The production of light by matter - from light bulbs to monolithic blue LEDs

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Context

The Nobel Prize in Physics 2014


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Å « for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources».

Outline

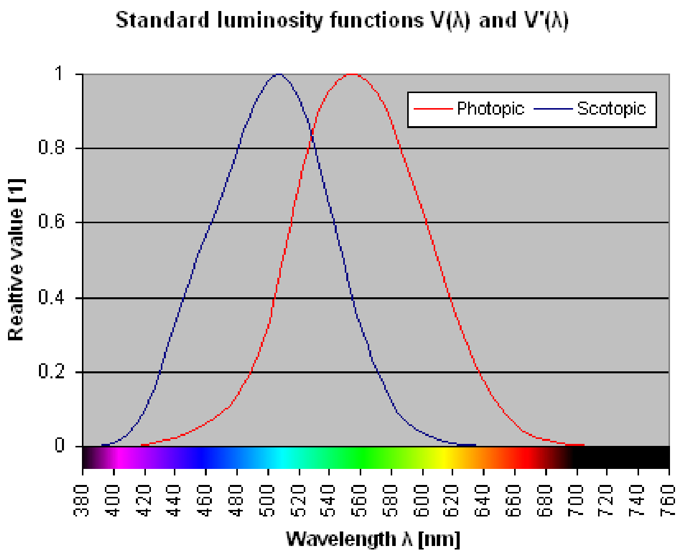
- Short review of white light sources
- Breaking down the light emitting diode
    - *Electronic states in bulk semiconductors*
    - *Light-matter interaction*
    - *PN-junction and electroluminescence*
    - *Characterizing and improving light emitters*
- Gallium nitride and the blue emitting diode
    - *Nitride growth*
    - *Control of doping*
    - *The blue diode*
    - *Nanostructures and perspective*

Comparing white light emitters

- **Luminous flux:** measure of the perceived power of light.

Luminous flux (Lm) = radiant flux (W) × luminosity function

- Luminosity function: spectral sensitivity of human visual perception of brightness.
- In daylight, the maximum sensitivity is at 555 nm (in the green region). This type of vision is called (*photopic vision*).
- In low light conditions, maximum sensitivity is at 507 nm (in the blue-green region) and red light is almost invisible (*scotopic vision*).



Comparing white light emitters

- **Luminous flux:** measure of the perceived power of light.

Luminous flux (Lm) = radiant flux (W) × luminosity function

- **Luminous efficacy:** ratio of flux to power consumption.

$$\text{Efficacy} = \frac{\text{Flux(Lm)}}{\text{Power (W)}}$$

- **Color rendering index (CRI) :** characterize the quality of the white light produced by a source. A value of 100 corresponds to the natural day light.

Incandescence light bulbs

- Invented by Joseph W. Swan in 1879, improved by Thomas Edison.
- **Principle:**
  - A tungsten filament is heated to a high temperature by an electric current passing through it until it glows.
  - The emitted light displays a "black body" spectrum: its shape is given by the Planck's law and depends only on temperature.

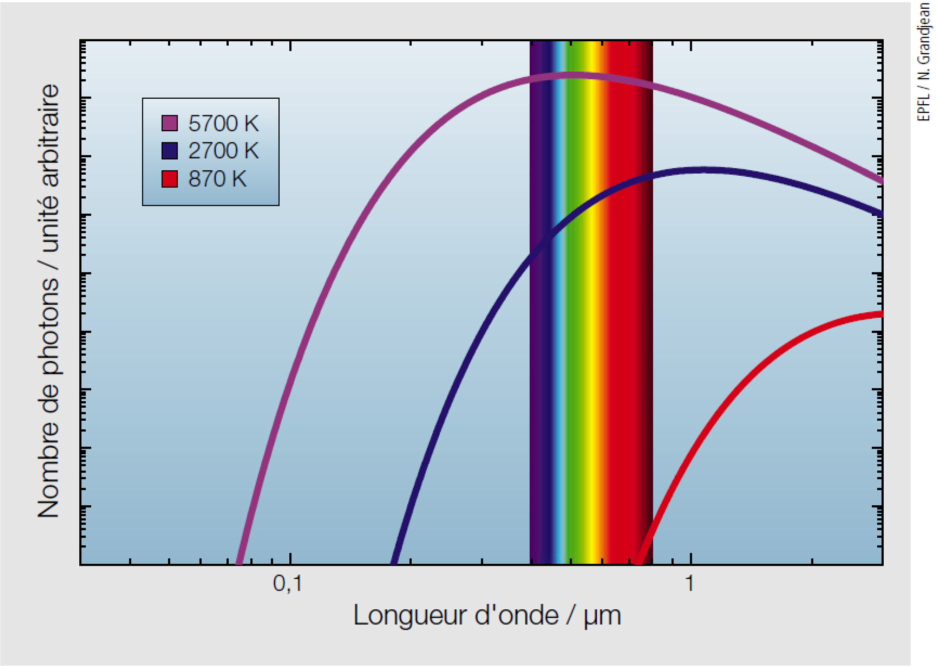
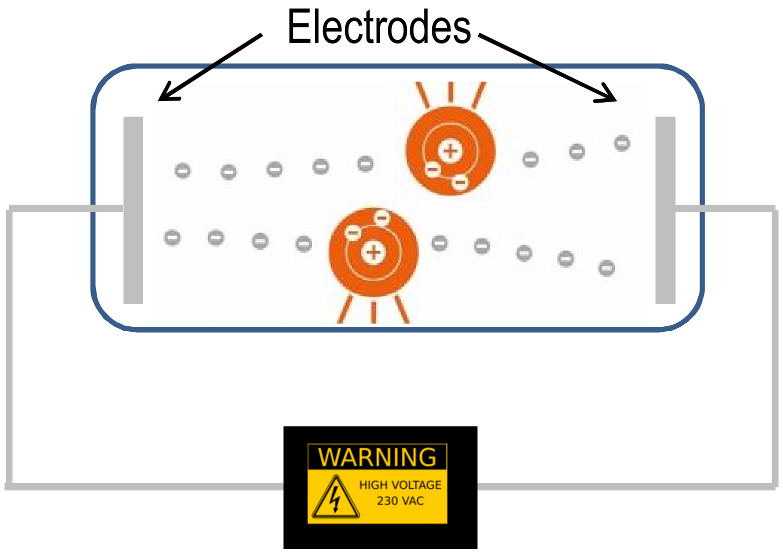


Figure 1 Spectre d'émission du corps noir pour différentes températures : soleil (5700 K), lampe à incandescence (2700 K) et 600 °C (870 K), ce qui correspond au début de l'émission dans le visible.

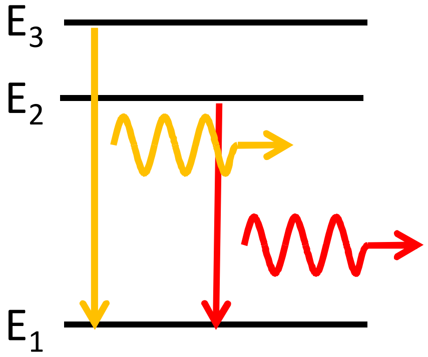
Efficacy (lm/W)	15
CRI	100
Lifetime(h)	1000

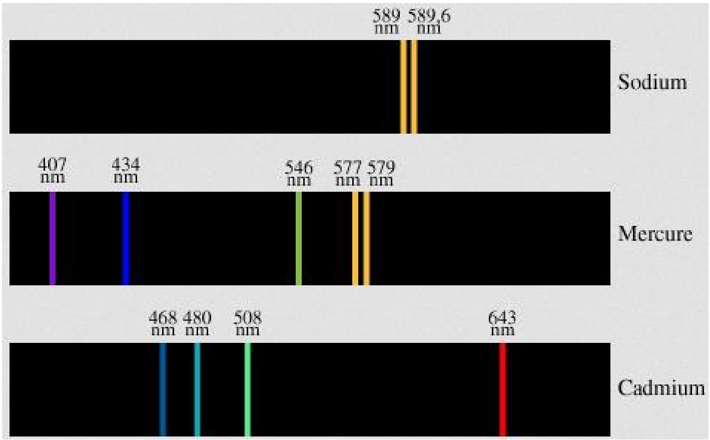
Gas-discharge lamps



- **Principle:**
  - A gas of atoms in a sealed tube is excited by an electric discharge.
  - In the plasma, mobile electrons collide with atoms, transfer energy to the atoms and elevate them to an excited state.
  - Atoms relax towards their ground state by emitting light.

Gas-discharge lamps





- **Principle:**
  - Electronic levels in atoms are discrete.
  - The emission spectrum displays series of line the wavelengths of which satisfy the equation:

$$\boxed{E_i - E_f = \frac{hc}{\lambda}}$$

⇨ *The emission spectrum is characteristic of the element.*

Gas-discharge lamps

- **Example:** High pressure sodium lamp, motorway lighting.

www.marjoy.com

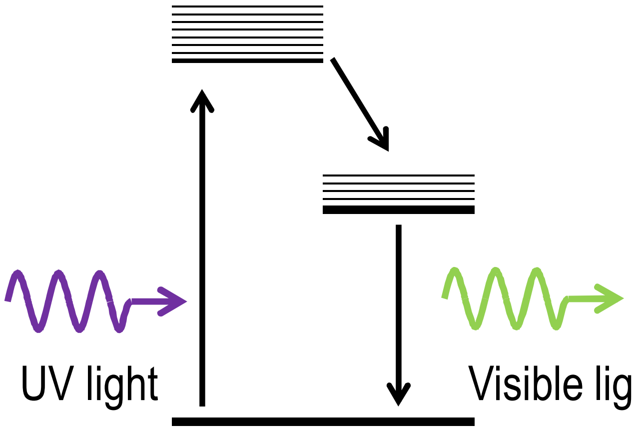
Efficacy (lm/W)	90-140
CRI	25
Lifetime(h)	25000

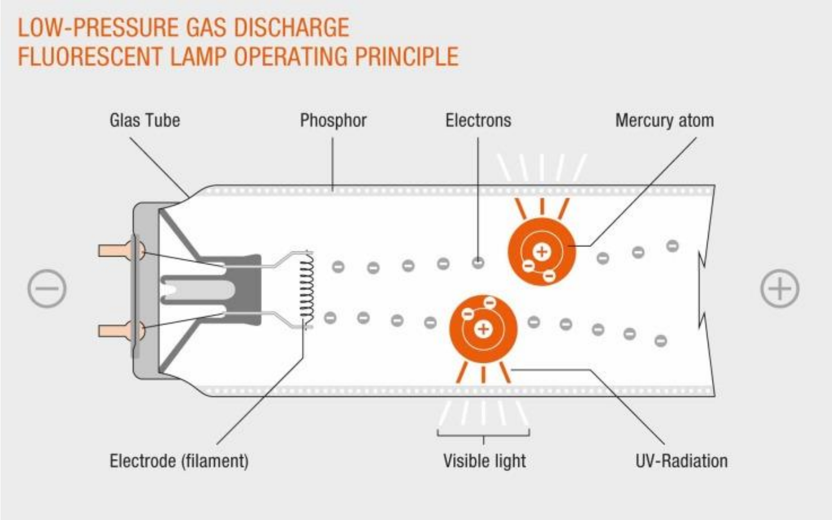
Compact fluorescent tubes

- **Principle:**

  A gas discharge mercury lamp radiates ultraviolet light. The emitted ultraviolet light is converted into visible light as it strikes the phosphorescent coating on the bulb.

Optical pumping of phosphorescent coating



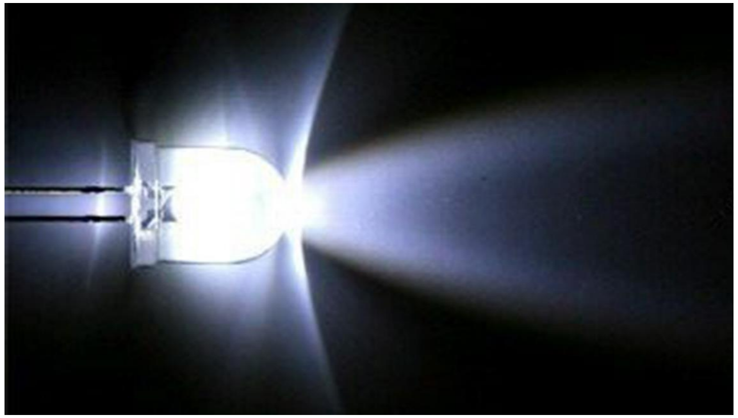


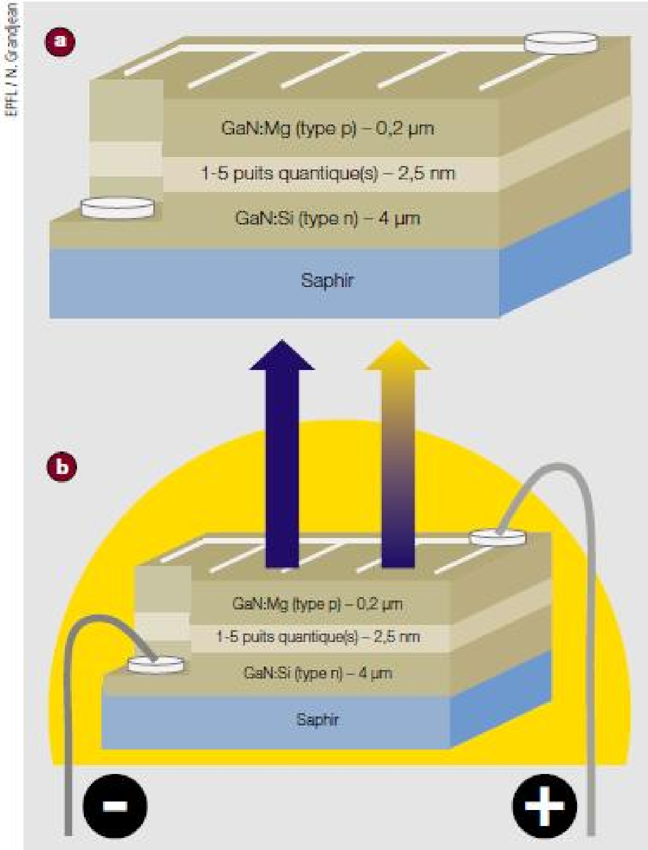
http://www.osram.com

Efficacy (Lm/W)	100 (tubes), 40-60 (bulbs)
CRI	Up to 85
Lifetime (h)	~10000

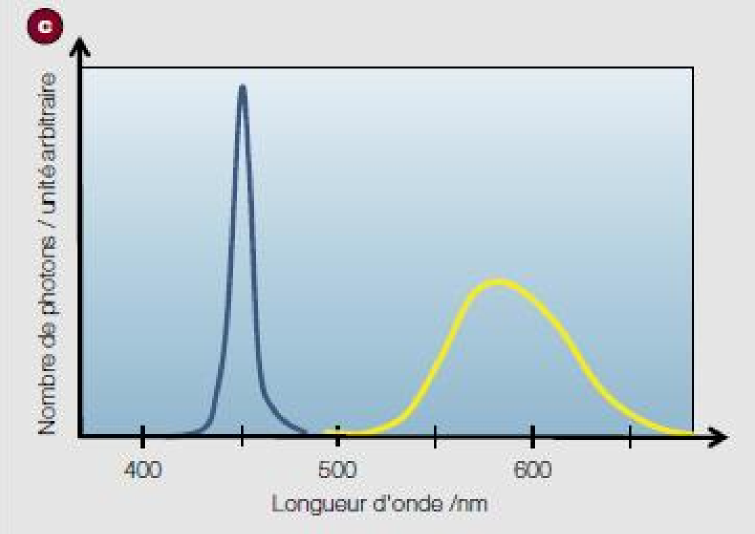
Electroluminescent diodes

- **Principle:**
  - Radiative recombination of negative (electrons) and positive charges (« holes ») that are electrically injected in a semiconductor diode.
  - Build around a blue emitting diode.




EPFL / N. Grandjean

White LEDs



Efficacy (Lm/W)	100
IRC	80-90
Lifetime (h)	> 15000

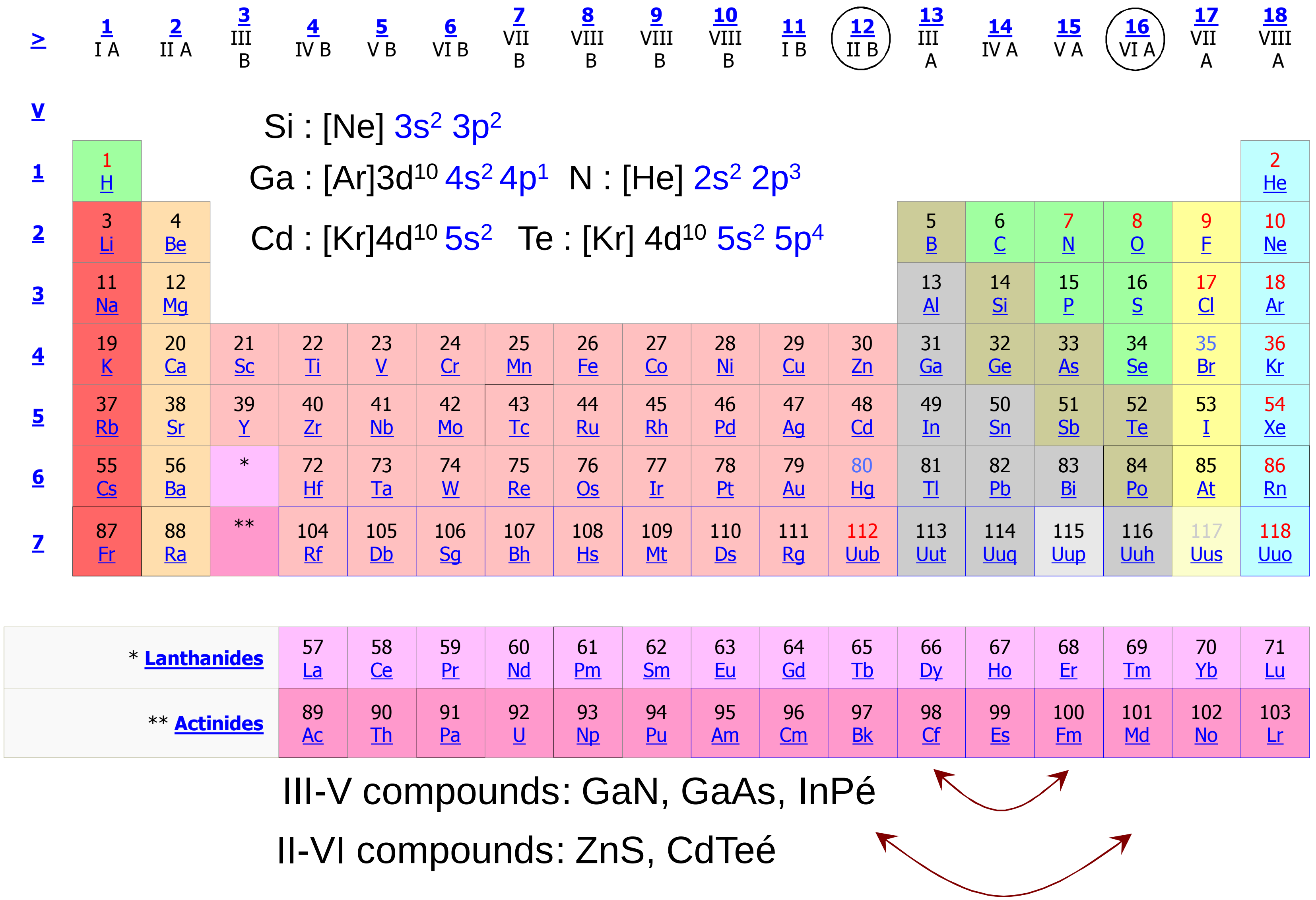
- The blue LED has a double function:
  - It supplies the blue part of the spectrum at 450 nm.
  - It Optical pumps a yellow phosphorescent compound.
- White light=blue emission from a LED (450-460 nm) + yellow emission from a phosphor.

LED history

- **1907:** H.J. Round (Marconi Electronics) discovers electroluminescence of SiC.
- **1961:** first infrared LED made of GaAs (Bob Biard and Gary Pittman, Texas instruments).
- **1962:** using GaAsP alloy enable the of the first visible LED (710 nm)(Nick Holonyak Jr. and Sam Bevacqua, General electric).
- **1960-70:** yellow and green LEDs.
- **1972:** GaN green emitting LED prototype (J.Pankove,RCA).
- **1989:** GaN UV emitting LED prototype (380 nm) (H. Akasaki & H. Amano).
- **1994:** InGaN based blue diode(450 nm) S.Nakamura, Nishia.

⇨ *Different materials emit light in distinct ranges of wavelength.*

Semiconductor compounds



Si : [Ne] $3s^2\ 3p^2$

Ga : [Ar]$3d^{10}\ 4s^2\ 4p^1$ N : [He] $2s^2\ 2p^3$

Cd : [Kr]$4d^{10}\ 5s^2$ Te : [Kr] $4d^{10}\ 5s^2\ 5p^4$

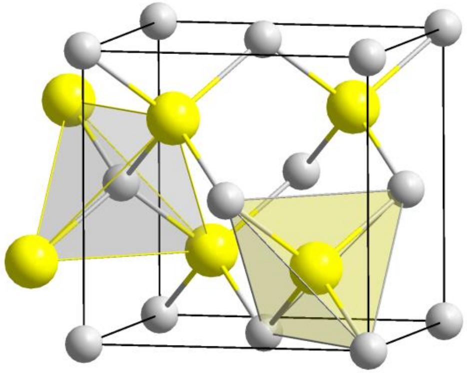
≥ v	1 I A	2 II A	3 III B	4 IV B	5 V B	6 VI B	7 VII B	8 VIII B	9 VIII B	10 VIII B	11 I B	12 II B	13 III A	14 IV A	15 V A	16 VI A	17 VII A	18 VIII A
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

* **Lanthanides**	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
** **Actinides**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

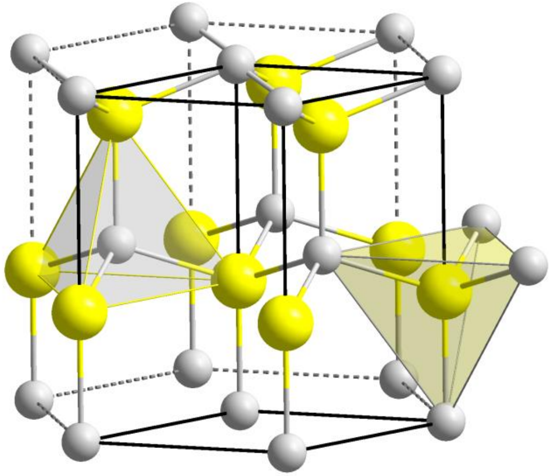
III-V compounds: GaN, GaAs, InPé

II-VI compounds: ZnS, CdTeé

Structure cristalline

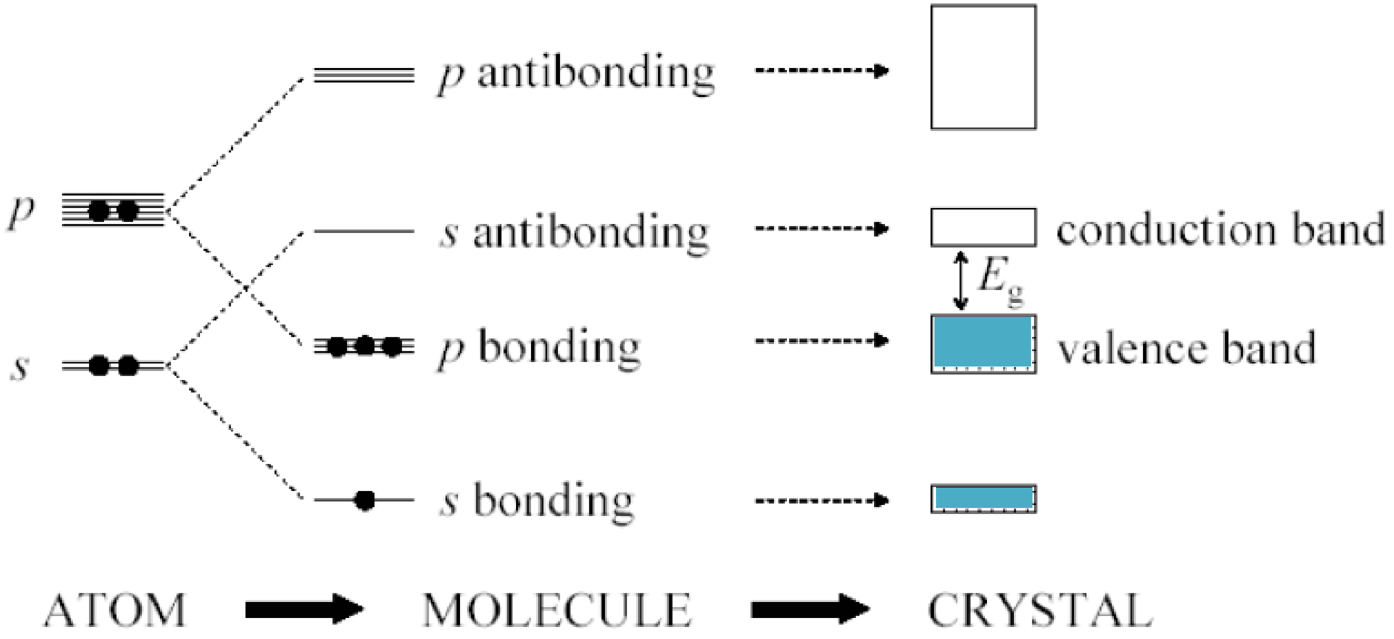


- zinc-blende (cubic) and wurtzite (hexagonal) structures are the most common.
- The arrangement of atoms is periodic in real space.
- Crystal electrons evolve in the periodic Coulomb potential created by atoms..



Semiconductor	Structure	Lattice parameter
Si	Diamond	a = 5,430 Å
GaAs	Zinc-blende	a = 5,653 Å
GaN	Wurtzite	a = 3,189 Å c = 5,185 Å

From atomic states to energy bands



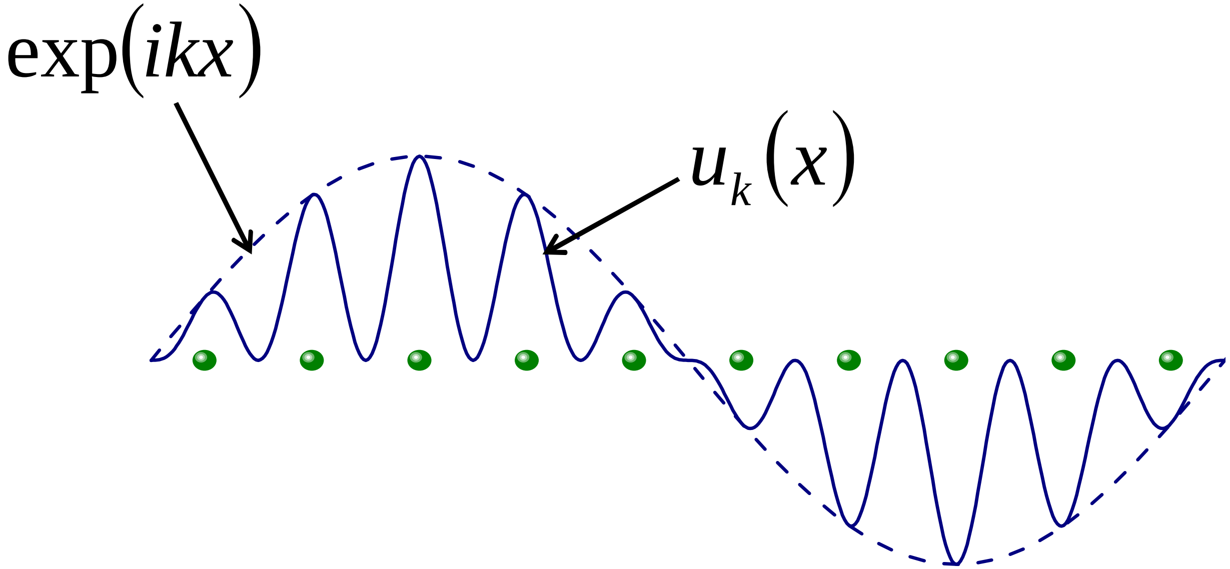
- The electronic states of the periodic lattice are built by coupling the valence states of the isolated atoms.
- The coupling lifts the degeneracy between the atomic states and opens bandgaps in the band structure.

⇨ *The bandgap energy is characteristic of a semiconductor.*

Electronic states

- Cristal: periodic arrays of atoms, translational symmetry.
- Electrons can delocalize on crystal atoms and are characterized by a wavefunction:

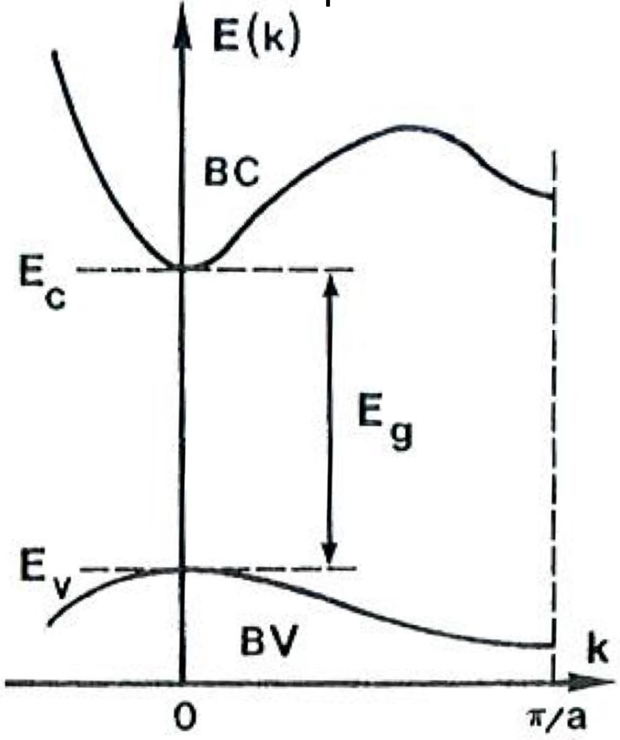
$$\psi_k(x) = \exp(ikx) \times u_n(x)$$



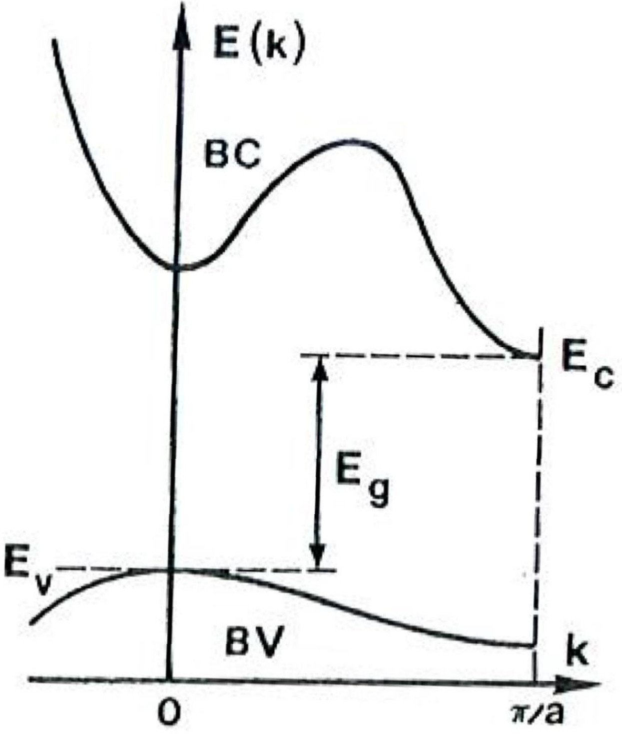
⇨ *Energy depends on quantum number **k***

Band structure in reciprocal space

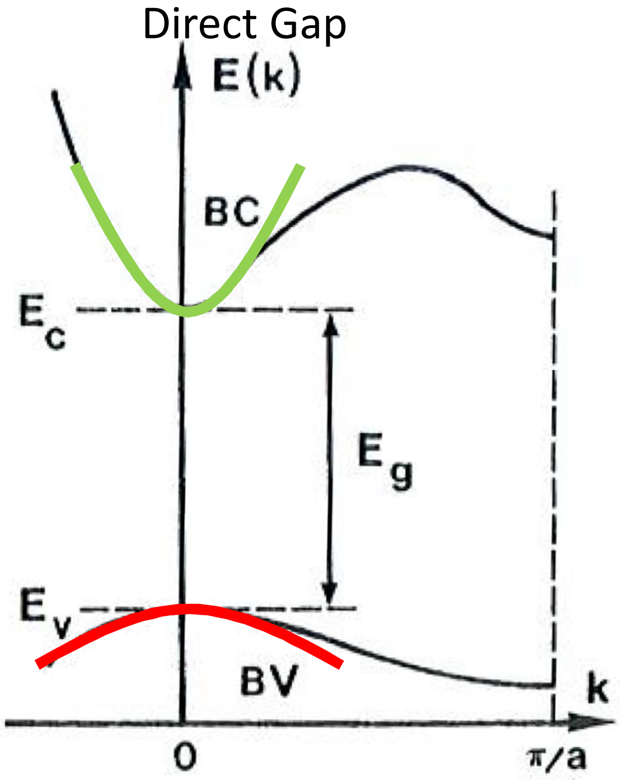
Direct Gap



Indirect Gap



Effective mass



Near the band maxima:

$$E(k) = E(k_0) + k\underbrace{\frac{\partial E}{\partial k}}_{=0} + \frac{k^2}{2}\frac{\partial^2 E}{\partial k^2} + \dots$$

By introducing the electron « effective mass »

$$m_e^* = \hbar^2 \left(\frac{\partial^2 E}{\partial k^2}\right)^{-1}$$

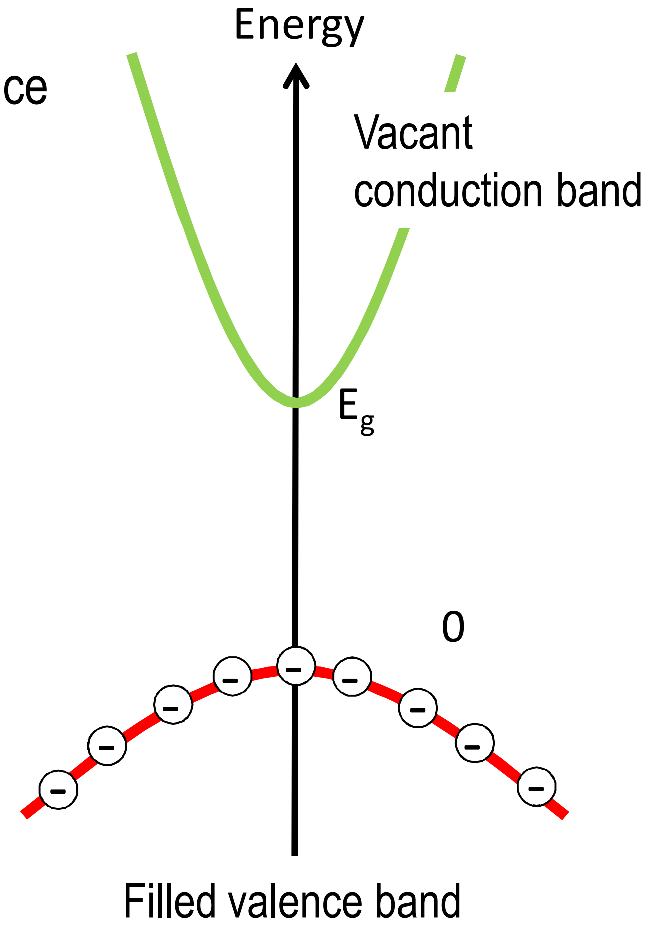
The energy dispersion is similar to the one of a free electron of mass m*.

$$\boxed{E(k) \approx E(k_0) + \frac{\hbar^2 k^2}{2m^*}}$$

⇨ *Effective medium with mass m_e^*.*

Intrinsic semiconductors

- At T= 0 K, all electrons occupy valence states.
- The crystal is insulant.

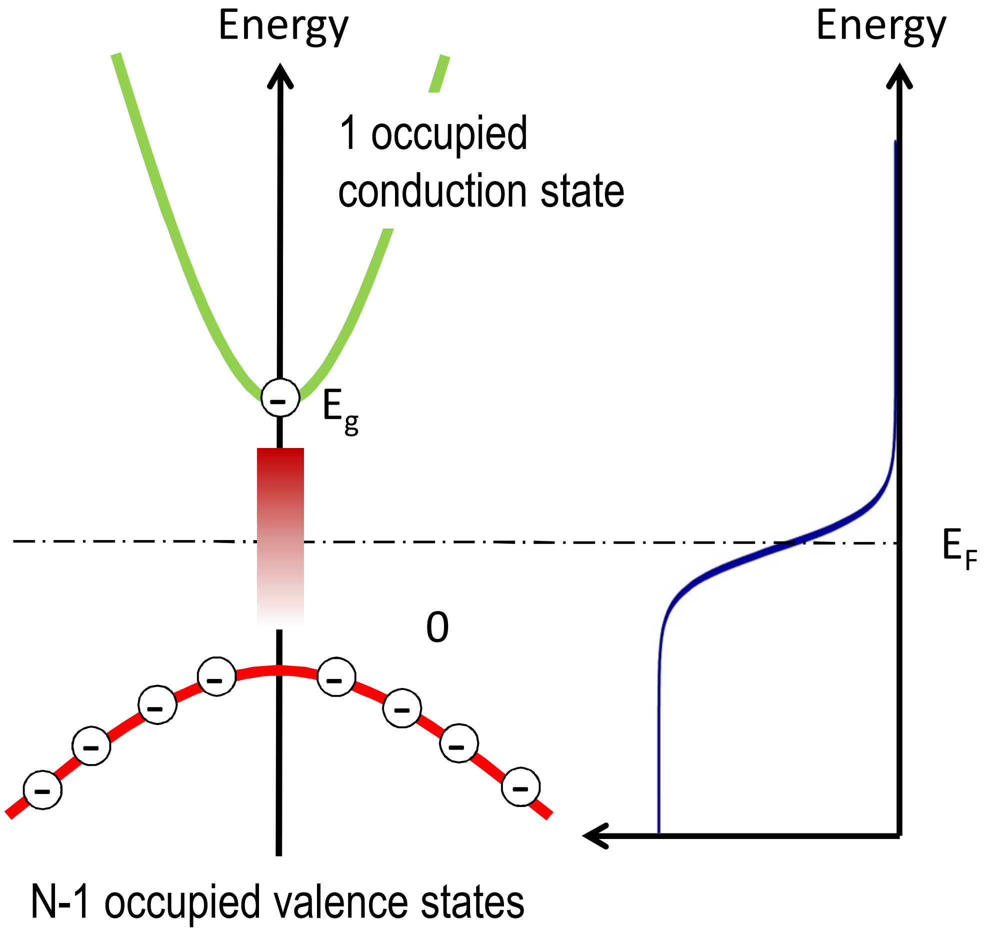


Intrinsic semiconductors

- For T ≠ 0, electrons can be thermally excited across the energy gap into the conduction band.
  - Conduction electrons = “free electrons”
- The probability that a state is occupied is given by the Fermi-Dirac distribution:

$$f(E)=\frac{1}{\exp\left(\frac{E-E_F}{k_BT}\right)+1}$$

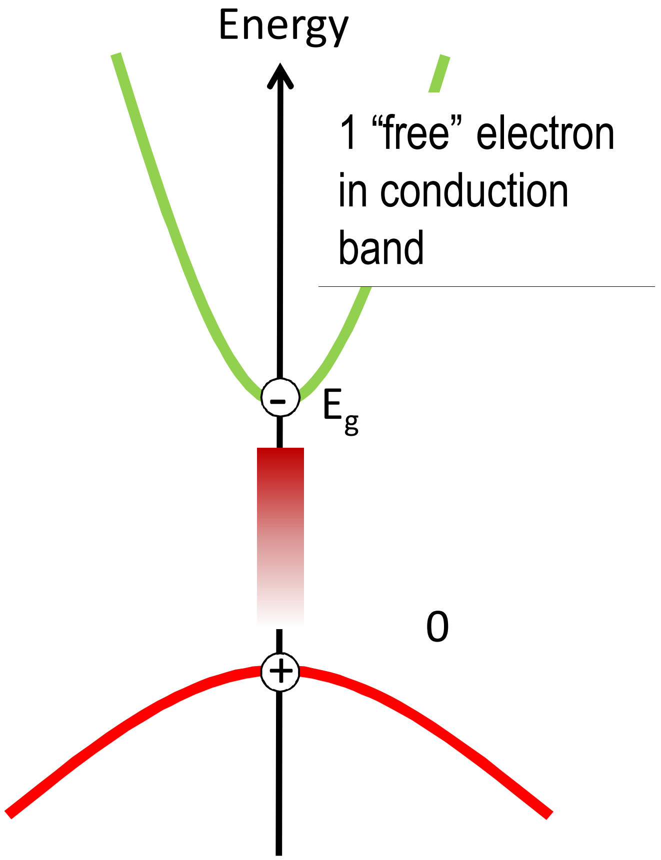
$$E_F \approx \frac{E_G}{2}$$



Intrinsic semiconductors

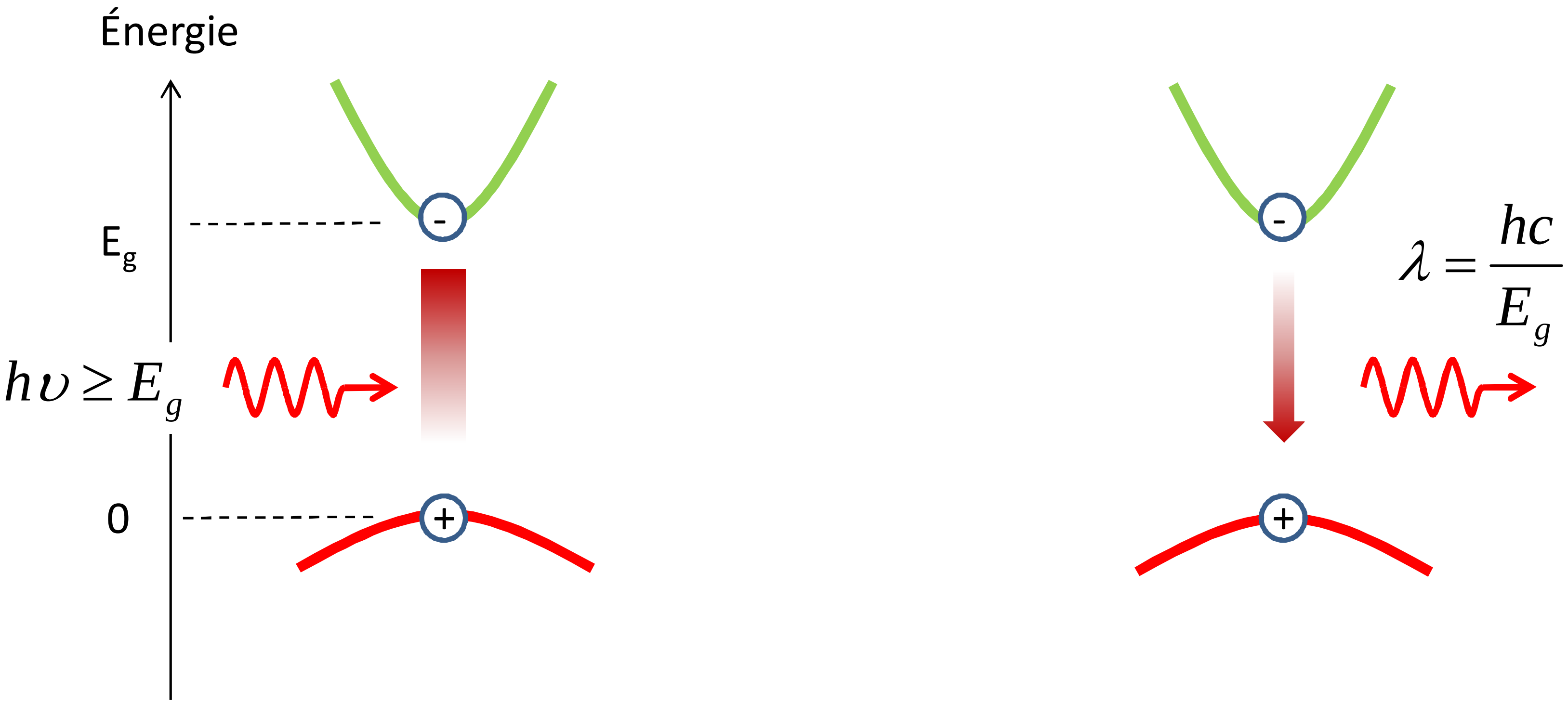
- The excited electron leaves behind one unoccupied states in the valence band that is equivalent to a quasi-particle carrying a positive charge.
- This lack of negative charge is called a “hole”.

⇨ *In semiconductors, electric current is mediated by electrons and holes.*



1 “free” hole in valence band

Optical processes



$$h\upsilon \geq E_g$$

$$\lambda = \frac{hc}{E_g}$$

- **Absorption:**

A photon which energy is larger than the bandgap Eg can be absorbed to create one electron in the CB and one hole in the VB.

- **Spontaneous emission:**

An electron at the bottom of the CB can recombine with a hole at the top of the VB to emit one photon which energy is close to the bandgap energy.

Selection rules

Quantum mechanics ⇨ probability of optical transition between from an initial state |i> to a final state |f>

Fermi's golden rule:

$$\underbrace{P}_{\text{Transition probability/s}} = \frac{2\pi}{\hbar} \underbrace{\left|\langle f|V|i\rangle\right|^2}_{\text{Matrix element of light-matter interaction}} \underbrace{\rho(f)}_{\text{Final density of state}} \underbrace{\delta\left(E_f - E_i \pm \hbar\omega\right)}_{\text{Energy conservation}}$$

Application to semiconductors

Eigen functions:

$$\left|\psi_{\vec{k}}\right\rangle = u_{\vec{k}}(\vec{r})e^{i\vec{k}\vec{r}}$$

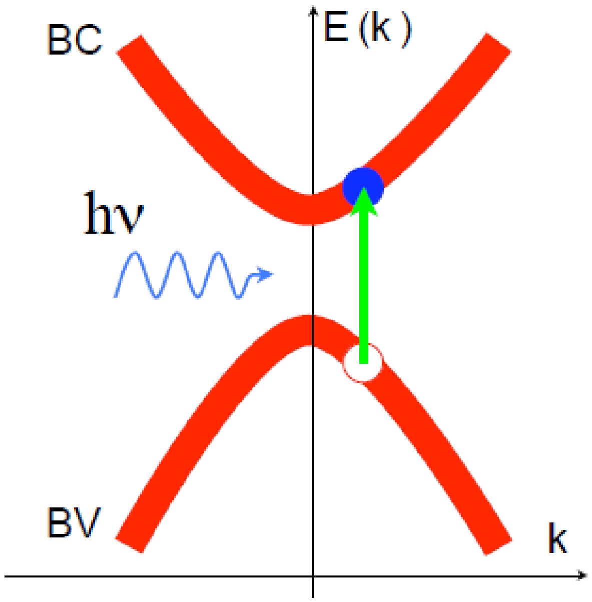
Periodic

Plane wave

Optical matrix element:

$$\left\langle f\middle|V\middle|i\right\rangle \propto \left\langle u_i\middle|V\middle|u_f\right\rangle \times \delta\left(\vec{k}_f - \vec{k}_i - \vec{q}\right)$$

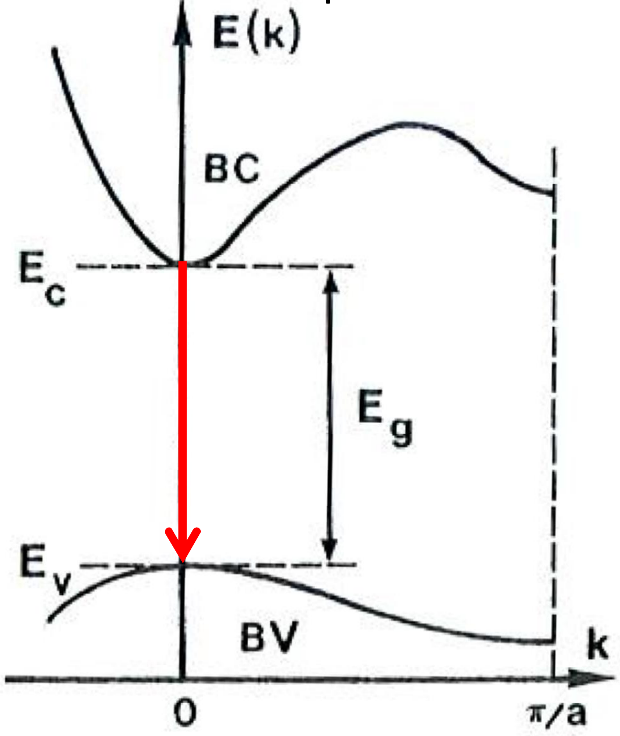
q = 2π/λ, light wavevector



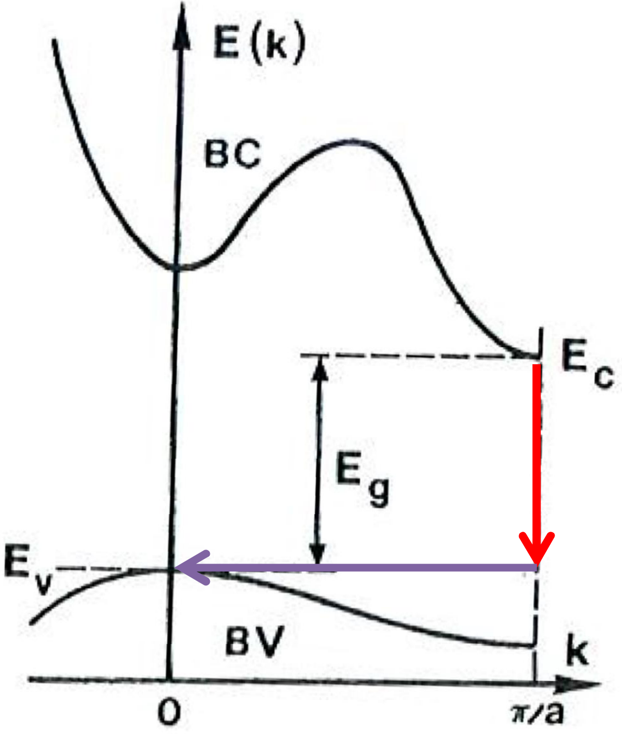
Selections rules show vertical transitions Δk=0

Direct and indirect bandgaps

Direct Gap

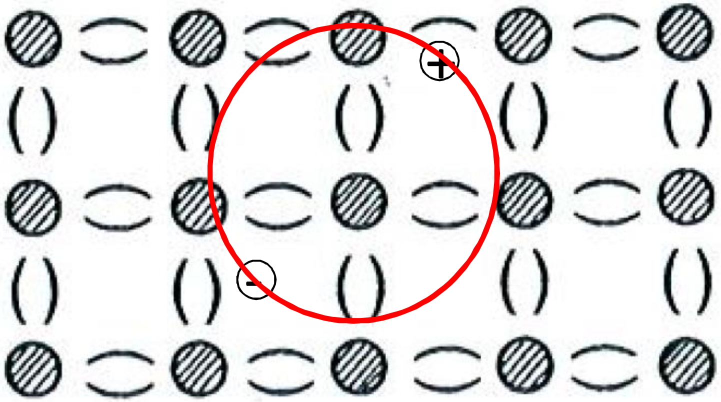


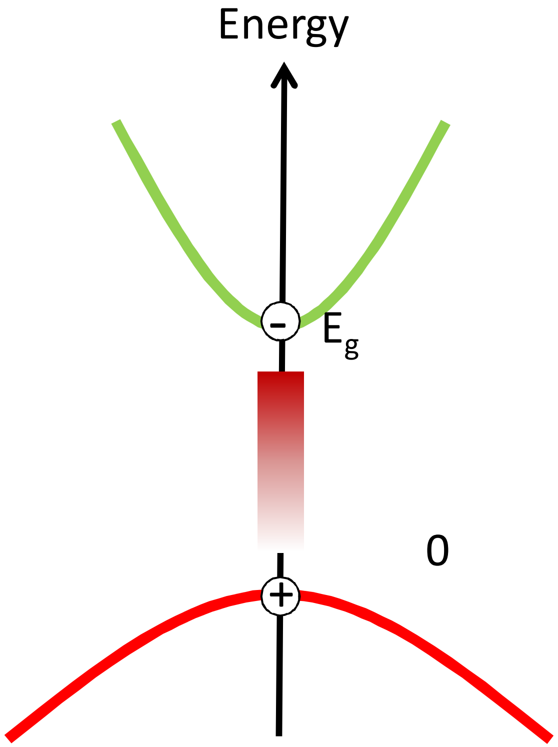
Indirect Gap



⇨ *Bulk semiconductors with indirect bandgap are weak light emitters.*

Excitons





- The electron and the hole are bound par Coulomb interaction.
- The exciton can freely propagate or localize on defects.

⇨ *It is a very fine probe of matter, very sensitive to imperfections..*

Hydrogen-like description

Exciton seen as an hydrogen atom in a effective medium *(defined by* m_e^**,* m_h^* *and* **Ů***)*

$$E_{ex}(n,K) = E_g - \frac{R_y^*}{n^2} + \frac{\hbar^2 K^2}{2M}$$

$$R_y^* = 13.6 \frac{\mu}{\varepsilon_r^2 m_0}$$

Exciton binding energy

$$M = m_e + m_h \qquad K = k_e + k_h$$

Mass and wave vector of the exciton

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}$$

Reduced mass for the relative motion

$$a_B^* = a_B \frac{m_0}{\mu \varepsilon_r} = 0.052 \frac{m_0}{\mu \varepsilon_r}$$

Bohr radius

Light-matter interaction in semiconductors

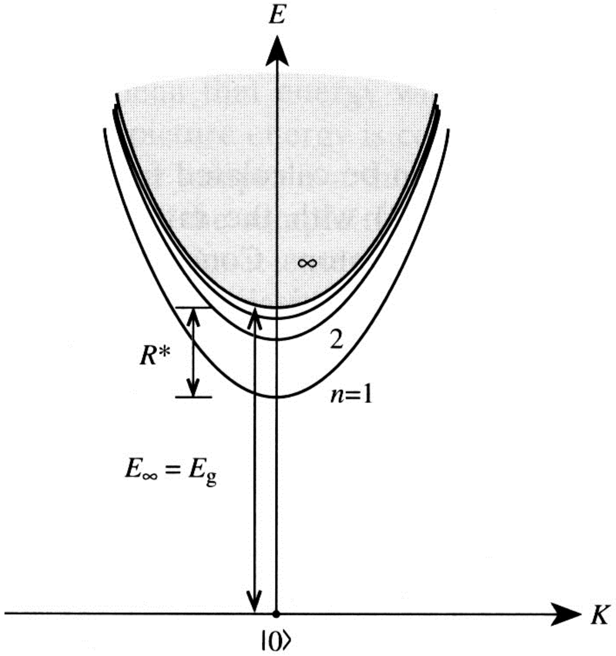
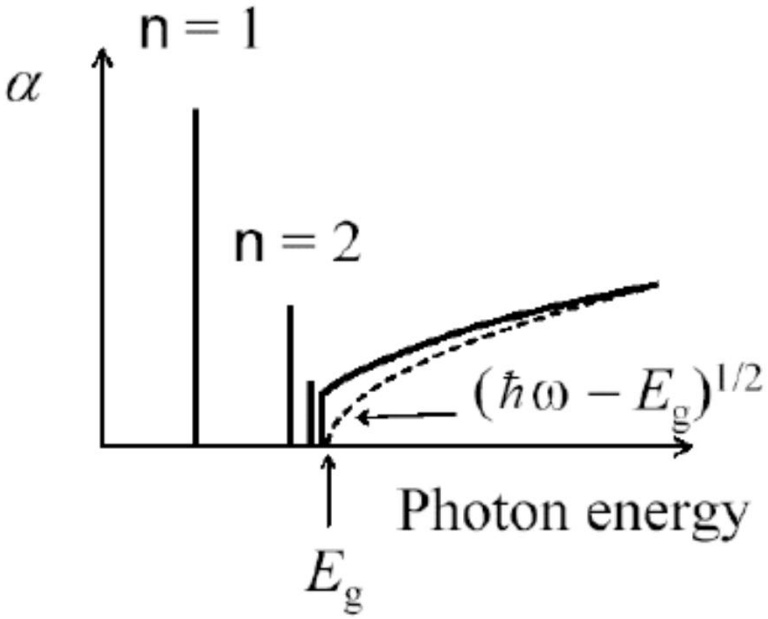


Fig. 6.21. The energy states of a Wannier exciton showing both its bound states $n = 1$ to 3 and the continuum states. E_g is the bandgap and R^* the exciton binding energy

Crystal	E_g (eV)	R_X (meV)	a_X (nm)
GaN	3.5	23	3.1
ZnSe	2.8	20	4.5
CdS	2.6	28	2.7
ZnTe	2.4	13	5.5
CdSe	1.8	15	5.4
CdTe	1.6	12	6.7
GaAs	1.5	4.2	13
InP	1.4	4.8	12
GaSb	0.8	2.0	23
InSb	0.2	(0.4)	(100)

R_y increases with E_g

Light-matter interaction in semiconductors



ÅCoulomb interaction between e and h: bound states
ÅHydrogen-like lines
$E_x = E_g$ ï R_y/n^2
ÅAbsorption increased if compared to the results of a simple band-to-band absorption model for ***ƙɤ*** > *E*g
ÅObservable in good quality crystals
ÅThe excitonic signature disappears for *kT* > *R*y

⇨ *In good quality crystals, excitons are responsible for strong and sharp resonances in optical spectra (absorption, reflexion and photoluminescence).*

Light-matter interaction in semiconductors

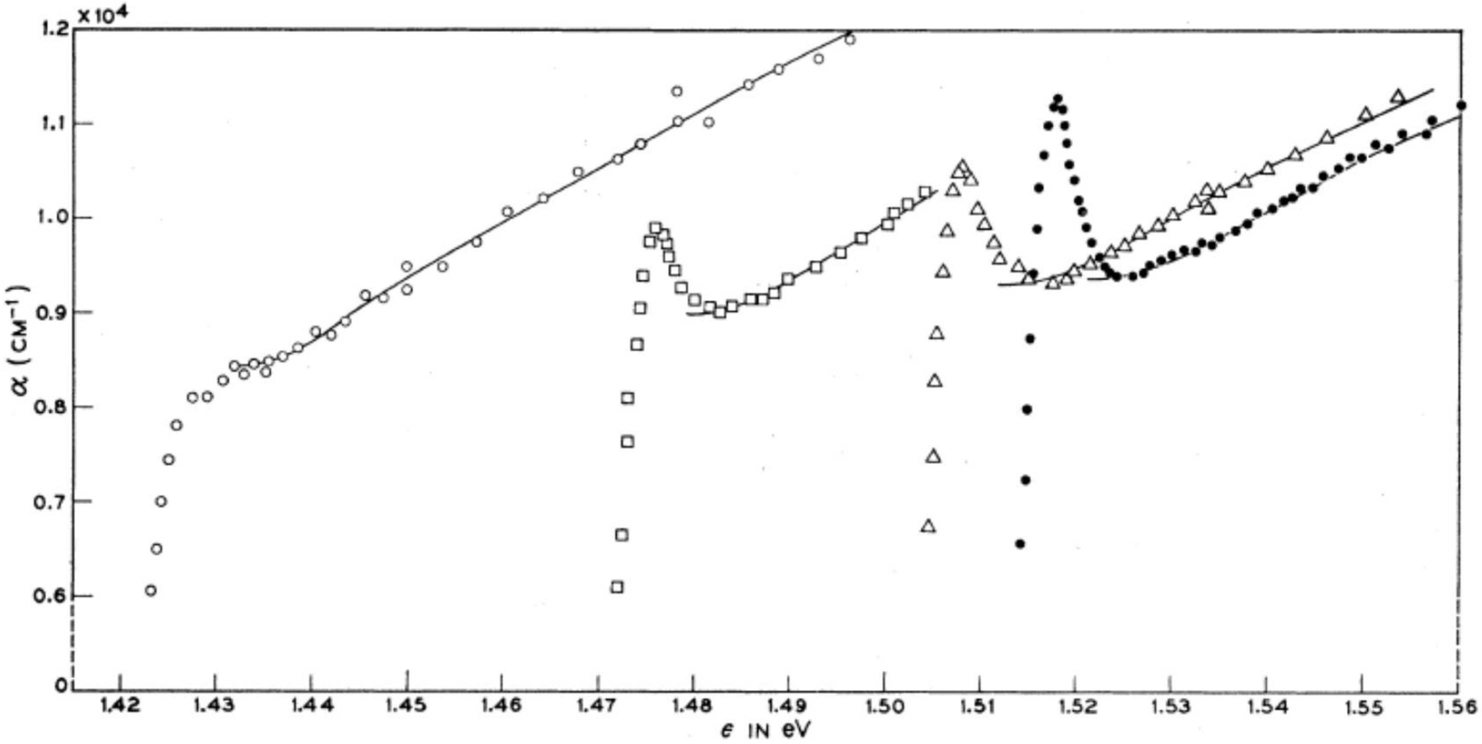
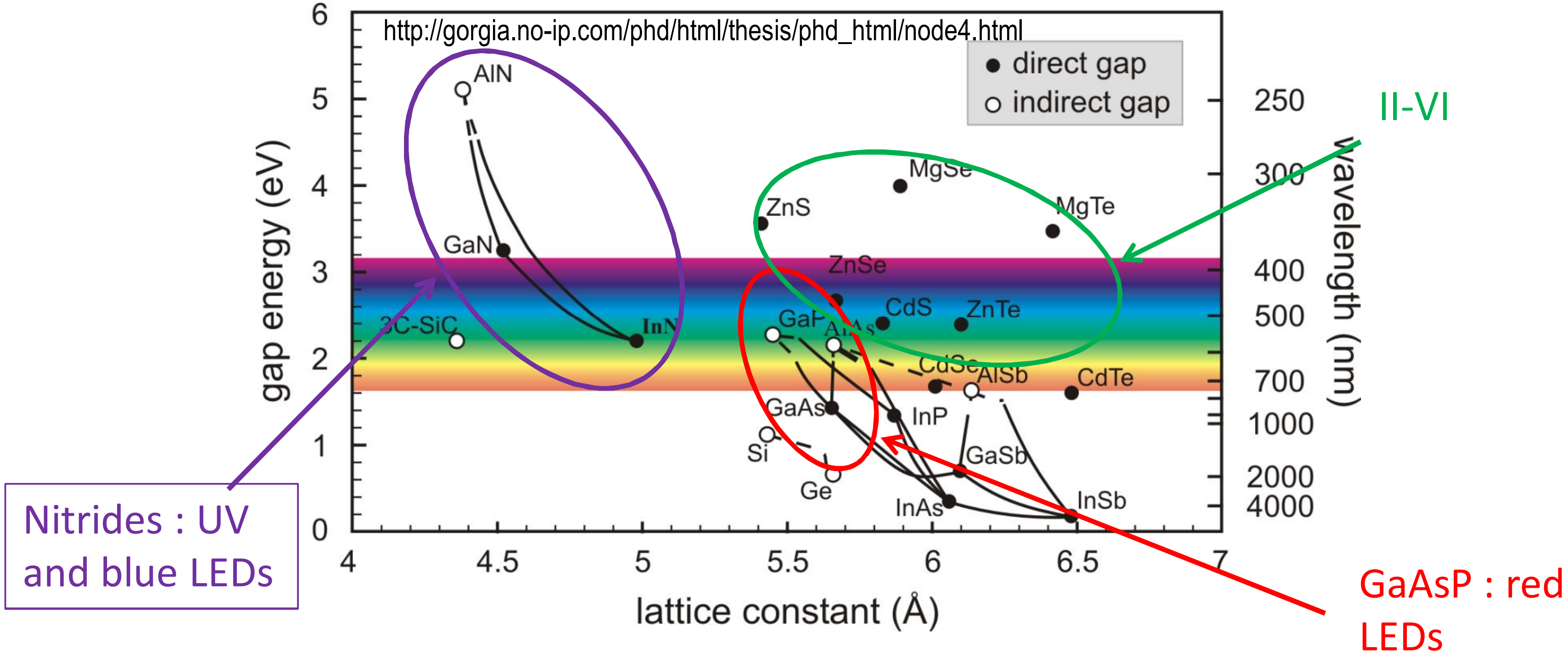


FIG 3 Exciton absorption in GaAs; ○ 294°K, □ 186°K, △90°K, ● 21°K.

- For a free exciton, as well as for a confined exciton, one searches for an exciton which is stable at high temperature: high exciton binding energy or high confinement.

Application

- The emission wavelength depends on the bandgap energy that is an intrinsic property of a semiconductor.
- By synthetizing different semiconductor alloys it is possible to generate all wavelengths from the UV to infrared.



http://gorgia.no-ip.com/phd/html/thesis/phd_html/node4.html

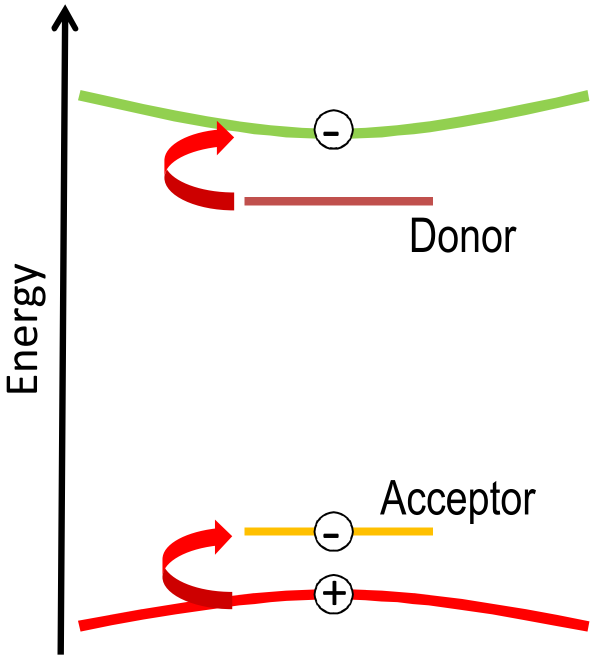
Nitrides : UV and blue LEDs

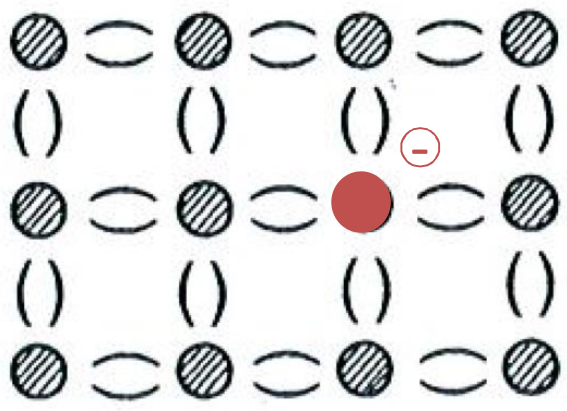
II-VI

GaAsP : red LEDs

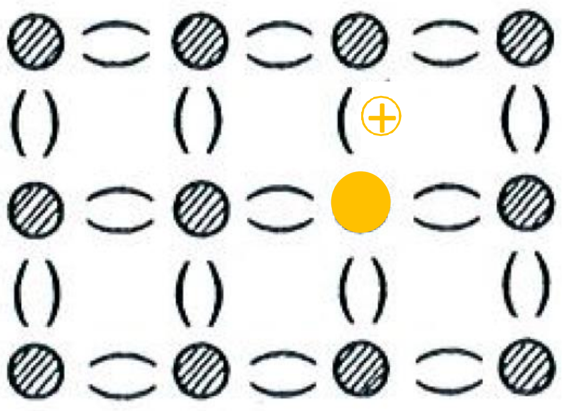
Doping

- Making optoelectronic devices requires the control of free carrier density.
- Addition of extrinsic atoms:
  - Impurity with one extra valence electron ⇨ *donor*
  - Impurity with one less valence electron ⇨ *acceptor*
- Typical impurity density ~10^{16}-10^{18} cm^{-3}



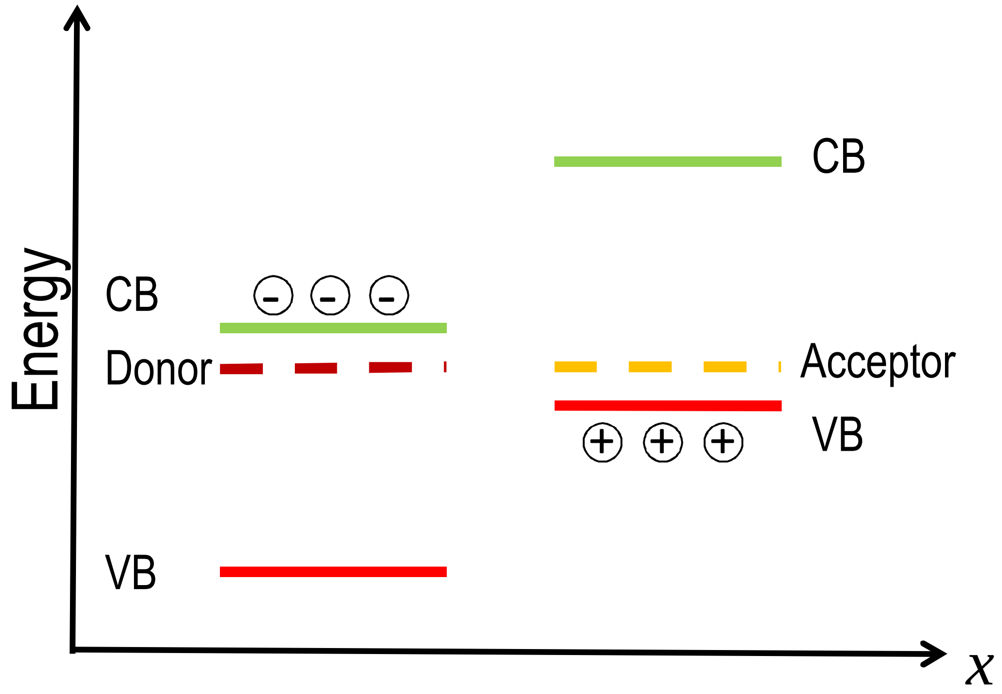


n doping

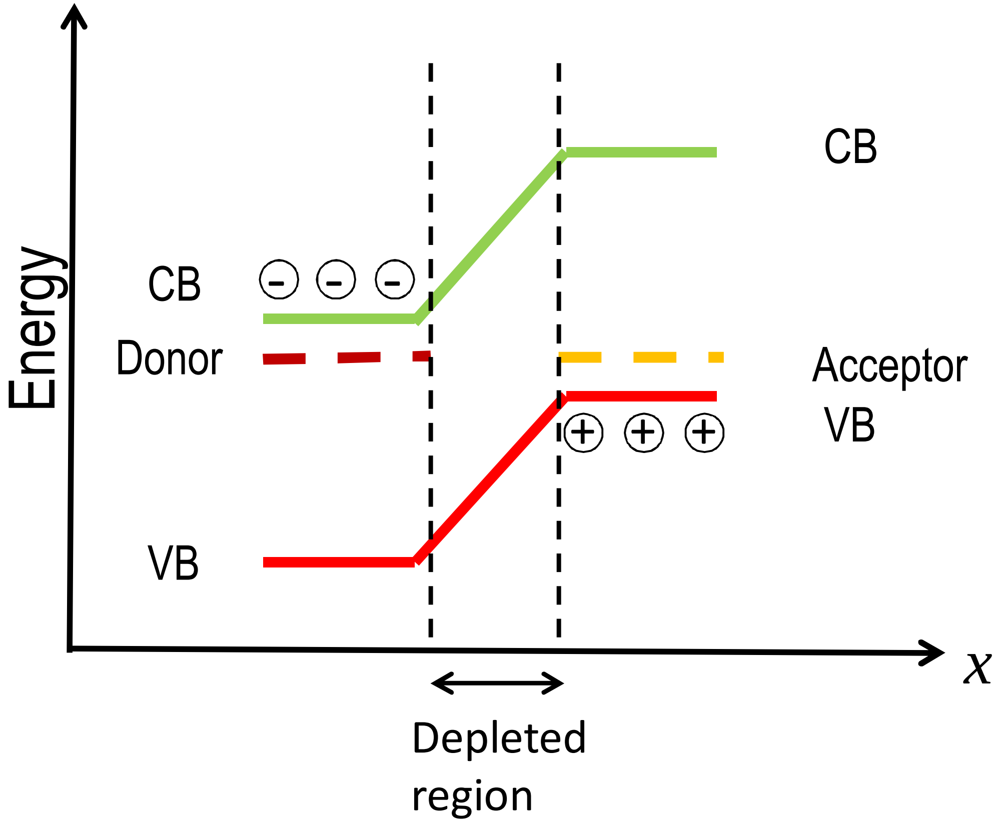


p doping

PN junction

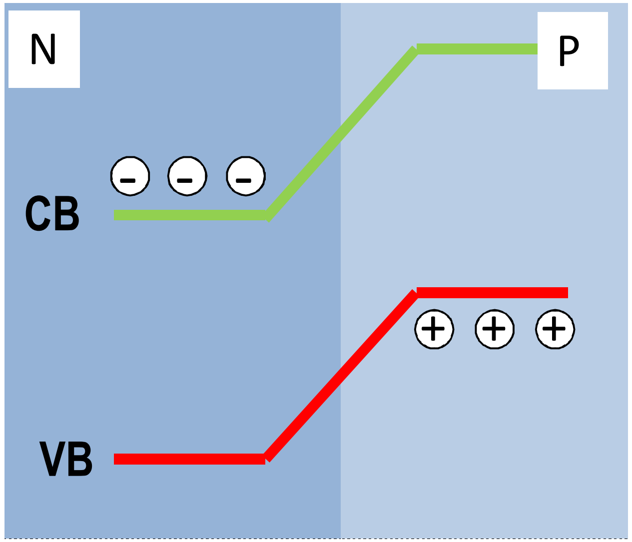


PN junction



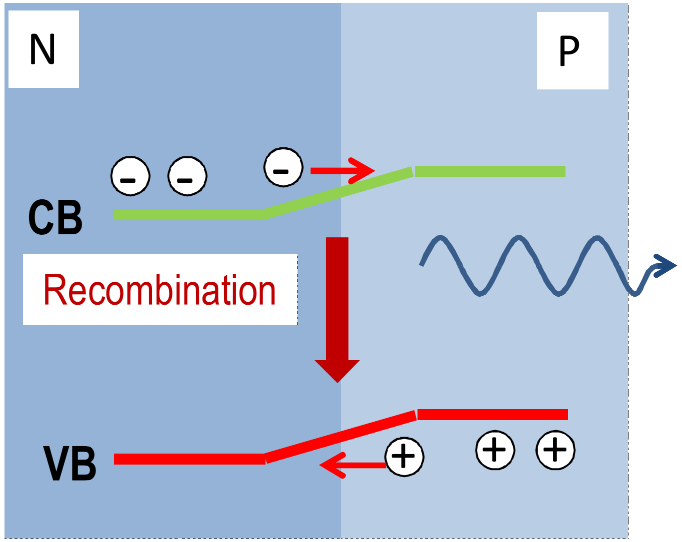
PN Junction electroluminescence

Zero bias



- A potential barrier hinders the diffusion of electron and hole across the depletion zone.

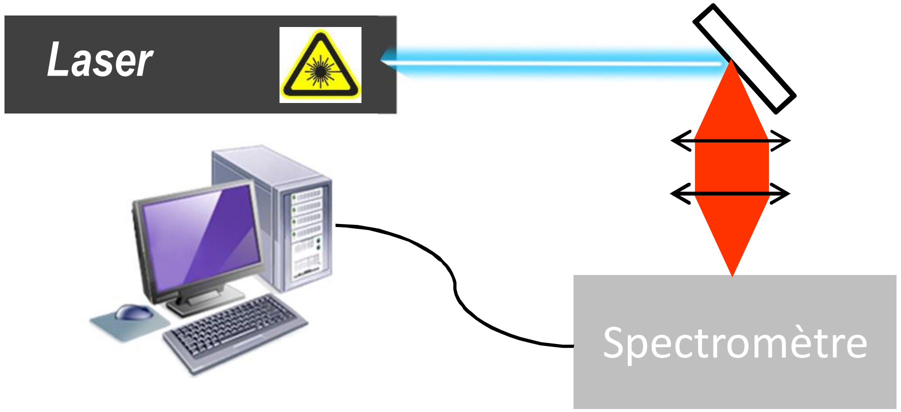
Forward bias



- Electron from n region *n* and holes from *p* region diffuse and meet in the depletion zone where they recombine to emit light.

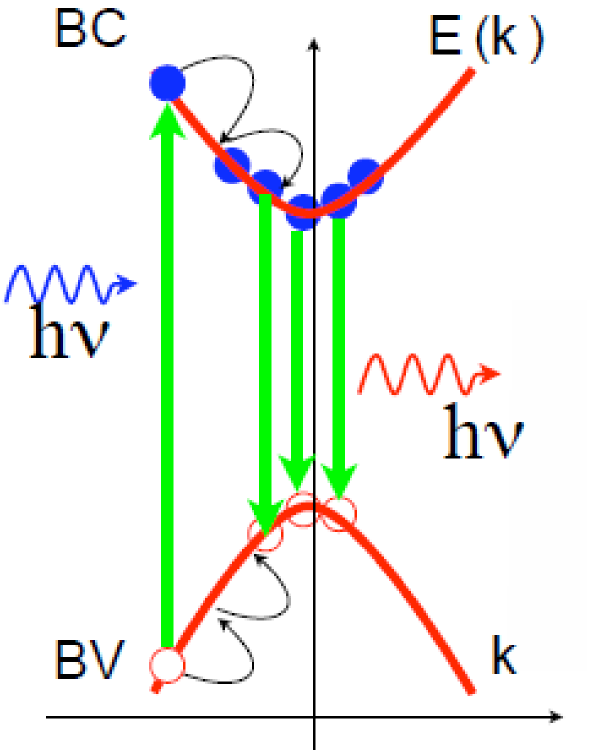
$$\text{Quantum efficiency} = \frac{\text{Number of emitted photons per unit time}}{\text{Number of injected electrons per unit time}}$$

Photoluminescence

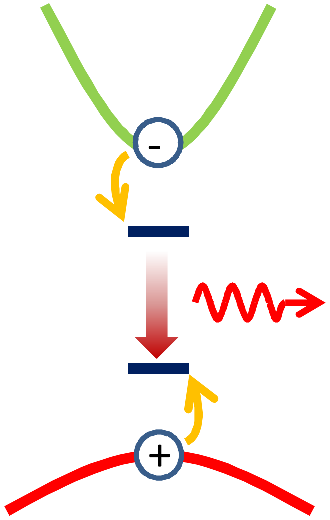


Laser

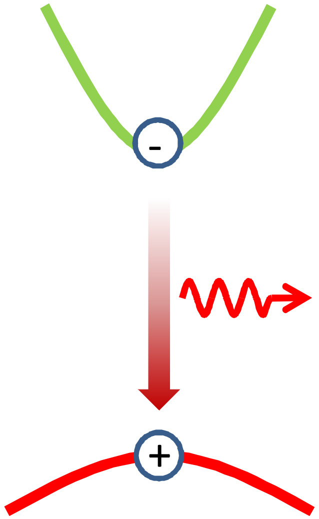
Spectromètre



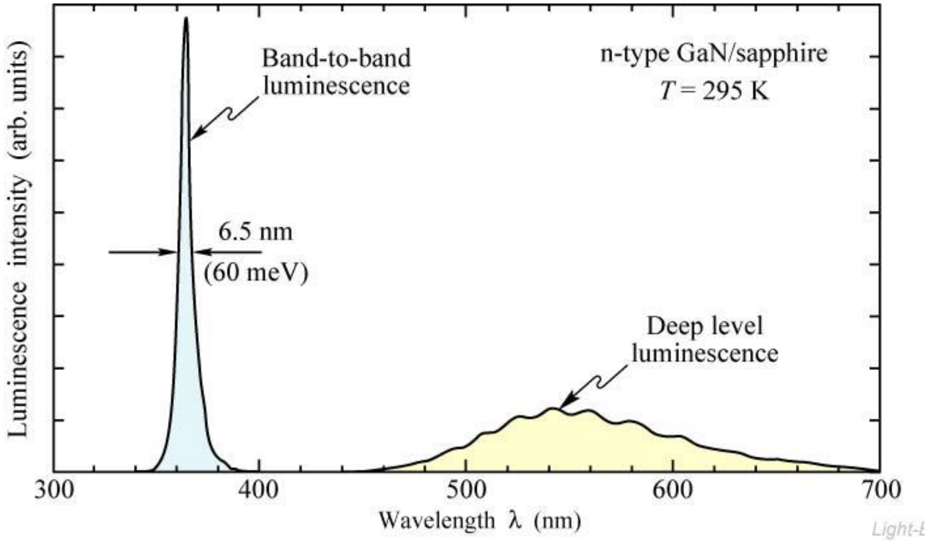
Photoluminescence



Intrinsic PL
Band to band



Extrinsic PL



⇨ *Photoluminescence reveals the crystal purity and gives information on the presence of doping impurities .*

Lifetime and radiative efficiency

Soit une population de n paires électron-trou :

$$\frac{dn(t)}{dt} = -n(t)\left(\boxed{\frac{1}{\tau_R}} + \boxed{\frac{1}{\tau_{NR}}}\right)$$

Probability of radiative recombination

Probability of non-radiative recombination

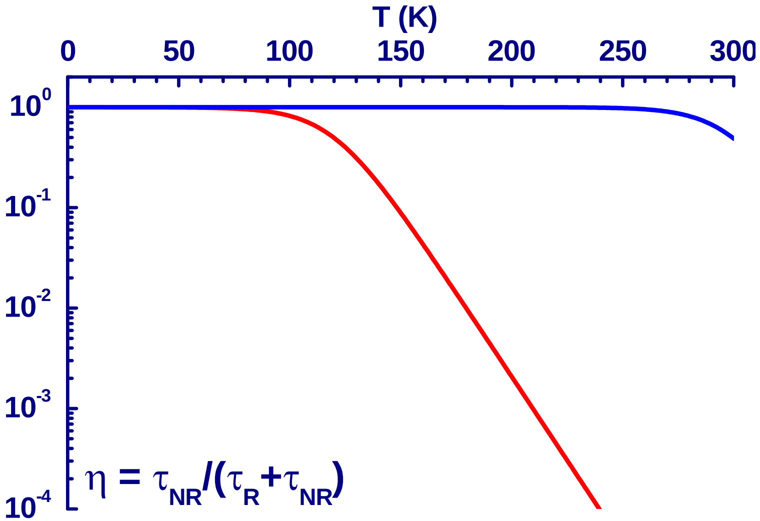
Radiative efficiency :

$$\eta = \frac{1}{1+\frac{\tau_R}{\tau_{NR}}}$$

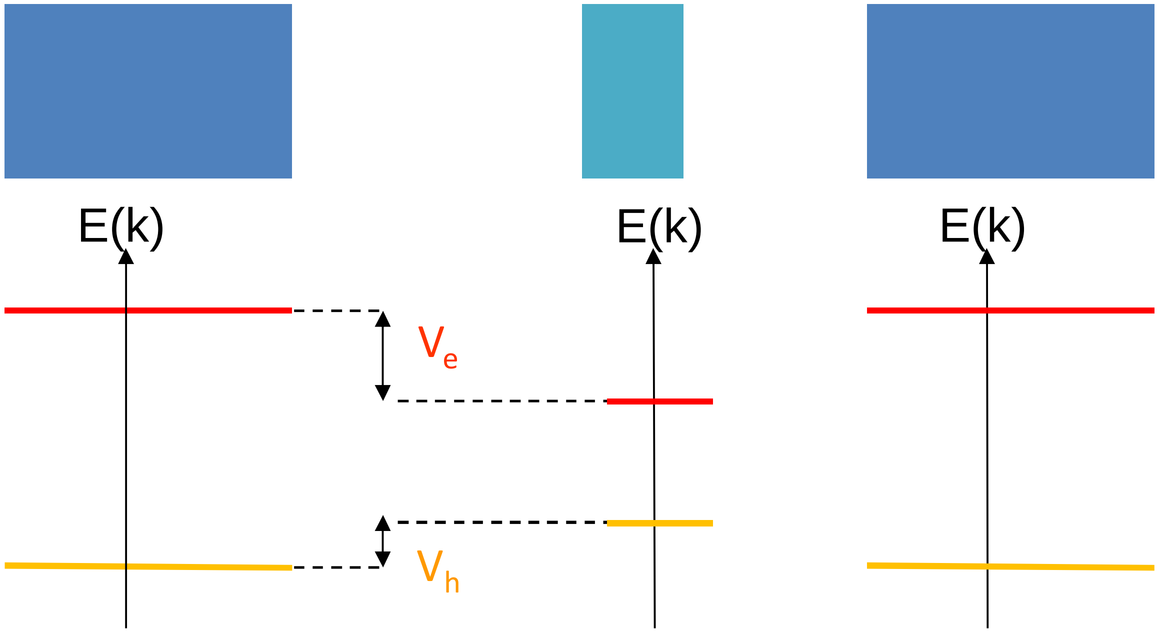
For light-emitting applications, need to maximize the radiative efficiency by decreasing τ_R / τ_{NR}:

⇨ *improve crystalline quality*

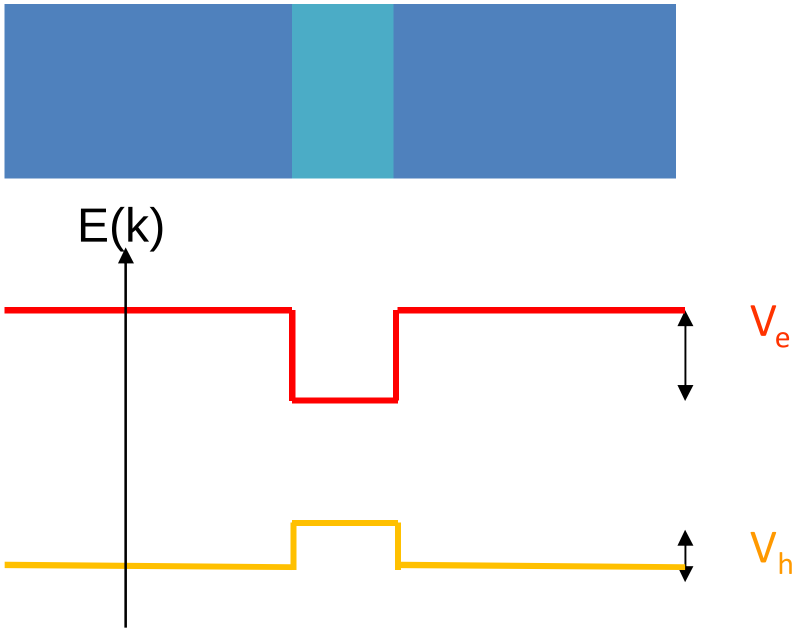
⇨ *Localize carriers (excitons)*



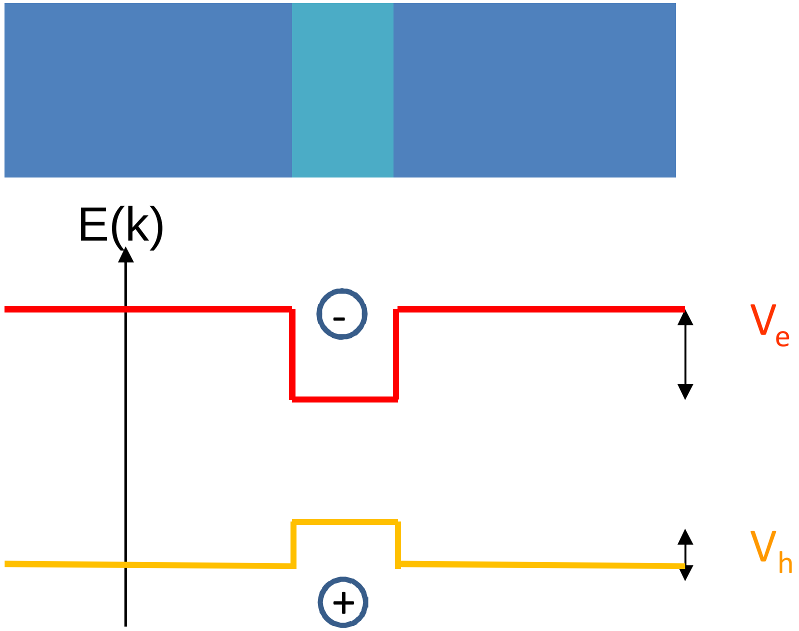
Heterojunctions, quantum structures



Heterojunctions, quantum structures



Heterojunctions, quantum structures



- ⇨ *Electrons and holes are confined in the same region of the sample.*
- ⇨ *Energies of optical transitions depend on the well width.*

Electronic states in QWs

Bulk material: carriers free to propagate in 3D

k=(k_x k_y k_z)

$$\psi_c\left(\vec{k},\vec{r}\right)=\frac{1}{\sqrt{V}}e^{i\vec{k}\vec{r}}u_c\left(\vec{k},\vec{r}\right)$$

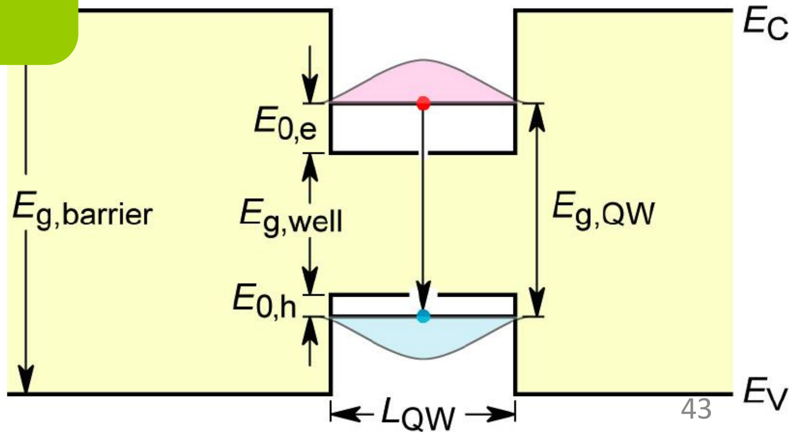
envelope
= plane wave

Periodic part

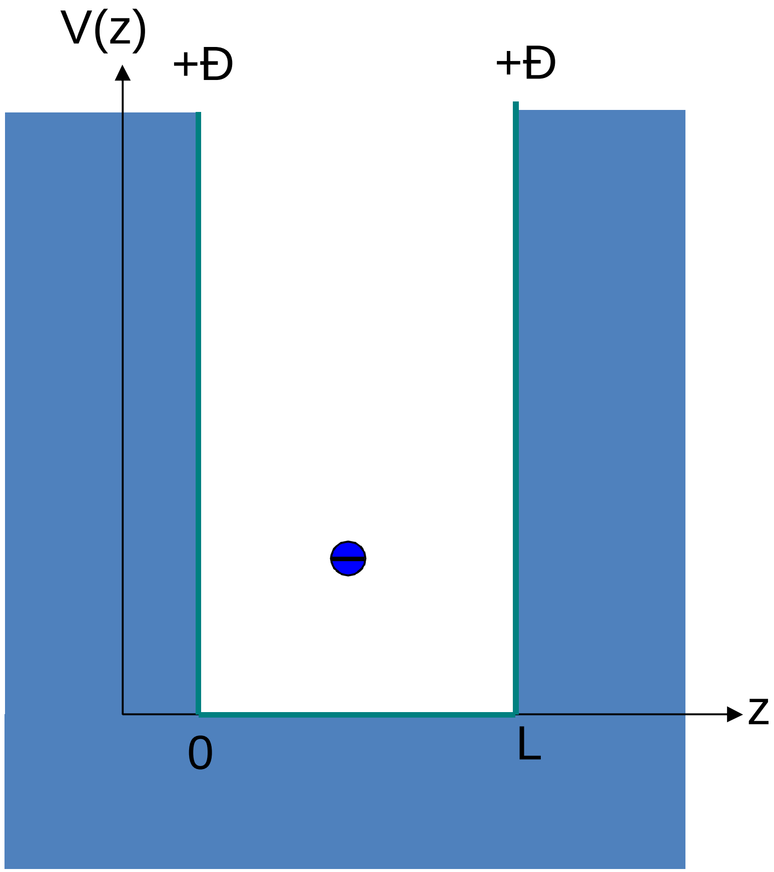
Nanostructure: The confinement potential breaks the translation symmetry in one or several direction.

$$\psi\left(\vec{k},\vec{r}\right)=\frac{1}{\sqrt{N}}F(\vec{r})u\left(\vec{k},\vec{r}\right)\cong\frac{1}{\sqrt{N}}F(\vec{r})u_c(0,\vec{r})$$

envelope
= localized function



Quantum well with infinite barriers



Envelope function equation :

$$\left[\frac{\hbar^2}{2m^*}\frac{\partial^2}{\partial z^2}-E_n\right]f_n(z)=0$$

Boundary condition :

$$f_n(0)=f_n(L)=0$$

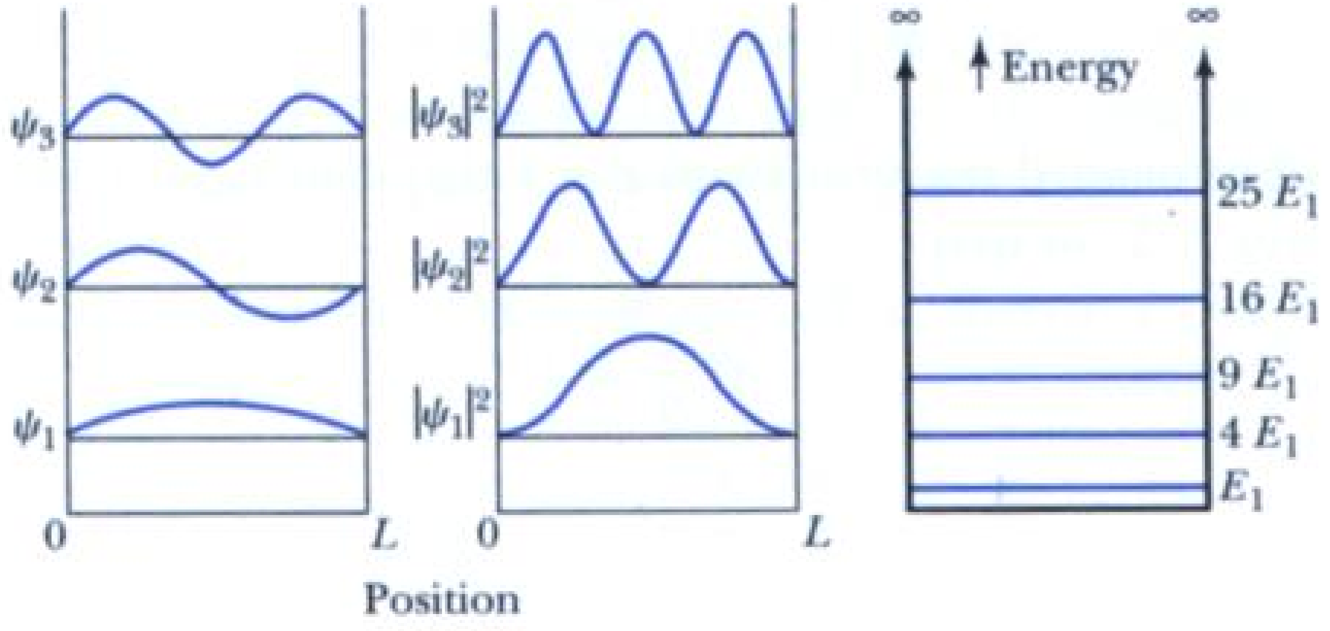
Solutions :

$$f_n(z)=\sqrt{\frac{2}{L}}\sin k_n z$$ avec $k_n = n\pi/L$

$$\boxed{E_n=\frac{\hbar^2 k_n^2}{2m^*}=\frac{\hbar^2}{2m^*}\left(\frac{n\pi}{L}\right)^2}$$

Confinement: discretization of allowed $\mathbf{k}_z$ and discretization of energy states.

Envelope function and energy levels



Optical transition in QWs

Fermi's golden rule

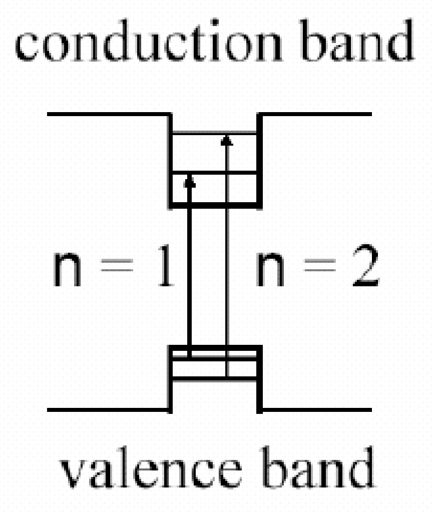
$$P_{i\to f\cong}=\frac{2\pi}{\hbar}\left|\langle f|p\varepsilon|i\rangle\right|^2 g(\hbar w)\cong\frac{2\pi}{\hbar}\left|\langle u_c|p\varepsilon|u_v\rangle\right|^2\left|\int f_e(z_e)f_h(z_h)dz\right|^2 g(\hbar w)$$

Envelope function overlap

QW with infinite barriers

$$\int f_n^e(z_e)f_m^h(z_h)dz=\frac{2}{L}\int_0^L\sin(k_n z)\sin(k_m z)dz=\delta_{n,m}$$

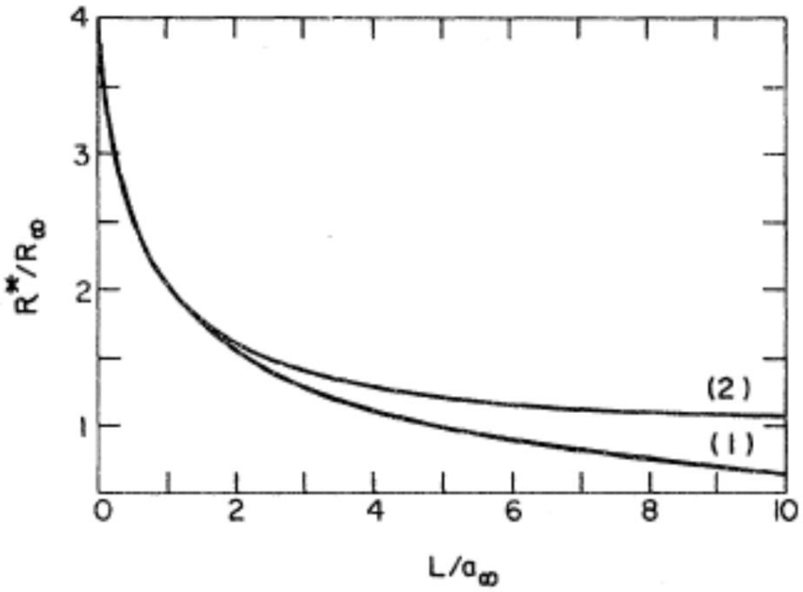
Alowed transition : **Δn = 0**



Excitons in QWs

2D hydrogenoid function

$$\psi_1 = N_1 \cos\frac{\pi z_e}{L} \cos\frac{\pi z_h}{L} \exp\left[\frac{-\rho}{\lambda_1}\right]$$

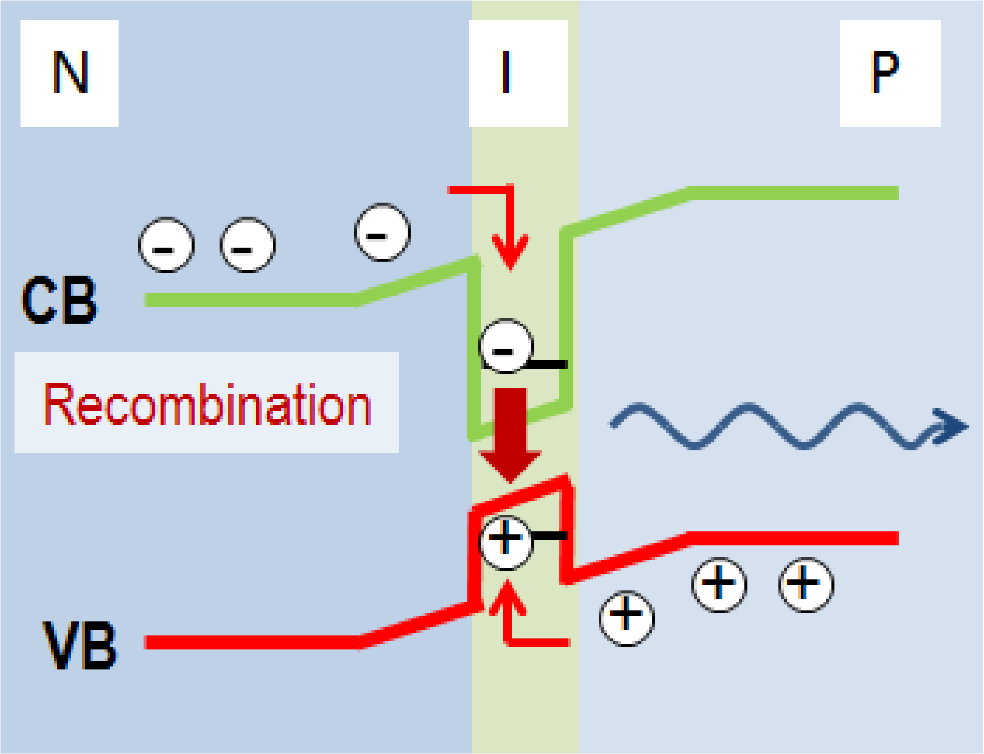


Quantum confinement enhances the exciton binding energy.

Energy spectrum of bound excitonic states

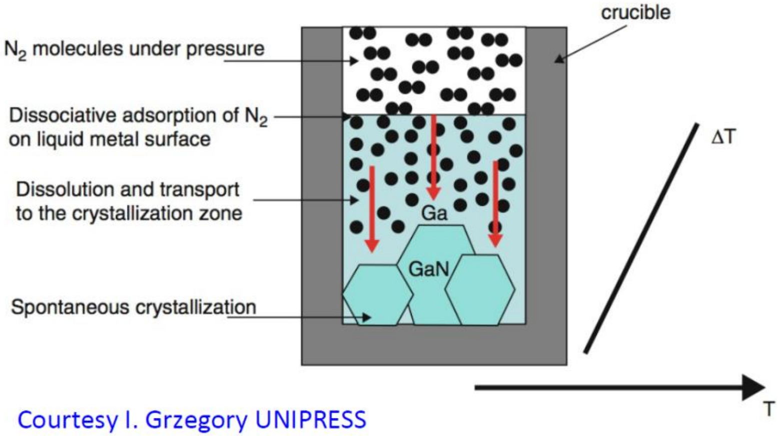
$$\mathbf{E_n = - R_y / (n - 1/2)^2}$$

Quantum well LED

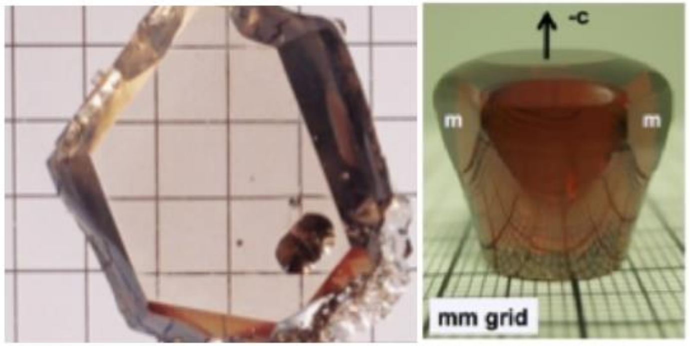


Growth of bulk GaN

- GaN is extremely complicated to synthetize.
- Growth of bulk GaN :1600°C, 20kbar.



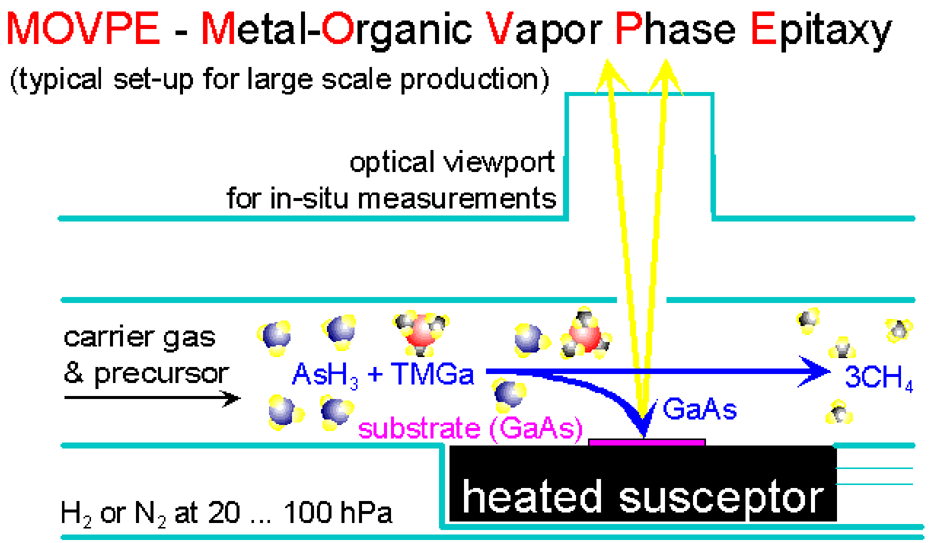
Courtesy I. Grzegory UNIPRESS



- Hetero-epitaxy:
  - ⇨ In a reactor, the chemical constituents of the crystal are deposited on a heated monocrystalline substrate that acts as a germ to initiate an oriented crystalline growth.

Metal-Organic chemical vapor deposition

- The principle is to pyrolyze metal-organic compounds (triethyl-gallium or trimethyl-gallium) and hydrides (NH3, SiH4) in the flow of a carrier gas (N2 or H2) in the vicinity of a heated substrate.

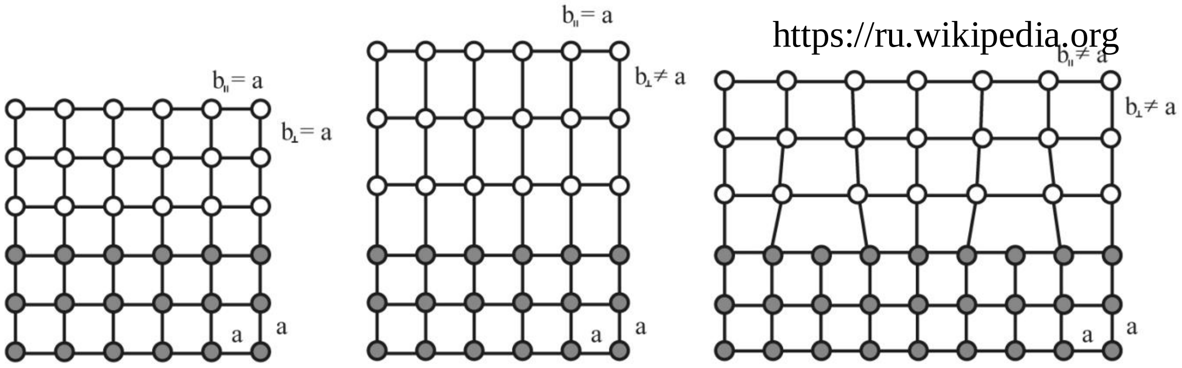


MOVPE - Metal-Organic Vapor Phase Epitaxy

(typical set-up for large scale production)

http://www.physik.tu-berlin.de/institute/IFFP/richter/new/research/monitor.shtml

Hetero-epitaxy

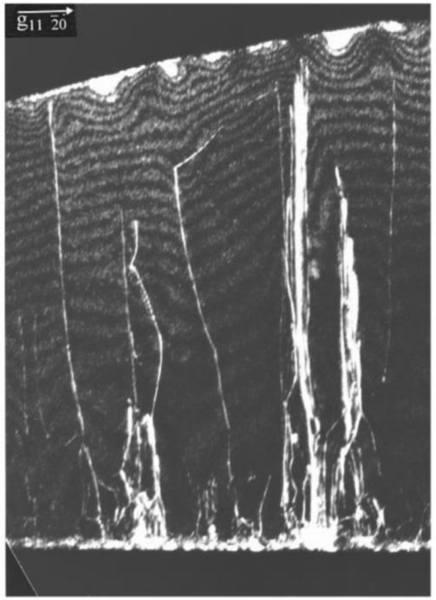


a) commensurate growth b) preudomorphic growth b) dislocation growth

https://ru.wikipedia.org

	GaN	Al_2O_3	6H-SiC	Si
a(Å)	3.189	4.758	3.08	5.430
a(T^{-1})	5.6	7.5	4.2	3.59

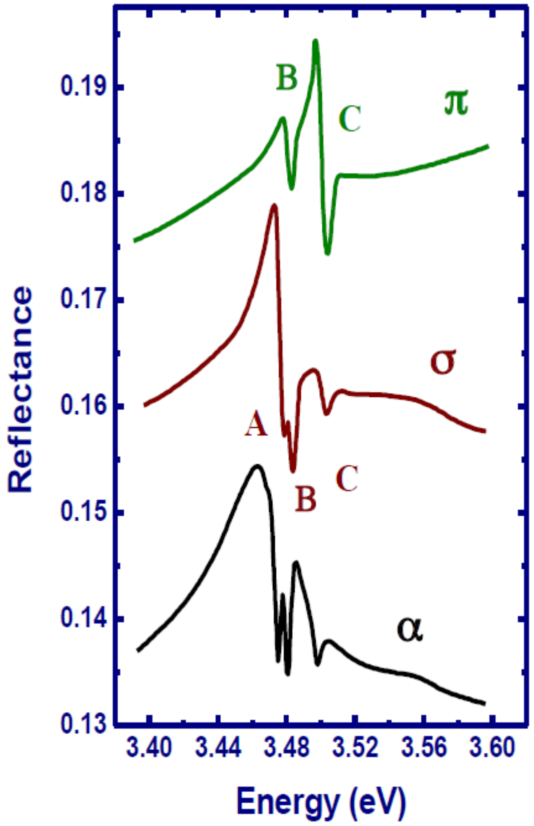
- **No matching substrate**
  - ⇨ Strained layers
  - ⇨ Structural defects (dislocations)



N. Grandjean, J. Massies, P. Vennéguès *et al.*, J. Appl. Phys. **83**, 1379 (1998)

⇨ *Dislocations are known to act as non-radiative centers in semiconductors.*

Optical investigations



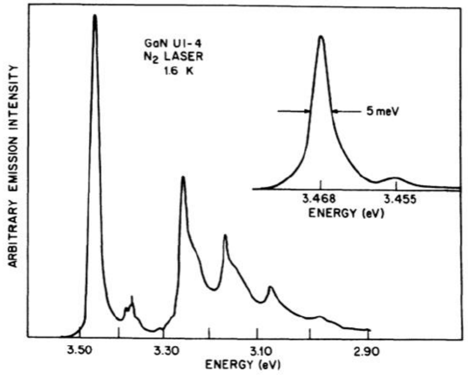
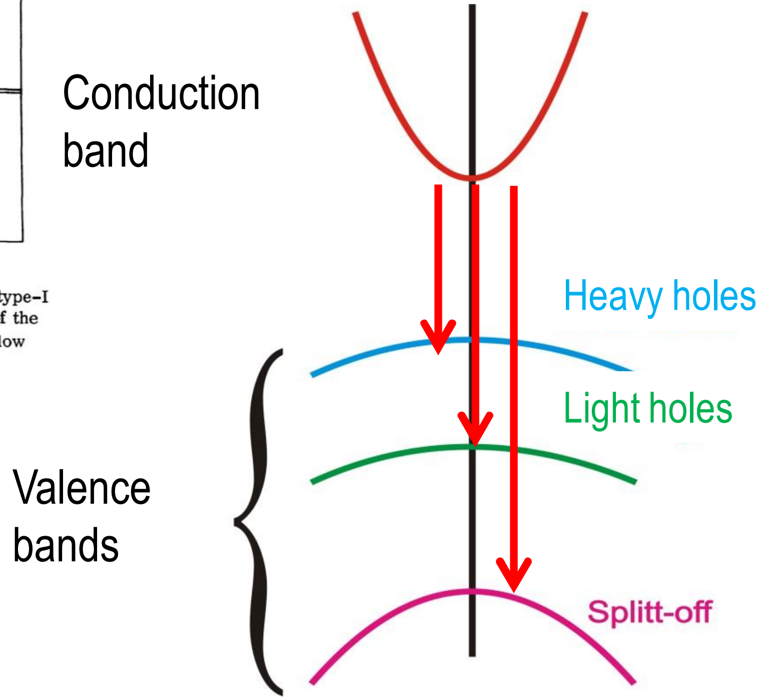


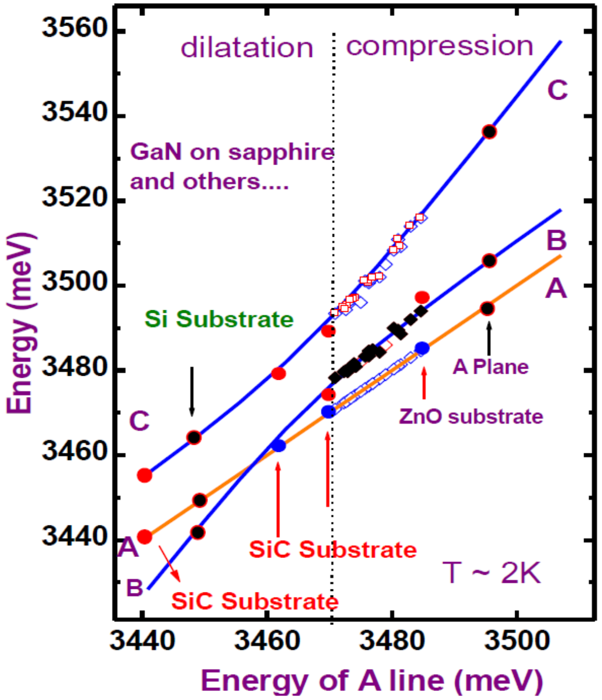
FIG. 5. Typical photoluminescence spectrum of type-I GaN at 1.6 K. The insert is a more detailed view of the strong high-energy peak near 3.468 eV, taken with low excitation intensity and high resolution.



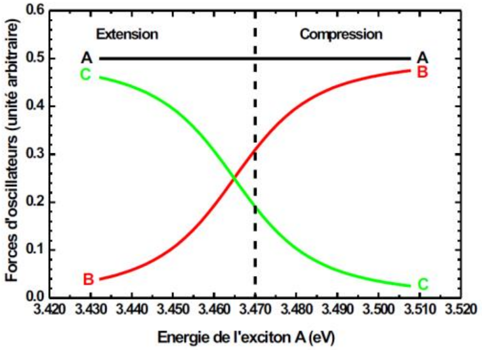
- Band gap measurement E_g=3,48 eV.
- Observation of excitonic transitions.
- Valence band structure.

R. Dingle, D.D.Sell,S.E.Stokowski and M.Ilegms, Phys. Rev. B, **4**, 1211 (1971)

Strain effect

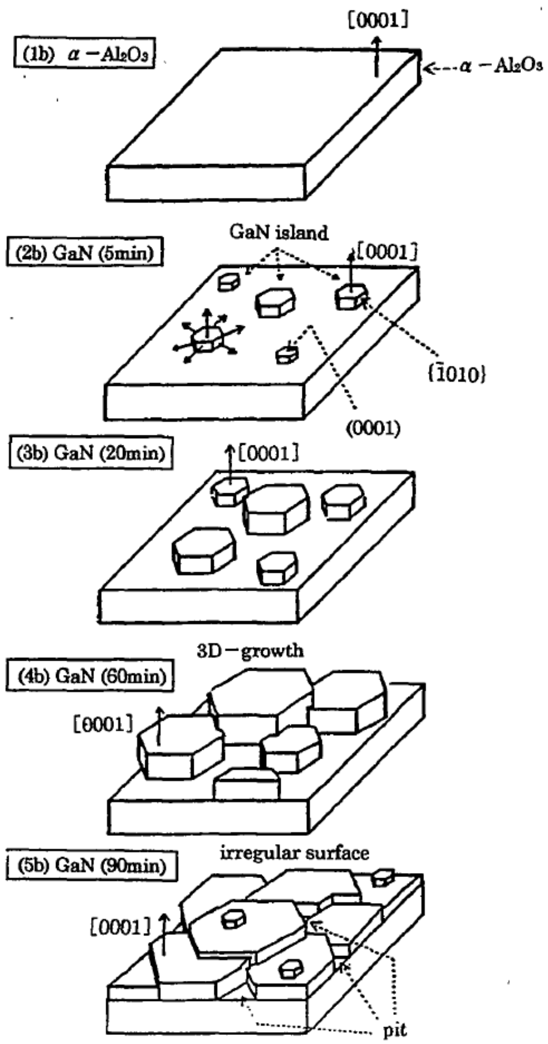


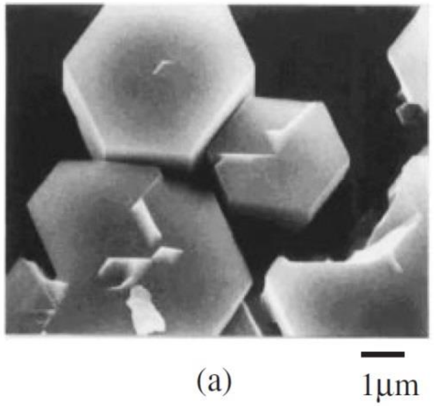
B. Gil, F. Hamdani and H. Morkoç Phys. Rev. B **54**, 7678 (1996)



- **Strain effect:**
  - Shifts the energy bands.
  - Modifies the coupling-strength between excitons and light.
  - Observable in optical experiments.

Growth of GaN by MOVPE



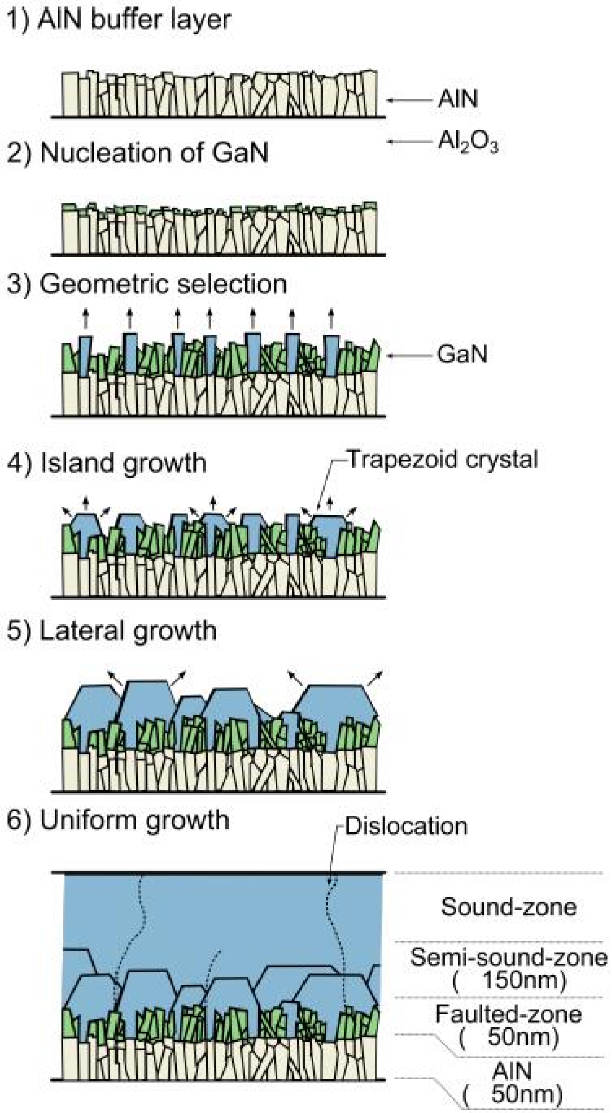


(a)

- **Hetero-epitaxy on sapphire (Al_2O_3)**
  - Island growth.
  - Rough polycrystalline layers, large density of structural defects.
  - Strong residual n-doping.

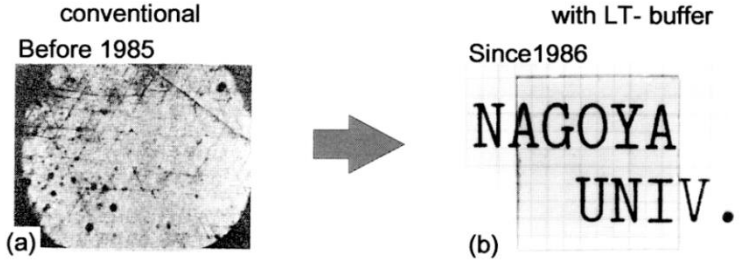
I. Akasaki and H. Amano, Jpn. J. Appl. Phys. **36** 5393 (1997)

Buffer layer



Benefits:

- ○ Supply of a high-density nucleation centers having the same orientation as the substrate.
- ○ Promotion of the lateral growth of the epitaxial film due to the decrease in interfacial free energy between the substrate and the epitaxial film.
- ○ Augmentation of grain size, diminution of dislocation density.



Many cracks, pits	⟶ Crack-free, pit-free
Rough surface	⟶ Specular surface
Dislocations > 10^{11} cm^{-2}	⟶ Dislocations 10^8~10^9 cm^{-2}
Electron mobility ~ 20-30 cm^2/Vs	⟶ Electron mobility ~ 700 cm^2/Vs
Weak luminescence	⟶ Intense luminescence (Sharp edge emission)

H. Amano, N. Sawaki, I. Akasaki I and Y. Toyoda, Appl. Phys. Lett. **48,** 353 (1986)

Control of p- doping

- Using AlN buffer layers, the residual donor density was drastically decreased.

  ⇨ *What about p-doping?*

- First attempts to incorporate p-impurities, such as Zn, showed no change in resistivity measurements.

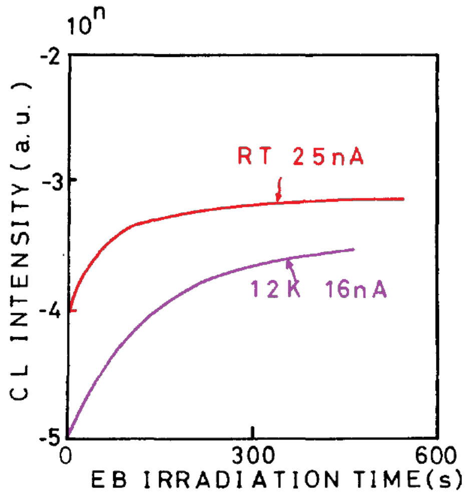
Doping activation

- Using AlN buffer layers, the residual donor density was drastically decreased.

  ⇨ *What about p-doping?*

- First attempts to incorporate p-impurities, such as Zn, showed no change in resistivity measurements.

- In 1987, H. Amano found that the intensity of Zn-related luminescence increases when Zn-doped GaN is irradiated with electron beam during CL measurement.



- Activation of Zn acceptors that were added during growth.

H. Amano, I. Akasaki, T. Kozawa, K. Hiramatsu, N. Sawaki, K. Ikeda and Y. Ishii, J. Lum. **40**&**41**, 121 (1988)
H. Amano, M. Kito, K. Hiramatsu and I. Akasaki, Jpn. J. Appl. Phys. 28, L2112 (1989)

Doping activation

- In 1992, S. Nakamura found that a thermal annealing at 800°C enables to reduce the resistivity of Mg-doped GaN layers.

Interpretation: acceptors are passivated by an hydrogen excess. Post-growth annealing breaks the Mg-H bound and activates the doping.

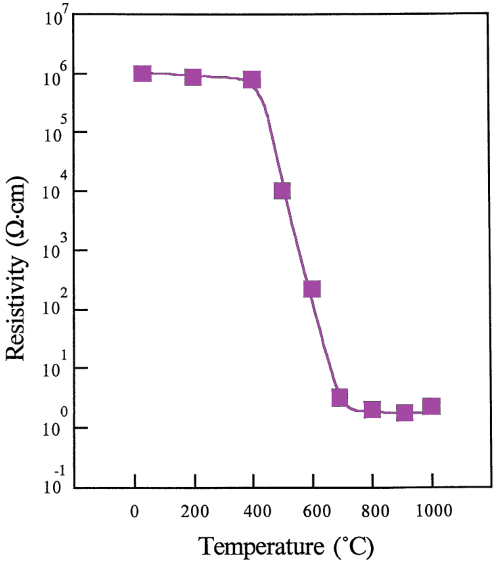


Fig. 1. Resistivity of Mg-doped GaN films as a function of annealing temperature.

S. Nakamura, T. Mukai, M.Senoh and N. Iwasa, Jpn. J. Appl. Phys. **31**, **L** 139-**L** 142 (1992)
S. Nakamura, N. Iwasa, M.Senoh and T. Mukai, Jpn. J. Appl. Phys. **31**, 1258-1266 (1992)

First GaN-based UV diode

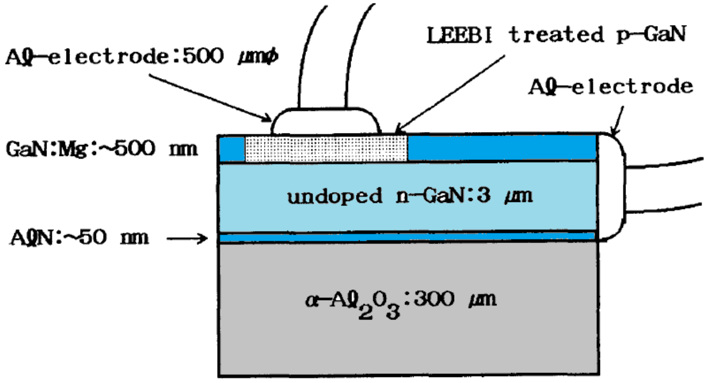
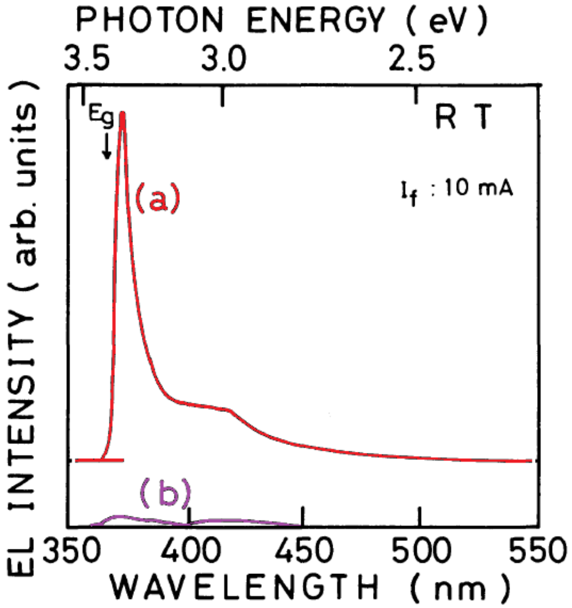


Fig. 3. The structure of the p-n junction LED.



- Built around a GaN:Si–GaN:Mg homojunction.
- Emission wavelength ~380 nm at room temperature.

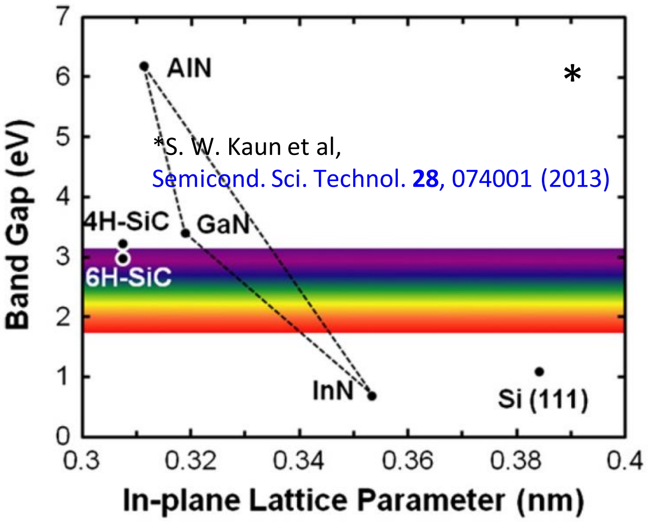
⇨ *Need to decrease the bandgap energy to achieve blue emission.*

H. Amano, M. Kito, K. Hiramatsu and I. Akasaki, Jpn. J. Appl. Phys. 28, L2112 (1989)

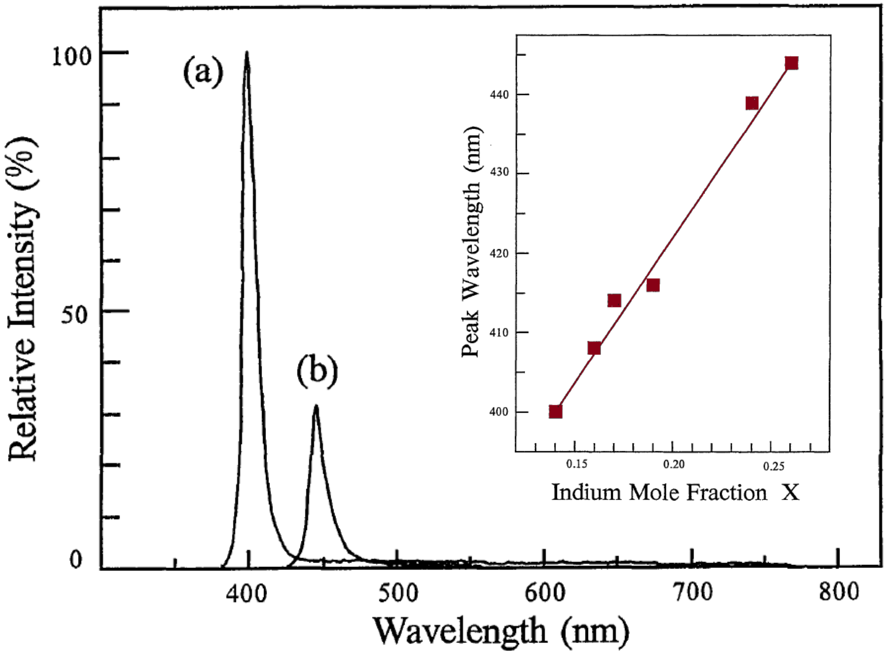
The blue diode

How blue can you get?

- Adding indium in GaN should shift the bandgap towards the visible range.
- A blue emission at ~ 450 nm needs to master the growth the alloy $In_xGa_{1-x}N$ for concentrations around 25-30%..

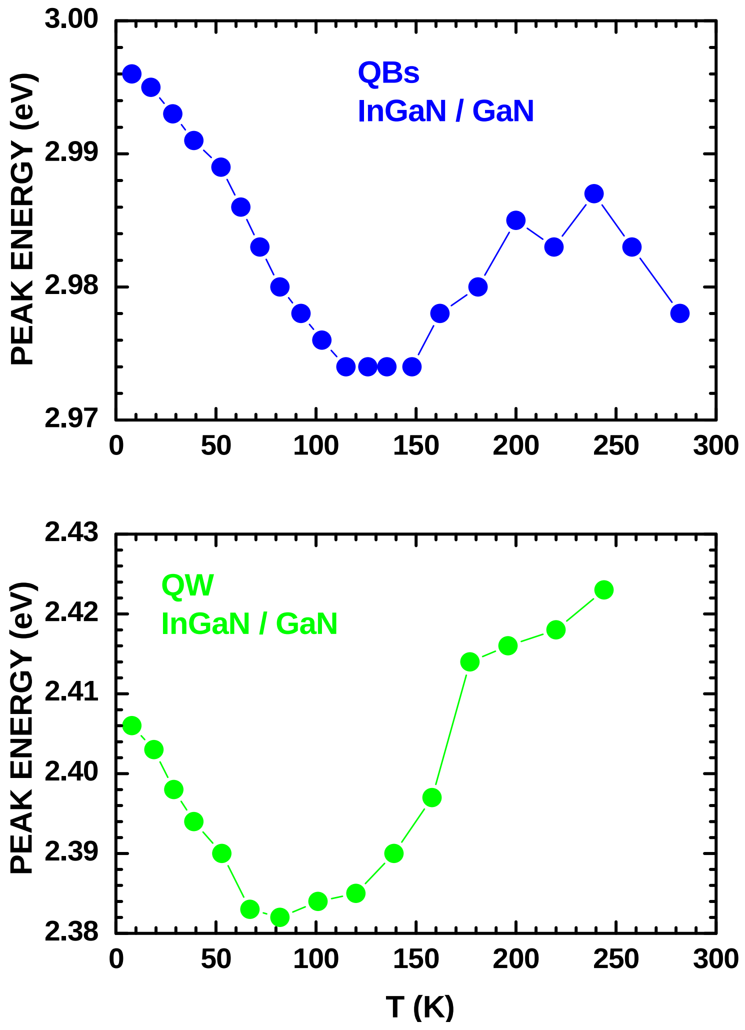


*S. W. Kaun et al, Semicond. Sci. Technol. **28**, 074001 (2013)

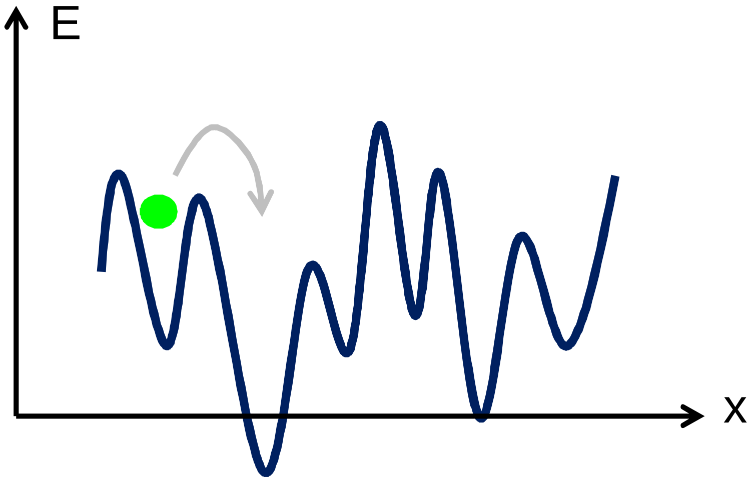


- In 1991, S. Nakamura develop a specific skill to growth InGaN using MOVPE.
- Strong photoluminescence whose wavelength depends on the indium fraction.

Advantage of InGaN



- The radiative efficiency of InGaN layers and quantum wells are not affected by dislocations.
- Localization of electron-hole pairs on potential fluctuations due to alloy disorder.
- Confirmed by the evolution of photoluminescence with T.



First blue diode

P–GaN/N–InGaN/N–GaN Double-Heterostructure Blue-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

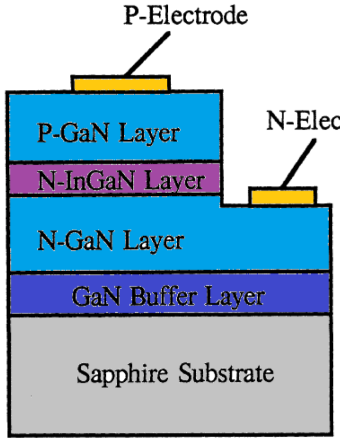


Fig. 1. The structure of the p-GaN/n-InGaN/n-GaN double-heterostructure blue LED.

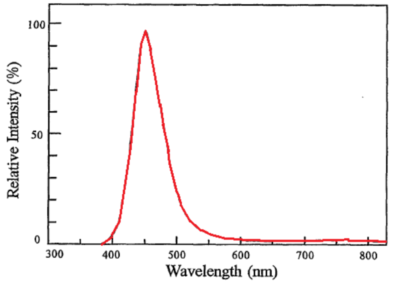


Fig. 5. Room-temperature photoluminescence spectrum of the top layer (Mg-doped p-type GaN layer) of the p-GaN/n-InGaN/n-GaN double-heterostructure after the 15 kV electron-beam irradiation treatment.

Quantum efficiency~0.2%

Candela-class high-brightness InGaN/AlGaN double-heterostructure blue-light-emitting diodes

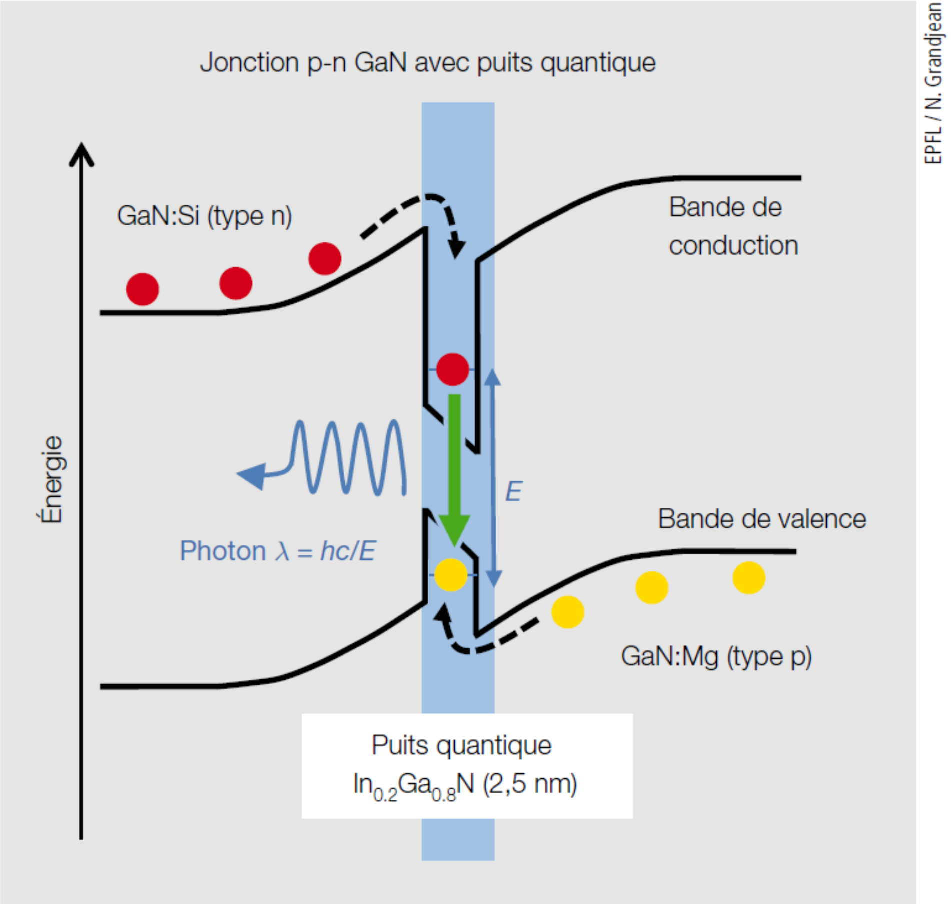
Shuji Nakamura, Takashi Mukai, and Masayuki Senoh
Department of Research and Development, Nichia Chemical Industries, Ltd., 491 Oka, Kaminaka, Anan, Tokushima 774, Japan

(Received 2 December 1993; accepted for publication 5 January 1994)

Quantum efficiency~3%

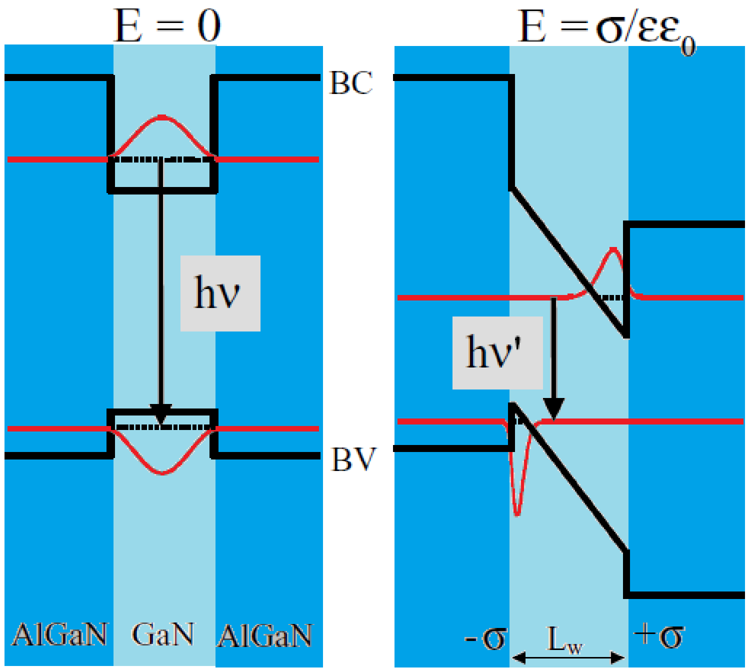
- ⇨ *Double heterostructure.*
- ⇨ *The next generation of components embeds quantum wells.*

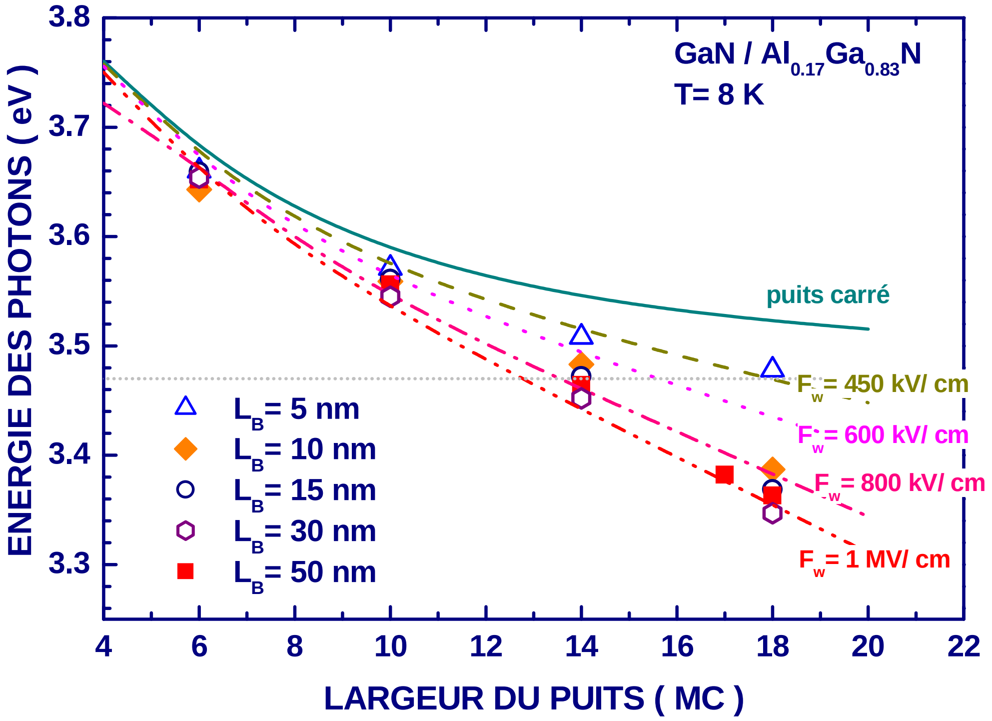
Quantum wells



EPFL / N. Grandjean

Quantum wells & quantum dots

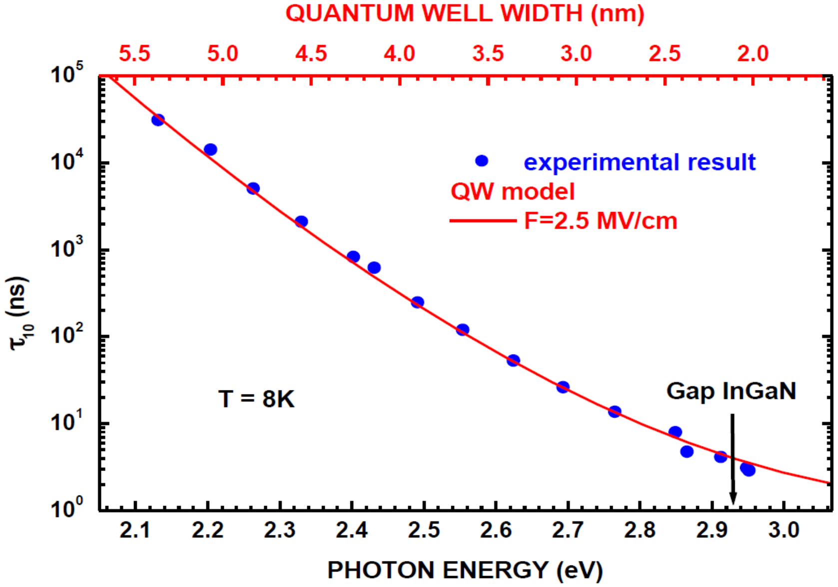


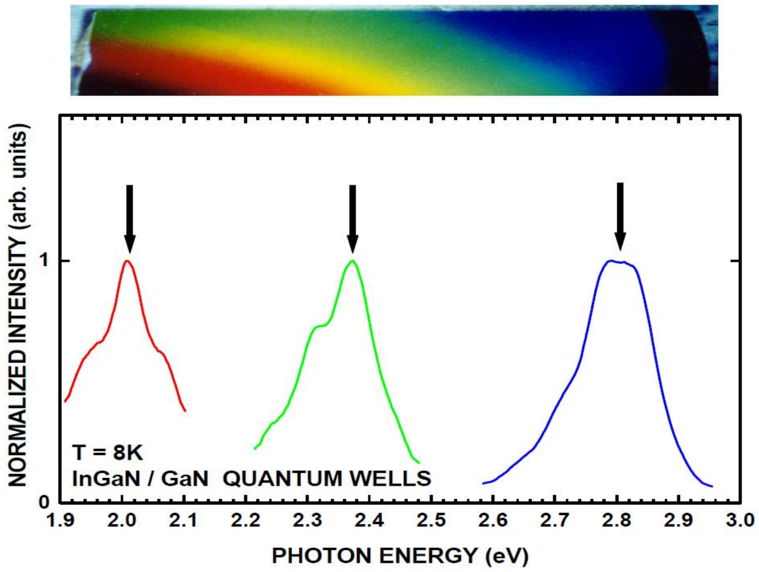


- Because of their wurtzite structure, nitride materials are piezoelectric.
- Existence of built in polarization fields in quantum wells that separate electrons and holes along the growth axis.

⇨ *Quantum confined Stark-effect.*

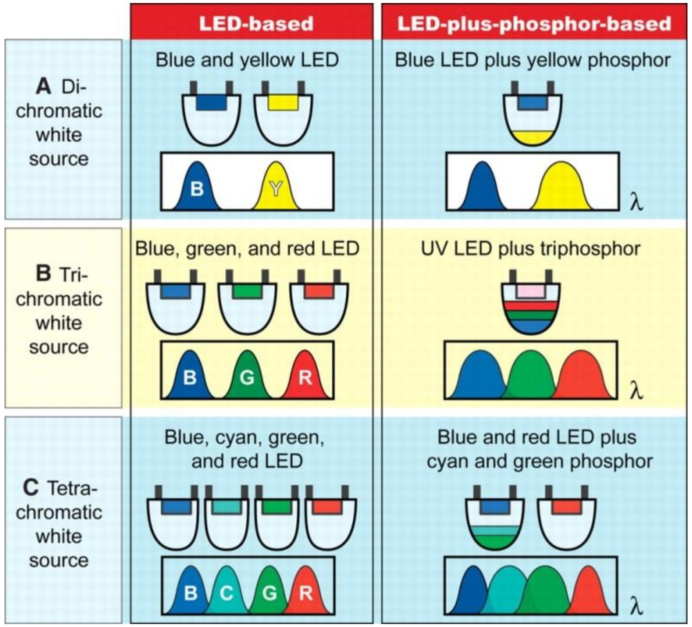
Effect of built-in electric field



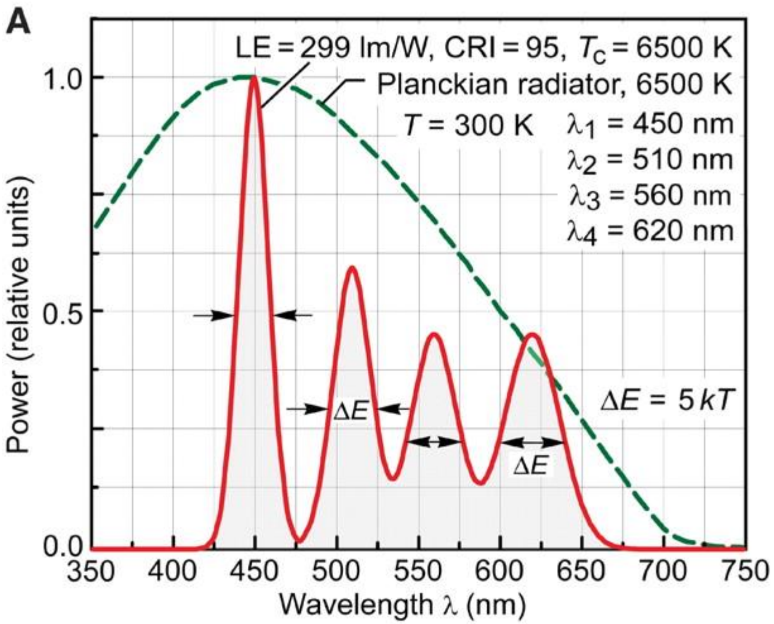


P. Lefebvre, A. Morel, M. Gallart, T. Taliercio, J. Allègre, B. Gil, H. Mathieu, B. Damilano, N. Grandjean and J. Massies, Appl. Phys. Lett. **78** (9), 1252-1254 (2001)

Improving the CRI



	LED-based	LED-plus-phosphor-based
A Di-chromatic white source	Blue and yellow LED	Blue LED plus yellow phosphor
B Tri-chromatic white source	Blue, green, and red LED	UV LED plus triphosphor
C Tetra-chromatic white source	Blue, cyan, green, and red LED	Blue and red LED plus cyan and green phosphor



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- Nitride based nanostructures are limited to light emission.
- Their wide bandgap and strong exciton binding energy makes them interesting for room temperature operation.
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⇨ *Here are some examples.*

Spin dynamics

Quantum dots

Quantum wells

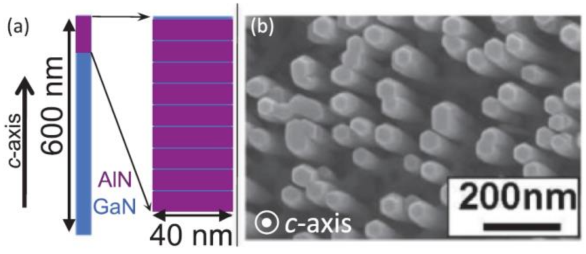
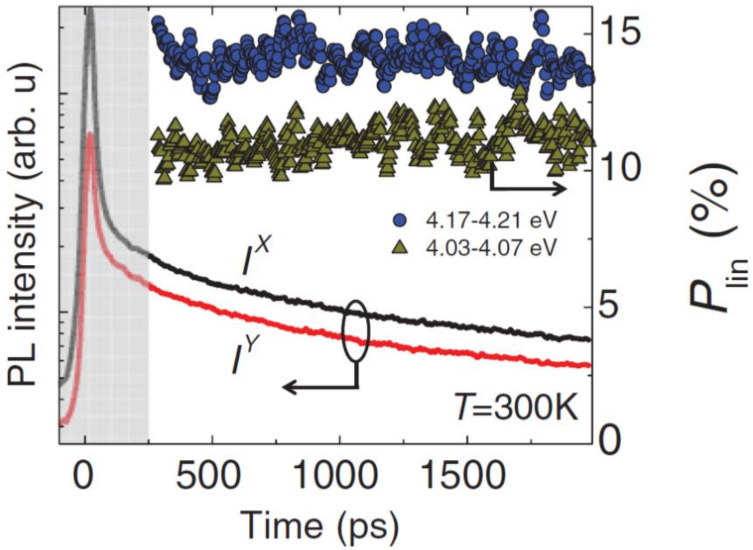
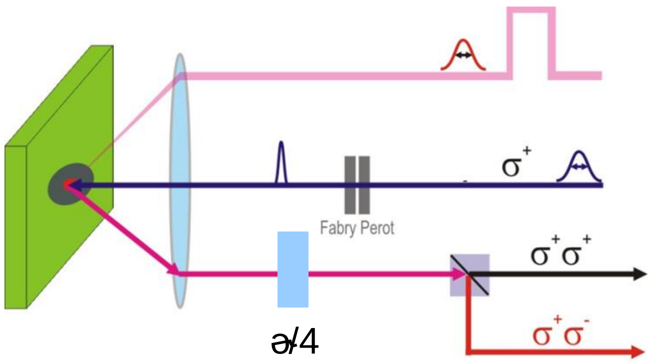
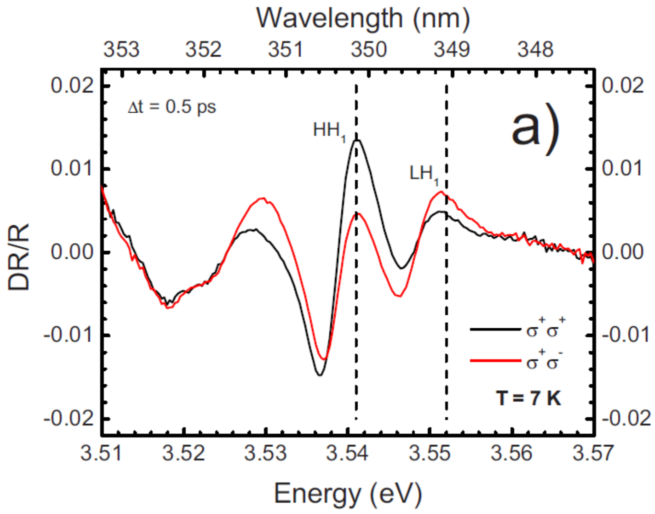


FIG. 1. (Color online) (a) Schematic representation of a single nanowire. (b) Top view SEM image of the nanowires.







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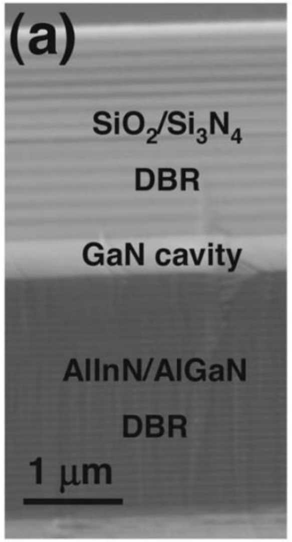
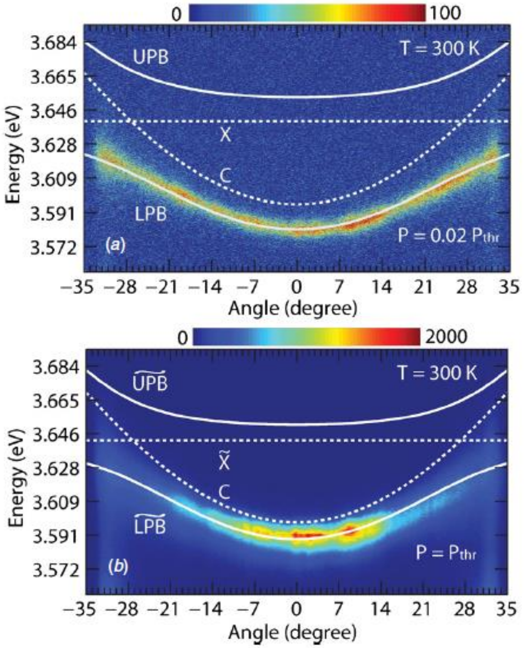
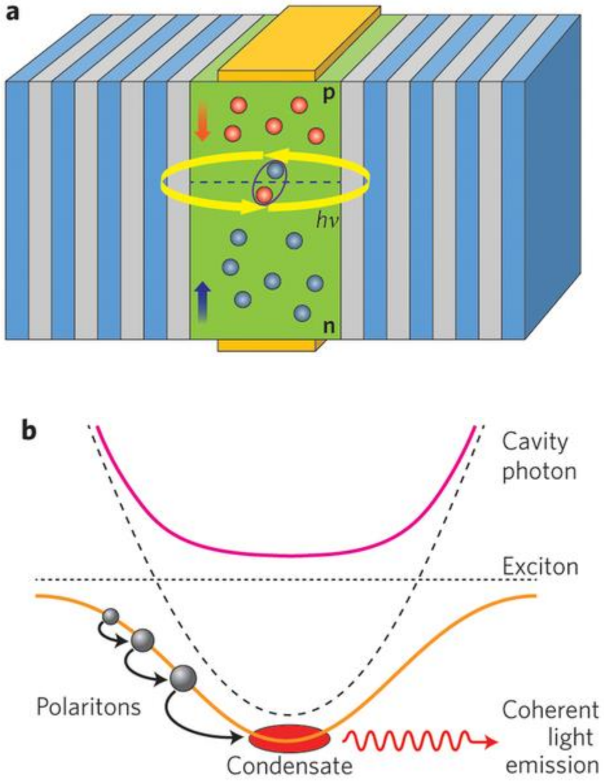
Polariton laser







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Single photon emitters

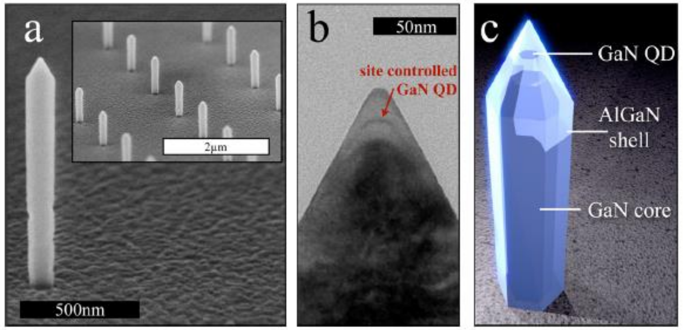

Figure 1. Images of site-controlled nanowire-QDs. (a) SEM image showing a single nanowire grown on a patterned SiO_2 substrate by selective area MOCVD. The inset shows an array of nanowires separated by 2 μm (a spacing of 20 μm was used for the optical experiments). (b) TEM image clearly showing the formation of a single QD near the tip of a single nanowire. (c) Schematic of a nanowire containing a single QD.

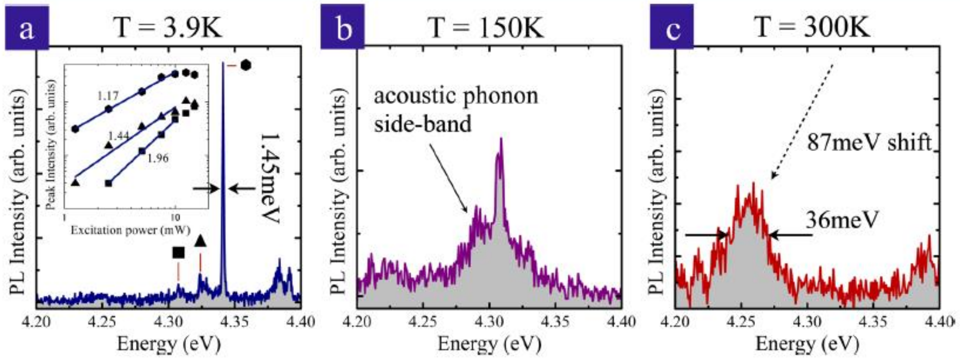

Figure 2. Emission spectra from a single nanowire-QD measured at 3.9 K (a), 150 K (b), and 300 K (c) (measured with excitation powers of 5 mW, 10 mW, and 15 mW, respectively). The inset in (a) shows the power dependence of the peak intensity of the three peaks labeled with a hexagon, triangle, and square, respectively.

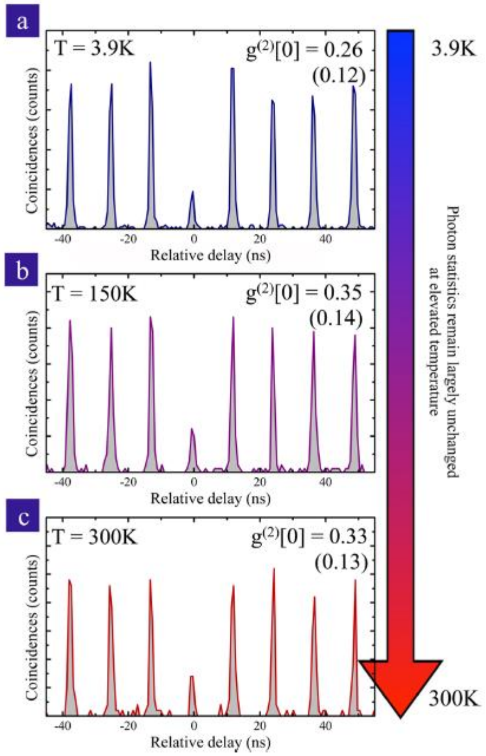

Figure 3. Coincidence counts histograms measured at 3.9 K (a), 150 K (b), and 300 K (c) from the same QD in Figure 2. The $g^{(2)}[0]$ values in parentheses are corrected for background and detector dark counts. The suppressed height of the peak at delay 0 is clear evidence of single photon emission, and the single photon statistics remain largely unaffected by temperature.

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Summary

- Focus on different white light sources and more specifically on light emitting diodes.
- Fundamentals of electronic and optical properties of semiconductors and their quantum heterostructures.
- Optics as a sensitive probe of matter.
- Story of the blue LED as an illustration of different technological steps to be taken.

Summary

- The three laureates demonstrated intuition and perseverance that lead to a revolution in lighting and light display.
- The mass marketing of nitride based lighting devices did not kill the fundamental research related to these materials.
- The success of the blue diode created a dynamics that brought a class of materials to maturity and created new perspectives in fundamental and applied research.