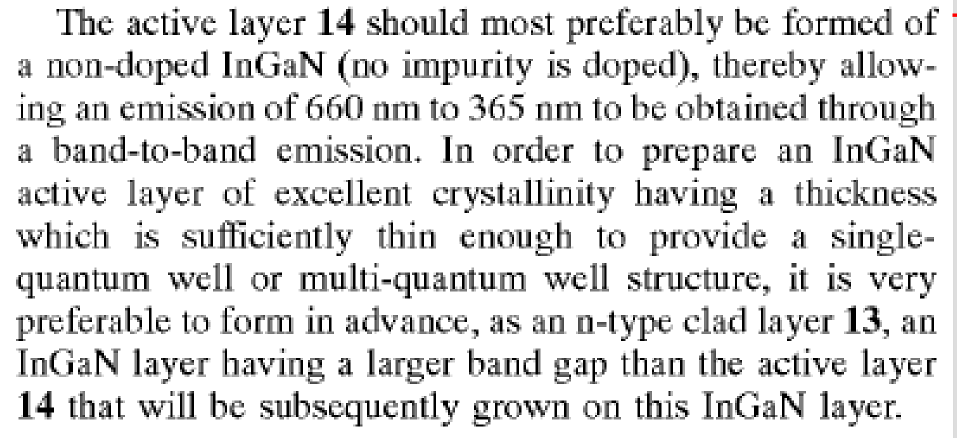
The n-type contact layer **12** may be formed of a n-type nitride semiconductor. If it is formed of a binary or ternary mixed crystal such as GaN or AlGaN, a contact layer of excellent crystallinity can be obtained. If the n-type contact layer **12** is formed of GaN in particular, an excellent ohmic contact with a negative electrode material can be achieved. A preferable n-conductivity can be obtained by doping the contact layer with a donor impurity such as Si, Ge or S. As for the materials for the negative electrode **18**, the use of a metallic material containing both Ti and Au, or both Ti and Al is preferable.



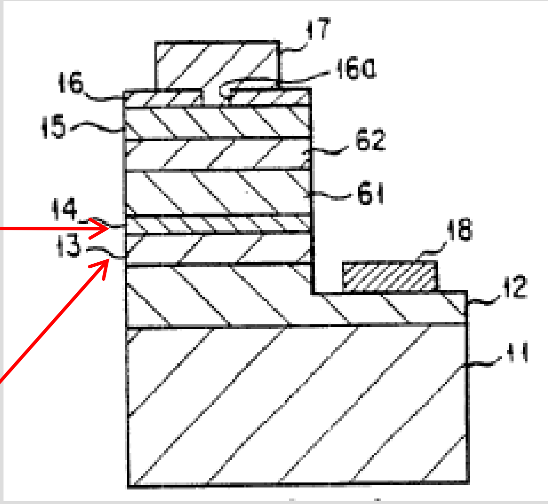
The substrate **11** may be made of sapphire (including the C-plane, R-plane and A-plane thereof), SiC (including 6H—SiC and 4H—SiC), Si, ZnO, GaAs, spinel ($MgAl_2O_4$, particularly (111) plane), and a monocrystalline oxide having a lattice constant which is close to that of the nitride semiconductor may be employed. Among them, sapphire and SiC are generally employed. Although a buffer layer is not specifically shown in FIG. **1**, a buffer layer formed of GaN or AlN several hundred angstroms in thickness is often formed between the substrate and the nitride semiconductor for the purpose of relieving the mismatching of lattice constants of these materials. Since, however, this buffer layer can be omitted if the substrate is formed of SiC or ZnO whose lattice constant is very close to that of the nitride semiconductor, the buffer layer is not shown in FIG. **1**.



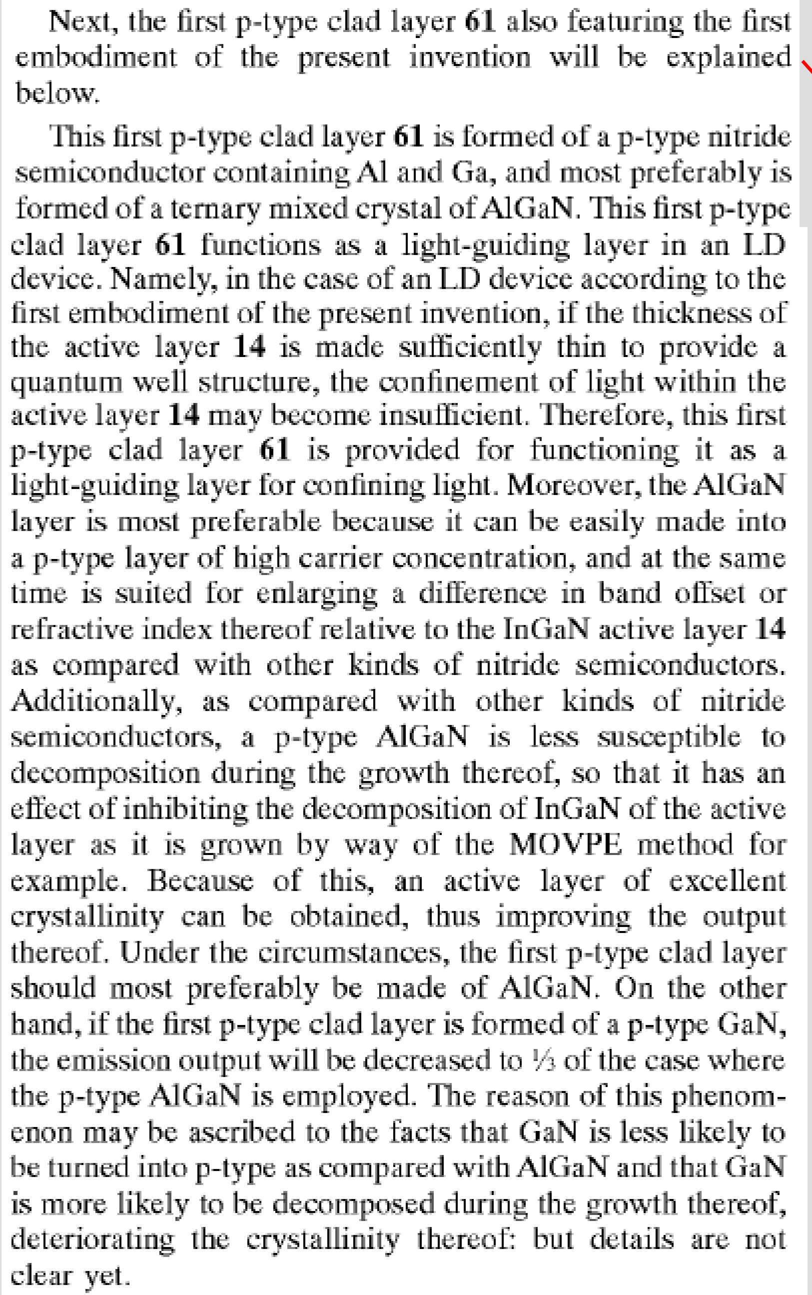
Komerční úspěch - patentová ochrana



The active layer **14** should most preferably be formed of a non-doped InGaN (no impurity is doped), thereby allowing an emission of 660 nm to 365 nm to be obtained through a band-to-band emission. In order to prepare an InGaN active layer of excellent crystallinity having a thickness which is sufficiently thin enough to provide a single-quantum well or multi-quantum well structure, it is very preferable to form in advance, as an n-type clad layer **13**, an InGaN layer having a larger band gap than the active layer **14** that will be subsequently grown on this InGaN layer.

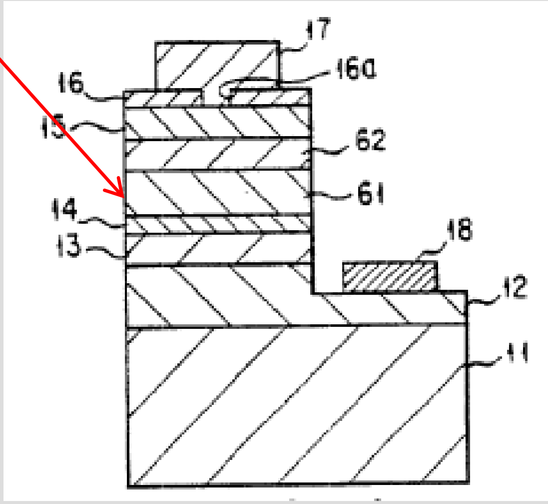


Komerční úspěch - patentová ochrana

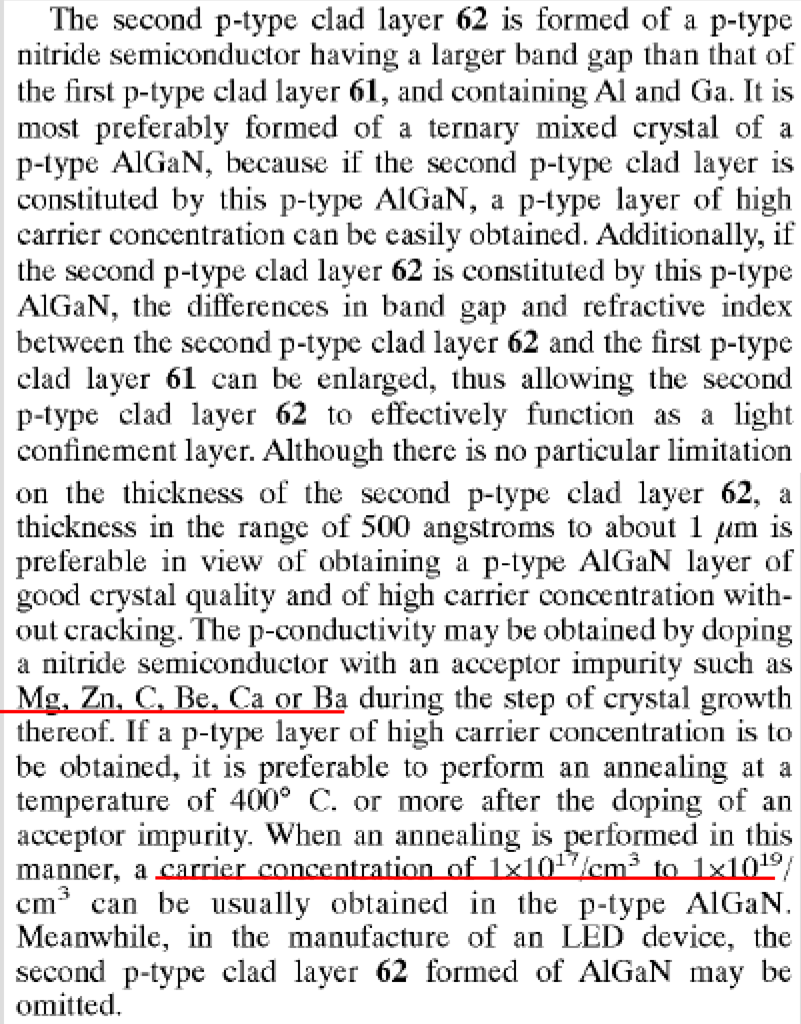


Next, the first p-type clad layer **61** also featuring the first embodiment of the present invention will be explained below.

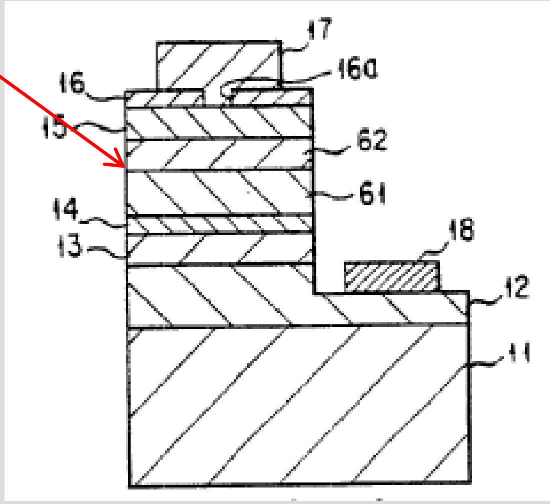
This first p-type clad layer **61** is formed of a p-type nitride semiconductor containing Al and Ga, and most preferably is formed of a ternary mixed crystal of AlGaN. This first p-type clad layer **61** functions as a light-guiding layer in an LD device. Namely, in the case of an LD device according to the first embodiment of the present invention, if the thickness of the active layer **14** is made sufficiently thin to provide a quantum well structure, the confinement of light within the active layer **14** may become insufficient. Therefore, this first p-type clad layer **61** is provided for functioning it as a light-guiding layer for confining light. Moreover, the AlGaN layer is most preferable because it can be easily made into a p-type layer of high carrier concentration, and at the same time is suited for enlarging a difference in band offset or refractive index thereof relative to the InGaN active layer **14** as compared with other kinds of nitride semiconductors. Additionally, as compared with other kinds of nitride semiconductors, a p-type AlGaN is less susceptible to decomposition during the growth thereof, so that it has an effect of inhibiting the decomposition of InGaN of the active layer as it is grown by way of the MOVPE method for example. Because of this, an active layer of excellent crystallinity can be obtained, thus improving the output thereof. Under the circumstances, the first p-type clad layer should most preferably be made of AlGaN. On the other hand, if the first p-type clad layer is formed of a p-type GaN, the emission output will be decreased to ⅓ of the case where the p-type AlGaN is employed. The reason of this phenomenon may be ascribed to the facts that GaN is less likely to be turned into p-type as compared with AlGaN and that GaN is more likely to be decomposed during the growth thereof, deteriorating the crystallinity thereof: but details are not clear yet.



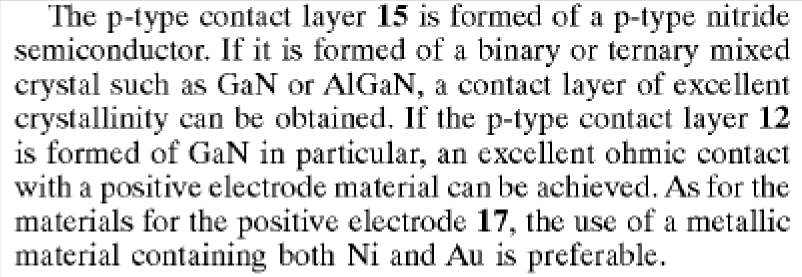
Komerční úspěch - patentová ochrana



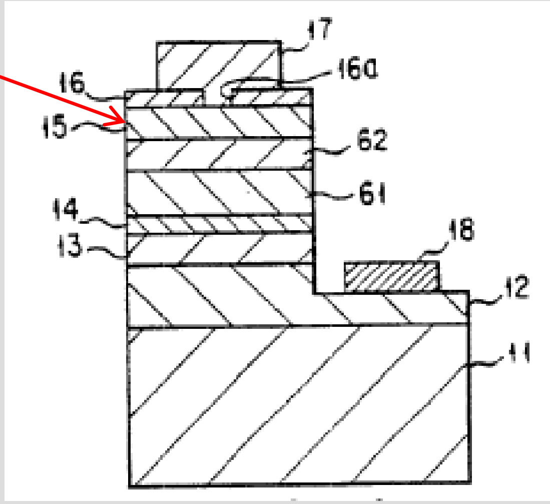
The second p-type clad layer **62** is formed of a p-type nitride semiconductor having a larger band gap than that of the first p-type clad layer **61**, and containing Al and Ga. It is most preferably formed of a ternary mixed crystal of a p-type AlGaN, because if the second p-type clad layer is constituted by this p-type AlGaN, a p-type layer of high carrier concentration can be easily obtained. Additionally, if the second p-type clad layer **62** is constituted by this p-type AlGaN, the differences in band gap and refractive index between the second p-type clad layer **62** and the first p-type clad layer **61** can be enlarged, thus allowing the second p-type clad layer **62** to effectively function as a light confinement layer. Although there is no particular limitation on the thickness of the second p-type clad layer **62**, a thickness in the range of 500 angstroms to about 1 μm is preferable in view of obtaining a p-type AlGaN layer of good crystal quality and of high carrier concentration without cracking. The p-conductivity may be obtained by doping a nitride semiconductor with an acceptor impurity such as Mg, Zn, C, Be, Ca or Ba during the step of crystal growth thereof. If a p-type layer of high carrier concentration is to be obtained, it is preferable to perform an annealing at a temperature of 400° C. or more after the doping of an acceptor impurity. When an annealing is performed in this manner, a carrier concentration of $1\times10^{17}/cm^3$ to $1\times10^{19}/cm^3$ can be usually obtained in the p-type AlGaN. Meanwhile, in the manufacture of an LED device, the second p-type clad layer **62** formed of AlGaN may be omitted.

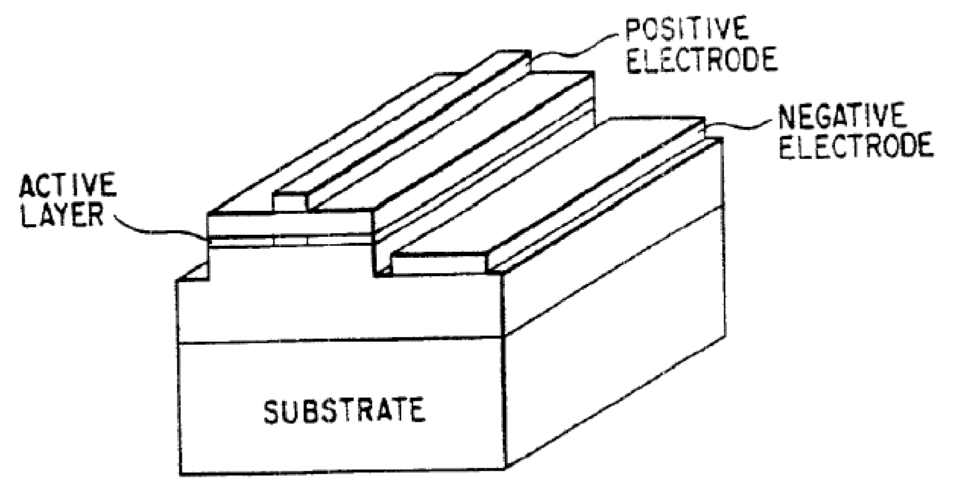


Komerční úspěch - patentová ochrana



The p-type contact layer **15** is formed of a p-type nitride semiconductor. If it is formed of a binary or ternary mixed crystal such as GaN or AlGaN, a contact layer of excellent crystallinity can be obtained. If the p-type contact layer **12** is formed of GaN in particular, an excellent ohmic contact with a positive electrode material can be achieved. As for the materials for the positive electrode **17**, the use of a metallic material containing both Ni and Au is preferable.





Komerční úspěch - patentová ochrana

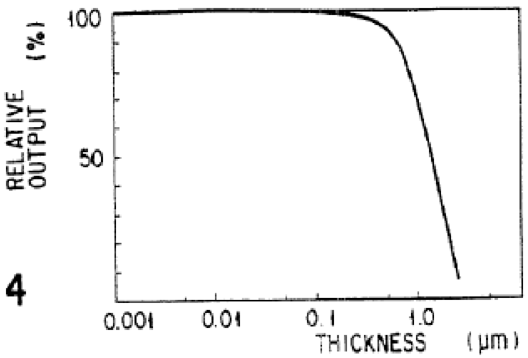


FIG. 4

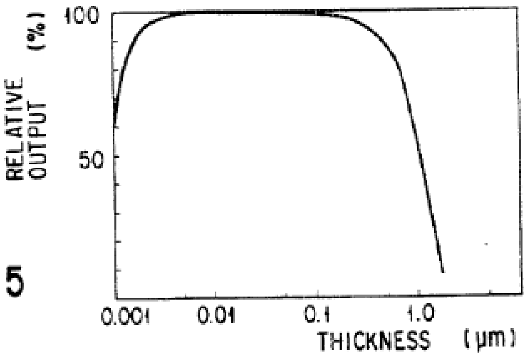


FIG. 5

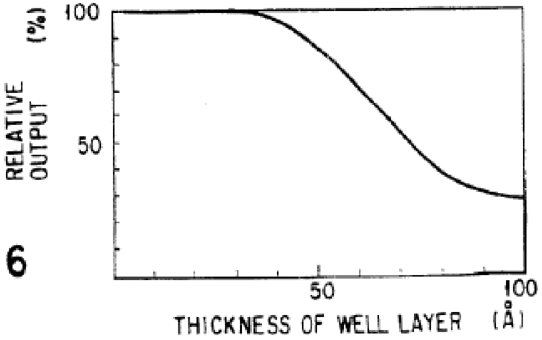


FIG. 6

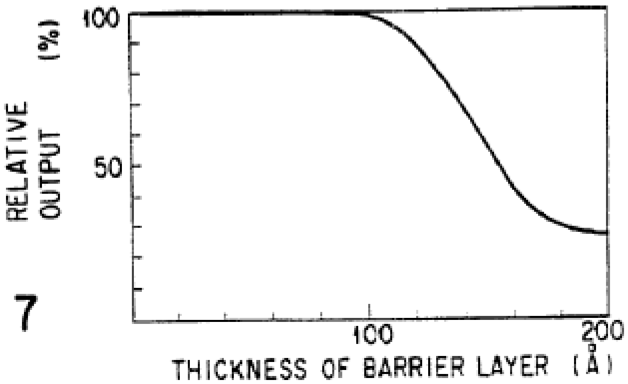


FIG. 7

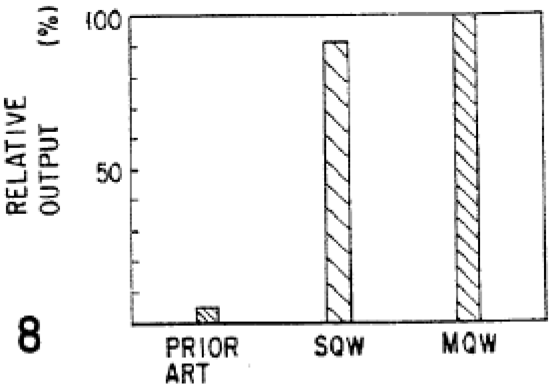
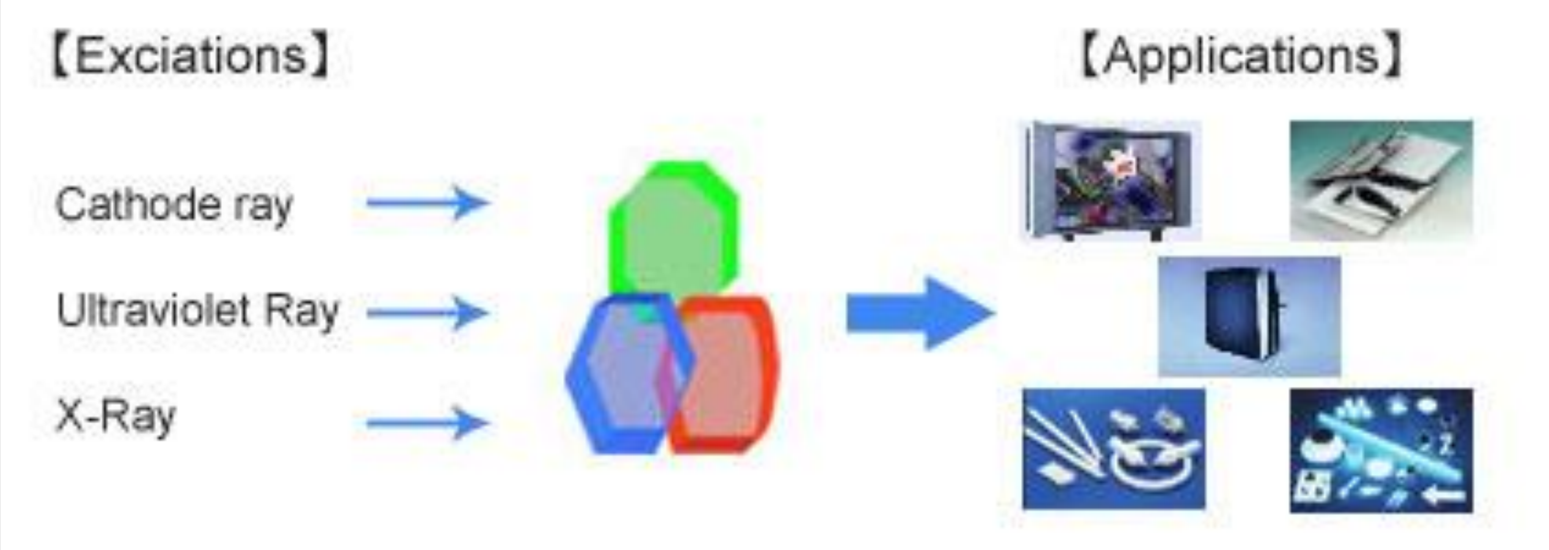


FIG. 8

UV + luminifor → bílé světlo

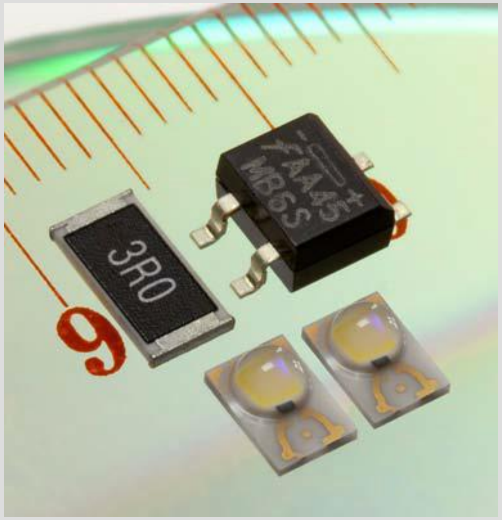
Luminifory („phosphors“) Nichia



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



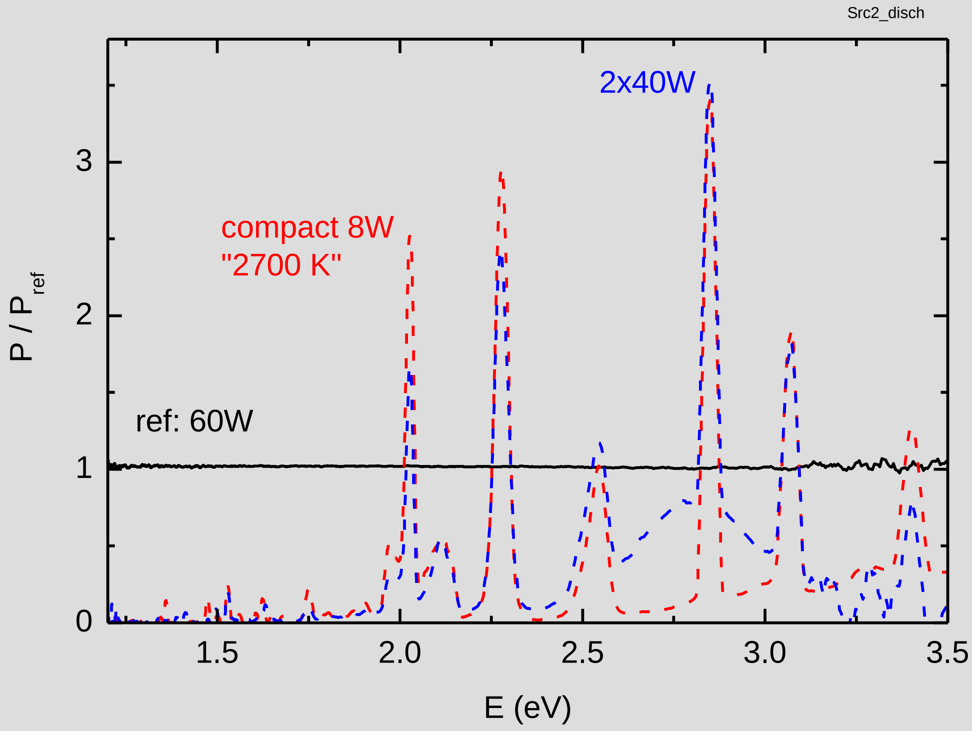
Nichia
Cree
OSRAM Opto
Philips Lumileds
Seoul Semiconductor
Toyoda Gosei

Srovnání účinnosti generace viditelného světla

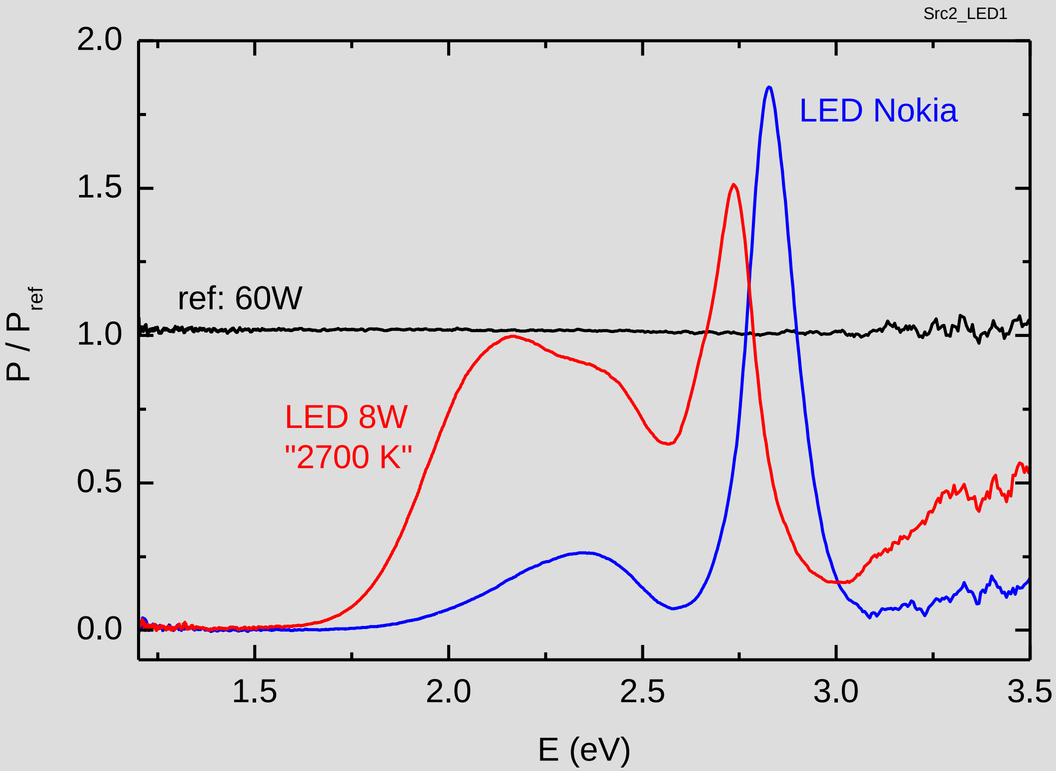
žárovka	5% max. (2% typ.)	15 lm / W (< 35)
zářivka	15%	
čip LED	40%	120 lm / W (< 240)
lampa LED	25%	

žárovka 100 W, 5 Kč/kWh ... spotřebuje 1000 Kč za
2000 h
83 dny nepřetržitě
500 dnů při 4 h/den

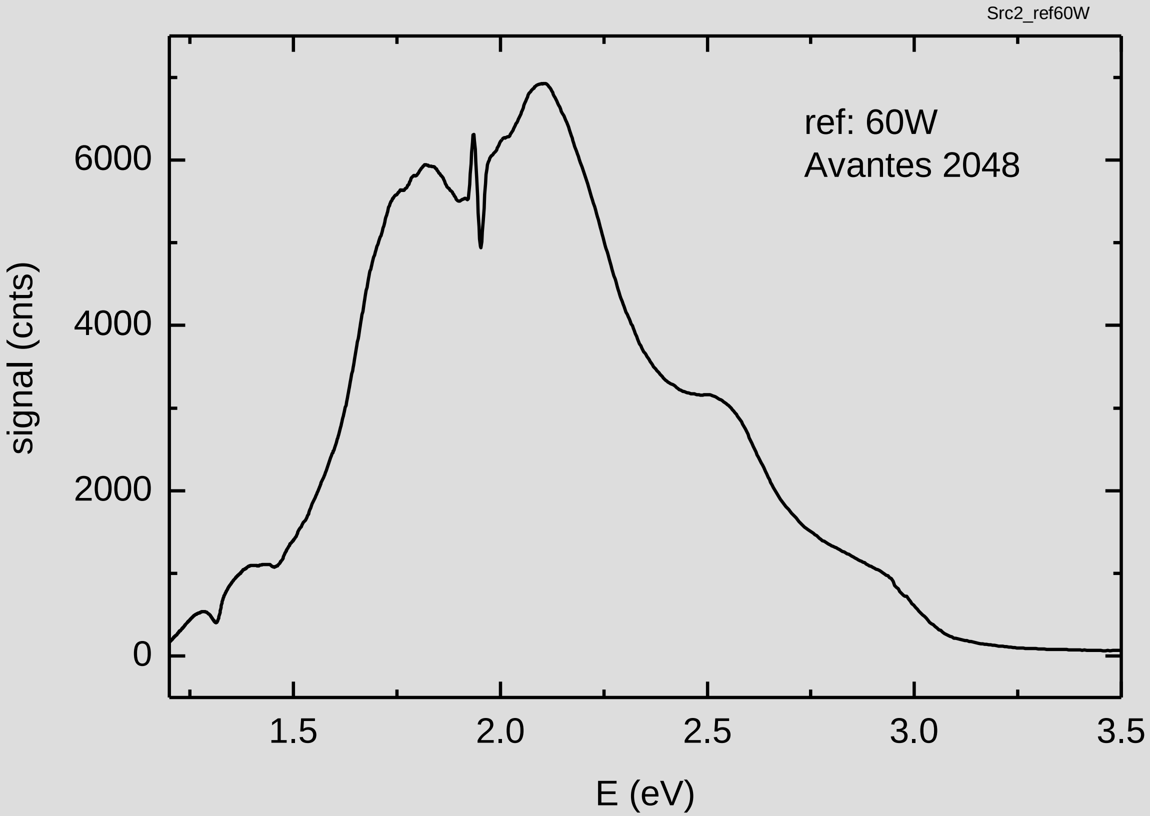
Spektrální charakteristiky „bílého“ světla : zářivky



Spektrální charakteristiky „bílého“ světla : LED



Signál referenčního zdroje, mnohakanálový spektrometr s Si detektorem



Závěr

Nitridové heterostruktury (AlGaIn)N

už vstoupily do

světlých zítřků

(na řadě jsou s dosti velkou pravděpodobností aplikace ve výkonové elektronice)