Optical Characterization of nanostructures emitting at short λs and in the DUV

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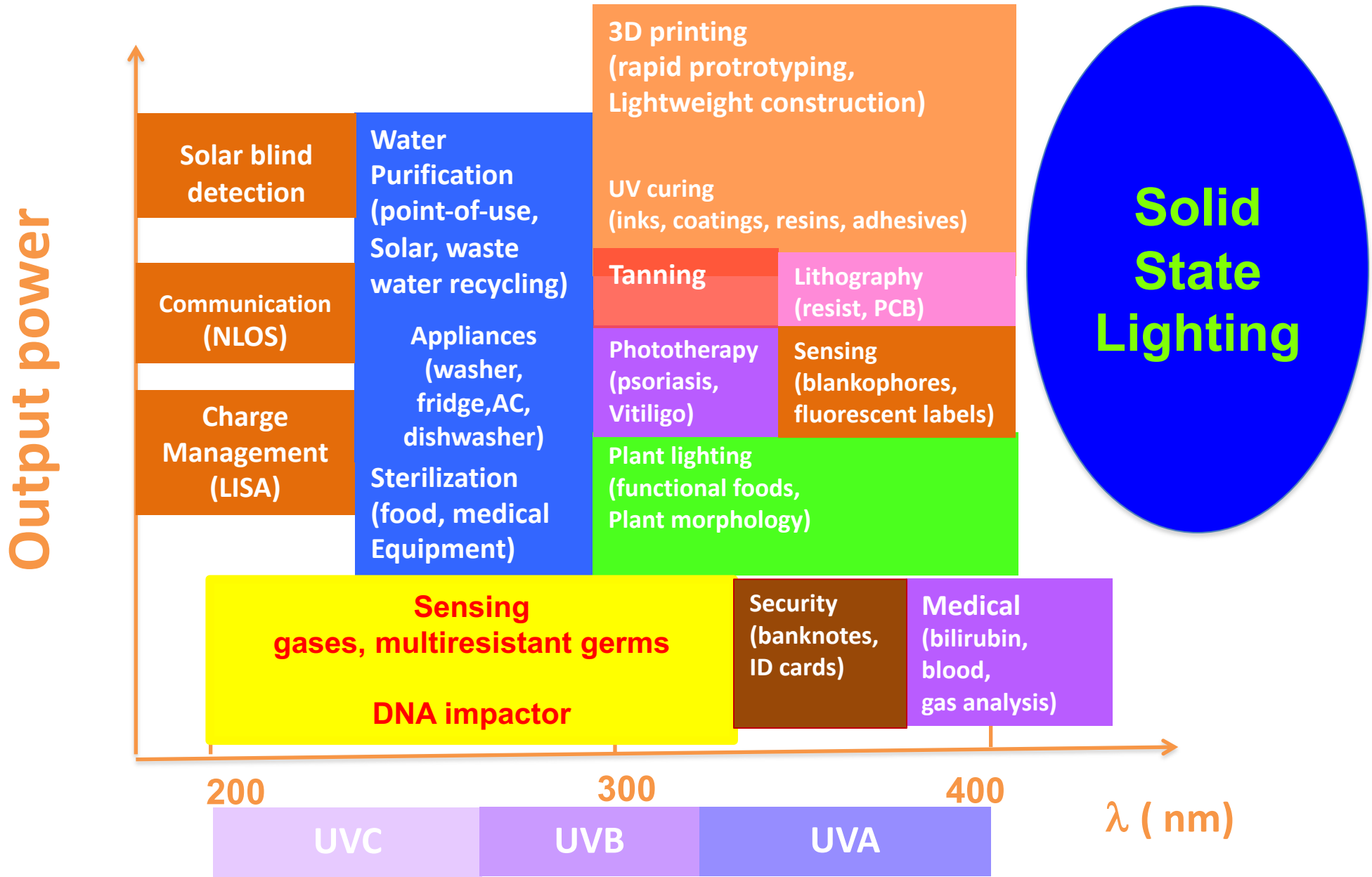
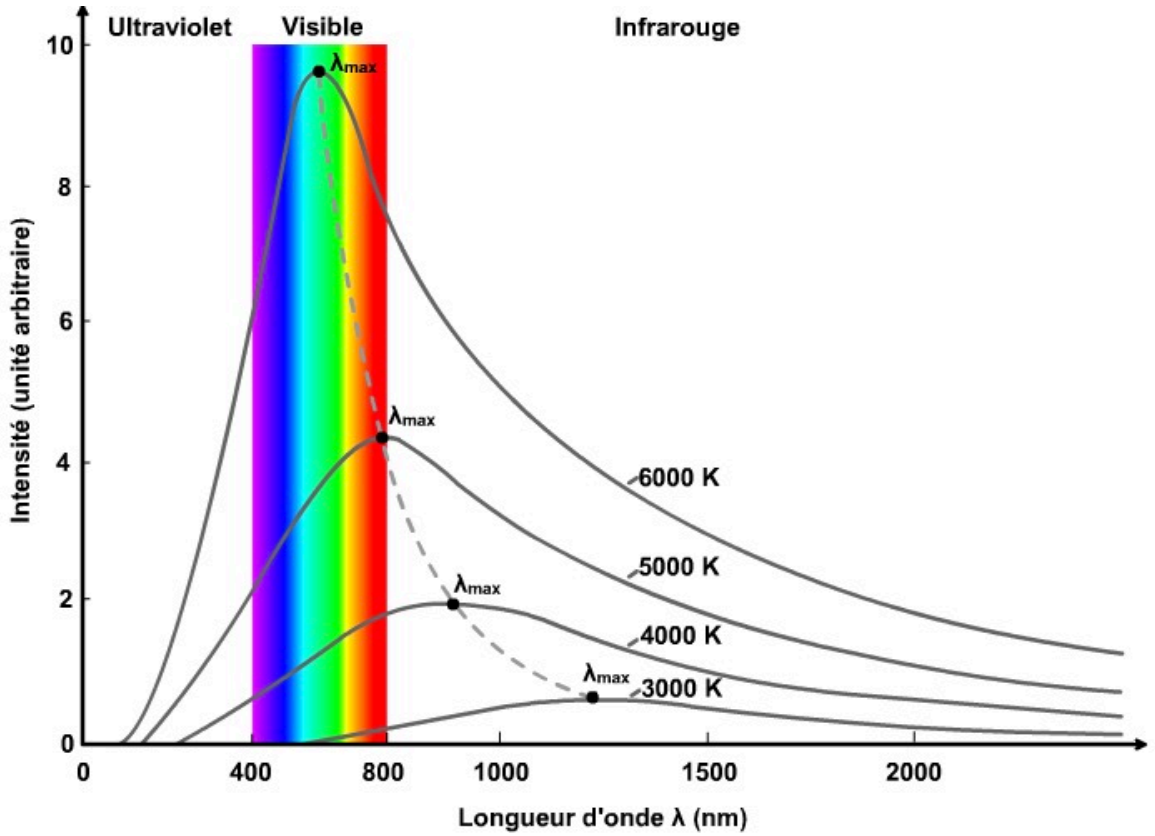
Specific thanks to :
A smart crystal grower, Julien Brault, DR CNRS
A smart crystal grower, B.Damilano, CR CNRS
A smart bulk crystal grower, Jim Edgar, KSU
A good friend: Guillaume Cassabois, PU UM
A handsome engineer: Pierre Valvin, IR CNRS
Many colleagues and students
The organisers

Why we need short λs light emitters/absorbers ?

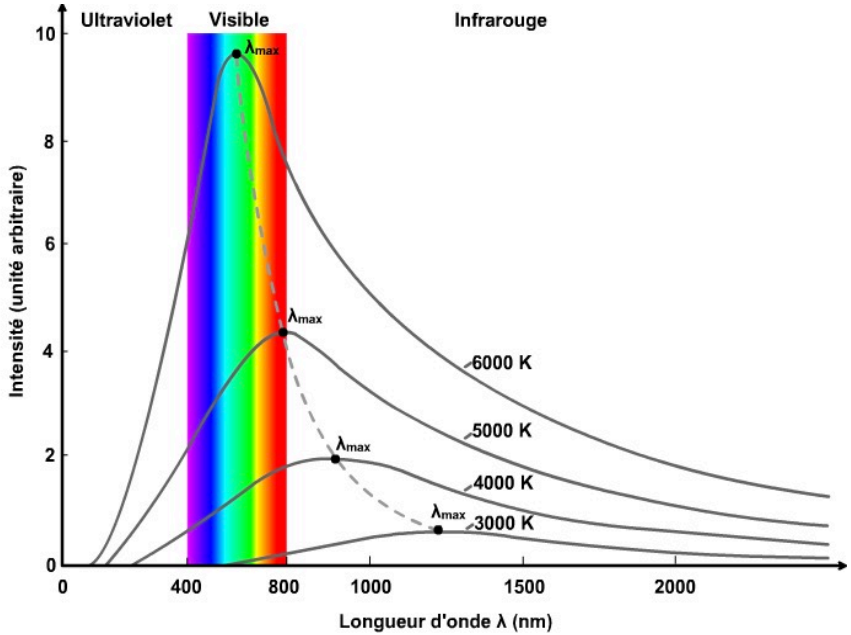
After Michael Kneissl's book

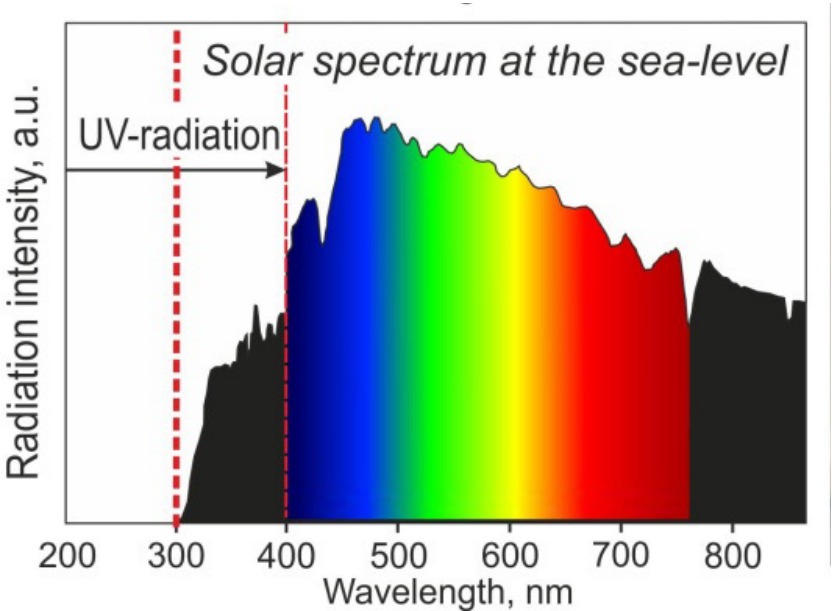


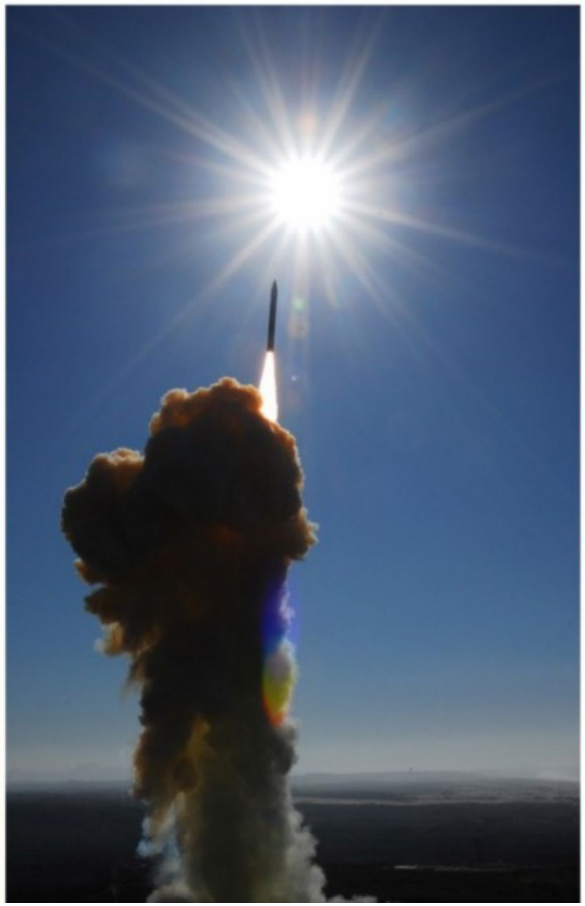
What about extending what is done in IR and *vis* in the UV for instance?

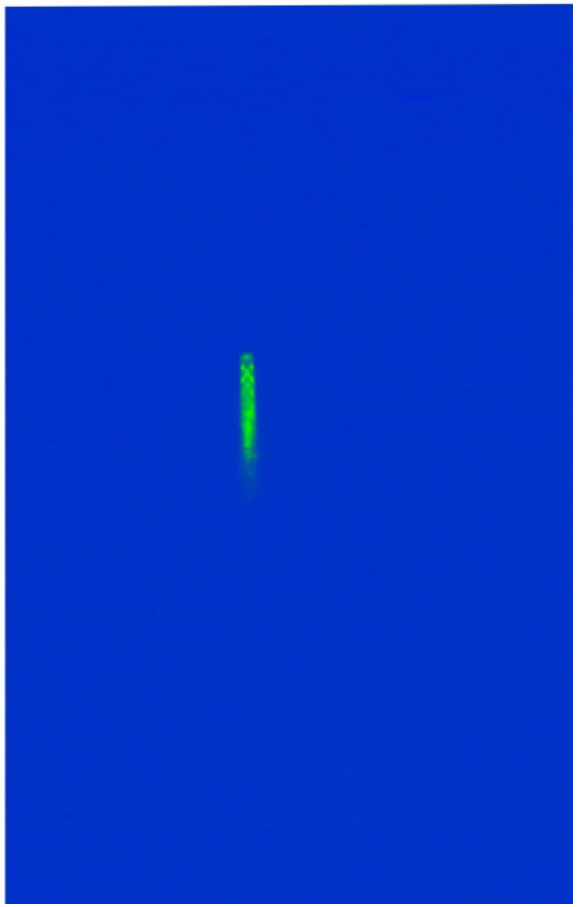


Solar Blind Flame Detection



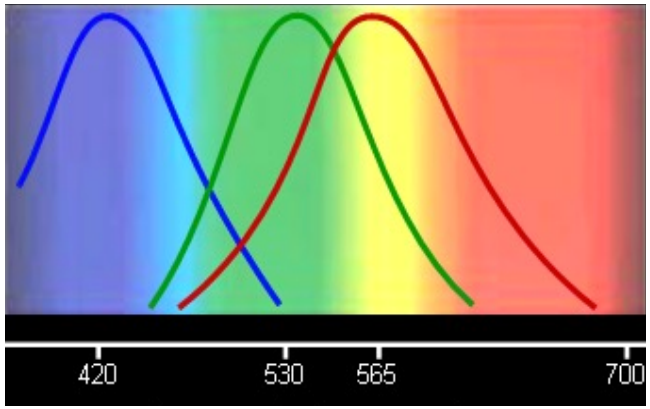


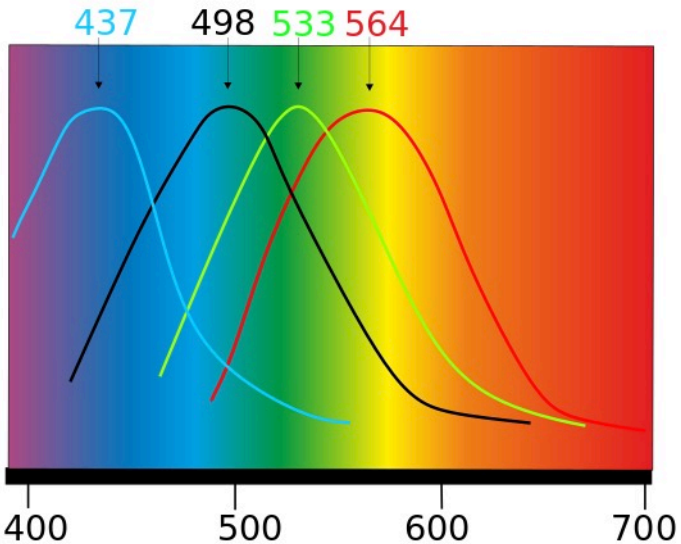




Quantum devices for multiwavelength imaging in hyper-degraded atmosphere

Analogy with the human vision *mutatis mutandis*



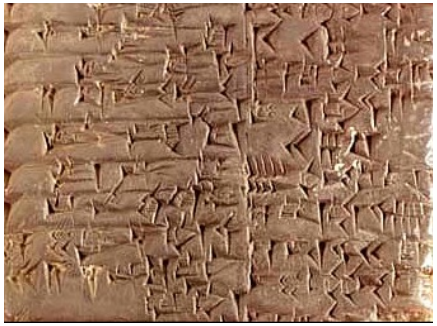


Multiwavelength imaging for probing scattering centres of different sizes

- UV
- Visible
- Middle Infrared (QCLs)
- THz
- Millimetric and centimetric waves

Classical cryptography, advanced encoding

Mesopotamia



Double or triple encryption:

- Dialect
- Secret encoding
- Almost nobody knows

how to read!

Nabuchodonosor

The same as left but message
is now hidden under the hair

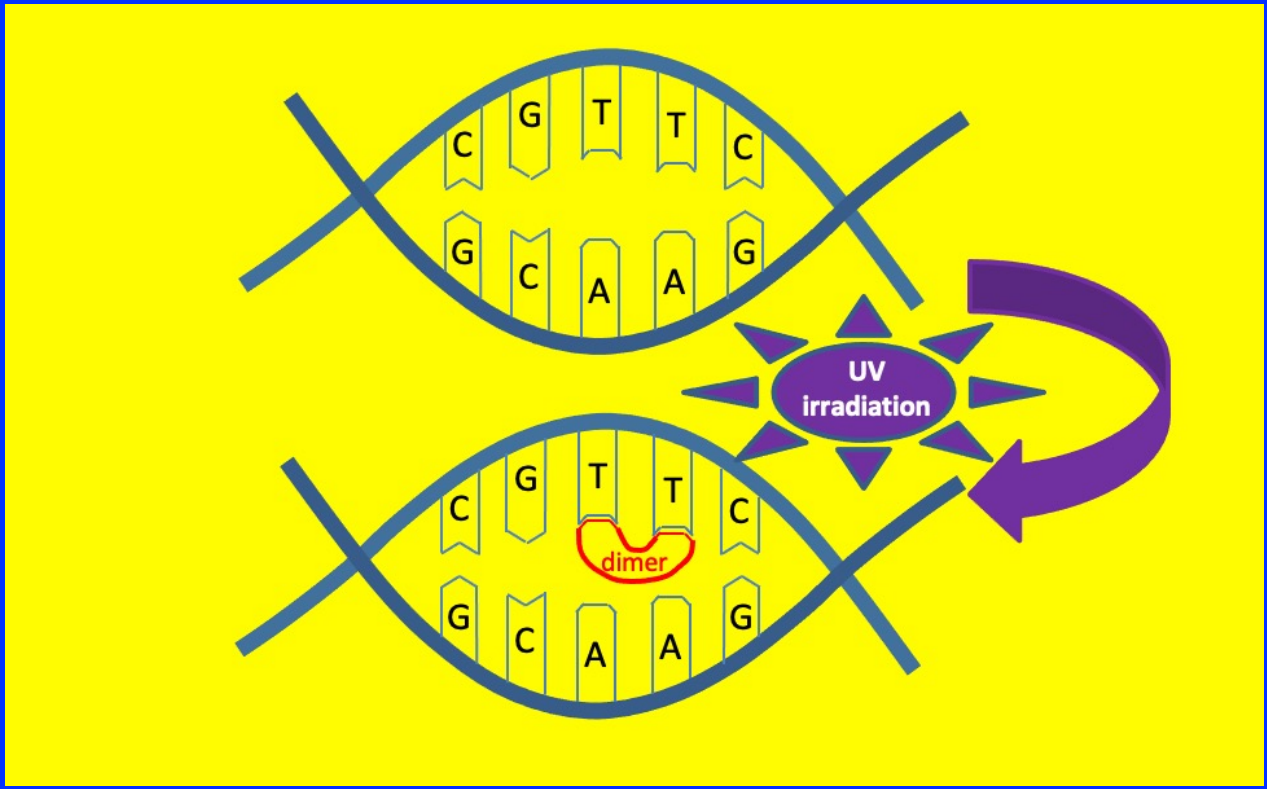
Enigma

Informatics

Encoding can be broken by computer assistance

Math, technology, encoding methods improve, code breaking methods get into sophistication

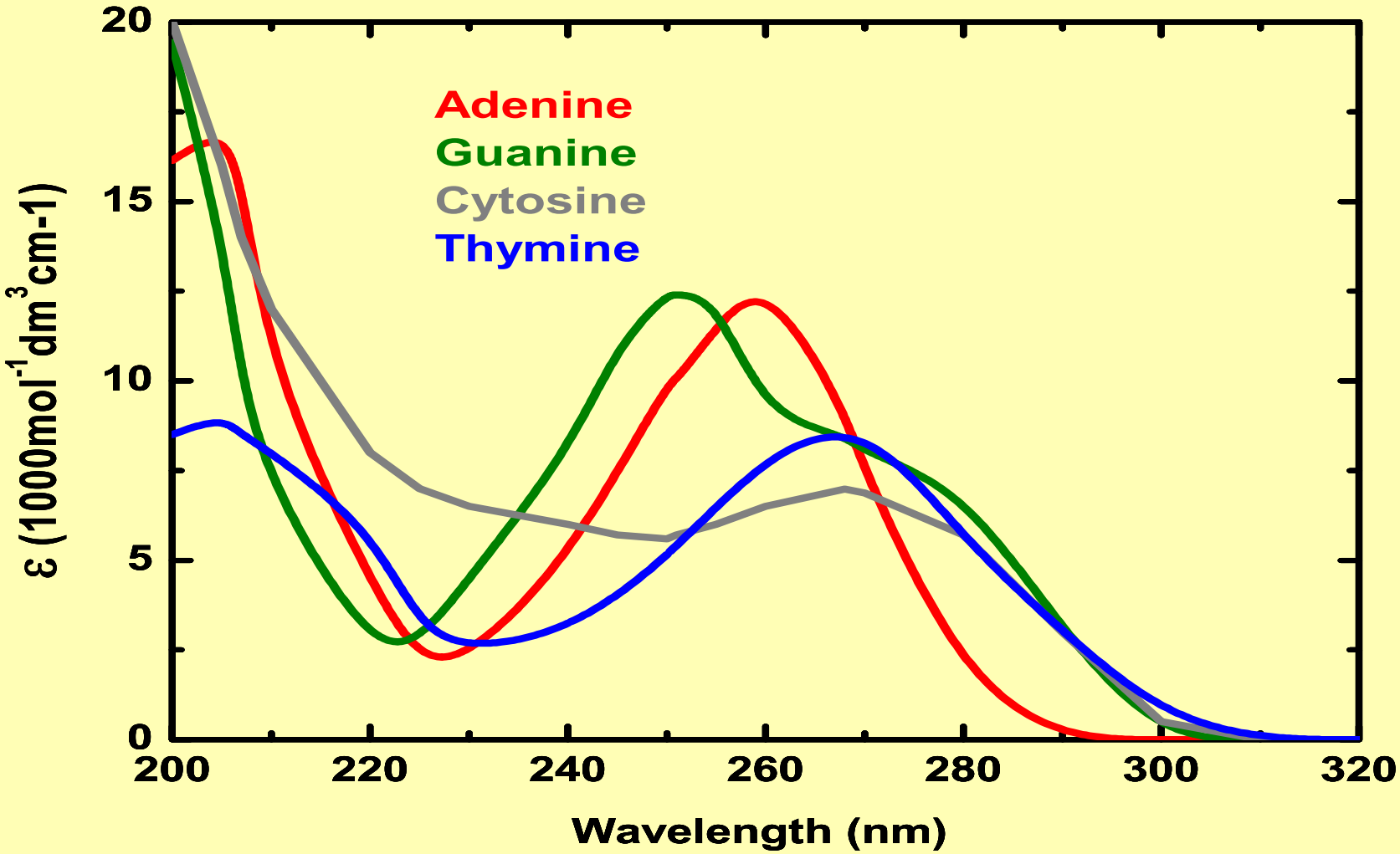
Dimerisation of Pyrimidines



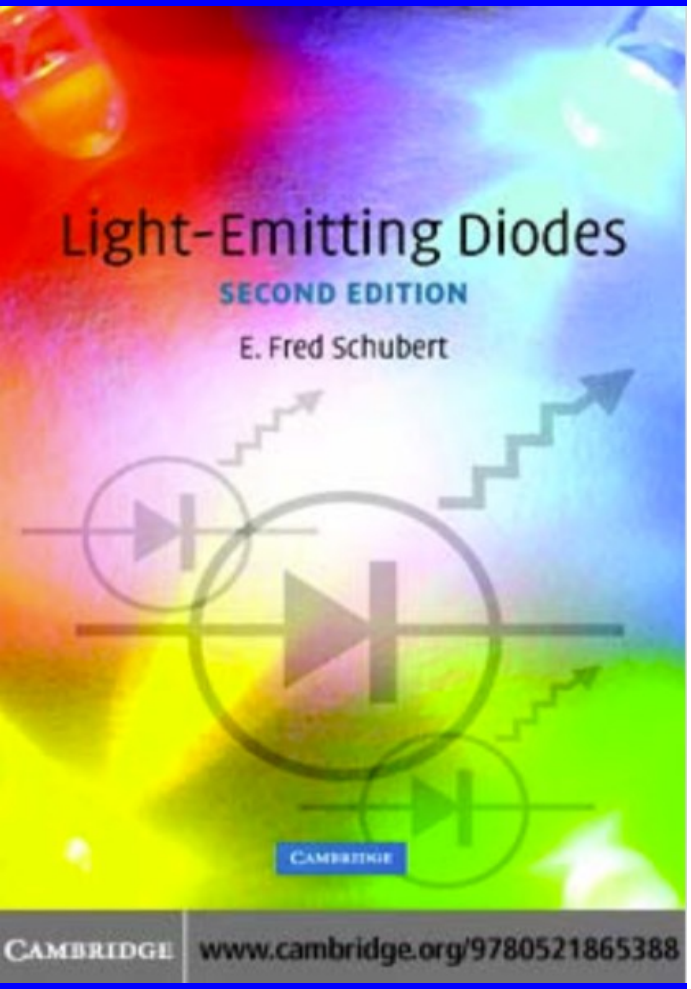
Thymine and Cytosine are the most reactive to UV, leading to formation of dimers blocking the NRA/DNA structure and thus its replication.

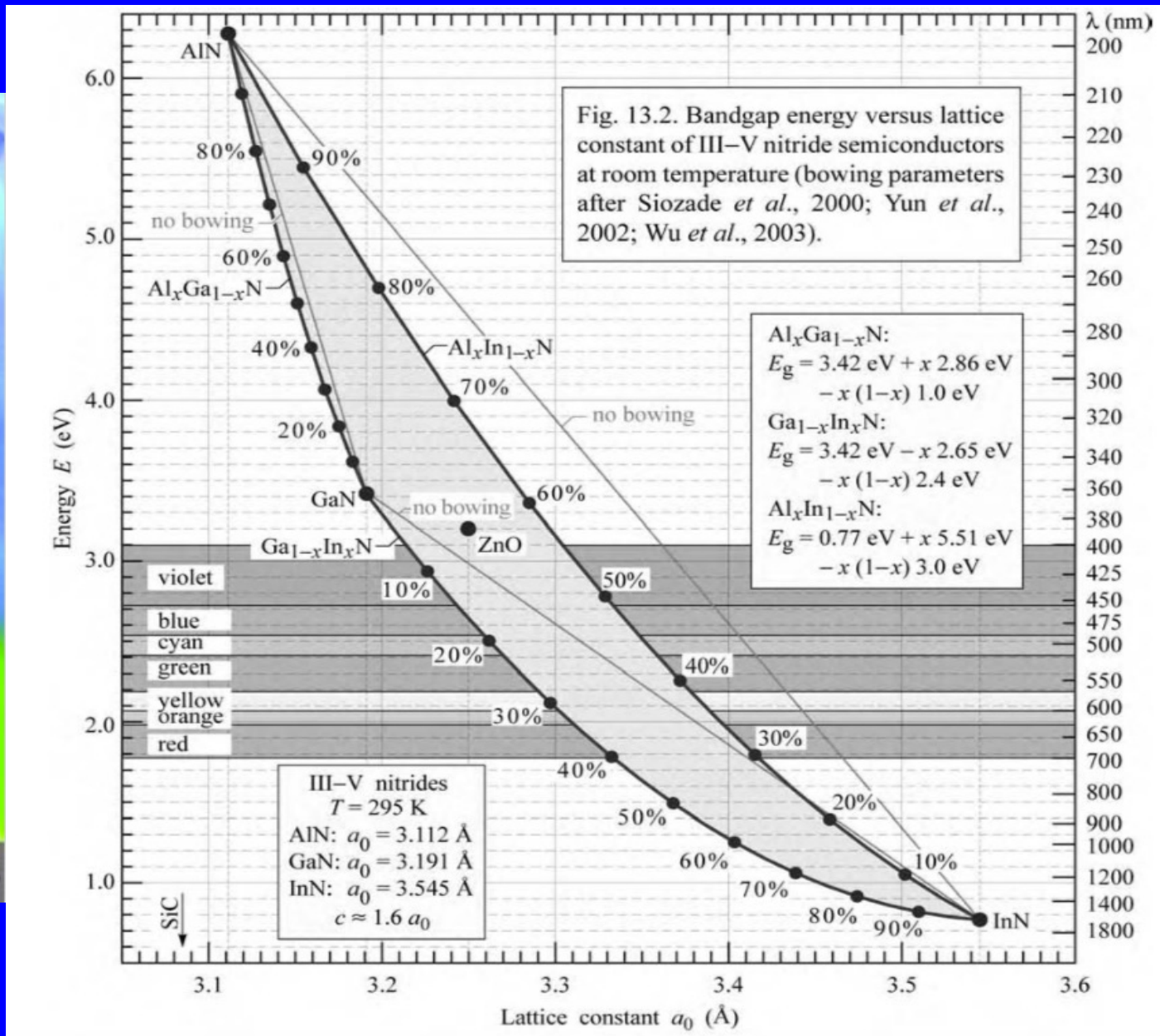
A. Rodger UV Absorbance Spectroscopy of Biological Macromolecules-in Encyclopedia of Biophysics -Gordon C. K. Roberts Ed. Heidelberg, New York Dordrecht London, Springer, 2013, pp. 2714–2718. https://doi.org/10.1007/978-3-642- 16712-6.

More about Ultra Violet light and the molecules of life

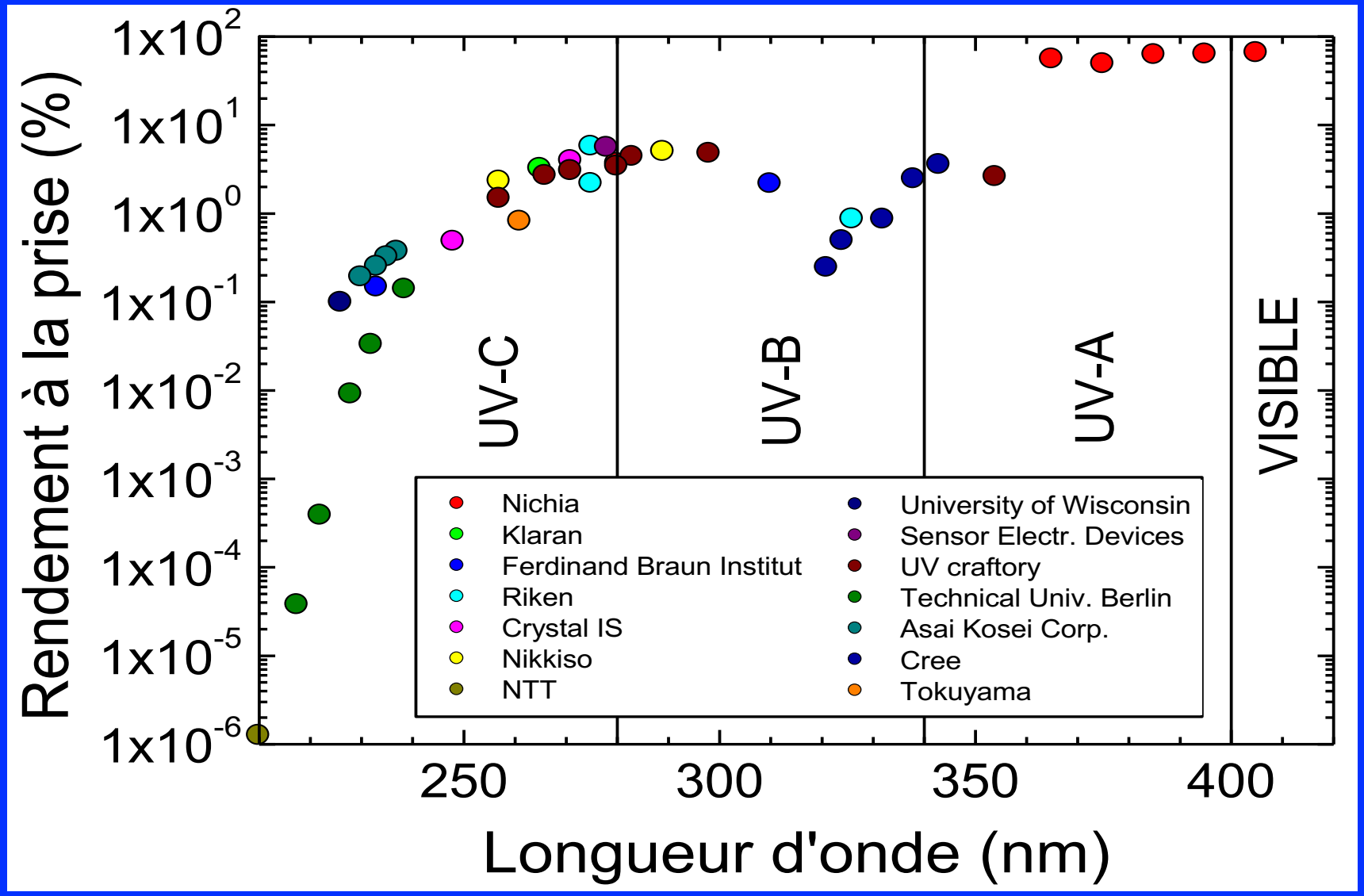


The GaN-AlN option



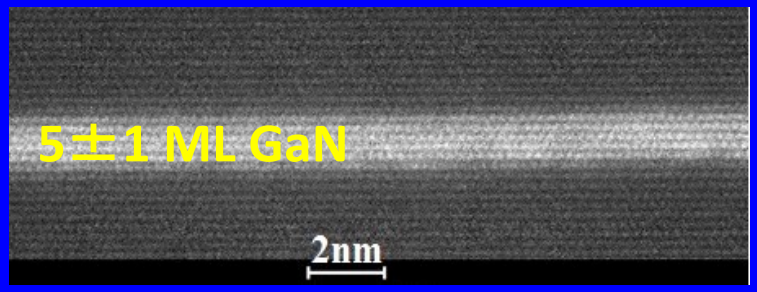


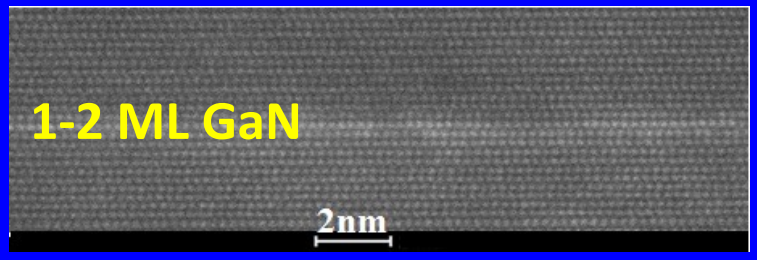
Wall plug efficiency of some DUV emitters against wavelengths of emission

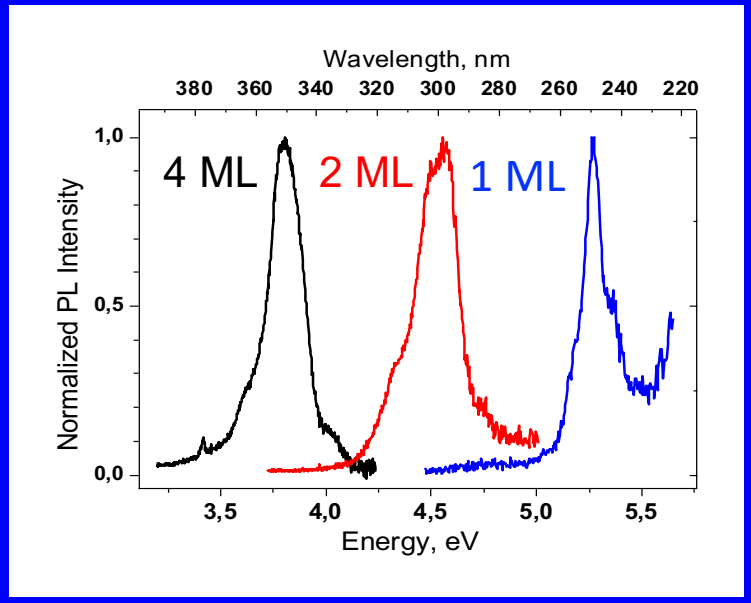


The GaN-AlN ultimate 2D stacking saturates at ≈ 235nm

Alexey Toropov and his colleagues @ IOFFE

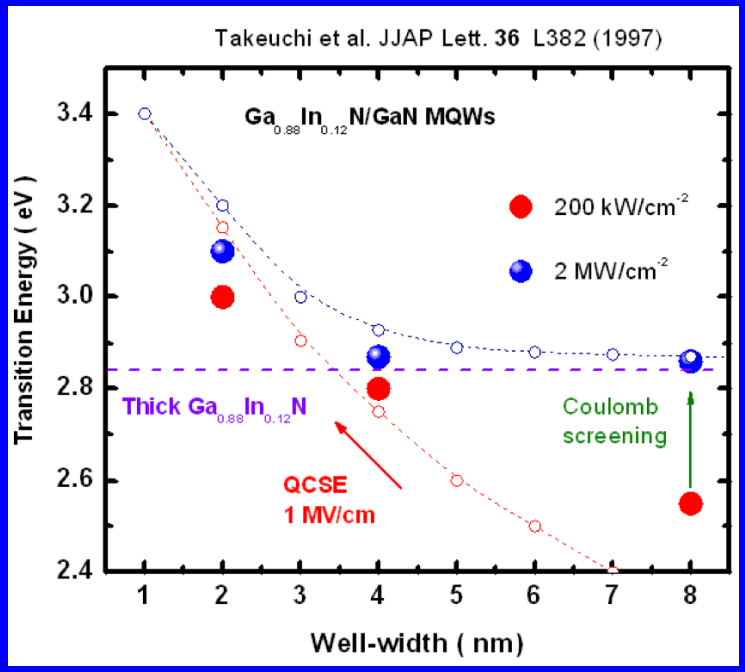






Toropov et al. Nano Letters (Letter) **20**, 158 (2020)

новое - это хорошо забытое старое?



Understanding The PL(T) through the whole series from 1 to 4 ML requires to describe the internal structure of the exciton and permits to reveal short range spin exchange interaction terms and energy harvesting from the low energy forbidden triplet state towards the higher energy singlet state.

Julien Brault: Reducing the wavelength using AlGaN or BN

- AlGaN/AlN QWs
- $Al_xGa_{1-x}N$/ $Al_yGa_{1-y}N$ QDs
- AlGaN/AlN QDs
- $Al_xGa_{1-x}N$/ $Al_yGa_{1-y}N$ QDs

$x < y$

Taking advantage of a profitable knowledge coming from InGaN-related experiences

BN could contribute to the writing the 100-year history of light emitted diode (LED)…..

O. V. Losev
(Soviet Union)

1927

SiC

Invented
the LED

N. Holonyak
(USA)

1962

(AlGaIn)As

Z. Alferov
(Russia)

197Xs-2000

Heterostructures

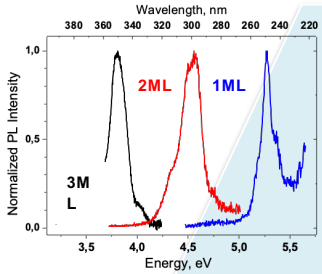
I.Akasaki,
H. Amano,
S.Nakamura

1989-2014

(AlGaIn)N

GaN/AlN
240 nm

BN ?



Experimental problems

- No cheap lasers at these wavelengths
- Cathodoluminescence (electron beam) is a serious but very expensive competitor
- There also exists UV emitting (expensive lamps) for exciting the electronic states of the crystals
- Use of mirrors instead of lens is mandatory
- Niche activity, not so many offers for optical devices in catalogs, compared with what is proposed for the visible or IR
- Absorption of UV radiations may be a problem (working under N_2 atmosphere)
- Severe working conditions have to be kept under constant control:

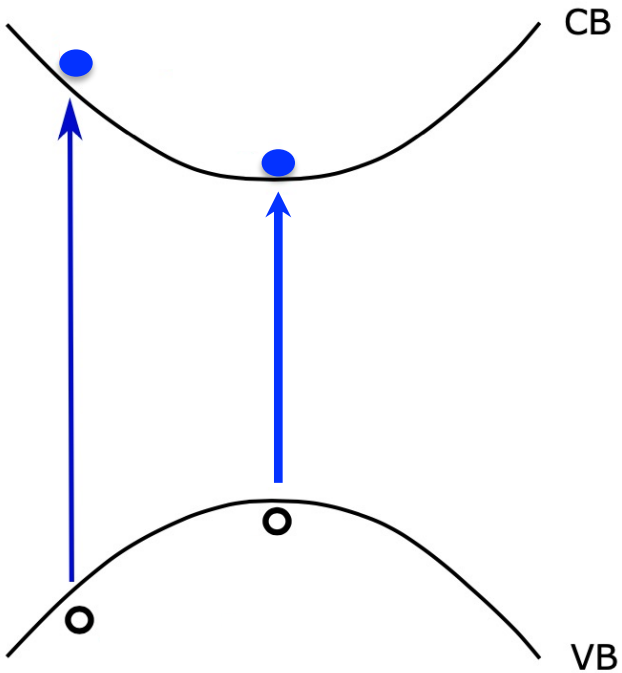
-Formation of O_3 control of O_2/N_2 composition when using an N2 flux to get rid of absorption,…

- Care with UV radiation (whatever the λ is, one has to be careful with lasers)
- Mandatory to use specific software to optimize the design of the set-up

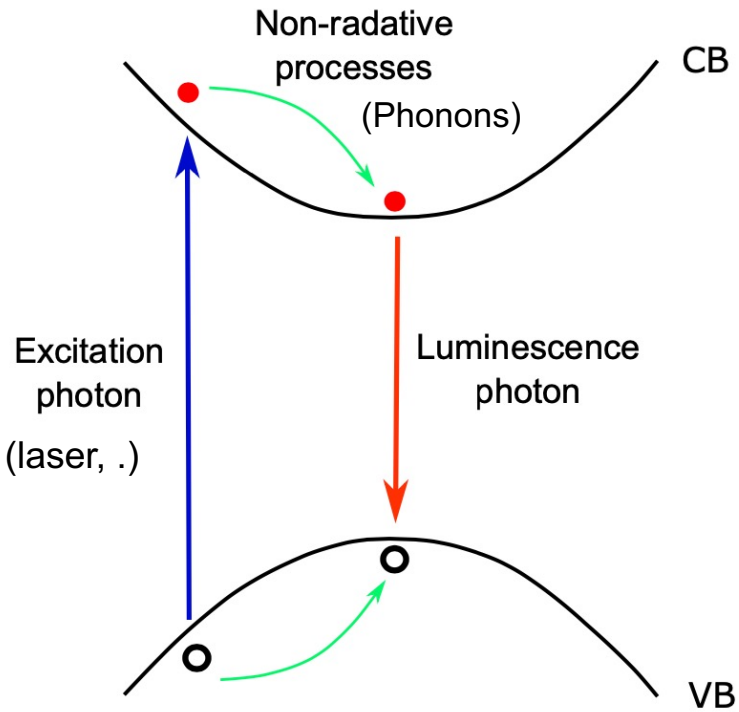
(Zemax ® for instance)

- A good CNRS-like neighbouring workshop for conceiving specific tools
- Optics is a very expensive characterization techniques

Reflectance and photoluminescence spectroscopies

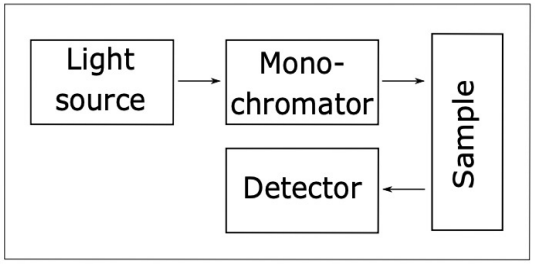


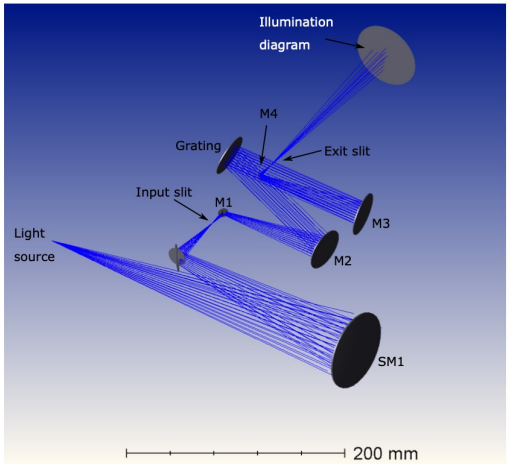
Vertical transition in K-space
Probes the dielectric function
Intensity ruled by selection rules and the joint density of states

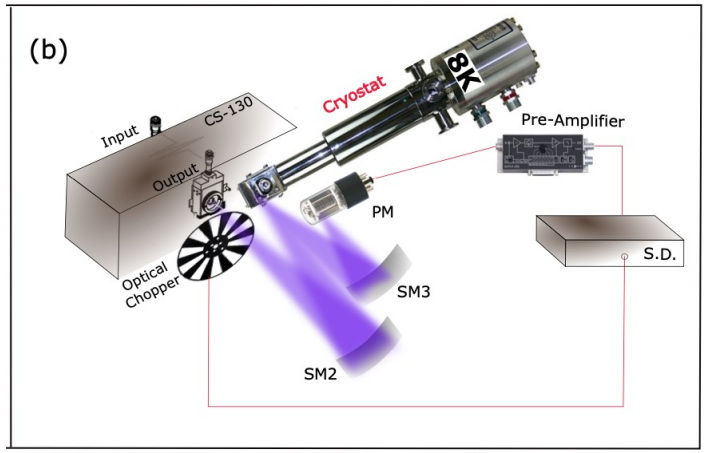


Thermalization process
Probes intrinsic and extrinsic states

Principle of reflectance (incl. in the UV range)







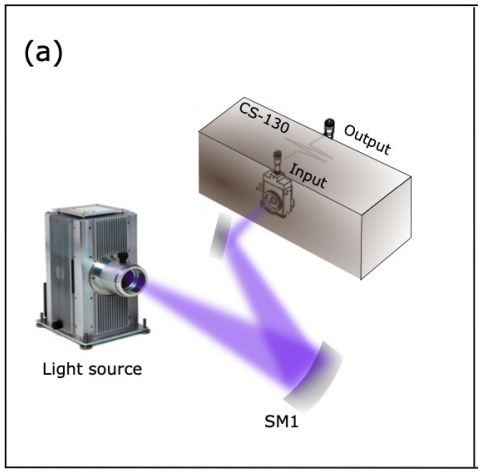


Figure 2.6: Simulation of our experiment using Zemax: The input and output slits of the monochromator are presented by two converging points. The dispersion of light by the monochromator is simulated by 3 mirrors and one grating with M2 being the one collimating the beam and M3 the one focusing the beam and giving the image at the exit plane; M4 is a flat mirror.

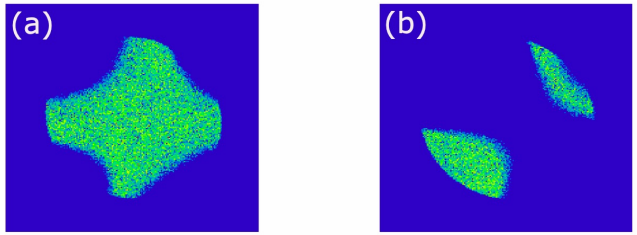


Figure 2.7: Illumination diagrams after the exit slit of the monochromator simulated using Zemax: (a) result of the simulation for slit width of about $30\mu m$; (b) result obtained for slit width of $150\mu m$ and by adding to the previous simulation a tiny off-center misalignment at the input slit of the monochromator.

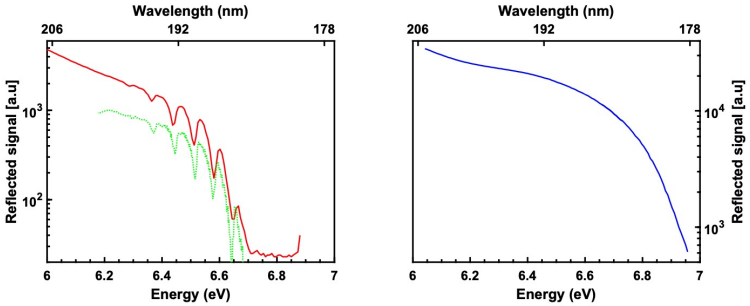


Figure 2.8: Intensity of the reflected light in the spectral range of the Schumann–Runge bands plotted in semi-log scale: (a) In red solid line is the spectrum measured by our setup from a reference sample, using a deuterium lamp and under ambient conditions; in green dotted line is plotted the spectrum of reflectance showing the Schumann-Runge bands. (b) same as solid line (a) under nitrogen-gas conditions.

Principle of cwPL and TRPL

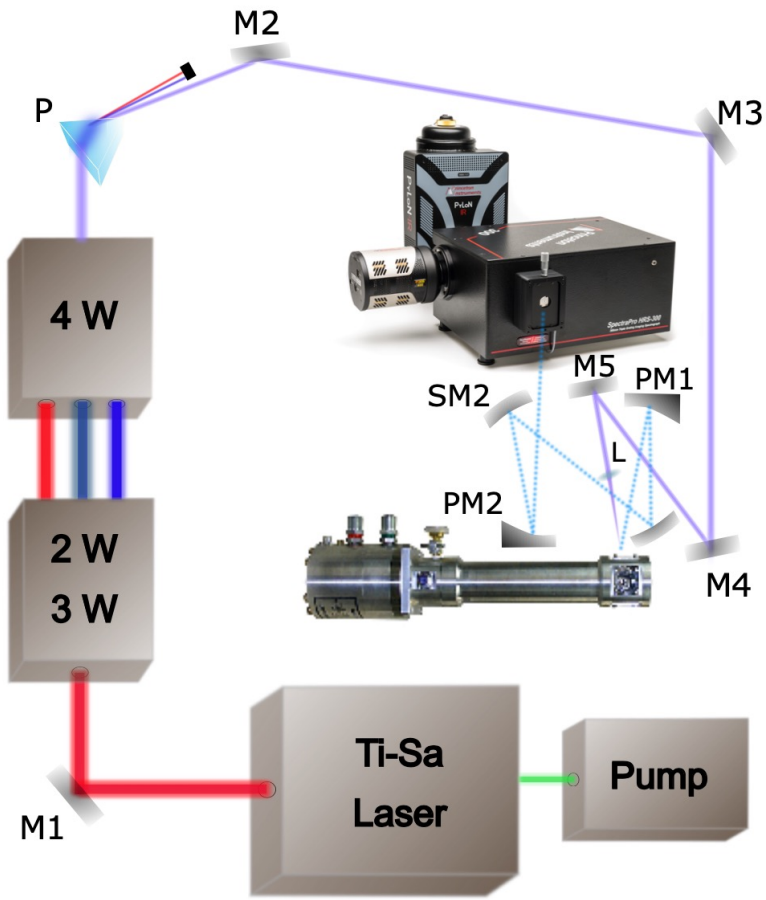
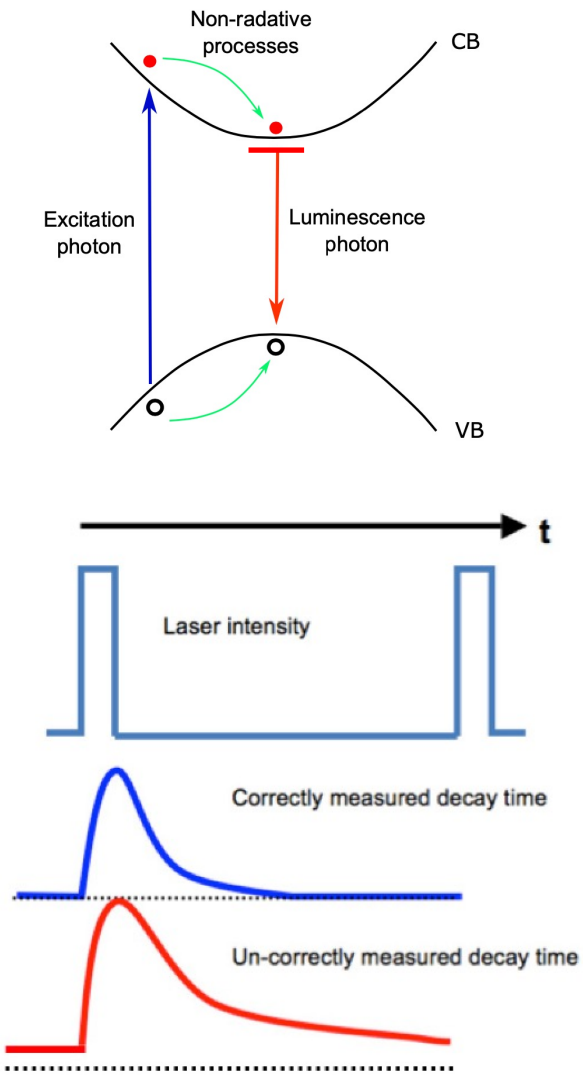
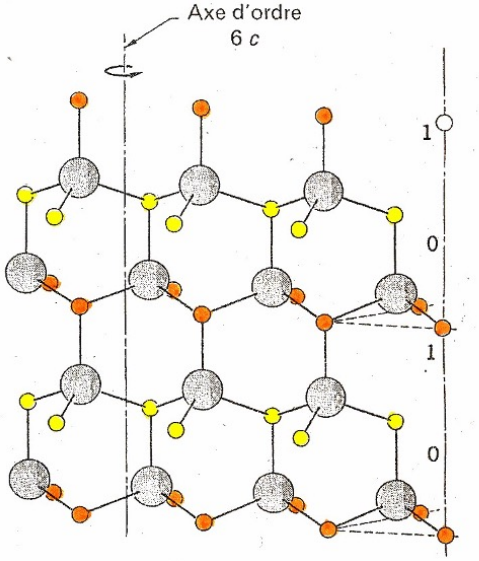


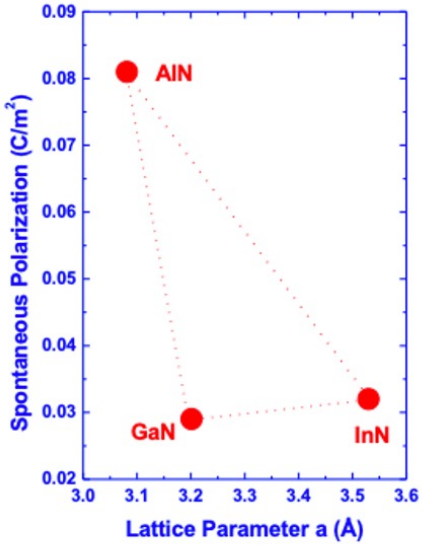
Figure 2.12: Scheme of our experimental setup used for PL measurements of h-BN samples: cryostat for temperature-dependent measurements, excitation beam provided by the fourth-harmonic of a Ti-Sa laser with wavelength varying from 192 and 196nm; (PM) = Parabolic mirrors; (SM) = Spherical mirrors; (M) = flat mirrors, (P) =



Application to wurtzitic Quantum wells



Hexagonal



$$\sigma_{W-B} = [\vec{P_W} - \vec{P_B}] \cdot \vec{n}$$

The conservation of the electric displacement vector $\vec{D}$ through the interface leads to write:

$$[\vec{D_W} - \vec{D_B}] \cdot \vec{n} = [\epsilon_W \vec{F_W} - \epsilon_B \vec{F_B}] \cdot \vec{n} = [\vec{P_B} - \vec{P_W}] \cdot \vec{n}$$

where the quantities ϵ_W and ϵ_B are the dielectric constants in materials W and B (they include ϵ_0).

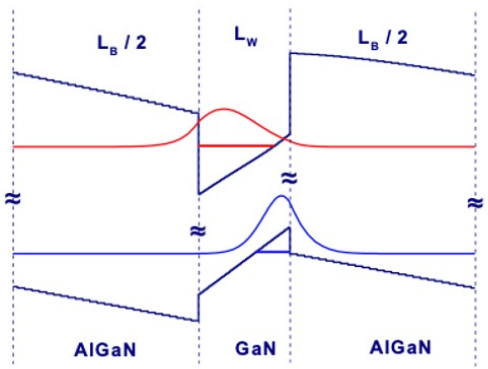
To express the discontinuity of the electric field F at the interface between W and B materials we applicate Born Von Karman cyclic conditions and the continuity of the electric field through a closed boucle:

$$\vec{F_W} \cdot \vec{n} L_W + \vec{F_B} \cdot \vec{n} L_B = 0$$

Then the electric field in materials W and B write:

$$\vec{F_W} \cdot \vec{n} = \frac{L_B}{\epsilon_W L_B + \epsilon_B L_W} [\vec{P_B} - \vec{P_W}] \cdot \vec{n}$$

$$F_B \cdot \vec{n} = -\frac{L_W}{\epsilon_W L_B + \epsilon_B L_W} [\vec{P_B} - \vec{P_W}] \cdot \vec{n} = -\frac{L_W}{L_B} \vec{F_W} \cdot \vec{n}$$



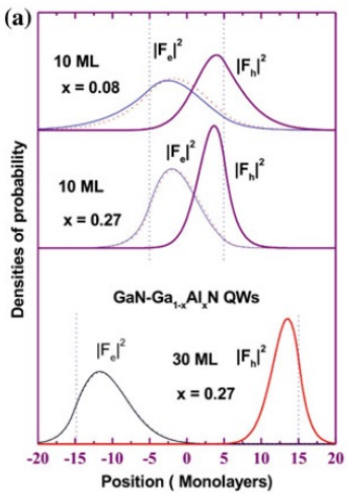
Energy decreases with L_W.

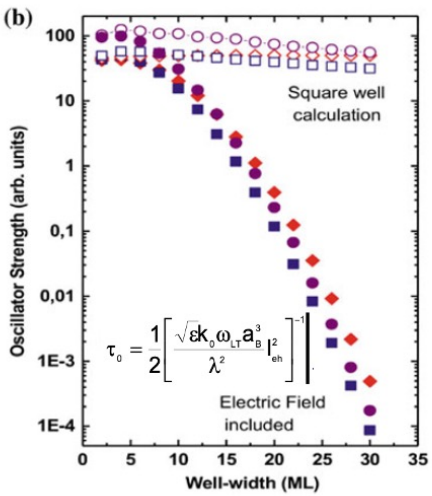
Oscillator strength déceases quasi-exponentialy.

Born-Von Karman approximation

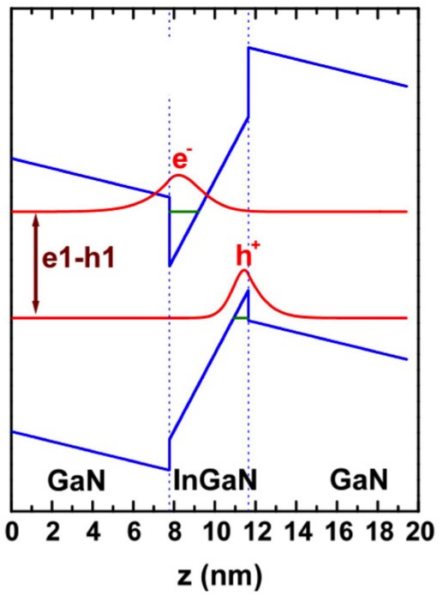
$F_W \sim \Delta P \,.\, L_B / (L_B + L_W)$

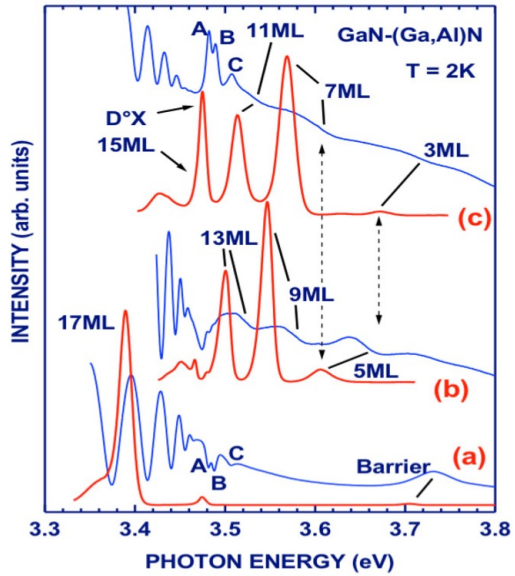
$F_B \sim \Delta P \,.\, L_W / (L_B + L_W)$

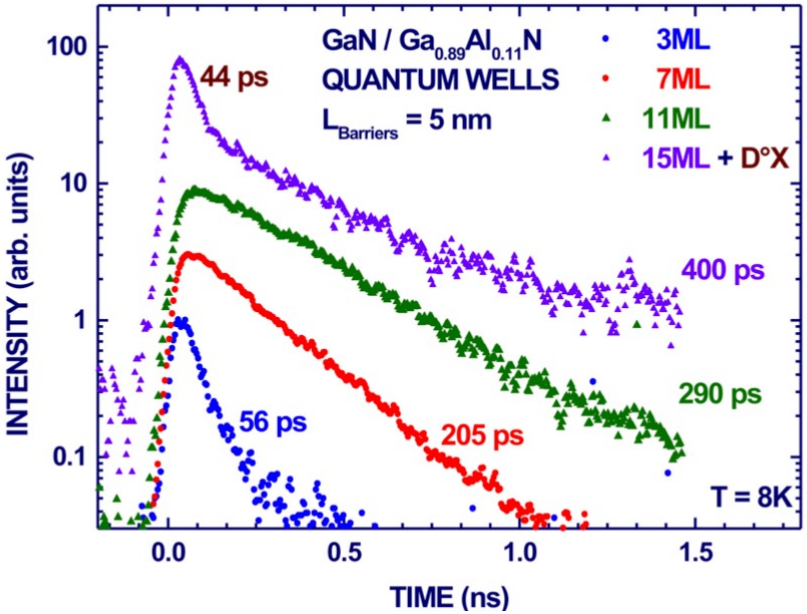


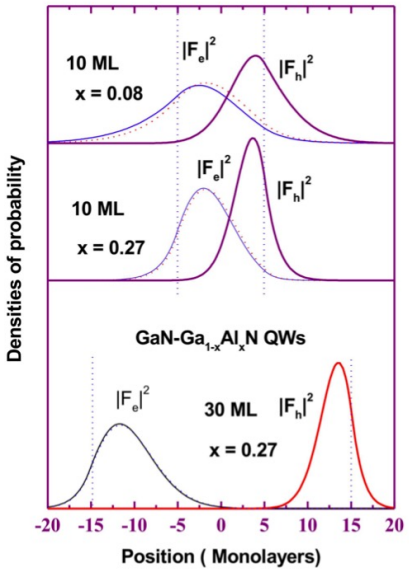


Quantum Confined Stark Effect

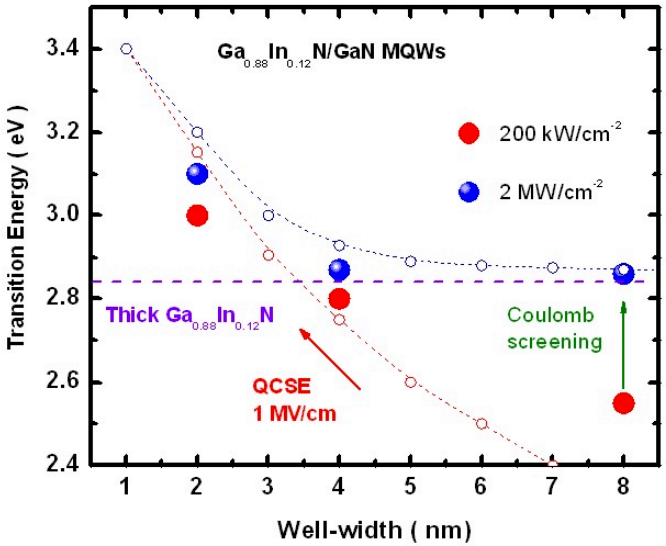


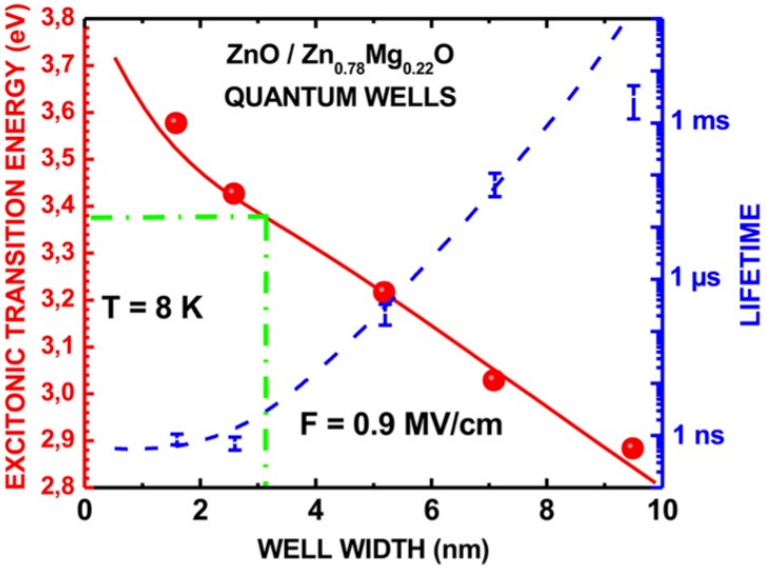




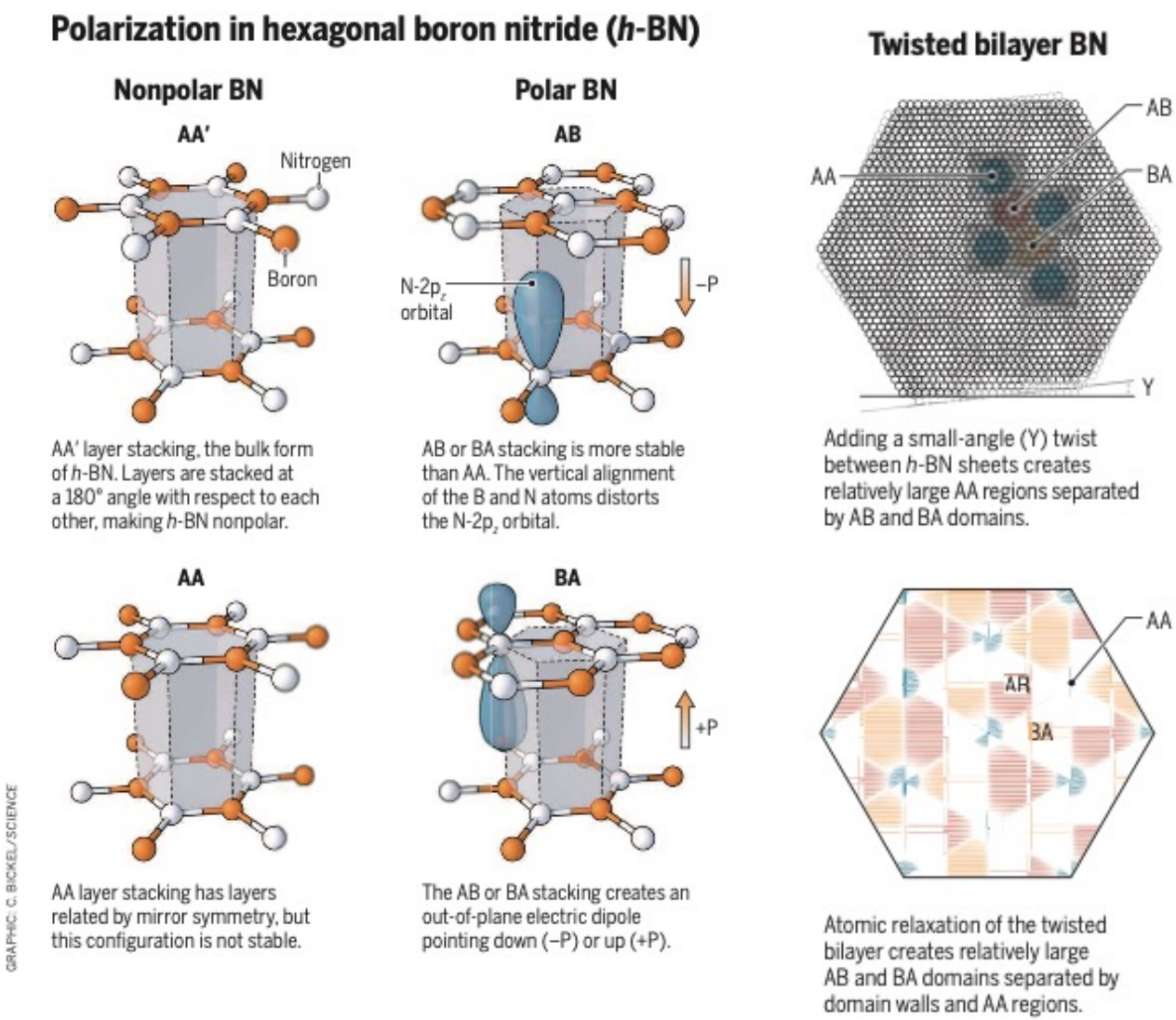


Takeuchi et al. JJAP Lett. **36** L382 (1997)

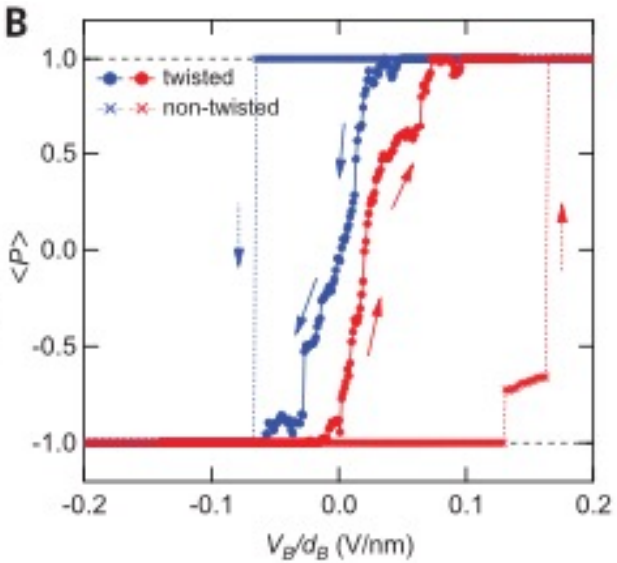




latent in singulis…



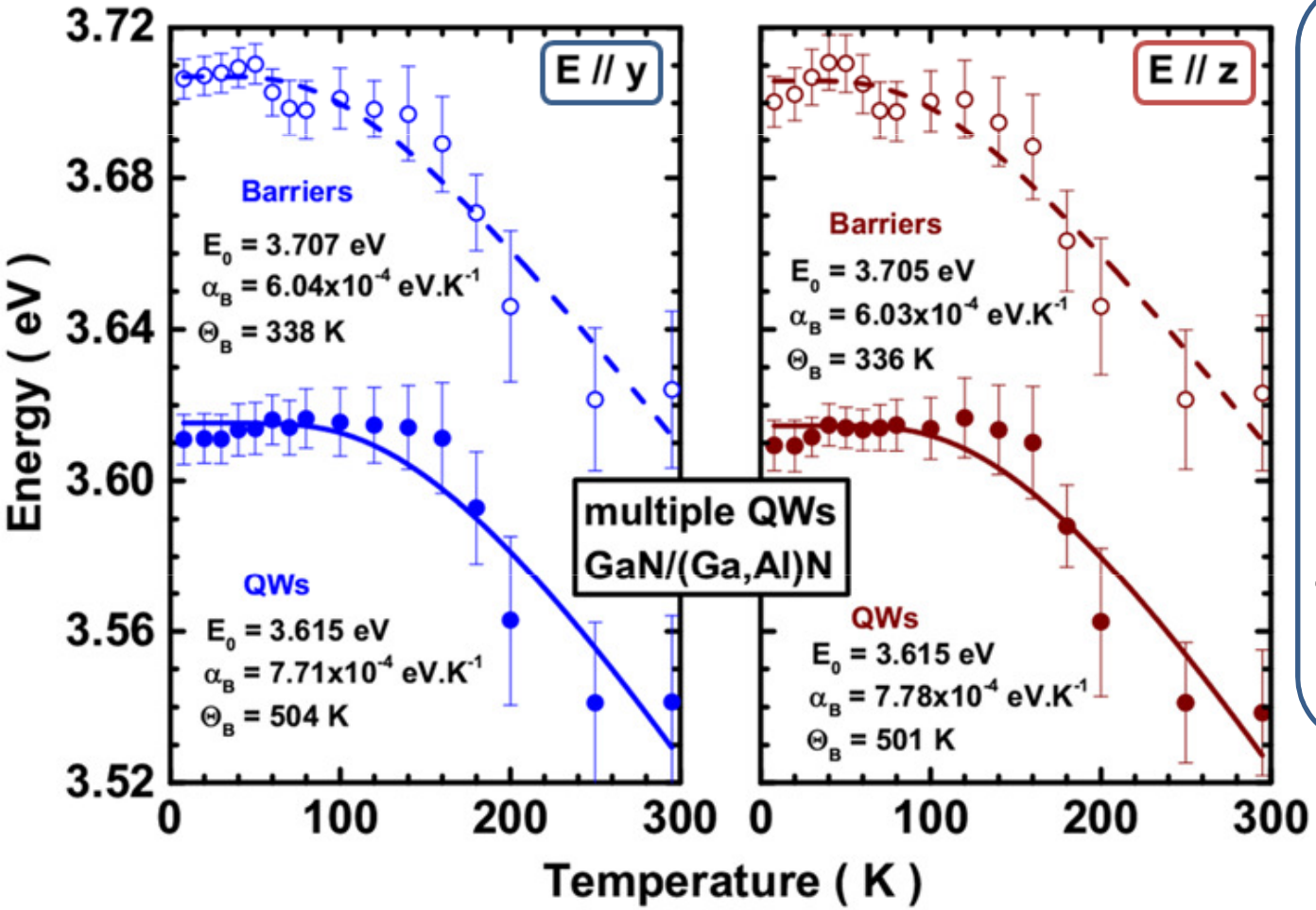
Ferroelectric switching in twisted bilayer BN.



Three papers about ferroelectricity in BN in the 25 june issue of Science:

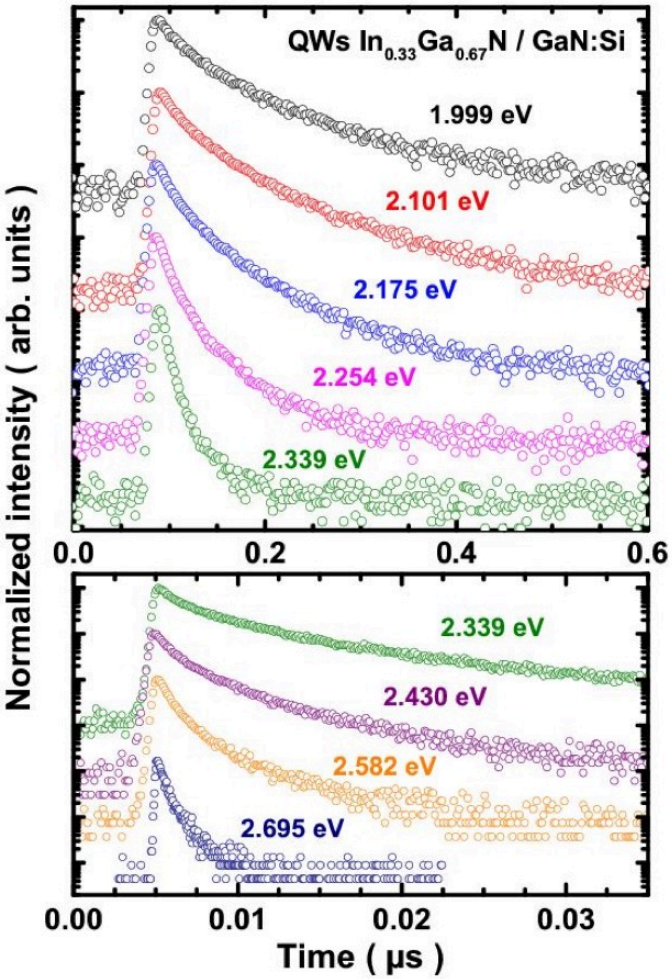
The place to be?

Photoluminescence energy against T in the weak localization case



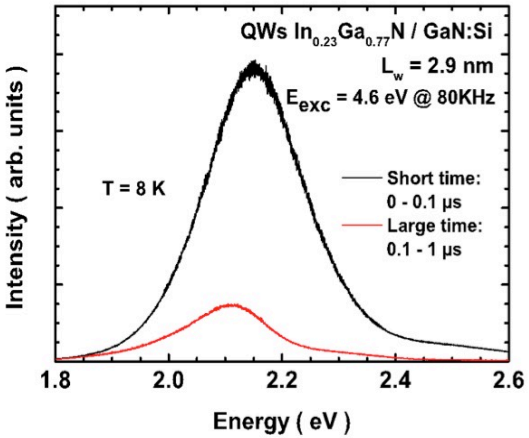
- Similar behaviors
- *E* more stable in QWs
- QWs: *E* cte until T ≈ 150K
- BLs: *E* ↓ for T > 50K
- Θ_B

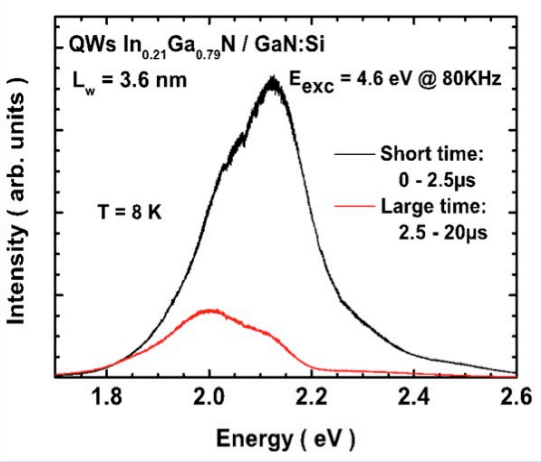
Direct experimental evidence localization phenomena by TRPL

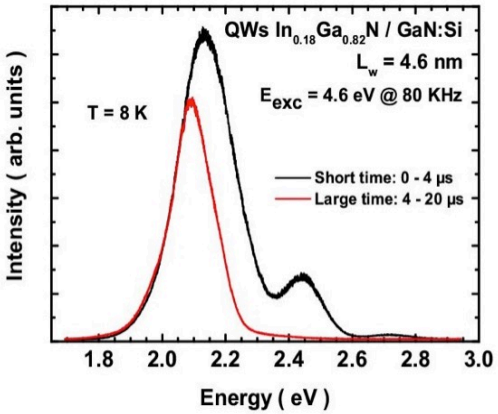


$$\frac{1}{\tau} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{nonrad}}$$

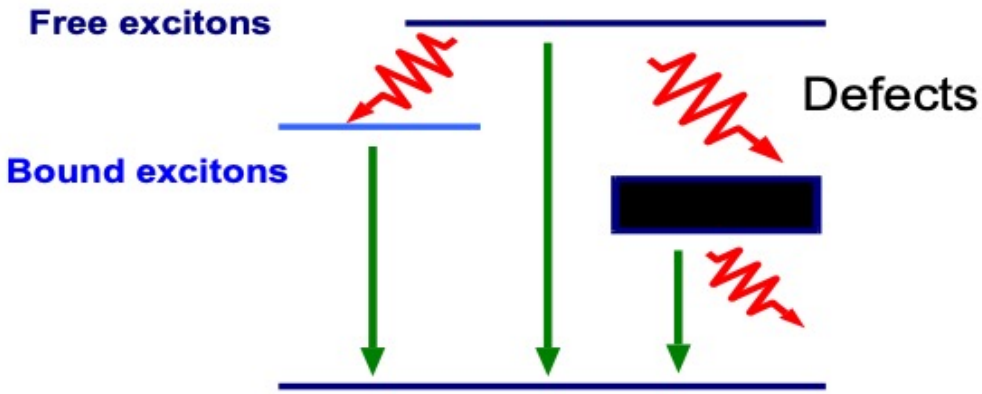
$$\tau_{(E)} = \frac{\tau_0}{1 + \exp(\frac{E - E_0}{\Delta_0})}$$







Decay times



$(\tau_{PL})^{-1} = (\tau_R)^{-1} + (\tau_{NR})^{-1}$ one measures it

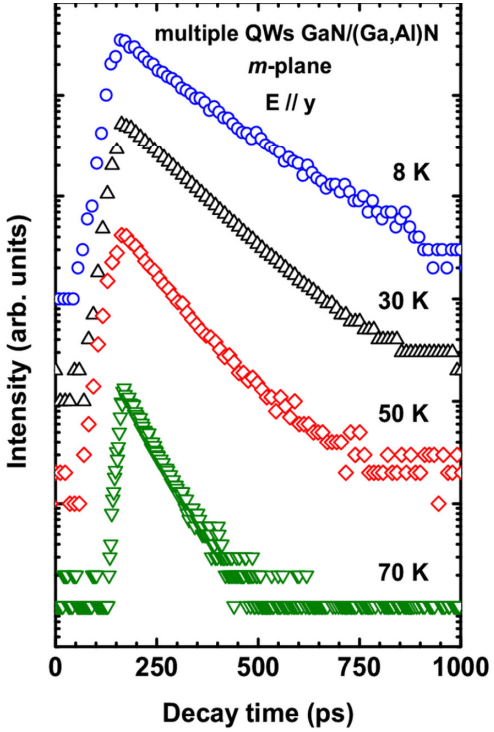
The PL intensity is given by :

$\eta = \tau_{NR} / (\tau_{NR} + \tau_R)$ one measures it

(one postulates $\eta \sim 1$ @ low T)

The radiative decay time is :

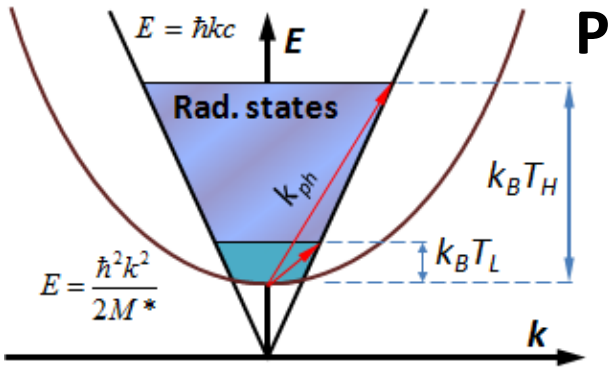
$\tau_R(T) = \tau_{PL}(T) / \eta(T)$



$$\frac{1}{\tau} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{nonrad}}$$

$$\tau_{rad} = \tau_0 T^{n/2}$$
$$\tau_{nonrad} = \tau_1 \exp(T_a/T)$$

Photoluminescence intensity against T



PL emission

G(T)

$k_{exc} \leq k_{ph}$

$$I(T) \propto \frac{1}{1+(\tau_{rad}/\tau_{nonrad})}$$

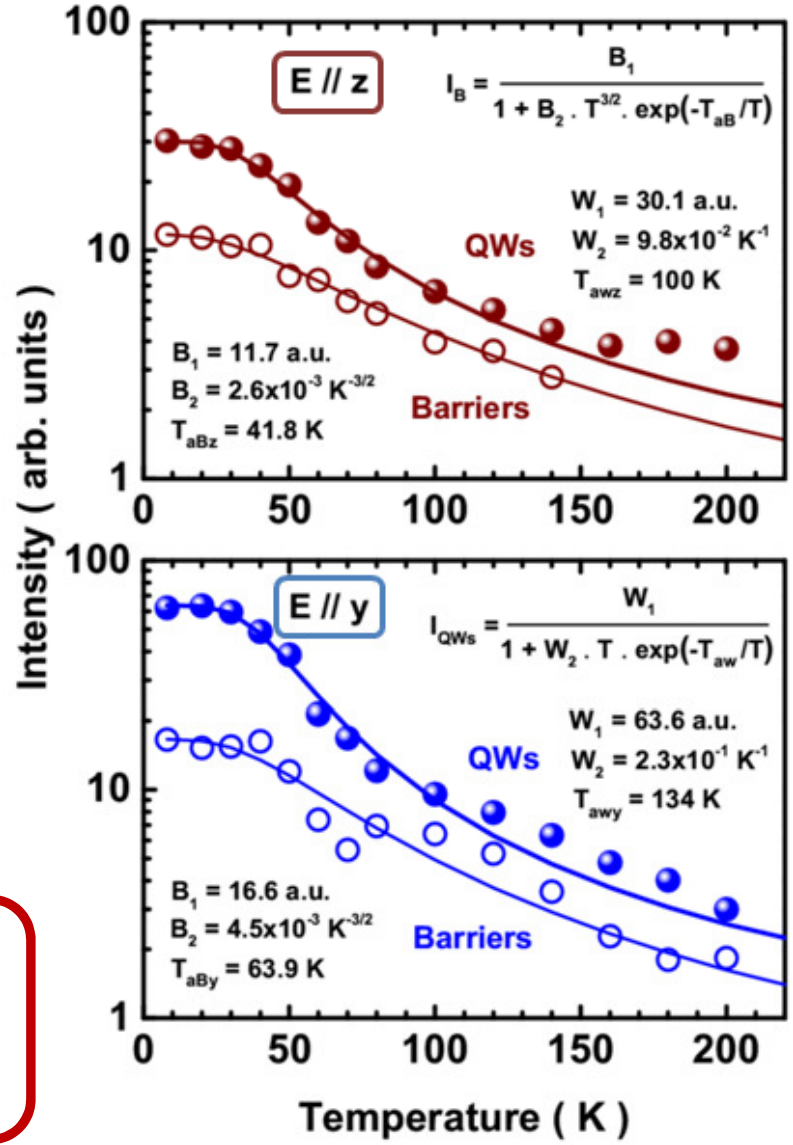
$$\tau_{rad} = \tau_0 T^{n/2}$$

$$\tau_{nonrad} = \tau_1 \exp(T_a/T)$$

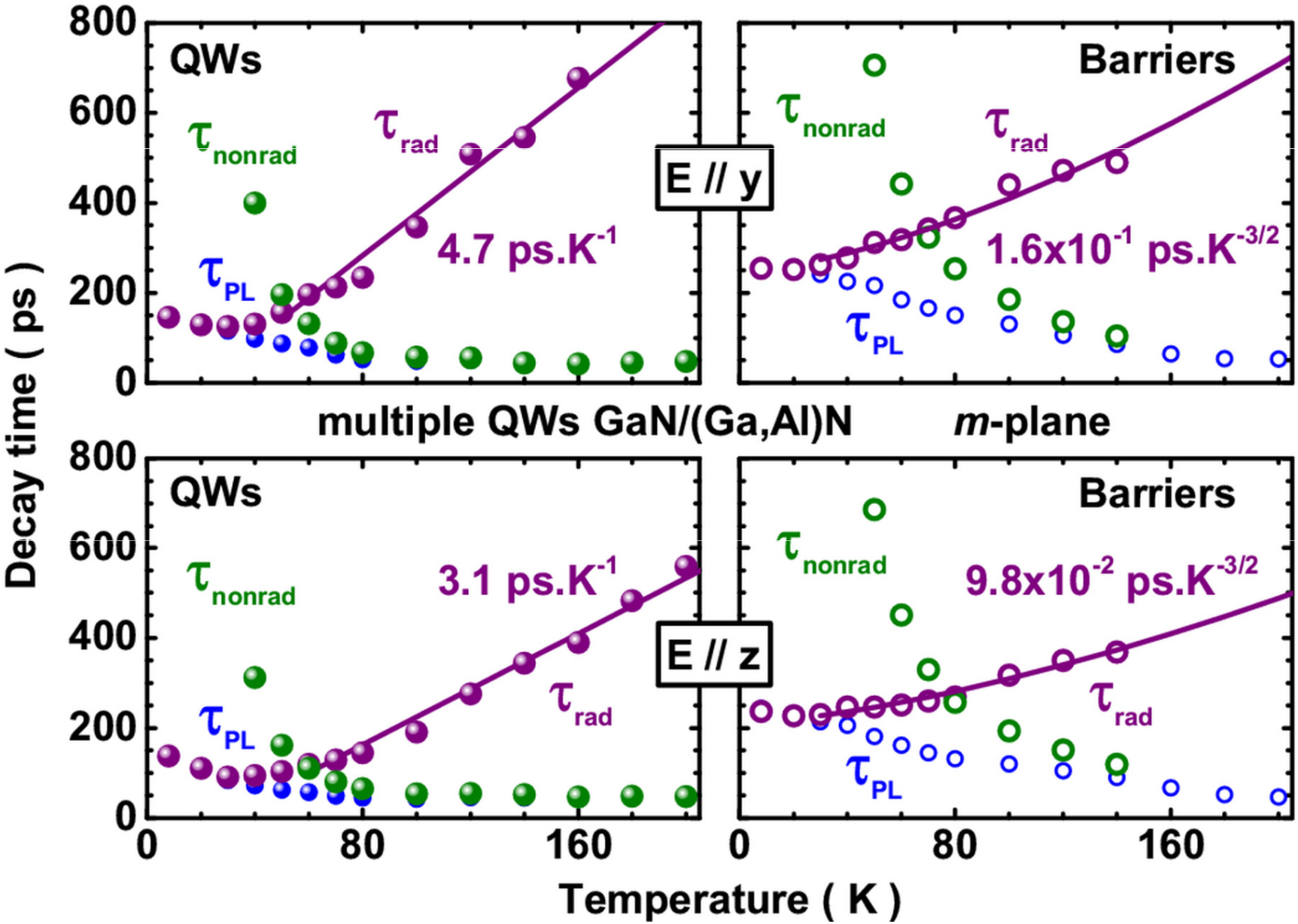
BLs:
n = 3

QWs:
n = 1

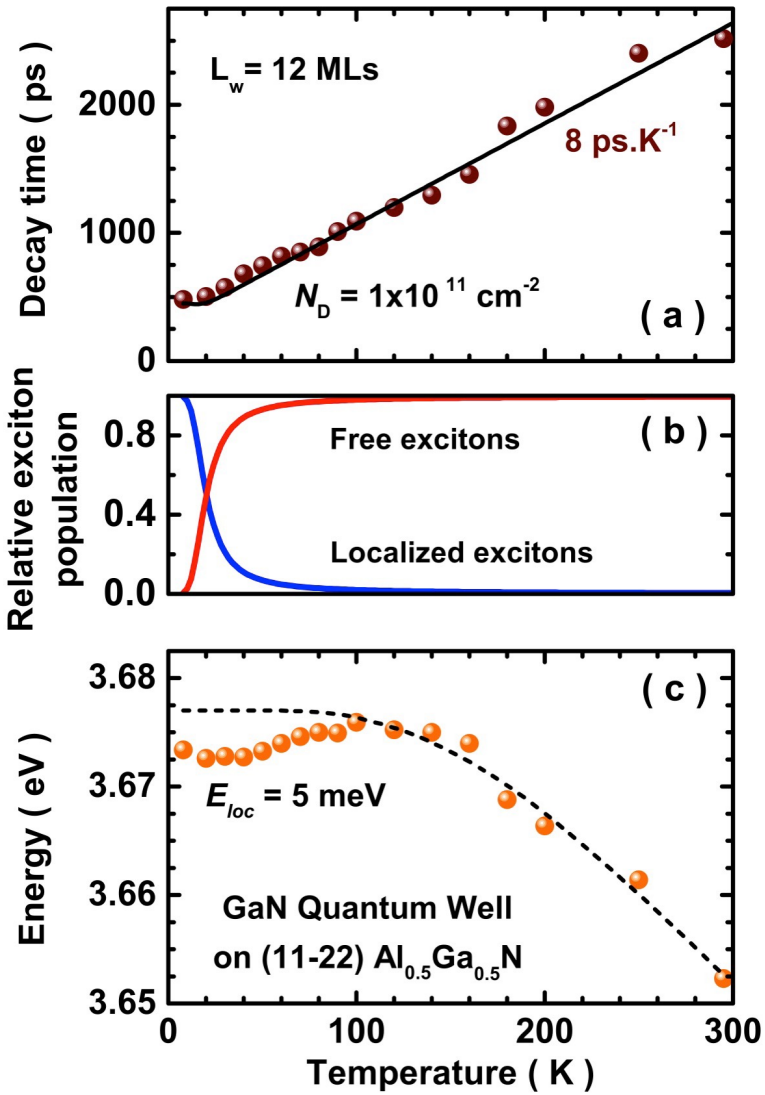
$$I(T) \propto \frac{1}{1+(\tau_0/\tau_1)T^{n/2}\cdot\exp(-T_a/T)}$$



Radiative and non radiative decay times



Relative populations of free and localized excitons



$$\frac{1}{\tau_{rad}} = \left[\frac{n_{loc}}{n_{free}+n_{loc}} \frac{1}{\tau_{loc}} + \frac{n_{free}}{n_{free}+n_{loc}} \frac{1}{\tau_{free-rad}} \right]$$

$$\frac{n_{loc}}{n_{loc}+n_{free}} = \frac{N_D \exp\left(\frac{E_{loc}}{kT}\right)}{N_D \exp\left(\frac{E_{loc}}{kT}\right) + 2\frac{Mm_0}{\pi\hbar^2}kT}$$

D.S. Citrin, Phys. Rev. B **47**, 3832 (1993)

$$\tau_{nfree-onrad} = \tau_1 \exp\left(\frac{T_a}{T}\right)$$

$\tau_1 = 74$ ps $\qquad T_a = 185$ K

$\tau_{free-rad} \approx \tau_0 T \qquad \tau_0 = 8\,\text{ps.K}^{-1}$

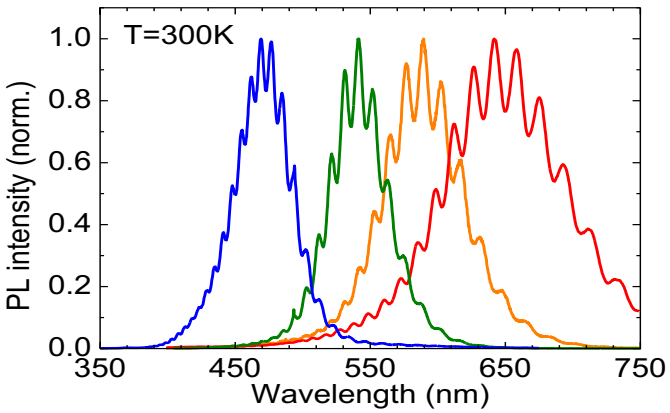
$\tau_{loc} = 400$ ps

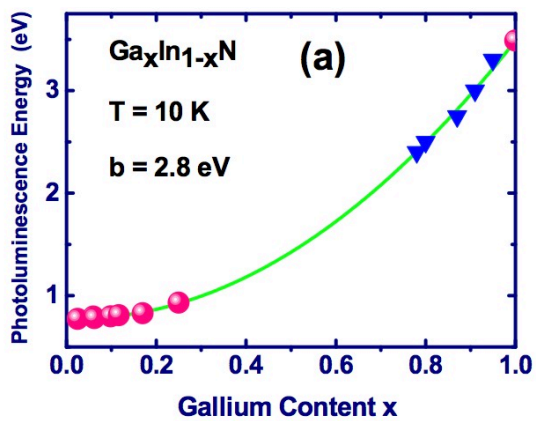
$E_{loc} = 5$ meV

$N_D = 1\text{x}10^{11}$ cm^{-2}

Effect of chemical disorder on PL of bulks

$$E_g(A_{1-x}B_xC) = (1-x)E_g(\mathrm{AC}) + \mathrm{xE_g(BC)} - \mathrm{bx(1-x)}$$





S.D Baranowski and A.L.Efros, Soviet Physics Semiconductors 12, 1328, 1978.

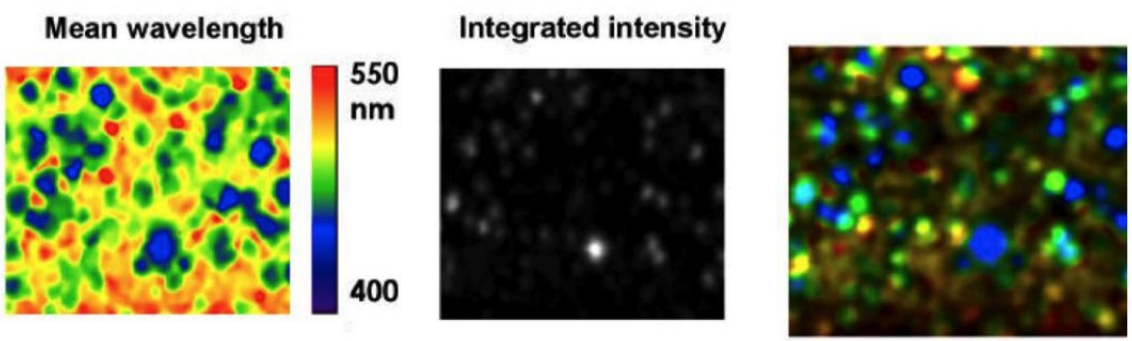
Excitonic broadening law :

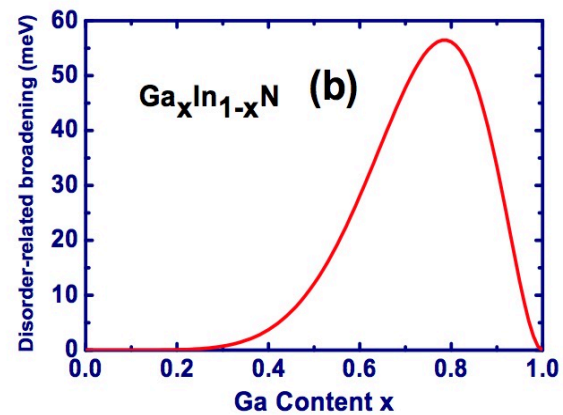
$$E_0 = \frac{1}{178}\frac{\alpha^4 M^3 x^2 (1-x)^2}{\mathrm{h}^6 N^2}$$

$$\alpha \equiv \frac{dE}{dx},$$

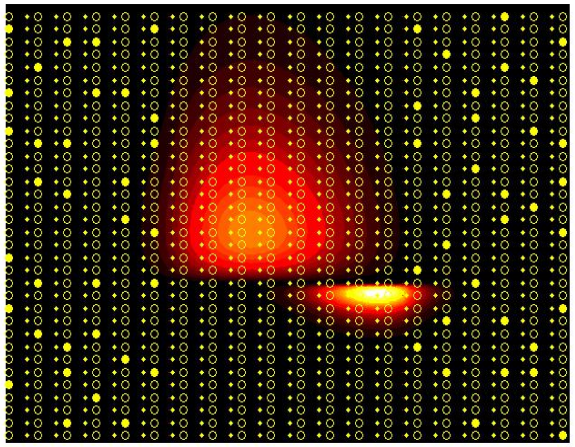
M exciton mass

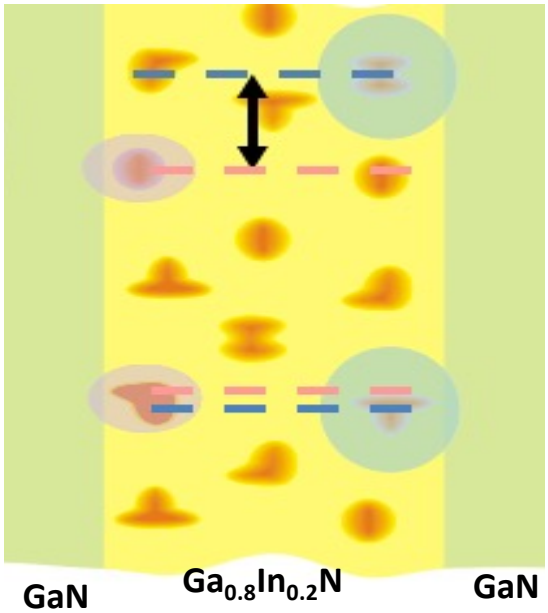
N volume density of atomic sites.

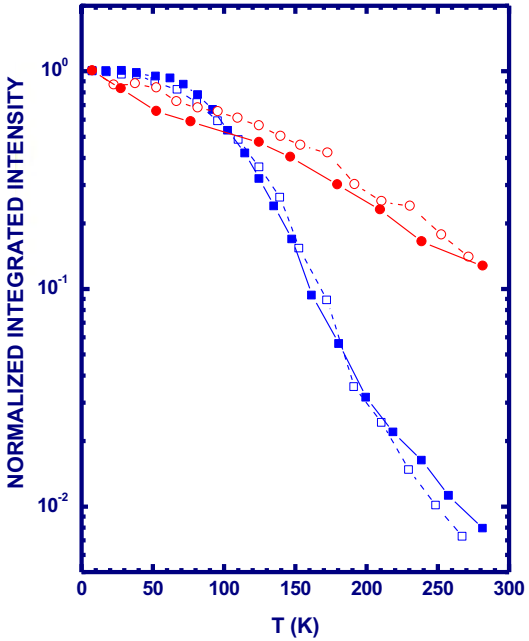


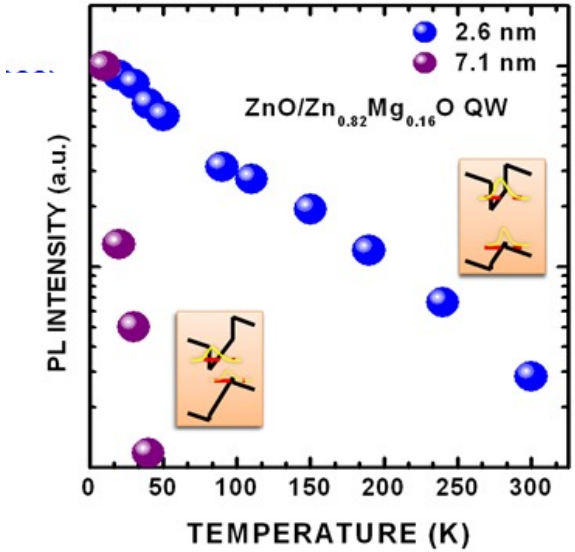


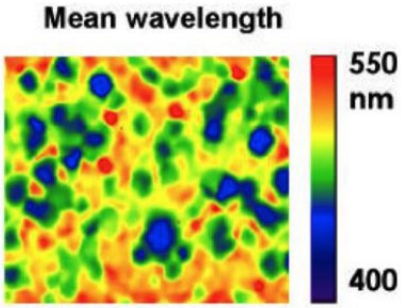
Quantum wells based on binary compound or ternary alloys

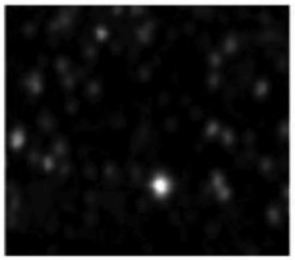


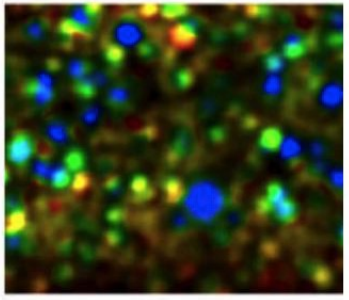




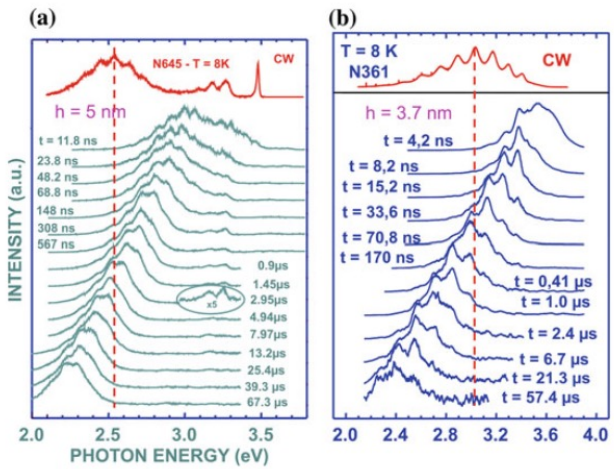




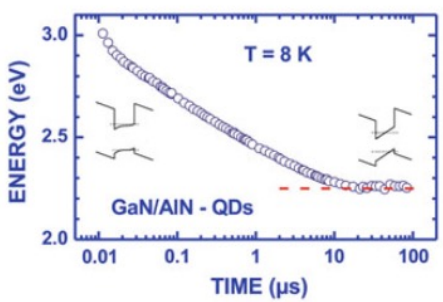


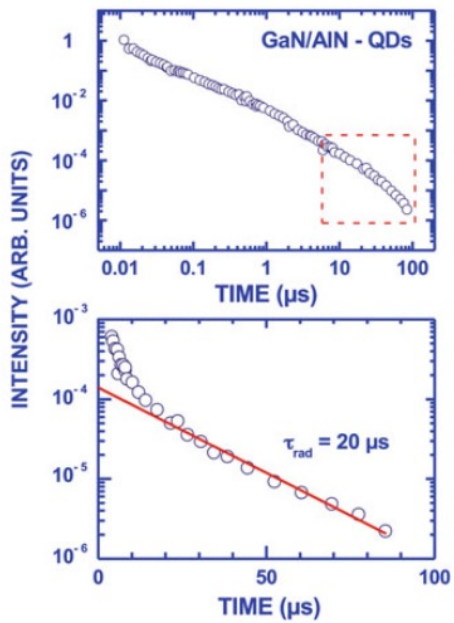


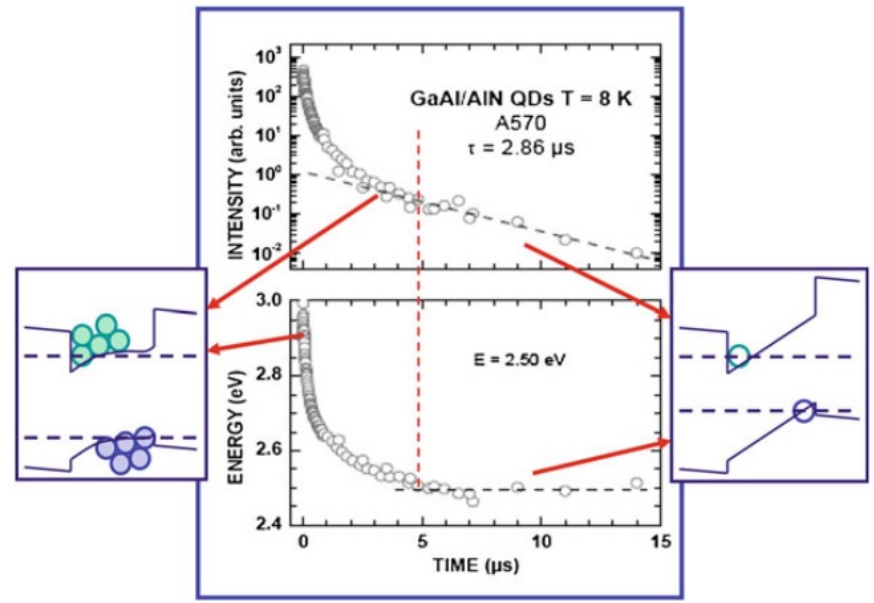
Low and high injections in LDS with QCSE: screening effects



The red-shift saturates



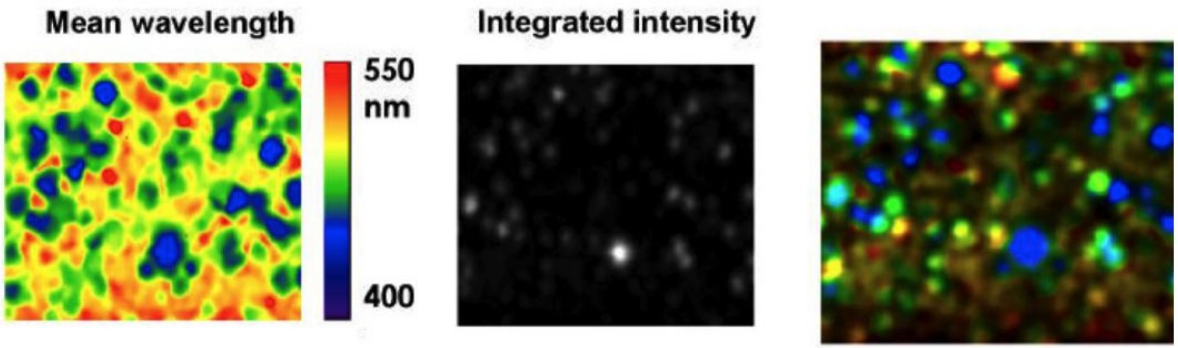


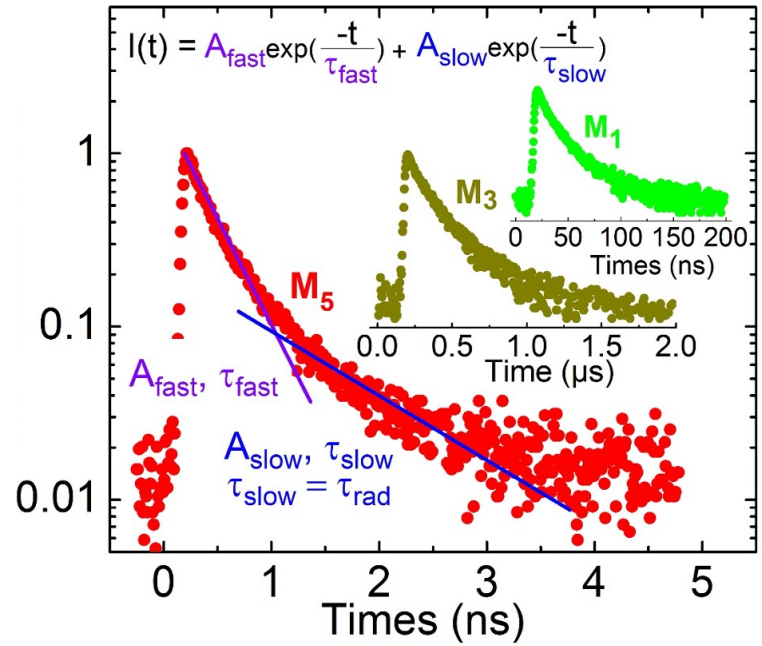


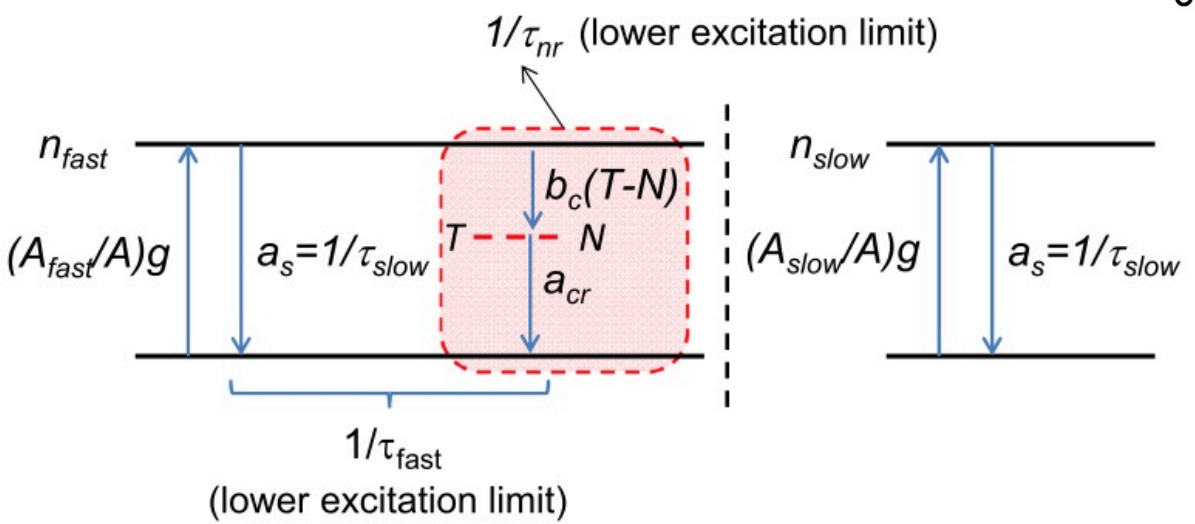
Needs to coherently solve Schrödinger and Poisson 's equations
Very tricky!

Measuring the IQE

IQE @LT using the Lotka-Volterra-type (prey-predator) equations







$$\frac{dn_{fast}}{dt} = \frac{A_{fast}}{A} g - a_s n_{fast} - b_c(T-N) n_{fast},$$

$$\frac{dN}{dt} = b_c(T-N) n_{fast} - a_{cr} N,$$

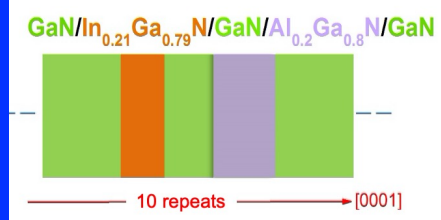
$$\frac{dn_{slow}}{dt} = \frac{A_{slow}}{A} g - a_s n_{slow},$$

$$i(t) = a_s n_{fast}(t) + a_s n_{slow}(t),$$

Yoshiya Iwata, Ryan G. Banal, Shuhei Ichikawa, Mitsuru Funato, and Yoichi Kawakami
Journal of Applied Physics 117, 075701 (2015)

Engineering and understanding of the carrier-localizing singularities

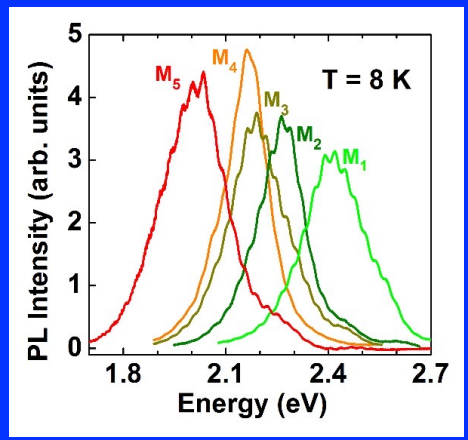
5 silicon doped samples:

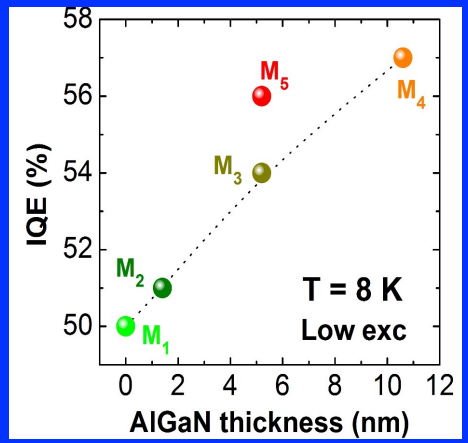


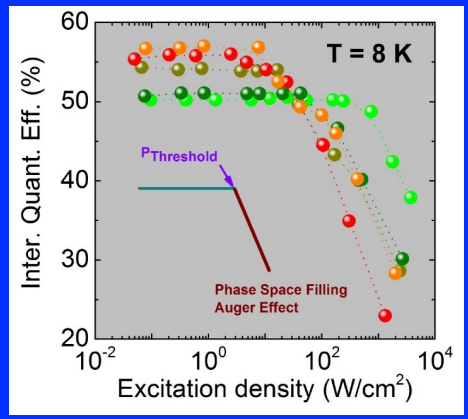
Fixed %In and well width

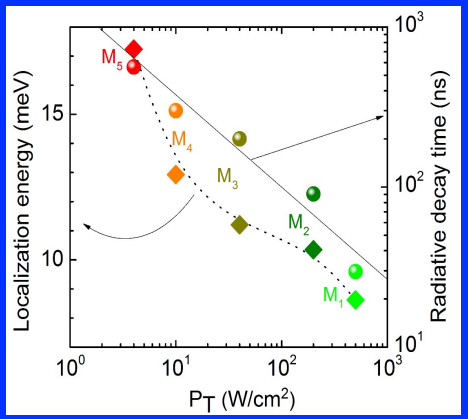
M_1 -> M_4: **increasing** AlGaN thickness

M_5 (M_3): changing In composition



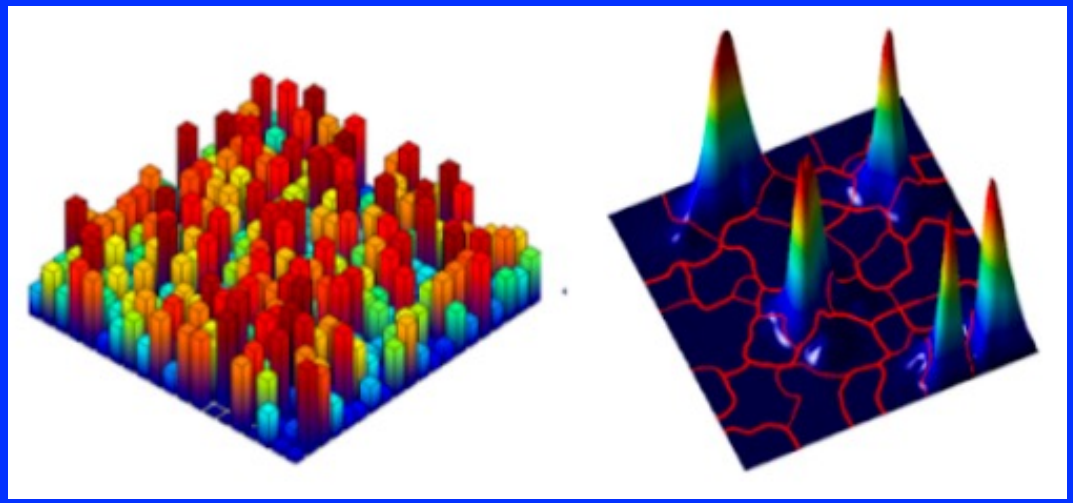






This triggers profound theoretical examinations
Marcel Filoche, Claude Weisbuch, ……

Since Anderson's seminal work in 1958, it is known that a sufficiently large structural disorder in the potential can lead to strongly localized quantum states.



Potential landscape | Energy landscape

$$E_0 = \frac{1}{178}\frac{\alpha^4 M^3 x^2 (1-x)^2}{\hbar^6 N^2}$$

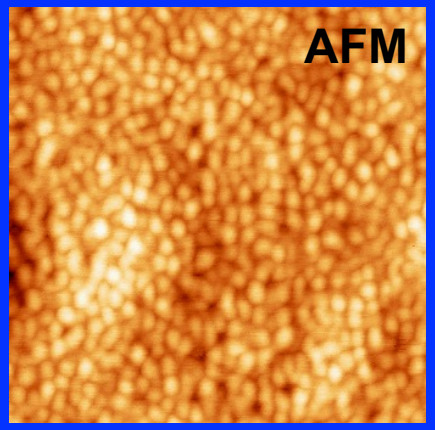
There is no confined level when:

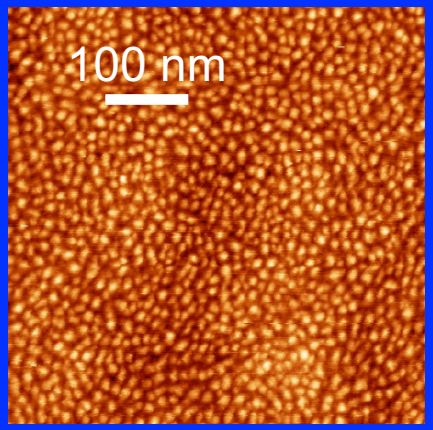
$$Va^2 \leqq \frac{\pi^2\hbar^2}{2m}$$

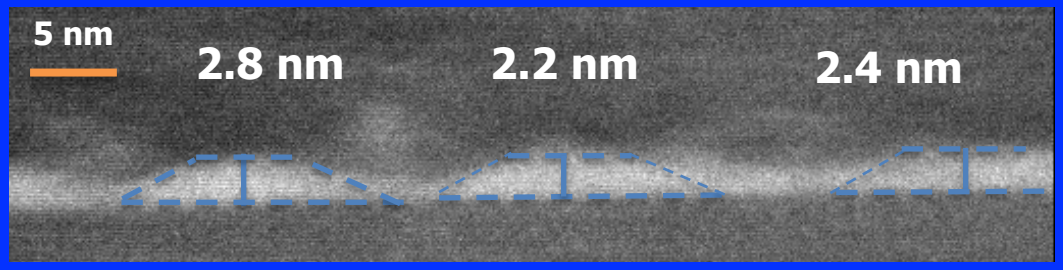
Growth of $Al_xGa_{1-x}N$/ $Al_yGa_{1-y}N$ QDs by MBE

➡ $Al_yGa_{1-y}N$ QDs grown on $Al_xGa_{1-x}N$ (0001)

QDs are grown (for $0.1 \leq x \leq 0.4$) with high densities between 2 – 6 x 10^{11} cm^{-2}

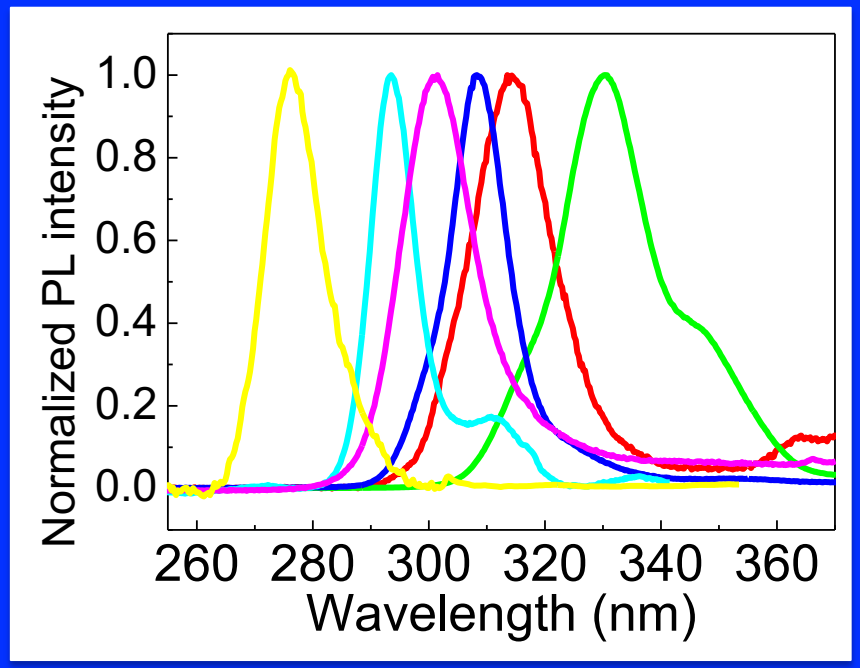






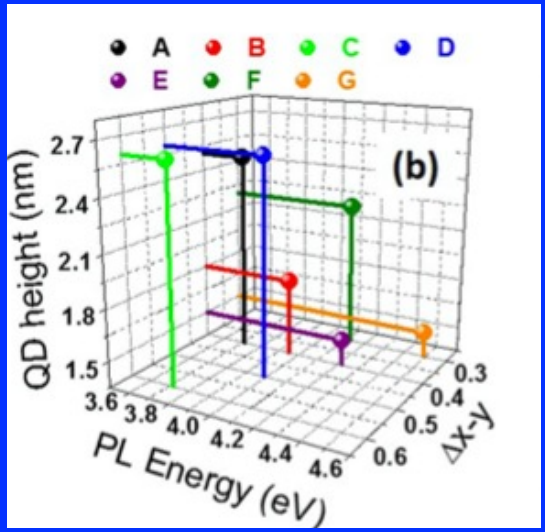
Cross-section TEM

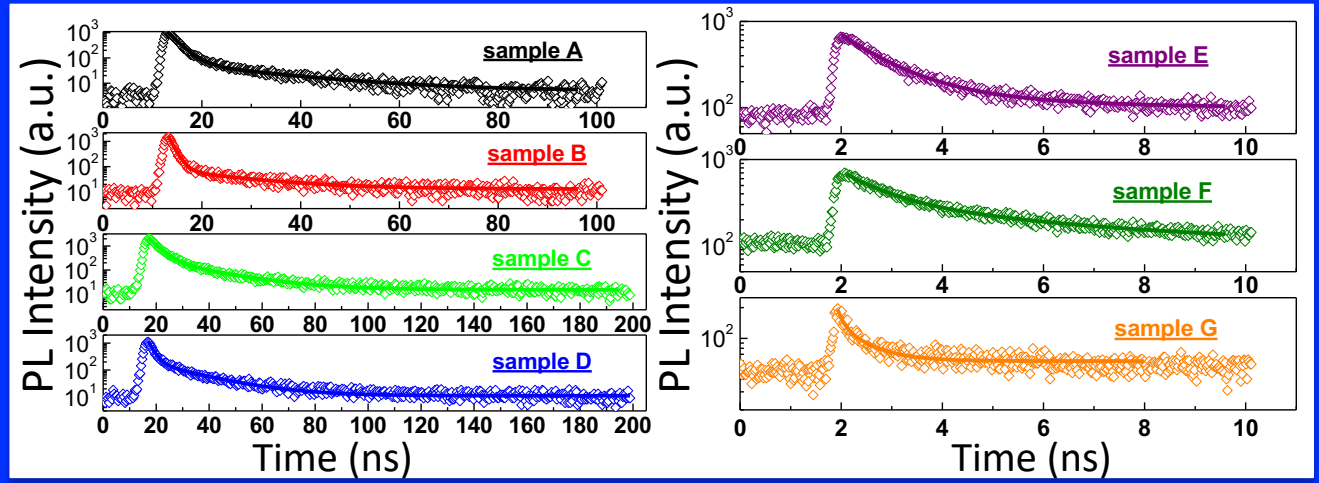
- Emission in the UVA to UVC range : from 340 nm ($Al_{0.1}Ga_{0.9}N$ QD) to 275 nm ($Al_{0.4}Ga_{0.6}N$ QD)

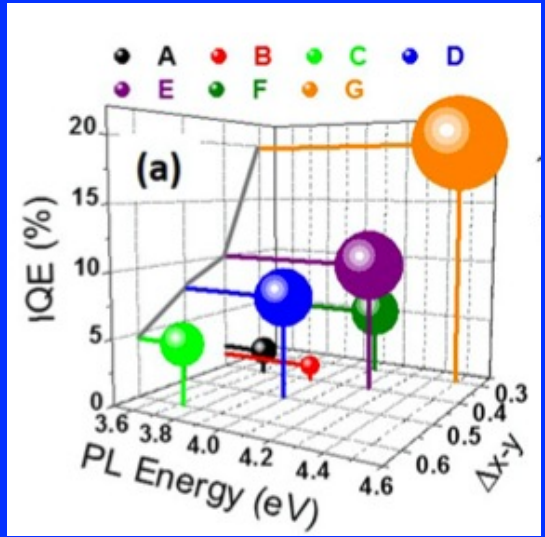


Internal quantum efficiencies of AlGaN quantum dots grown by molecular beam epitaxy and emitting in the UVA to UVC ranges

Sample	$Al_xGa_{1-x}N$ cladding layer Al composition	$Al_yGa_{1-y}N$ QDs Composition y	$Al_yGa_{1-y}N$ QDs Deposited amount (monolayers)	QD structural properties QD height (nm)	QD structural properties QD diameter (nm)	QD structural properties QD density (cm^{-2})
A	0.5	0.1	10	2.5 ± 0.5	10 ± 5	$5.0(\pm1) \times 10^{11}$
B	0.5	0.1	7	1.8 ± 0.5	8 ± 4	$1.5(\pm1) \times 10^{11}$
C	0.7	0.1	10	2.6 ± 0.3	10 ± 3	$2.4(\pm1) \times 10^{11}$
D	0.7	0.2	10	2.6 ± 0.3	10 ± 3	$5.4(\pm1) \times 10^{11}$
E	0.7	0.3	6	1.5 ± 0.3	8 ± 4	$2.2(\pm1) \times 10^{11}$
F	0.7	0.4	8	2.2 ± 0.4	10 ± 4	$2.6(\pm1) \times 10^{11}$
G	0.7	0.4	6	1.5 ± 0.4	8 ± 4	$4.8(\pm1) \times 10^{11}$



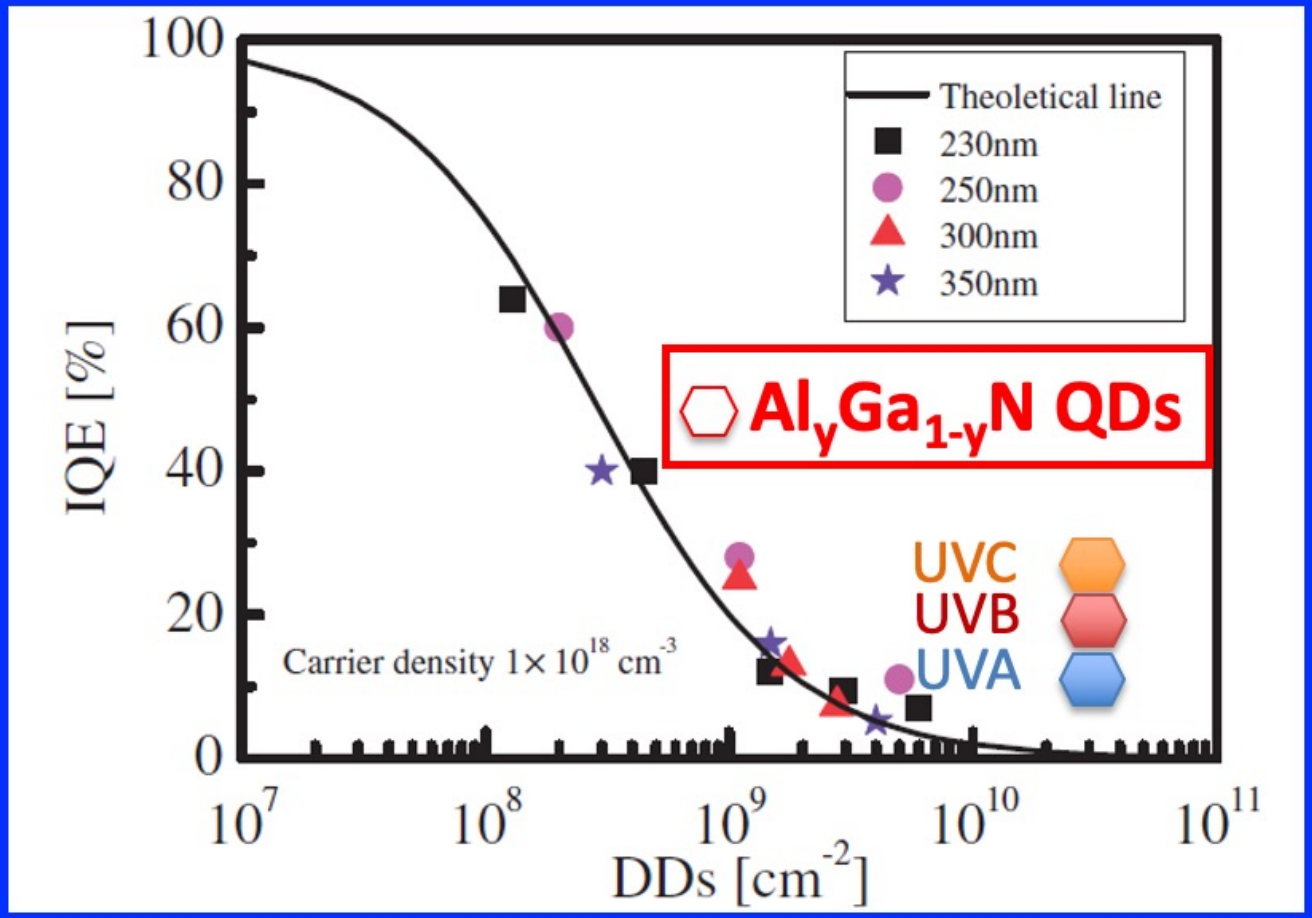




Y. Iwata, R. G. Banal, S. Ichikawa, M. Funato, and Y. Kawakami, J. Appl. Phys. **117**, 075701 (2015).

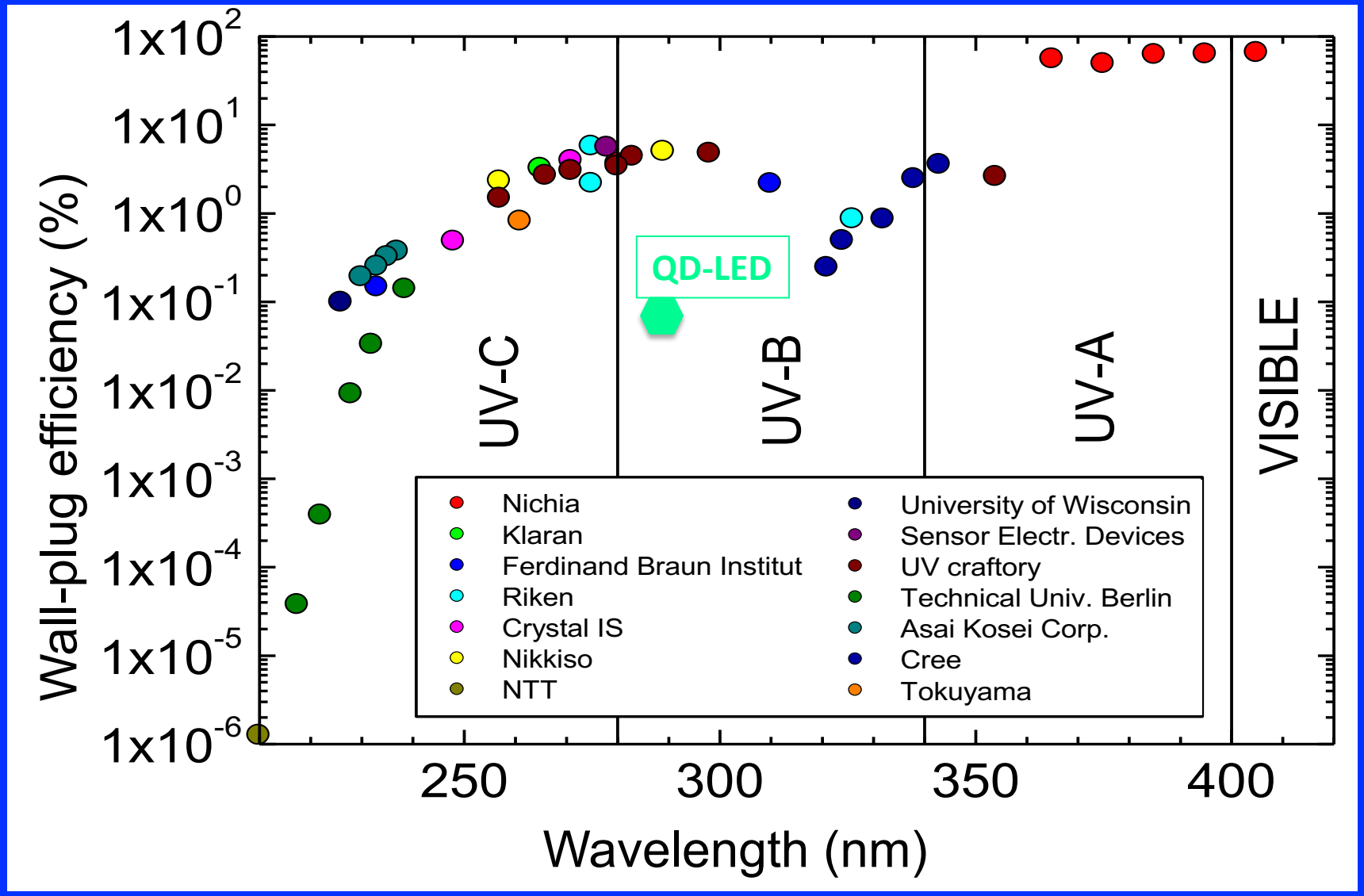
$$\text{IQE-LT} = \frac{A_{\text{fast}}\tau_{\text{fast}} + A_{\text{slow}}\tau_{\text{slow}}}{(A_{\text{fast}} + A_{\text{slow}})\tau_{\text{slow}}}.$$

Internal quantum efficiencies of AlGaN quantum dots grown by molecular beam epitaxy and emitting in the UVA to UVC ranges



Adapted from
[K. BAN et al., APEX 4, 052101 (2011)]

State-of-the-art of the wall plug efficiency of DUV emitters *v.s.* wavelengths of emission



A florilege of « to do » things

T_{aurad} depends on the materials and strongly with design if QCSE
d_{taurad}/dT slightly depends on the design of the heterostructure

Modelisations are needed to impact on the values of parameters of the non radiative decay time

Growing sample #n+1 , we believe it is better than #n

Checking what happens

Patenting if an inventing aspect rises from the shade

Writing a scientific article « after a reasonable amount of time » (be careful with Ostwald ripening)

Making a post-doc with smart people in the perspective of later joining us at CNRS in order to submit a lot of ANR projects

Never forget:

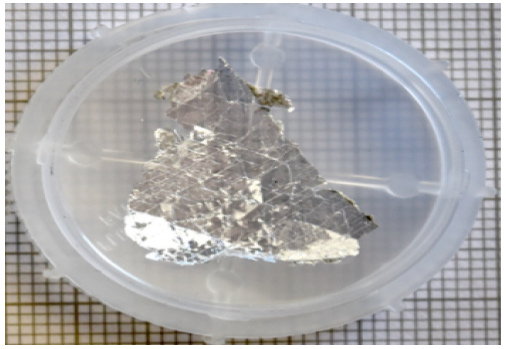
jerseywartunnels.com

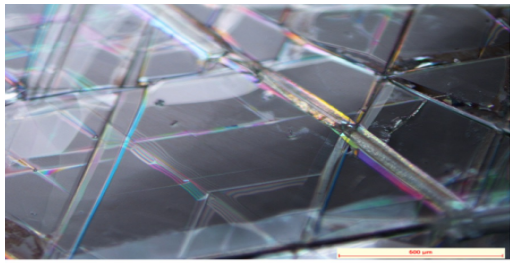
Two sides to every story.

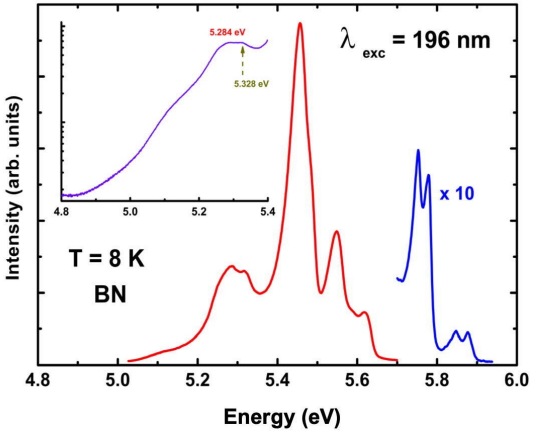
JERSEY

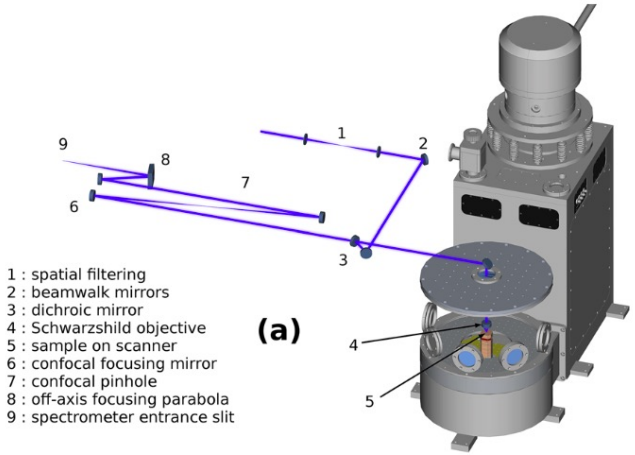
The CNRS option: dépasser les frontières

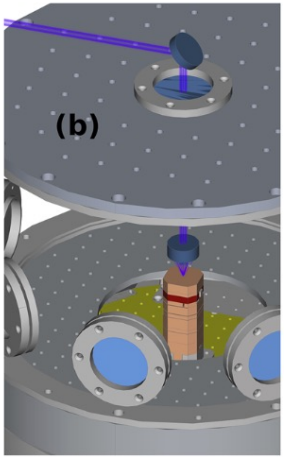
MicroPL @ 200 nm under the ultimate resolution (limited by diffraction)
Designed by Pierre Valvin and Guillaume Cassabois using ZEMAX ®
Constructed by Christian L'hénoret at our workshop

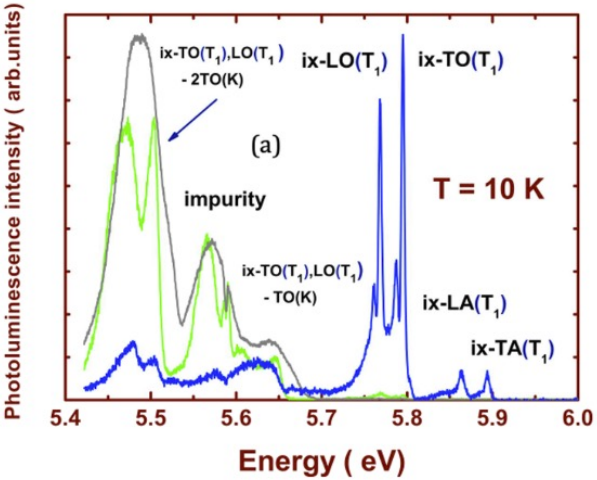


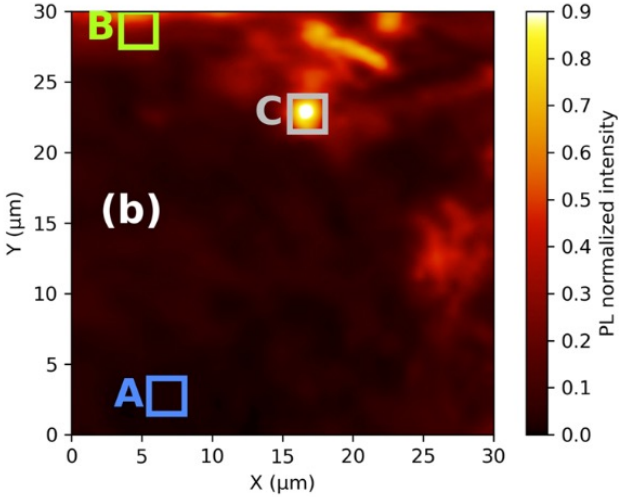












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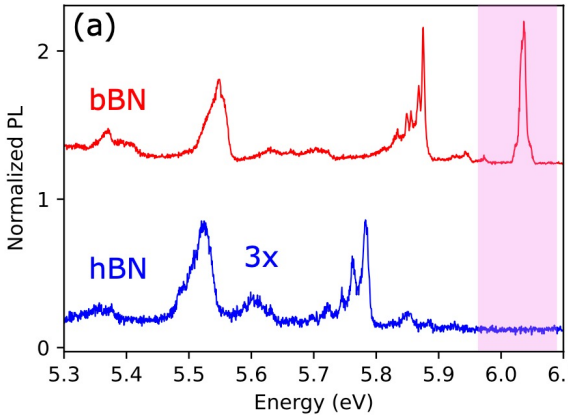
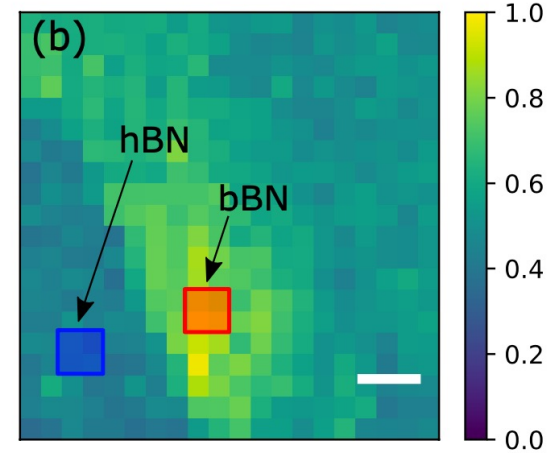
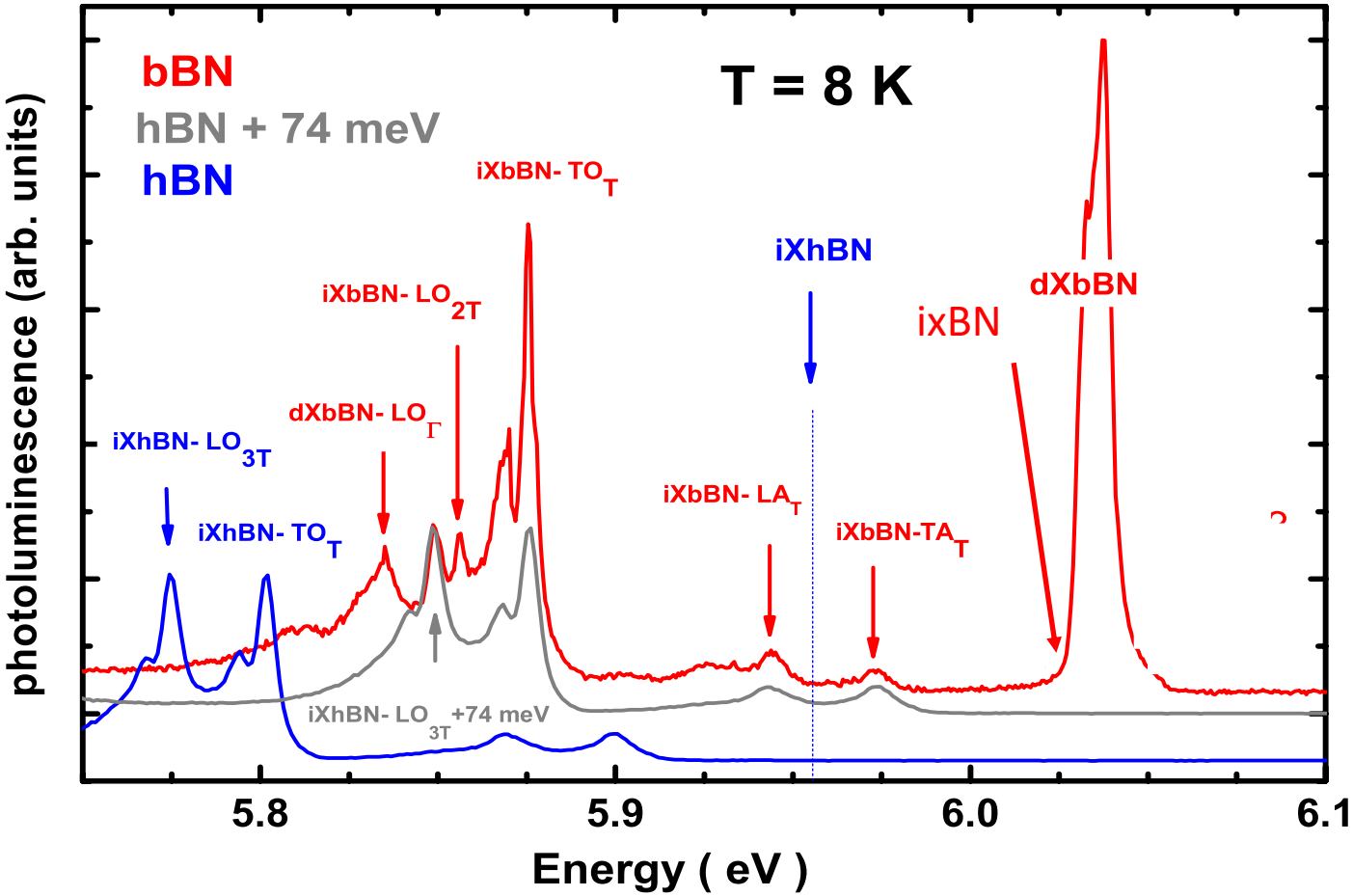
Probing intricate AA' and AB polymorph stackings in BN







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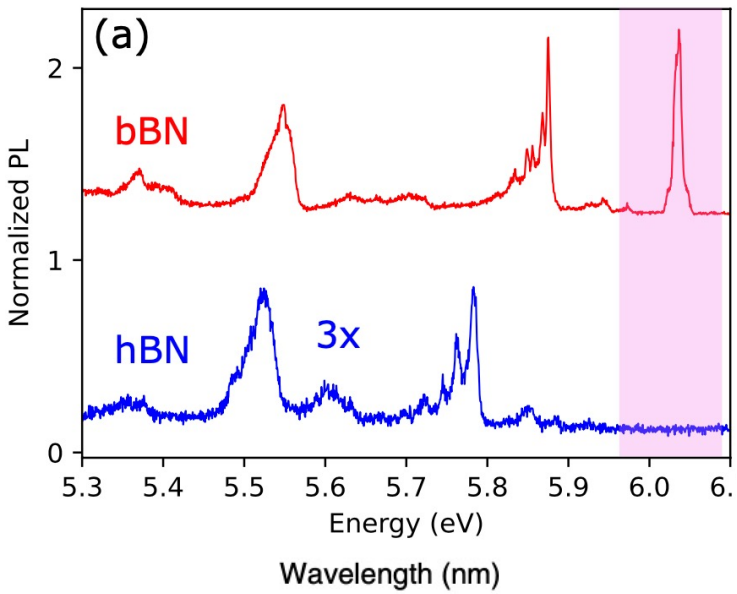
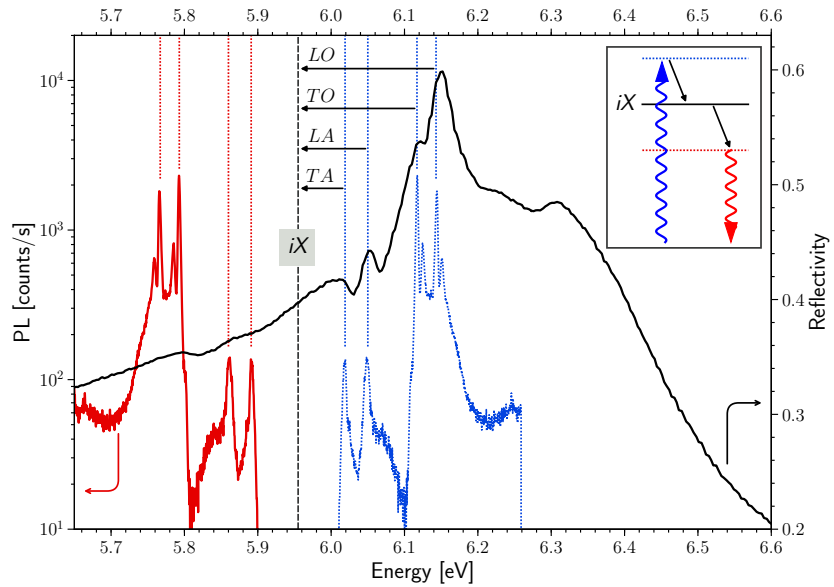
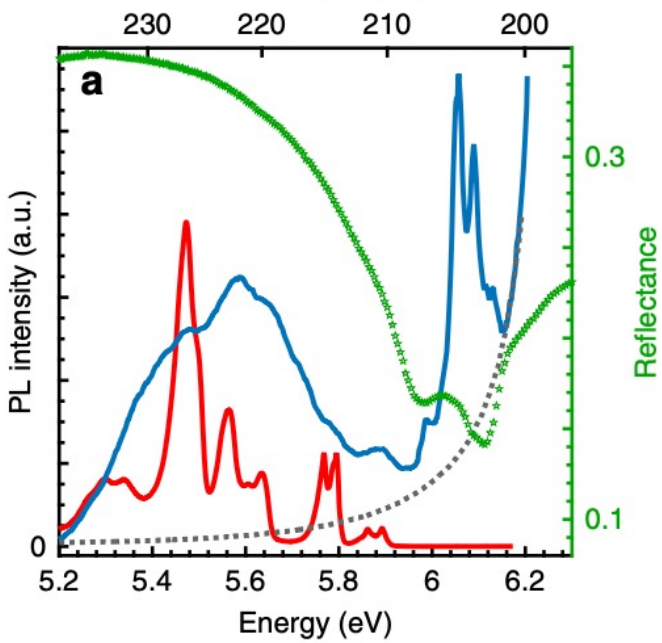
Localized probes are needed in materials science







Without localized optical probes we couln't have established to state that, at 8K:

The value of the indirect band gap of hBN is 5.955eV
The value of the indirect band gap of bBN is 6.029 eV

The value of the direct band gap of hBN is 6.125 eV
The value of the direct bandgap of bBN is 6.035 eV
The value of the direct band gap of mBN is 6.080 eV

Thank you for your attention