

Epitaxie de semiconducteurs II-VI :
ZnTe/ZnSe et CdTe:Se
Etude du confinement électronique de type-II
et du dopage isoélectronique

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Equipe mixte CEA-CNRS

« Nanophysique et Semiconducteurs »

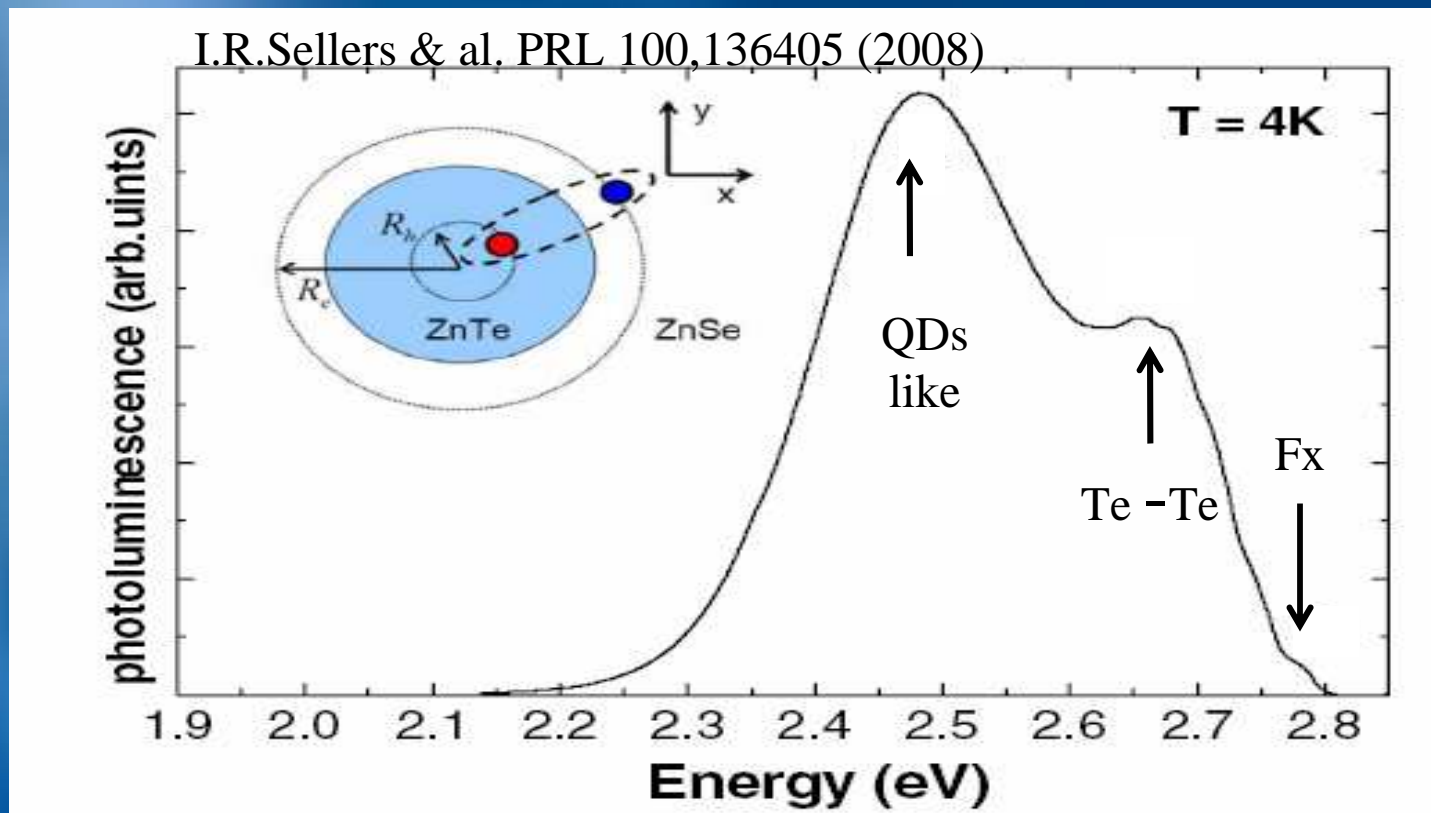
Institut NEEL – CNRS, Grenoble, France



Interest of telluride / selenide heterostructures

❖ Type-II interfaces

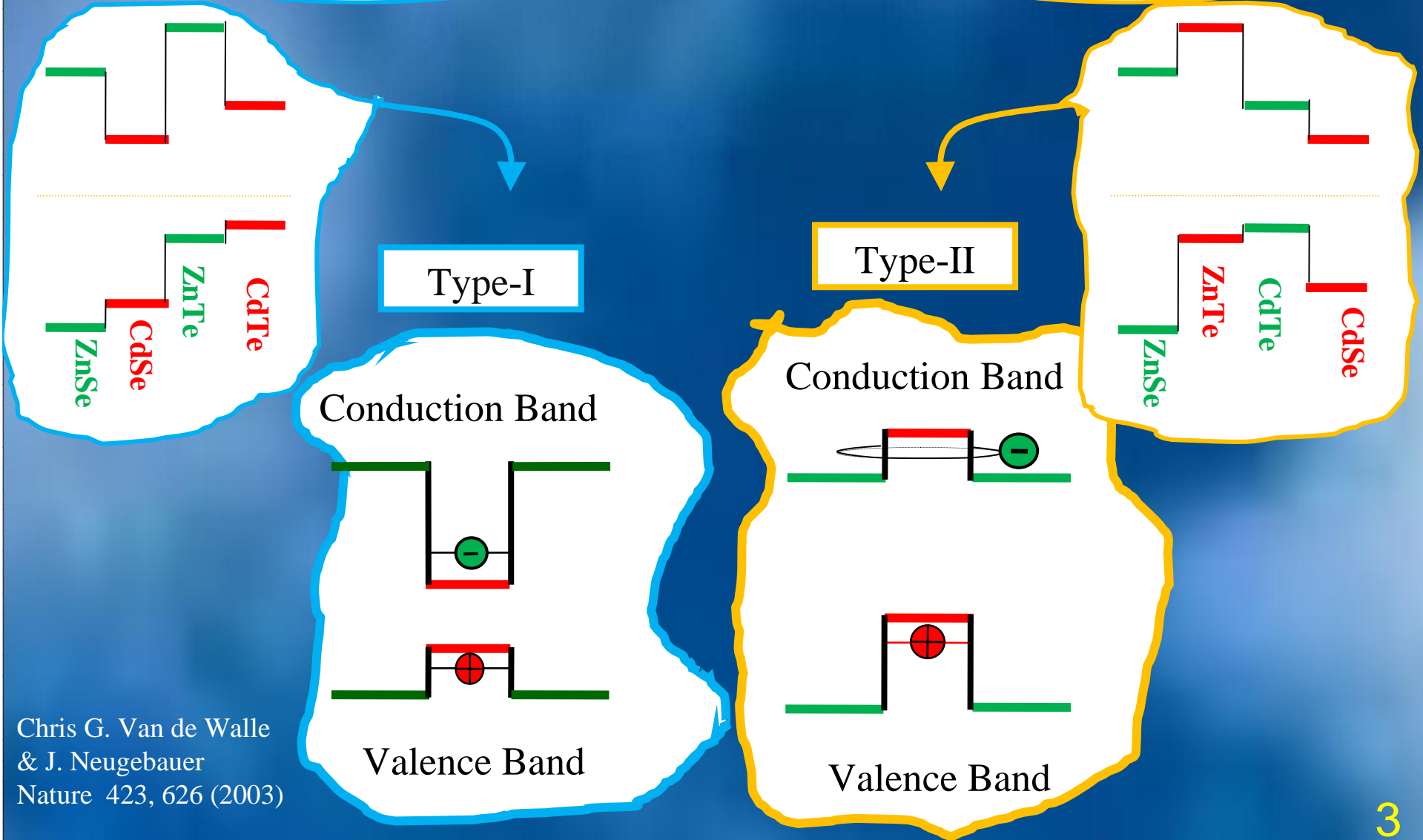
❖ Evolution of ZnSeTe system from isoelectronic centers to quantum dots and alloys



Energy band alignment

Common cation

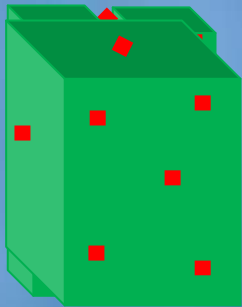
Common anion



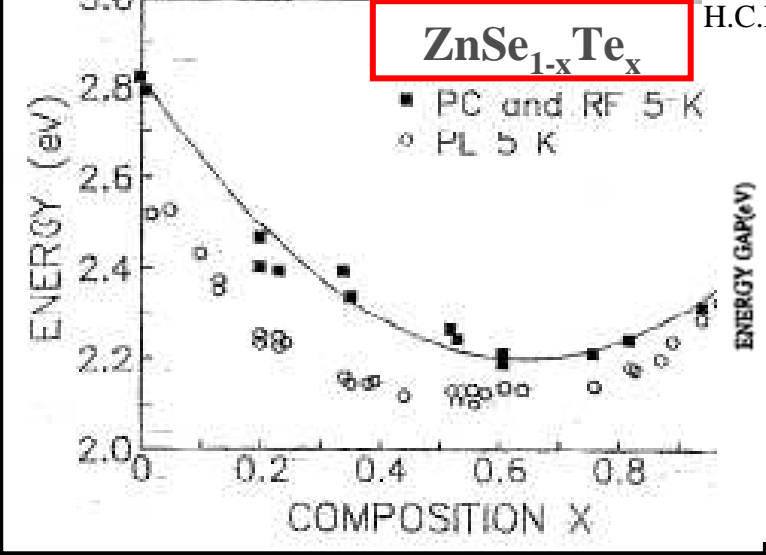
Chris G. Van de Walle
& J. Neugebauer
Nature 423, 626 (2003)

Tellurium and Selenium based alloys

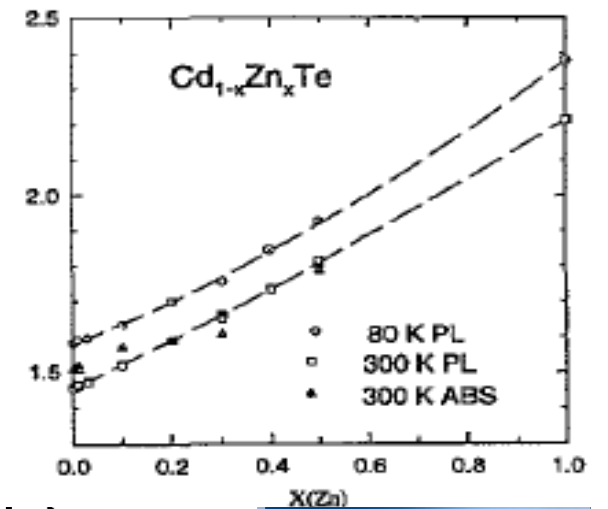
Isoelectronic centers



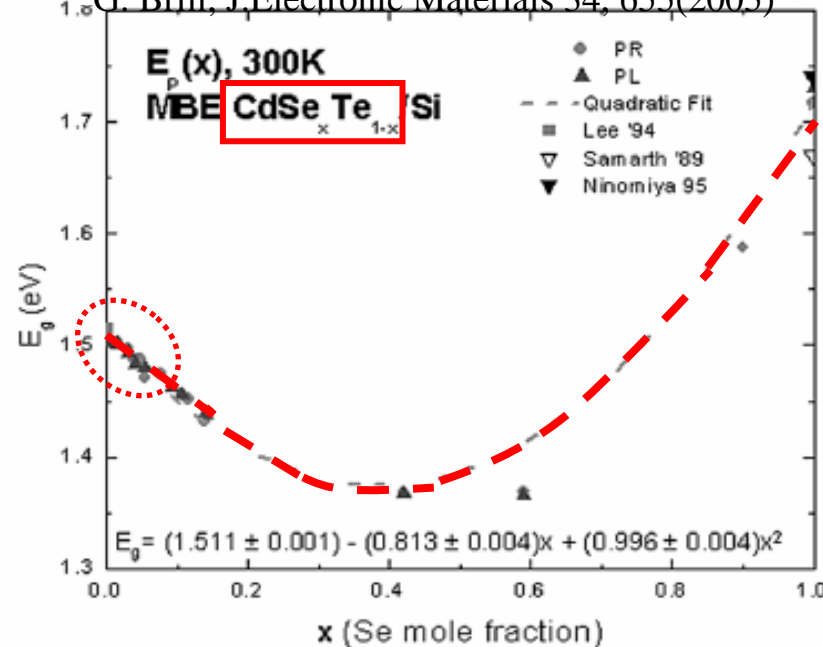
M.J.S.P. Brasil, App. Phys.Lett. 58, 2509 (1991)



H.C.POON, J.Phys.Condens.Matter 7,2783(1995)

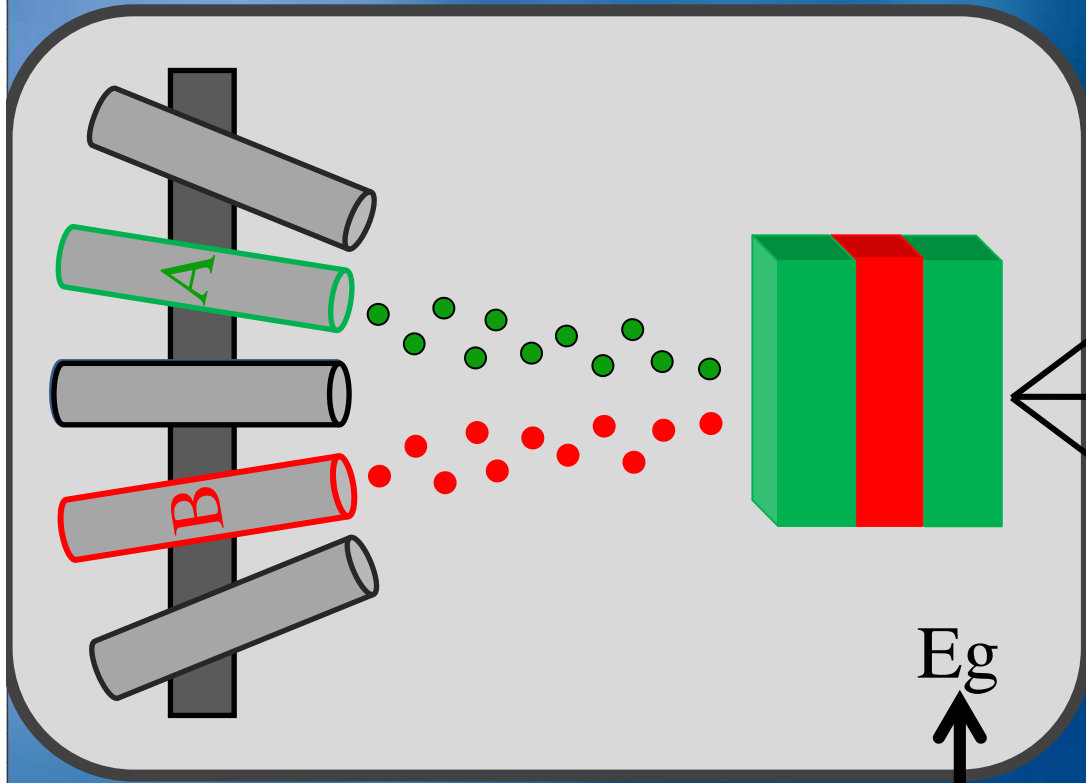


G. Brill, J,Electronic Materials 34, 655(2005)



B.

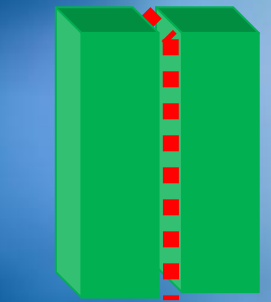
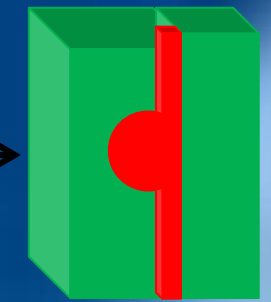
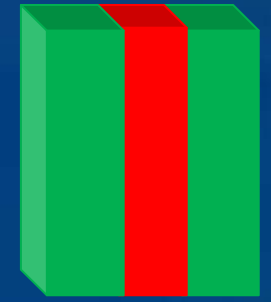
Heterostructures by MBE



Quantum well

Quantum dots

Isoelectronic centers



OUTLINE

❖ Introduction :

Tellurium & Selenium based Semiconductor?

1- Growth Mechanism of ZnTe/ZnSe QDs:

Islands formation ?

Capping difficulties & solutions ?

2- Optical Properties of Type-II QWs & QDs.

PL & Time Resolved PL Studies

3- Isoelectronic doping CdTe:Se.

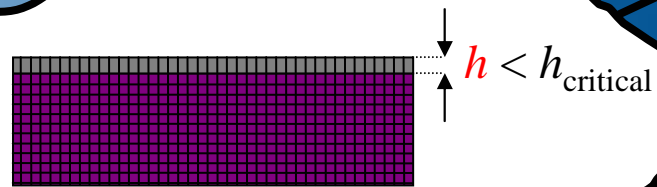
High purity samples

Optical studies

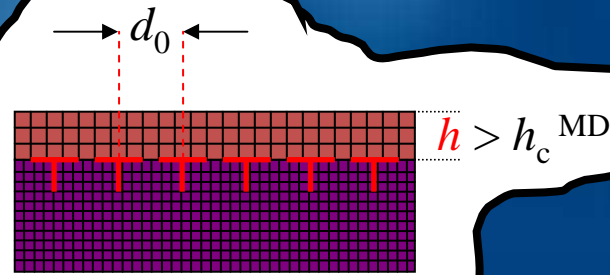
❖ Conclusion & Perspectives

Relaxation modes

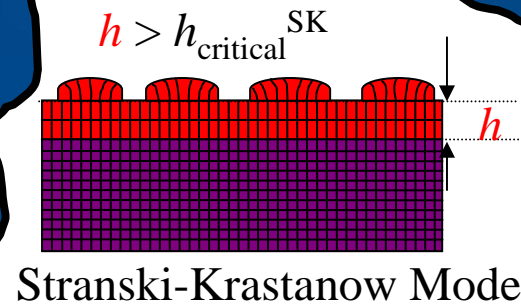
ZnTe/ZnSe :
7% of lattice mismatch



2D-coherent Mode:



2D-MD Mode



Stranski-Krastanow Mode

CdTe/ZnTe

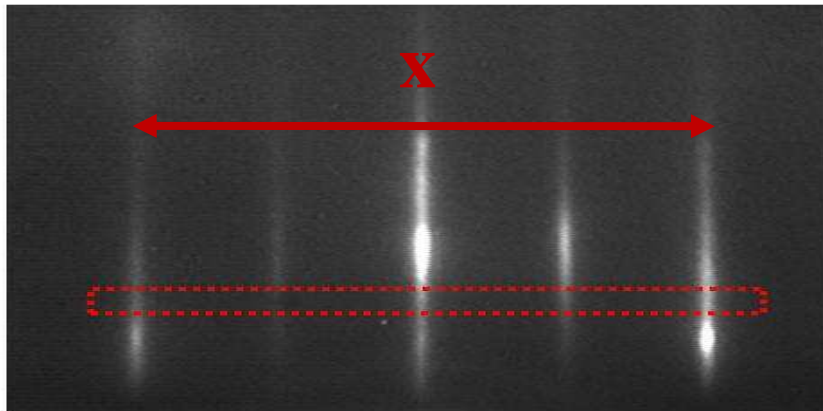
F.Tinjod
Thèse U.J.F
Grenoble (2003)

InAs/GaAs

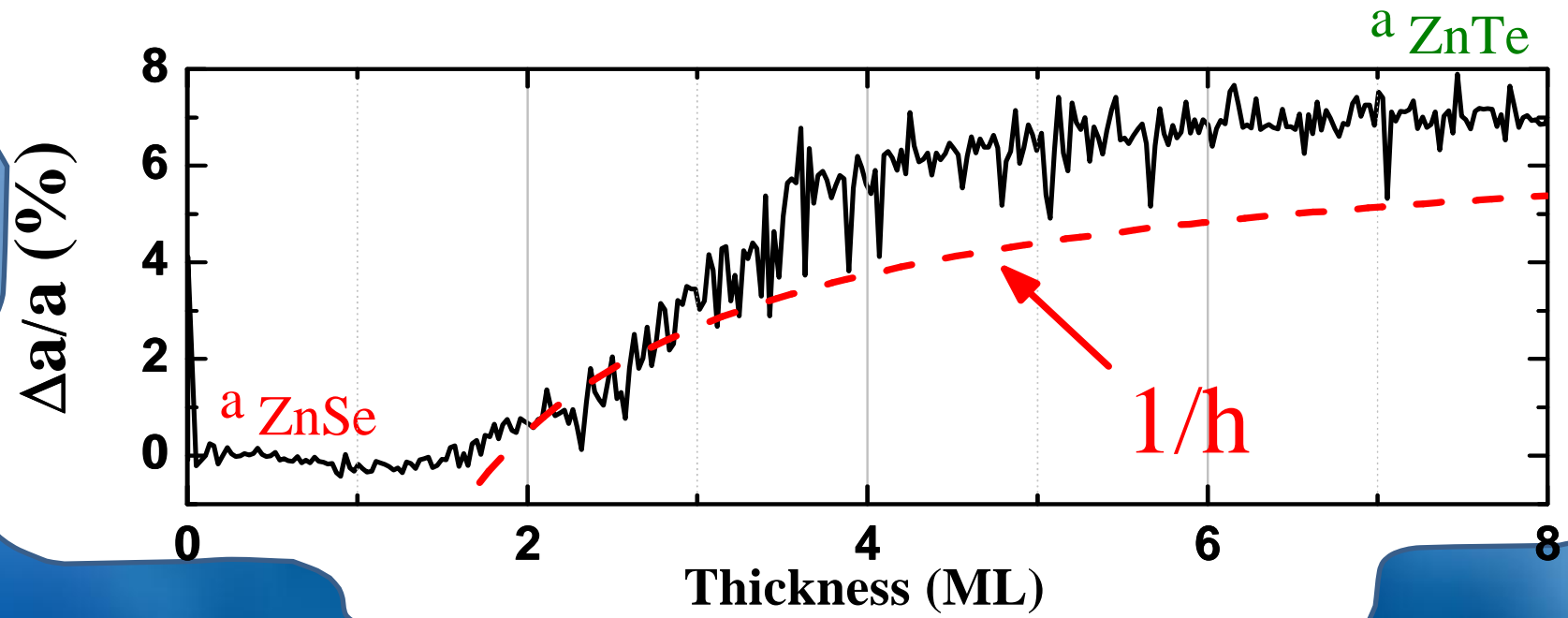
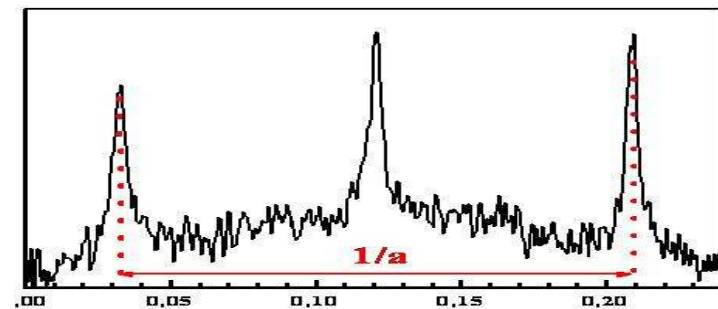
L.Goldstein
Appl.Phys.Lett.
47,1099,(1985)

Relaxation modes

Lattice parameter variation from RHEED:



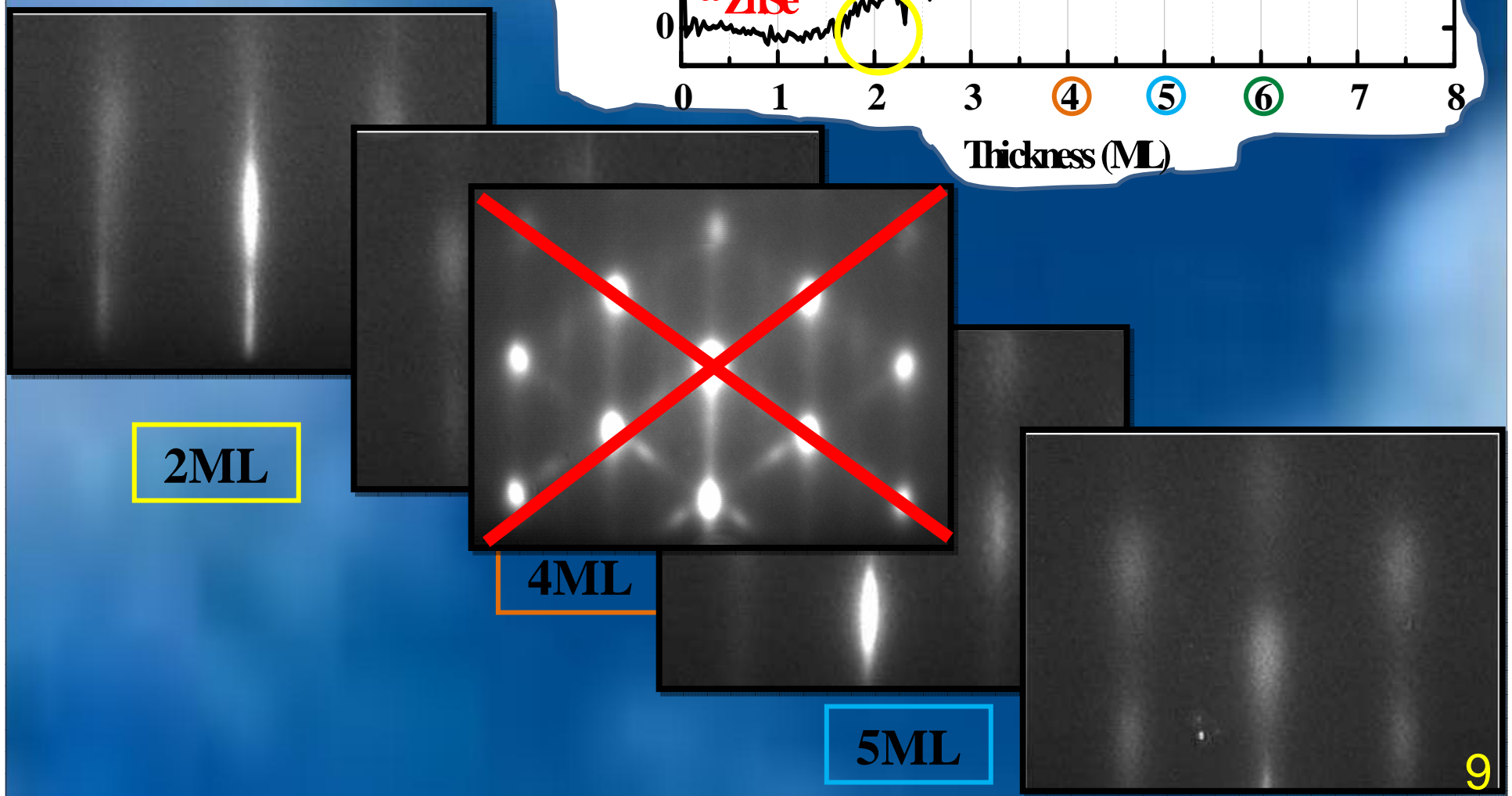
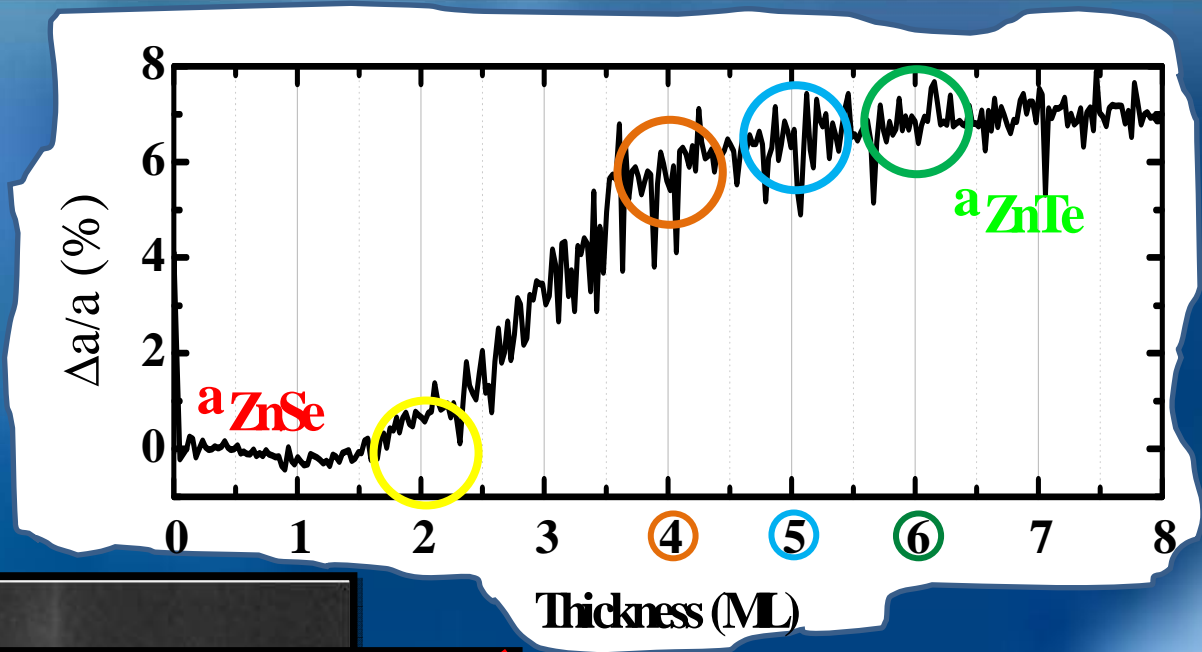
$$\frac{\Delta a}{a} = - \frac{\Delta x}{x}$$



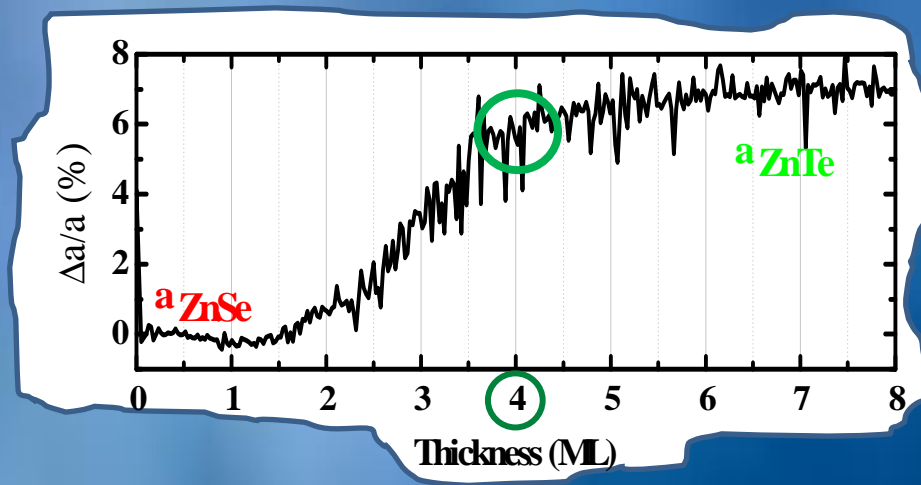
Critical thickness of ZnTe/ZnSe
 $hc = 2 \text{ MLs} = 0.6 \text{ nm}$

Relaxation modes

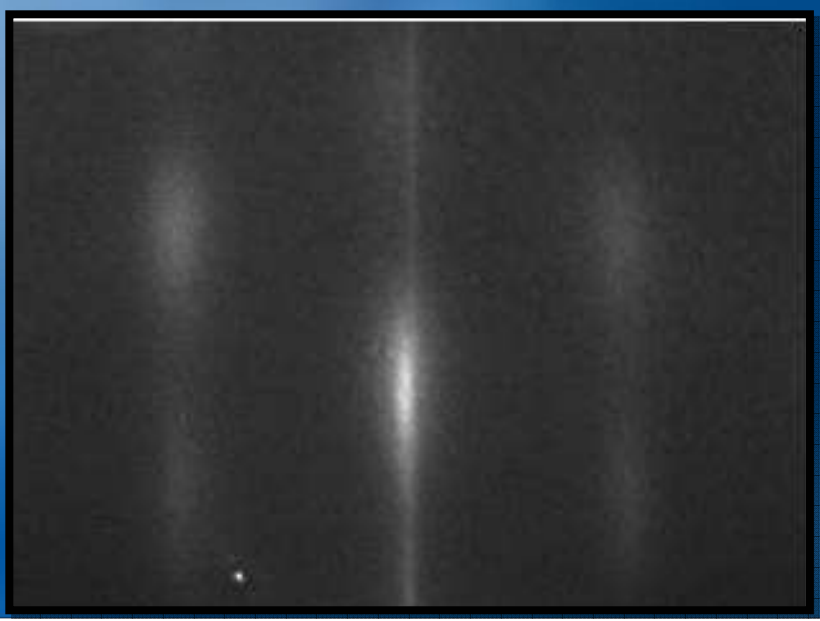
RHEED :
ZnTe Surface



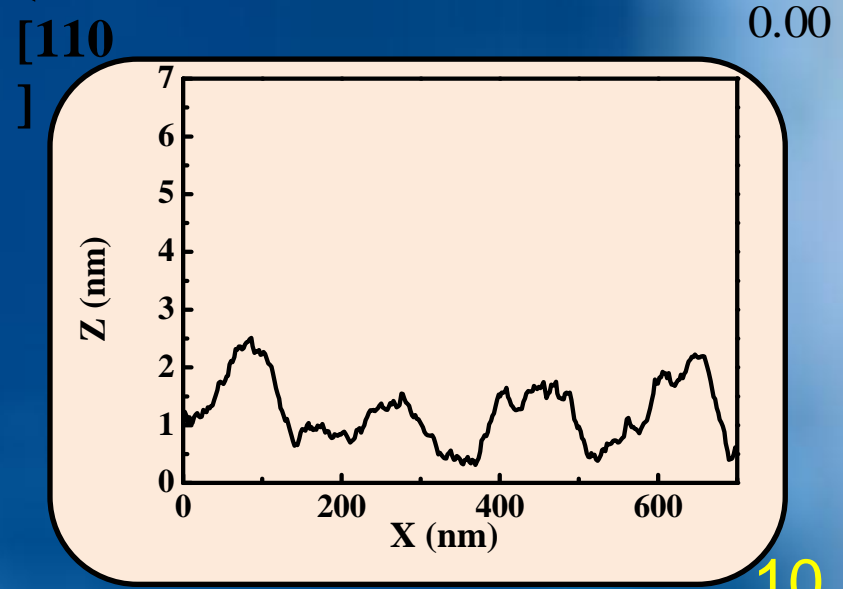
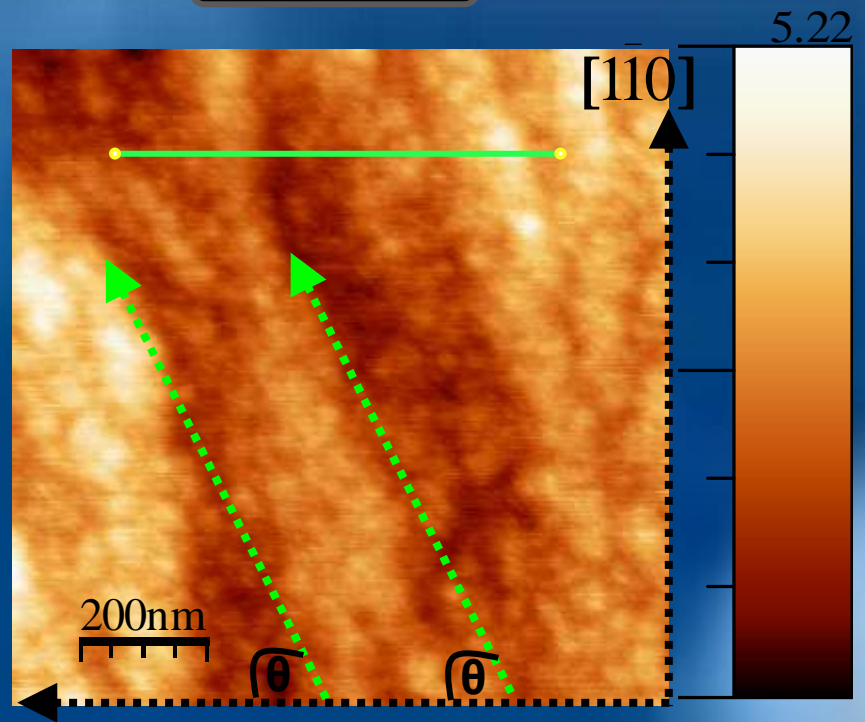
Relaxation modes



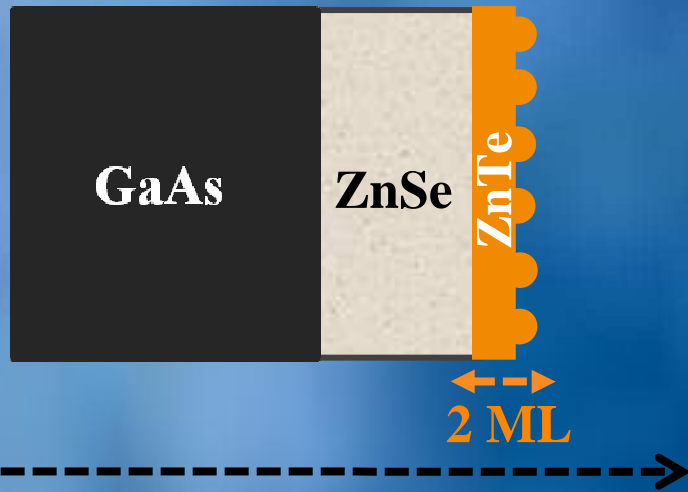
RHEED



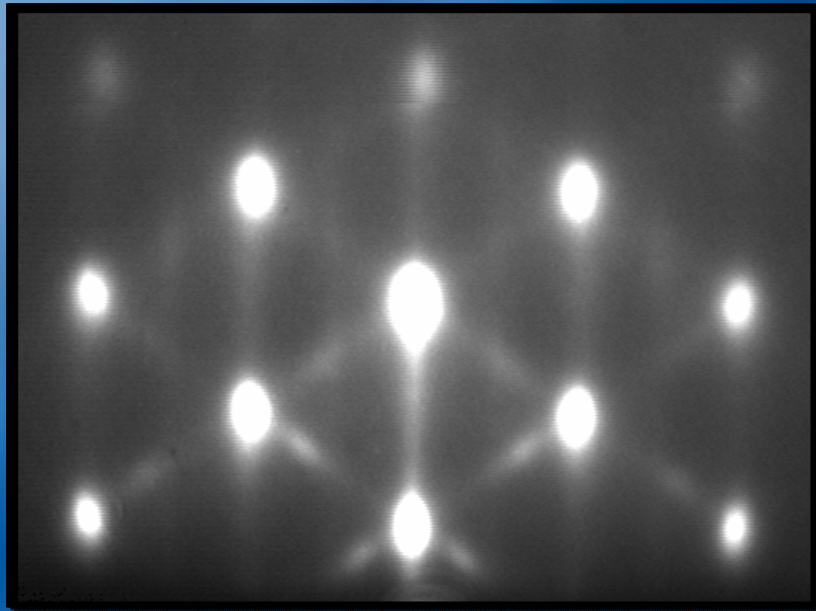
AFM



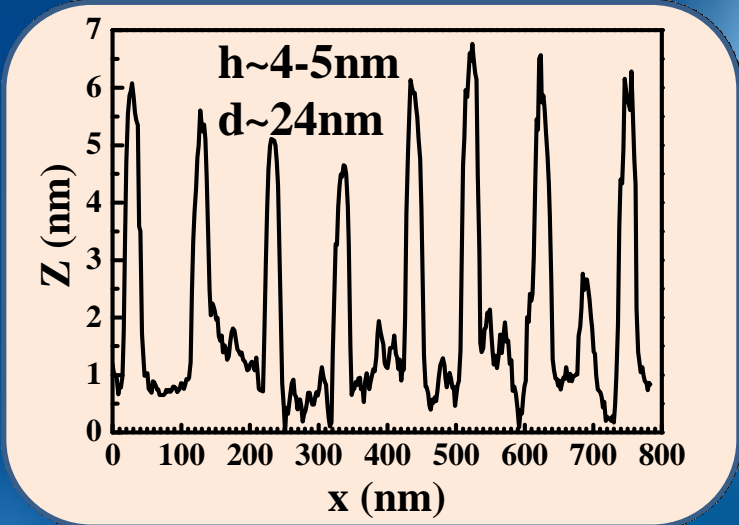
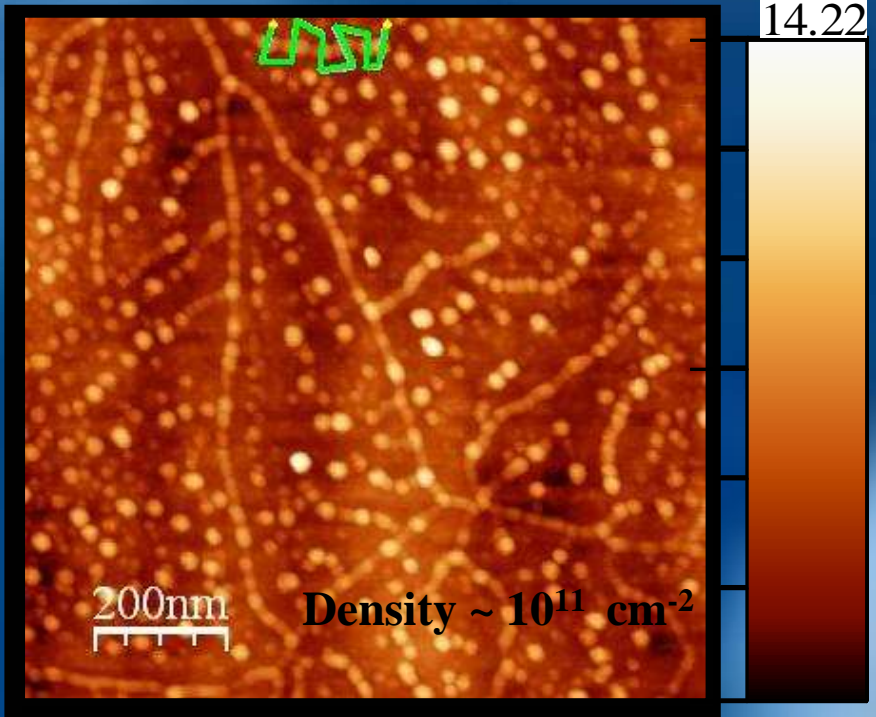
Sample's Growth : ZnTe/ZnSe



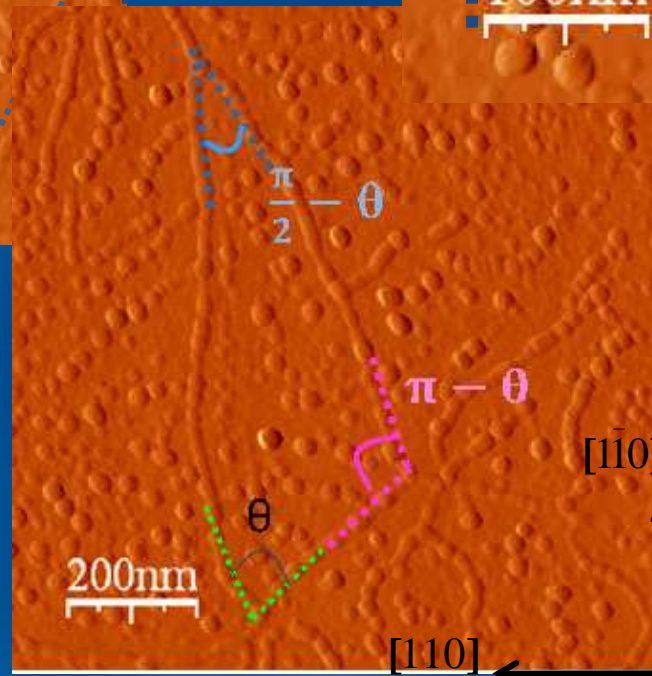
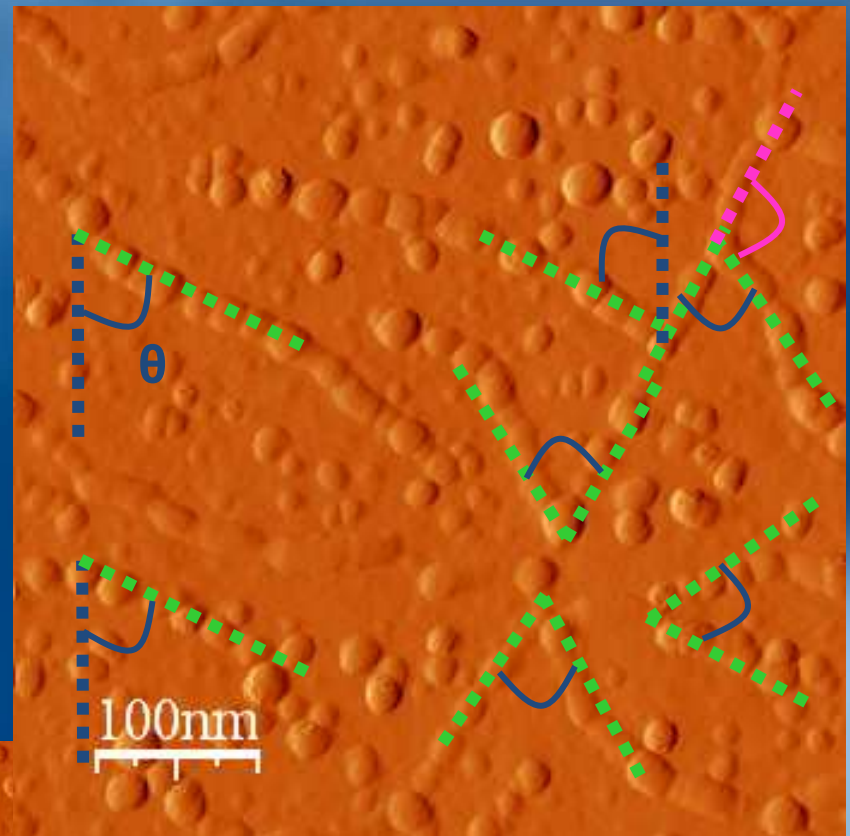
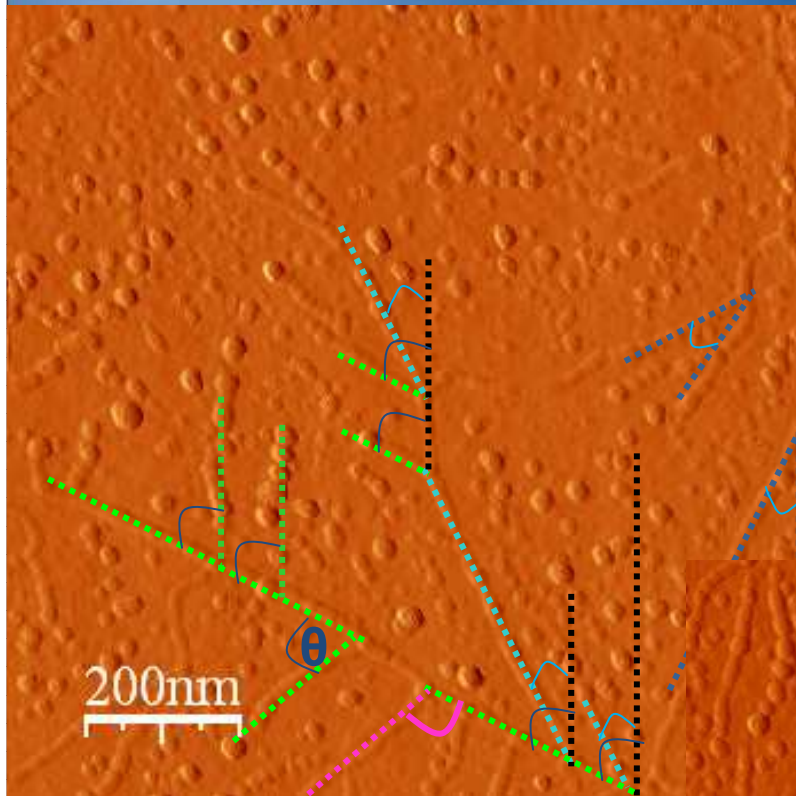
RHEED



AFM



Islands alignments



Oriented alignment :
[310]

Typical angle :
 $\theta = \pi/3$

OUTLINE

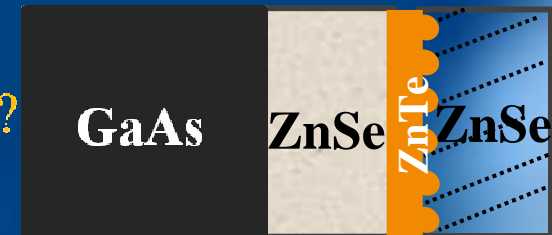
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❖ Conclusion & Perspectives

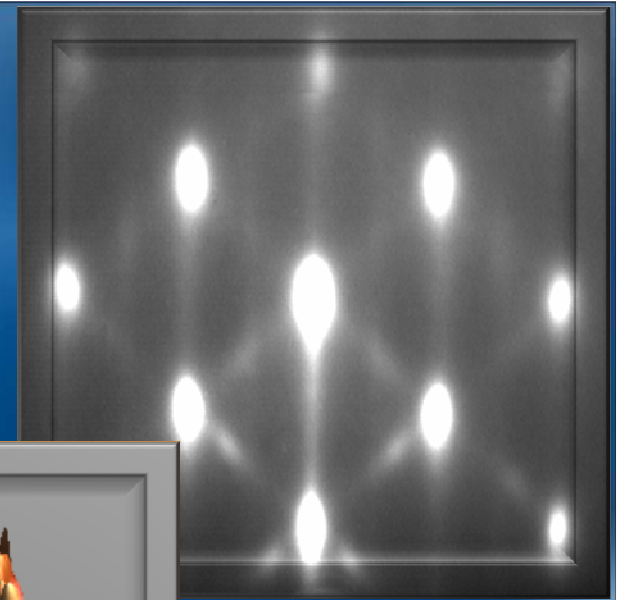
Islands after capping

Paradox?

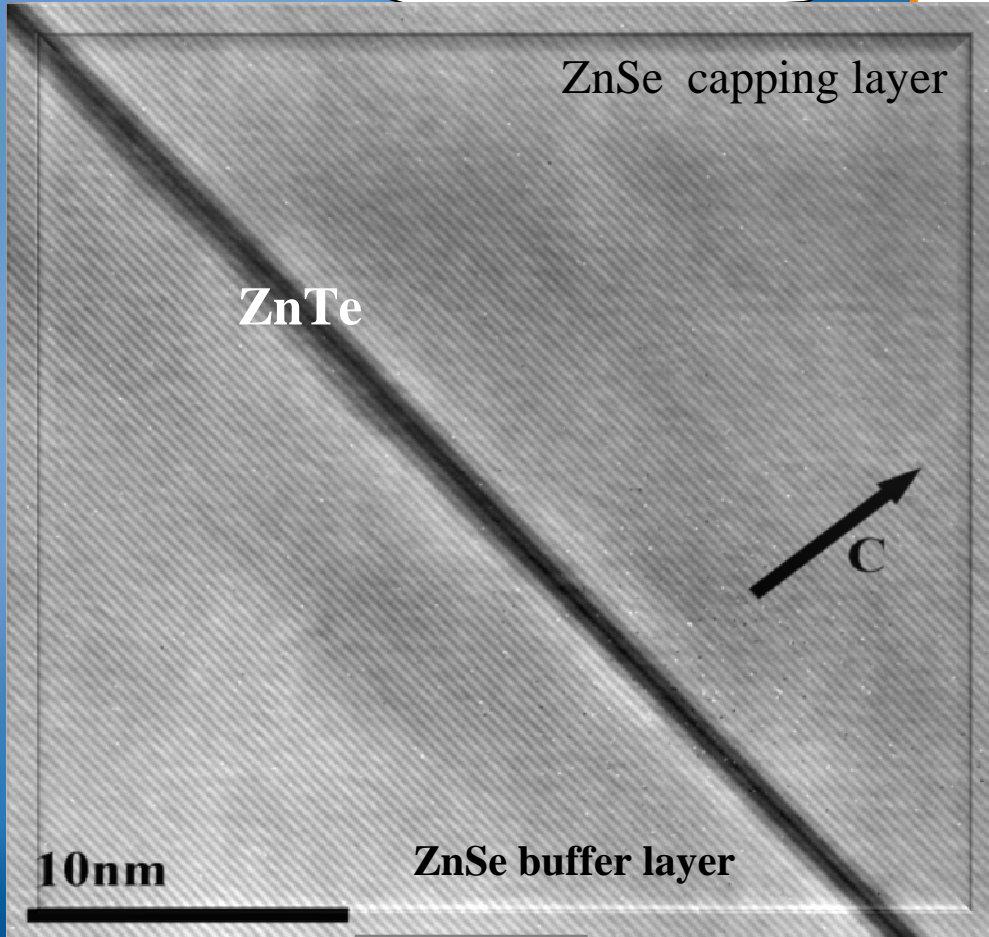
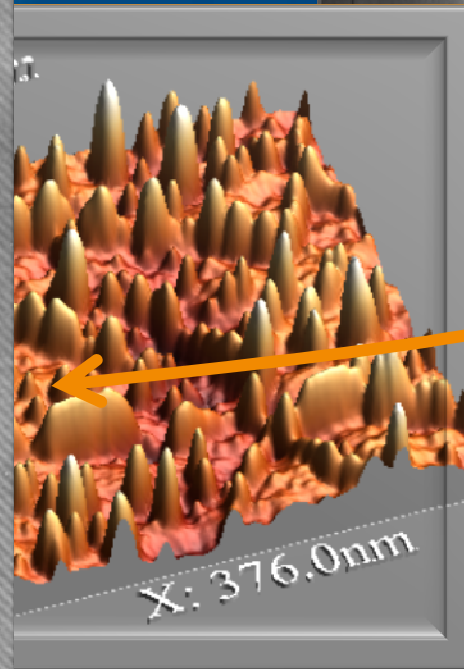
Flattening of ZnTe/ZnSe upper interface :

Disappearance of islands

AFM



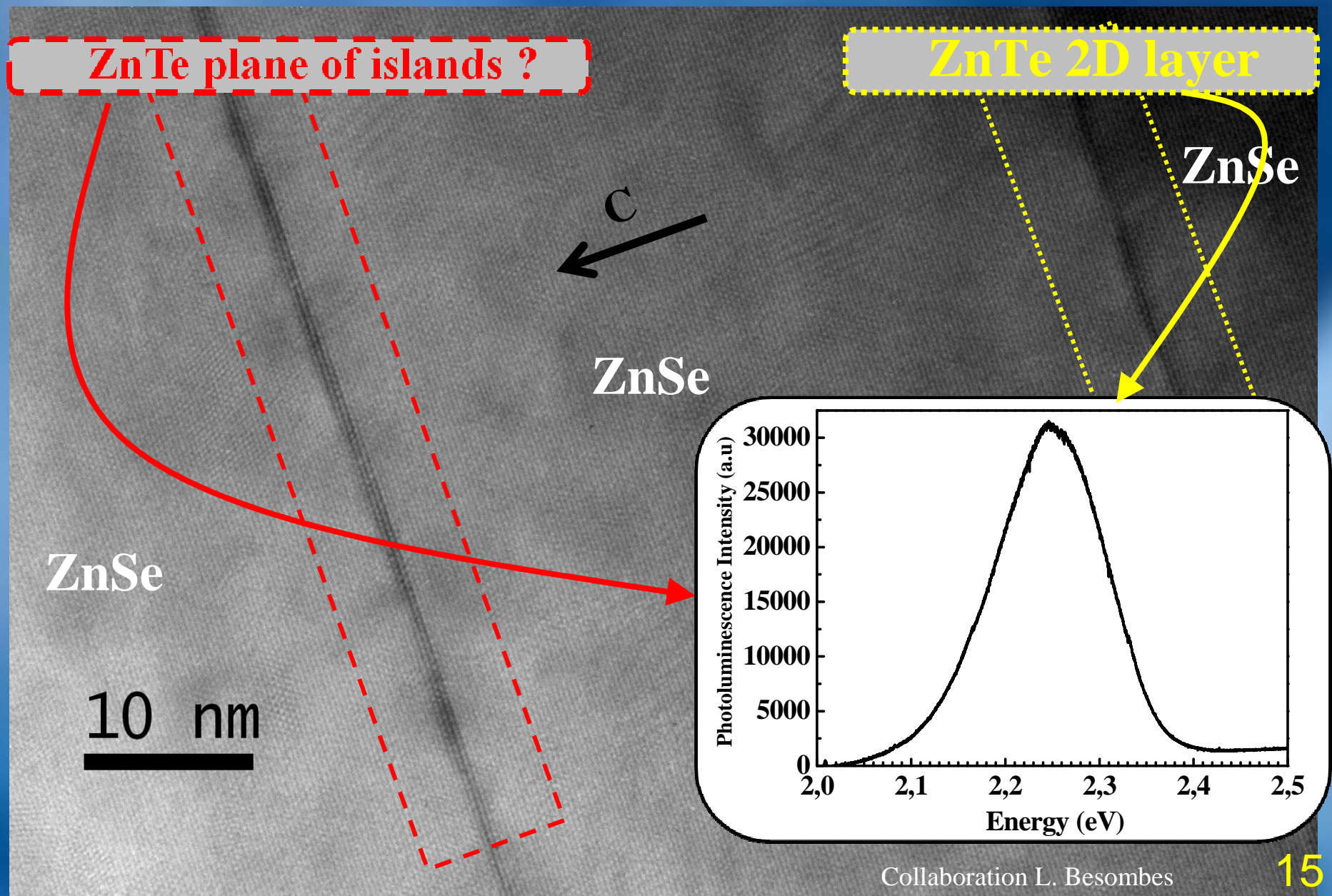
RHEED



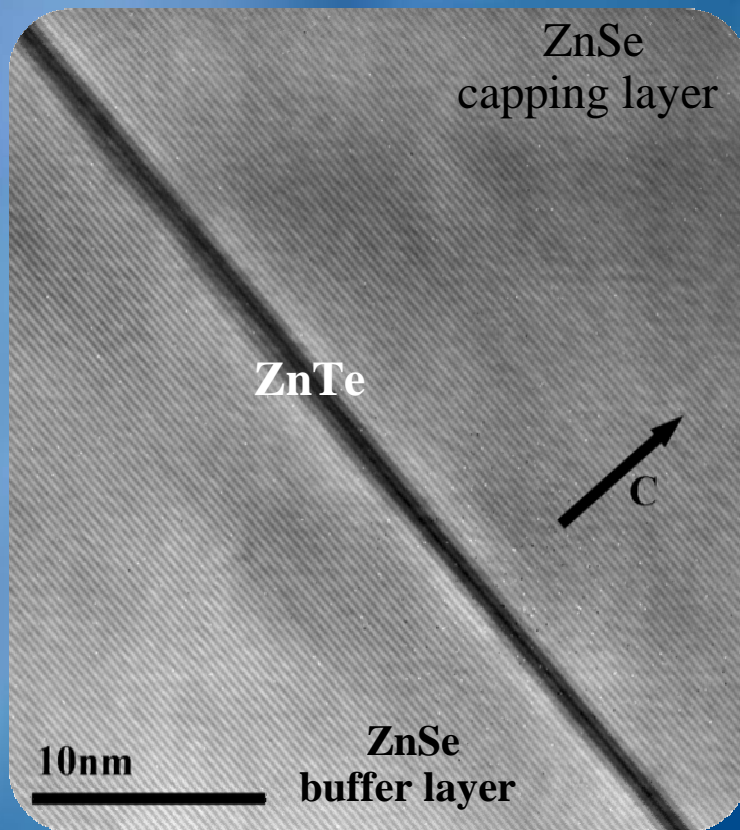
TEM

Collaboration C. Bougerol

Capping Consequences



Capping Consequences



Typical growth conditions of MBE of ZnSe :

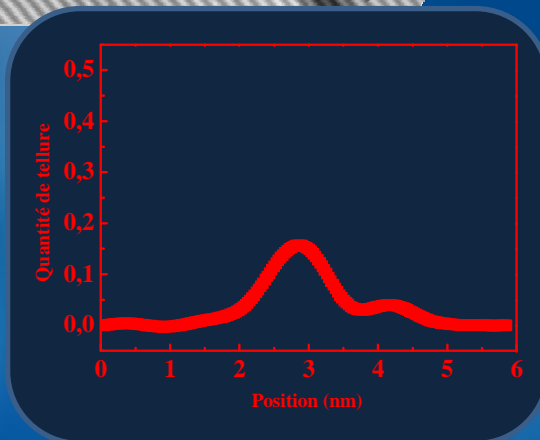
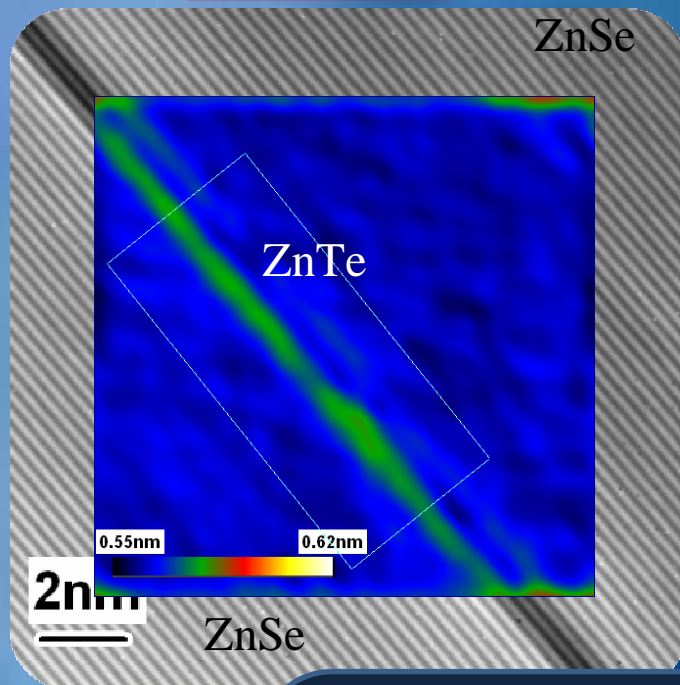
- Growth Temperature ~ 300°C
- Se:Zn= 3

Effect of growth conditions :

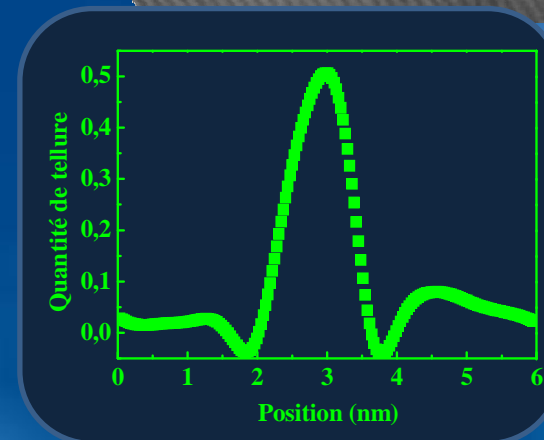
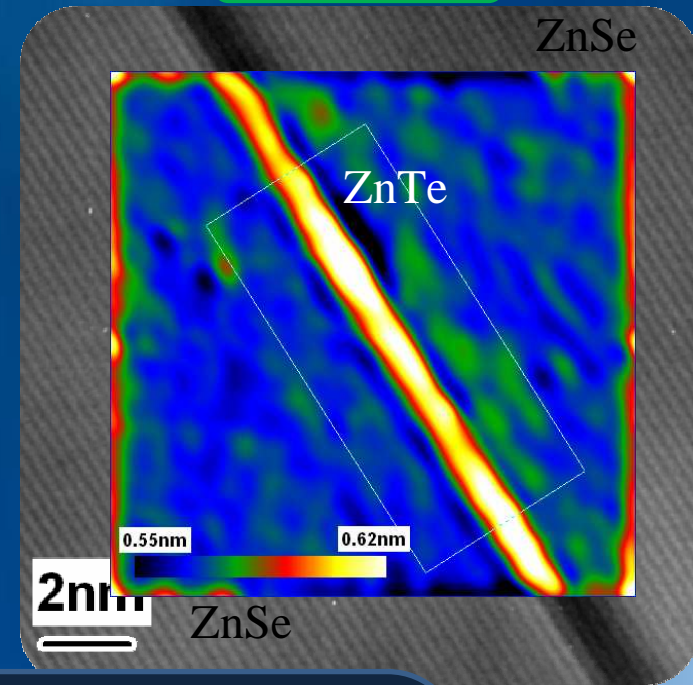
- Insensitive to substrate temperature (300°C → 150°C)
- flux ratio ...

Test of flux ratio Zn/Se on 2MLs QWs

Se : Zn = 3

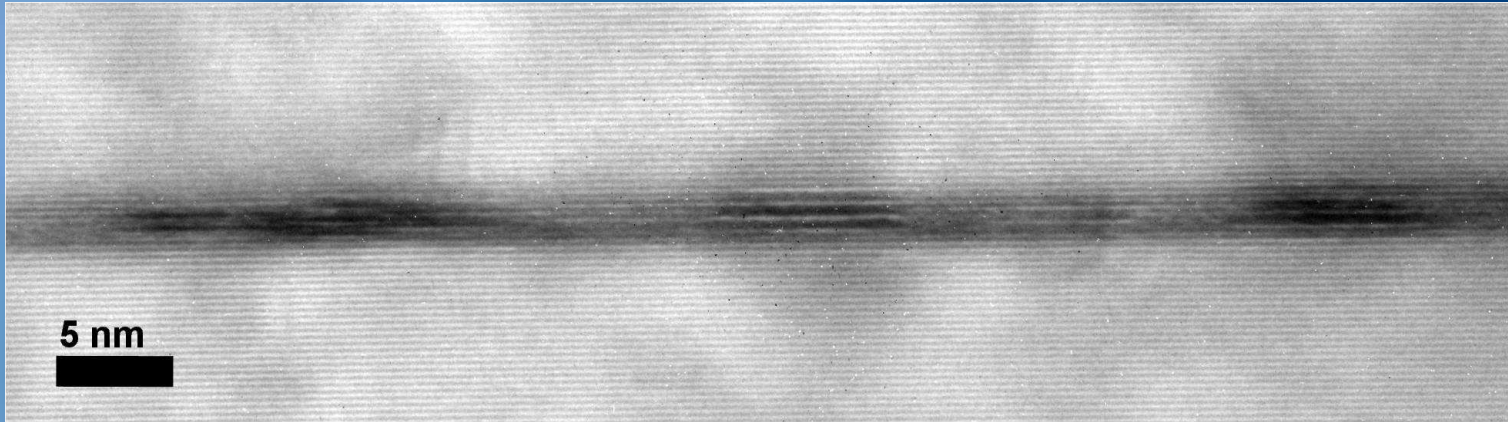


Se : Zn = 0.3

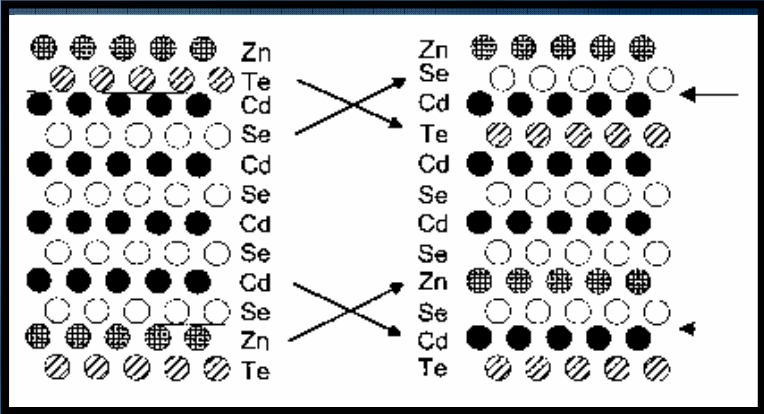


Spontaneous formation of ordered alloy

ZnTe quantum well capped under flux ratio Se:Zn = 0.3



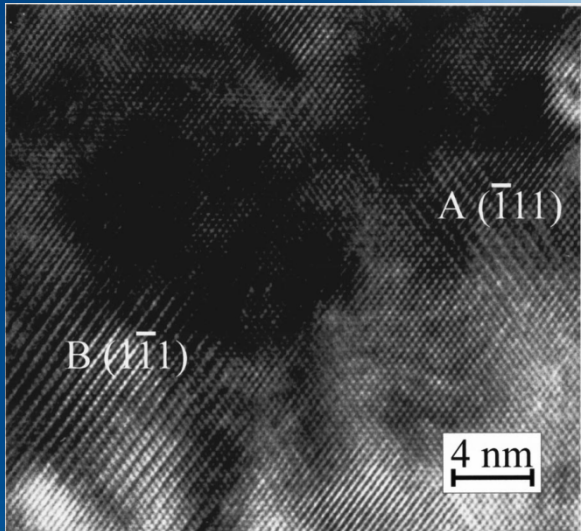
Atomic rearrangement
Te - Se at ZnTe/CdSe interface



K.M.Kemner & al.
Phys.Rev.B50,14327(1994)

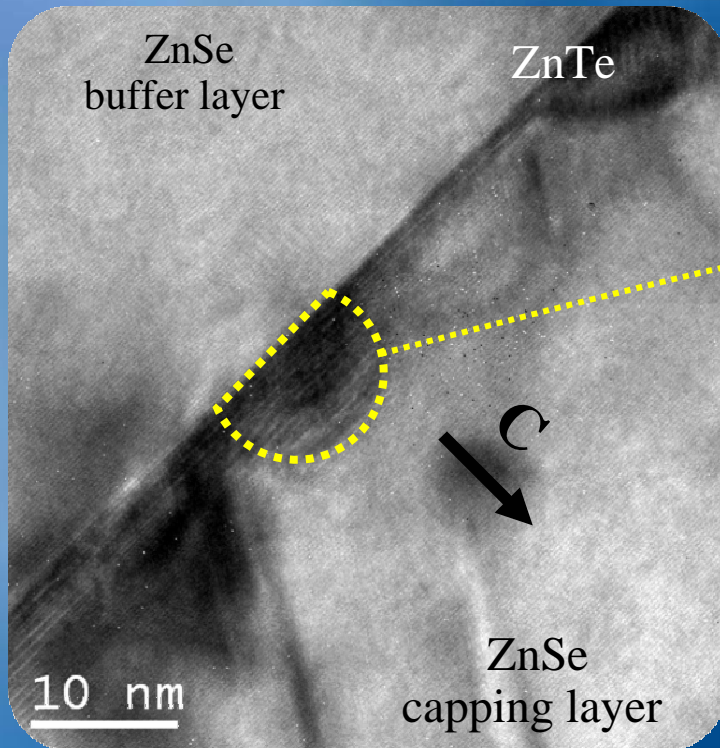
Ordered Structures
at ZnTe/ZnSe interface

H.S.LEE & al.
J.App.Phys.91,5657(2002)

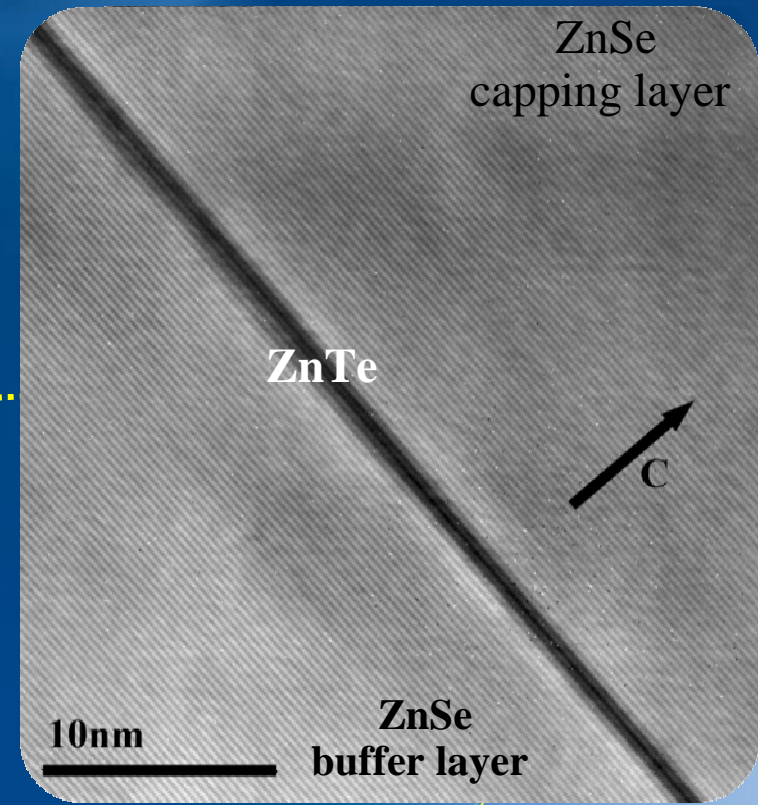


Effect of flux ratio Zn/Se on QD plane

Se : Zn = 0.3



Se : Zn = 3



periodicity in the dot

- Islands at ZnTe/ZnSe interface

Summary – Part 1

- “Non standard” Stranski-Krastanow relaxation for ZnTe/ZnSe
large scale undulations
- Surface treatment by amorphous Te
nanometer scale island’s formation
alignment along [310] directions
- ZnSe growth under Zn flux in excess
limitation of Se/Te competition & segregation
→ quantum dots preservation ←
- Atomic rearrangement at ZnTe/ZnSe interface
ordered alloys with double periodicity

OUTLINE

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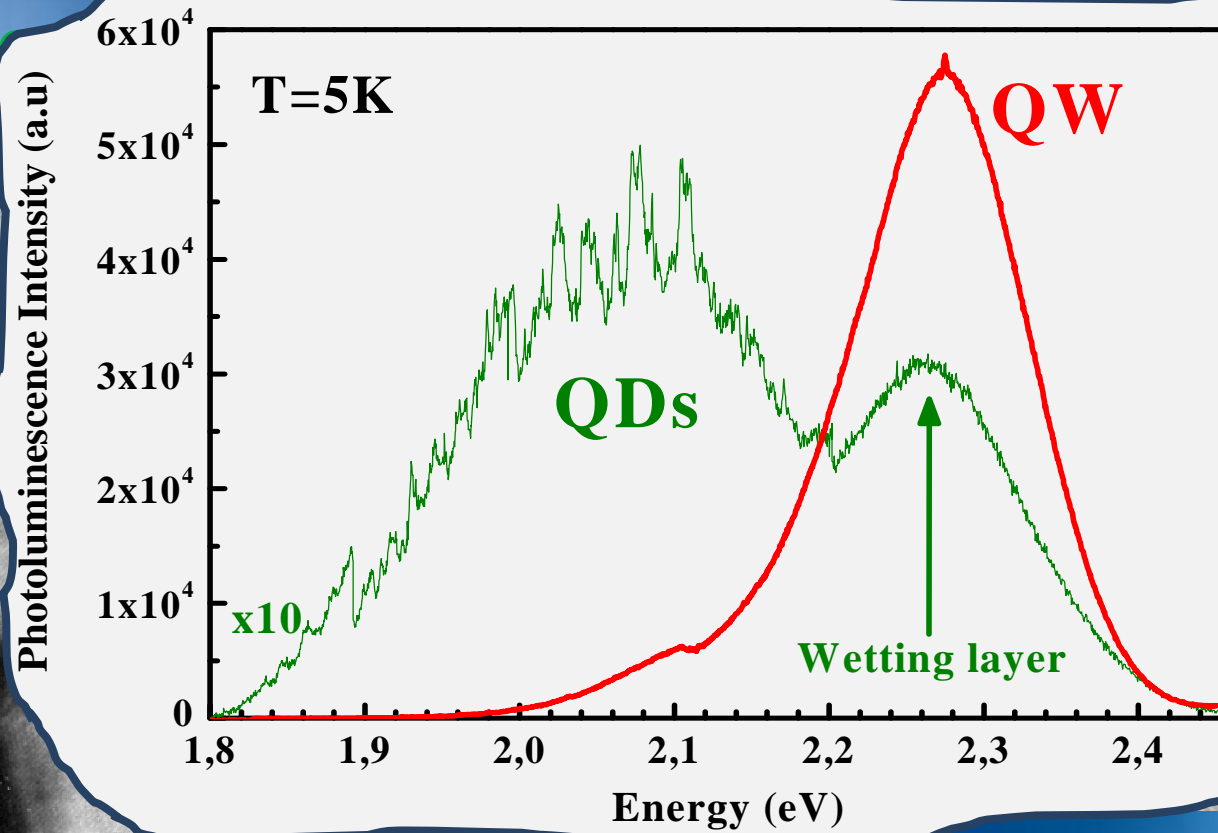
High purity samples

Optical studies

❖ Conclusion & Perspectives

Photoluminescence : Consequences of growth conditions

Se : Zn = 3



ZnSe
buffer layer

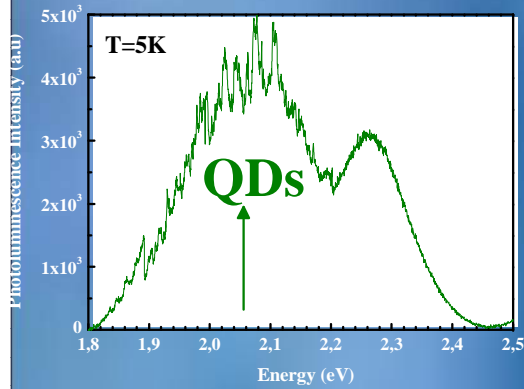
ZnSe
ing layer

c

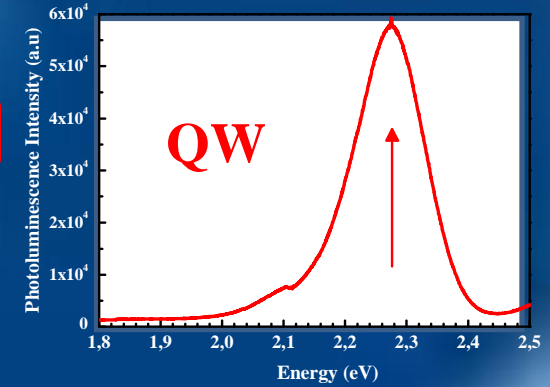
capping layer

10 nm

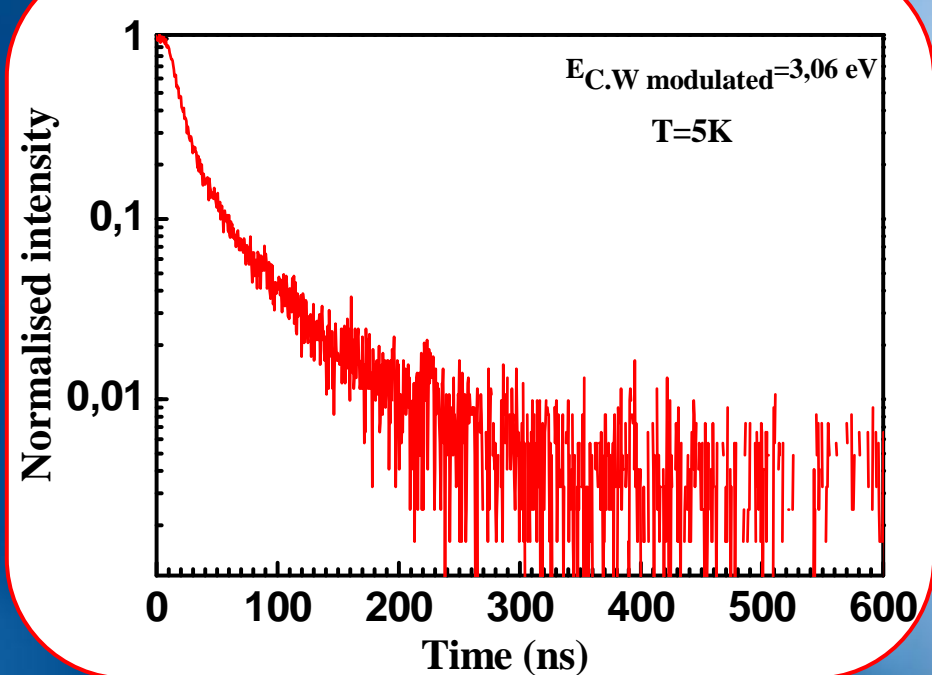
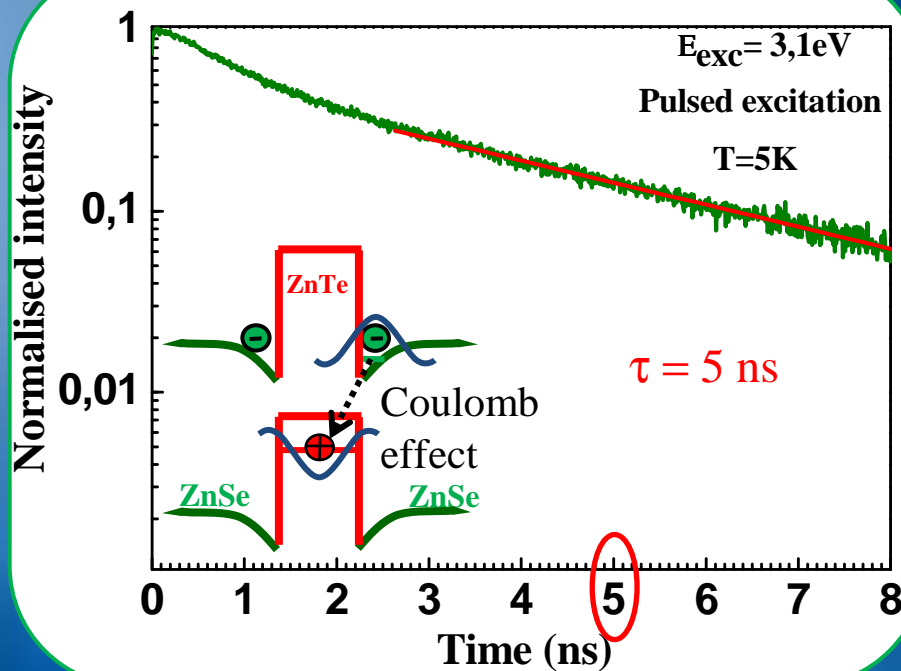
Photoluminescence decay



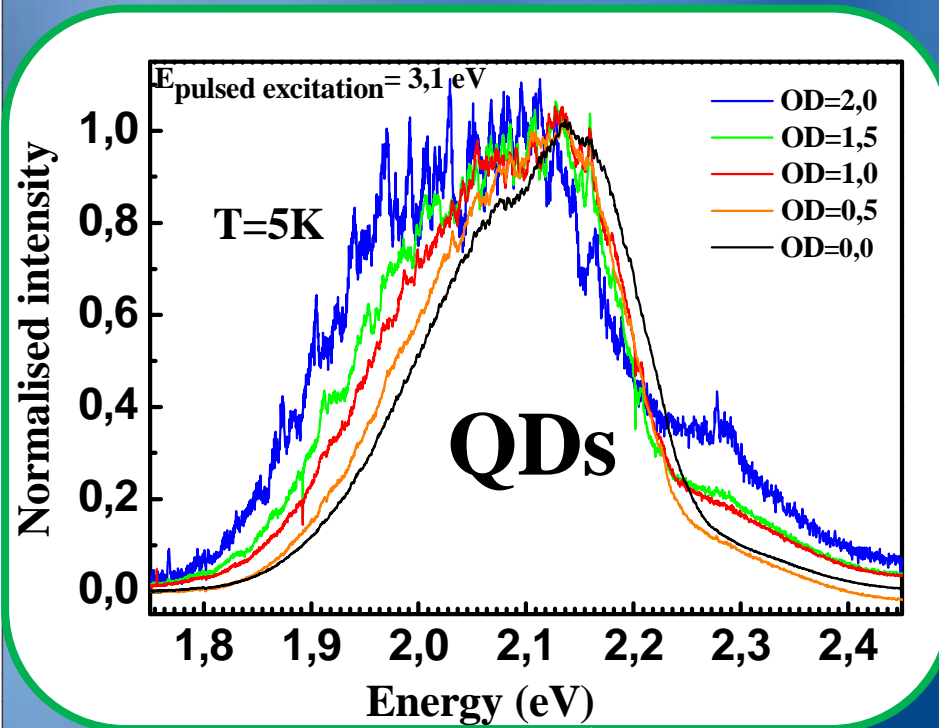
Se : Zn = 0.3



Se : Zn = 3



Photoluminescence : Excitation power dependence

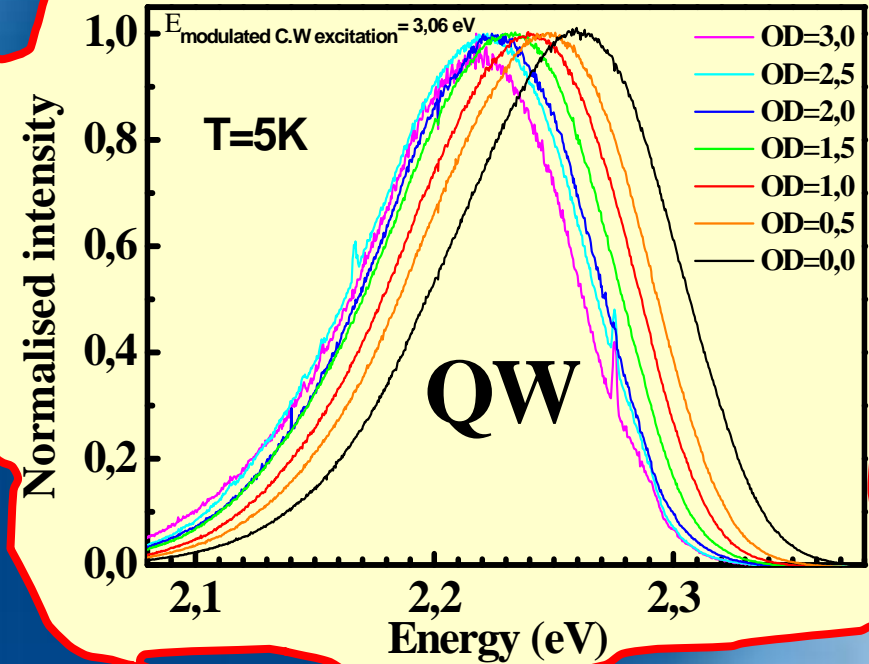


Excitation Spot ($2\mu\text{m}$): a few hundreds of dots

QD

Increase of power excitation :

- Narrowing of PL line
- Smoothing of the PL structures

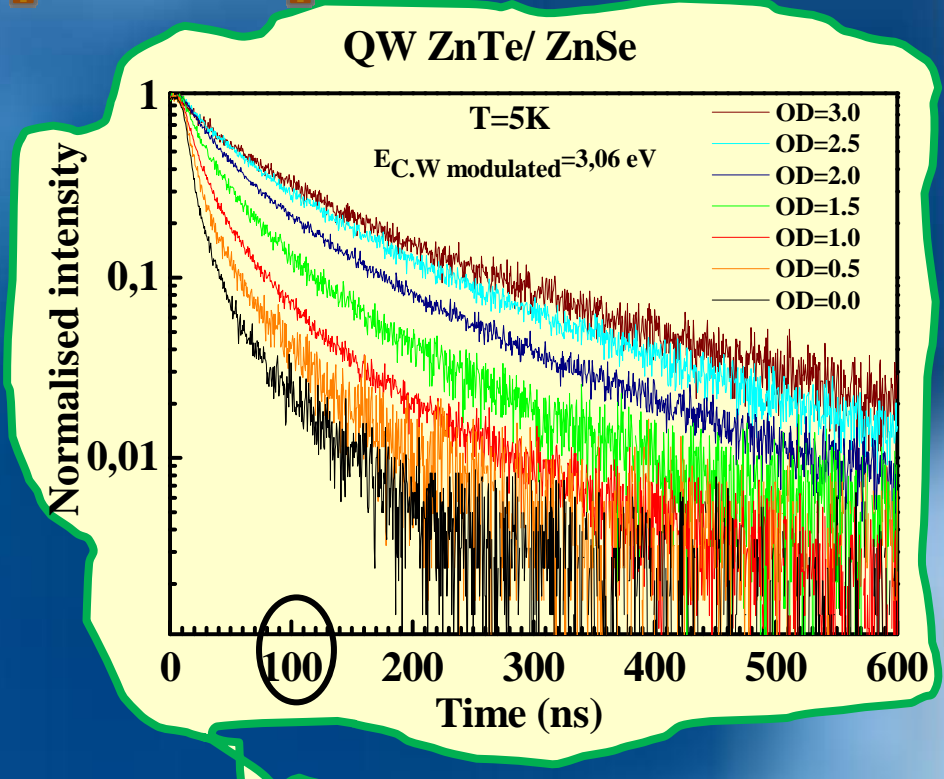
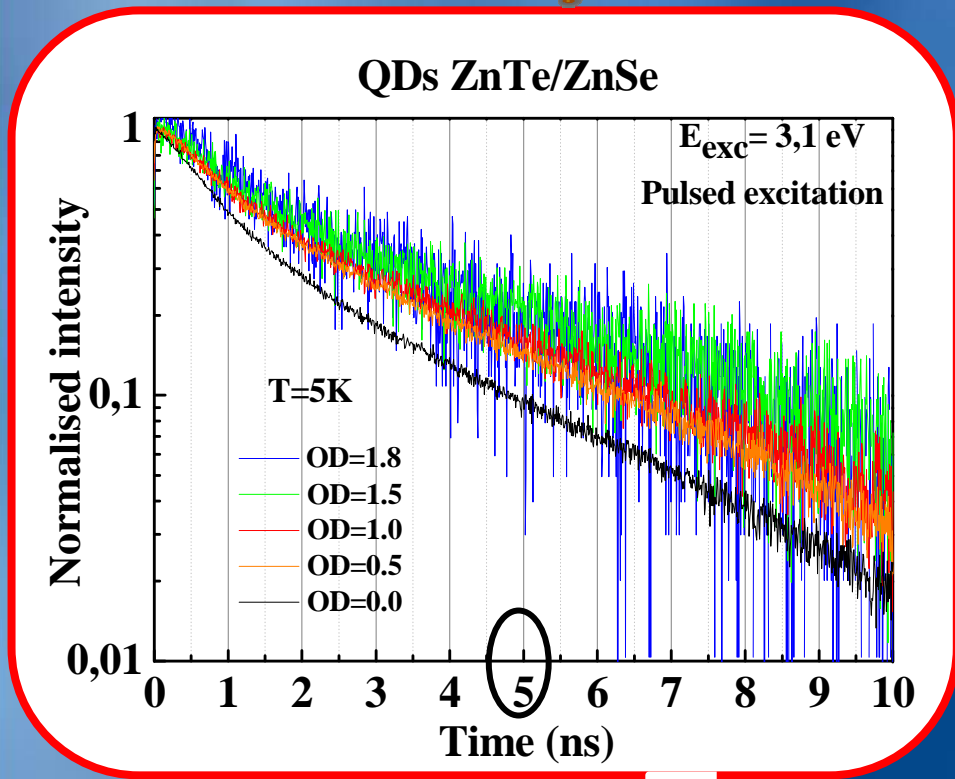


QW

Increase of power excitation :

- No change of the shape of the PL line
- excitation density: blue shift

Time decay : Excitation power dependence



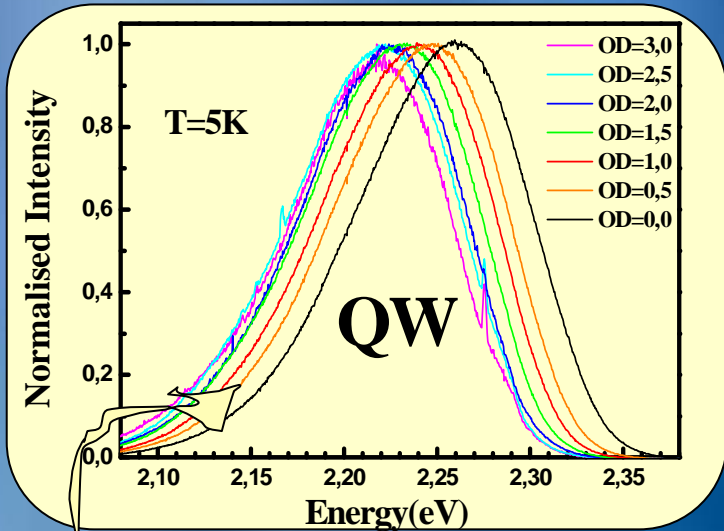
QD

QW

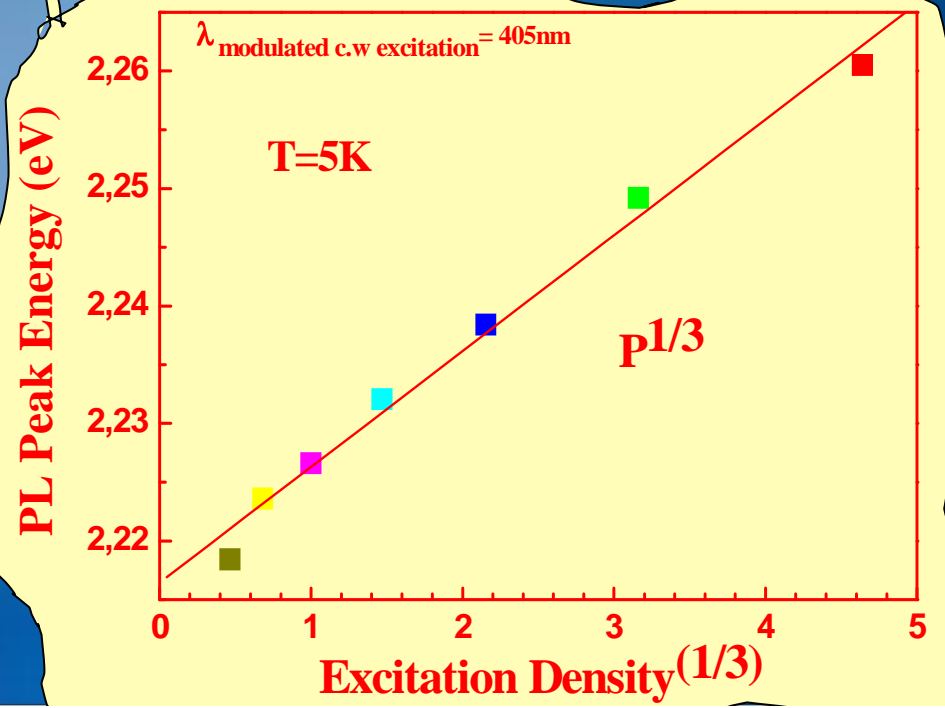
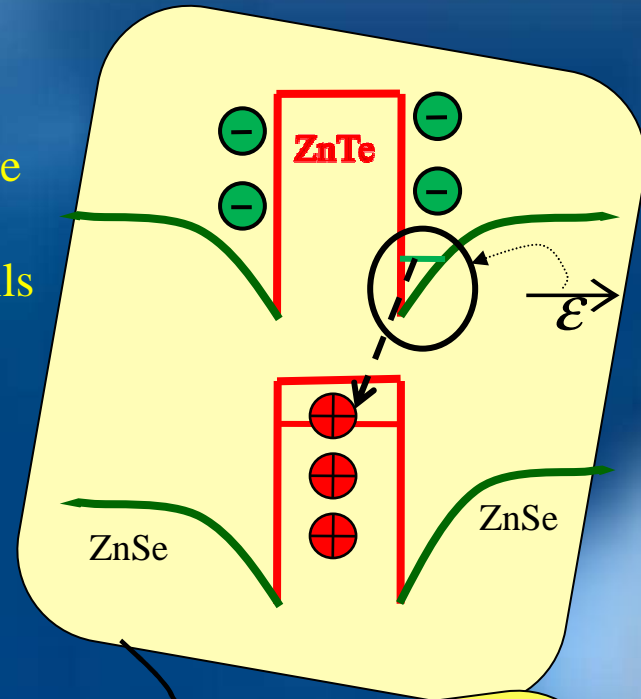
- PL decay (~ 5 ns) from excitons localized on an ensemble of QDs.
- close to mono-exponential.
- insensitive to excitation density.

- PL decay (~100ns)
- strongly time-stretched with respect to an exponential decay
- highly sensitive to the excitation density

Quantum well PL shift ?



Capacitor-like structure
&
triangular potential wells



Gauss theorem: $\|\mathcal{E}\| \propto n$

Schrödinger : $E_{conf} \propto \|\mathcal{E}\|^{2/3}$

Let assume : $n \propto \sqrt{P}$

$\Rightarrow E_{conf} \propto \|\sqrt{P}\|^{2/3} = P^{1/3}$

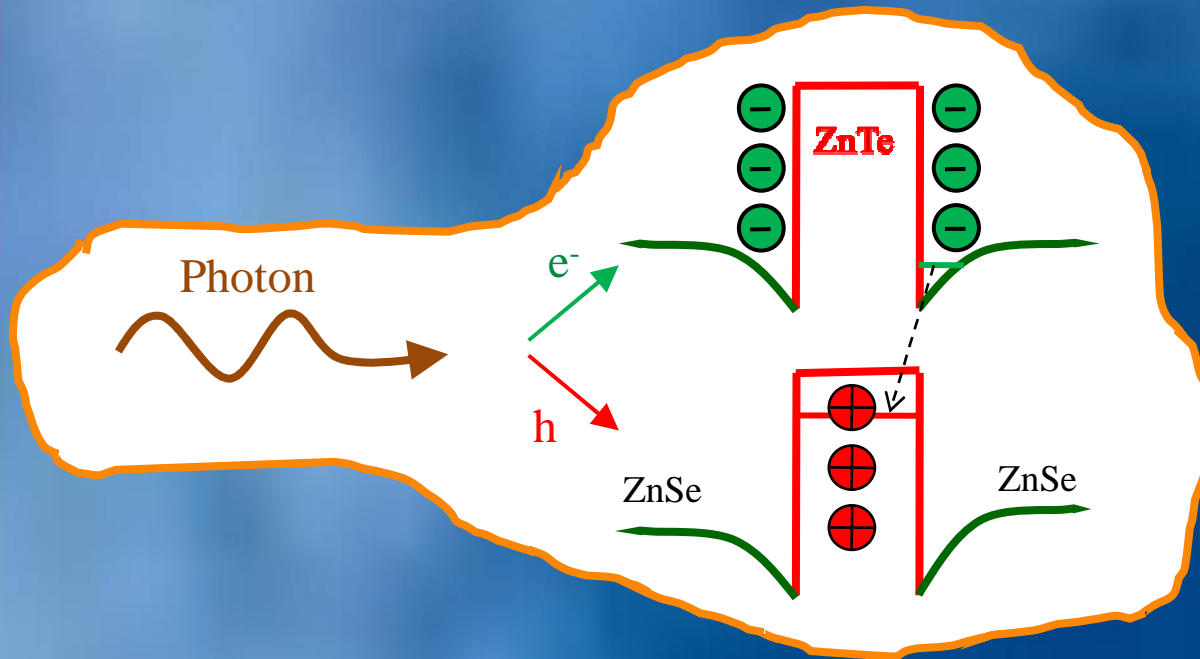
$$n \propto \sqrt{P} \quad ?$$

Type-II
QW:

$$\frac{dn}{dt} = AP - \gamma \cdot np$$

$\underbrace{\hspace{10em}}_{n^2}$

n : electrons
p : holes
n = p

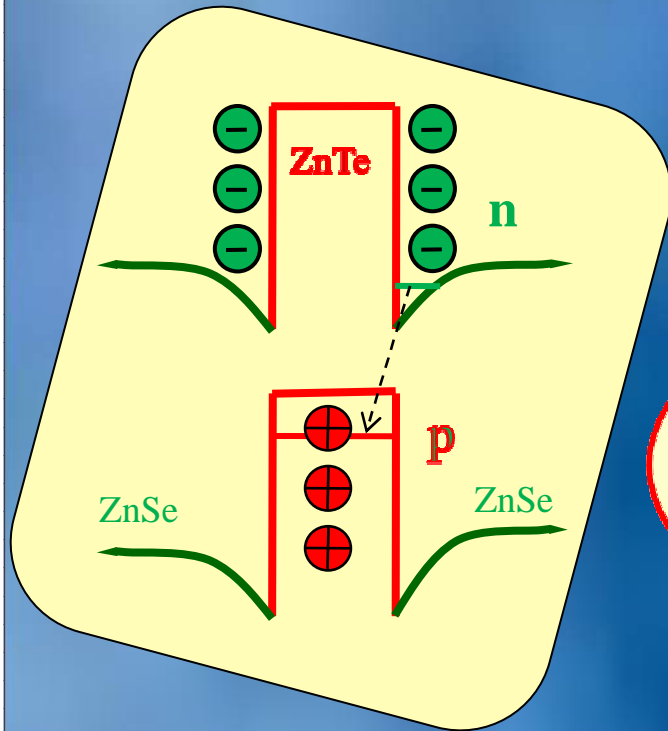


Stationnary solution :

$$\frac{dn}{dt} = 0$$

$$n^2 = \frac{AP}{\gamma} \Rightarrow n \propto \sqrt{P}$$

Photoluminescence decay



pulsed excitation :
 $AP=0$, $n(t_0)=p(t_0)=n_0$

Type-II
 QW:

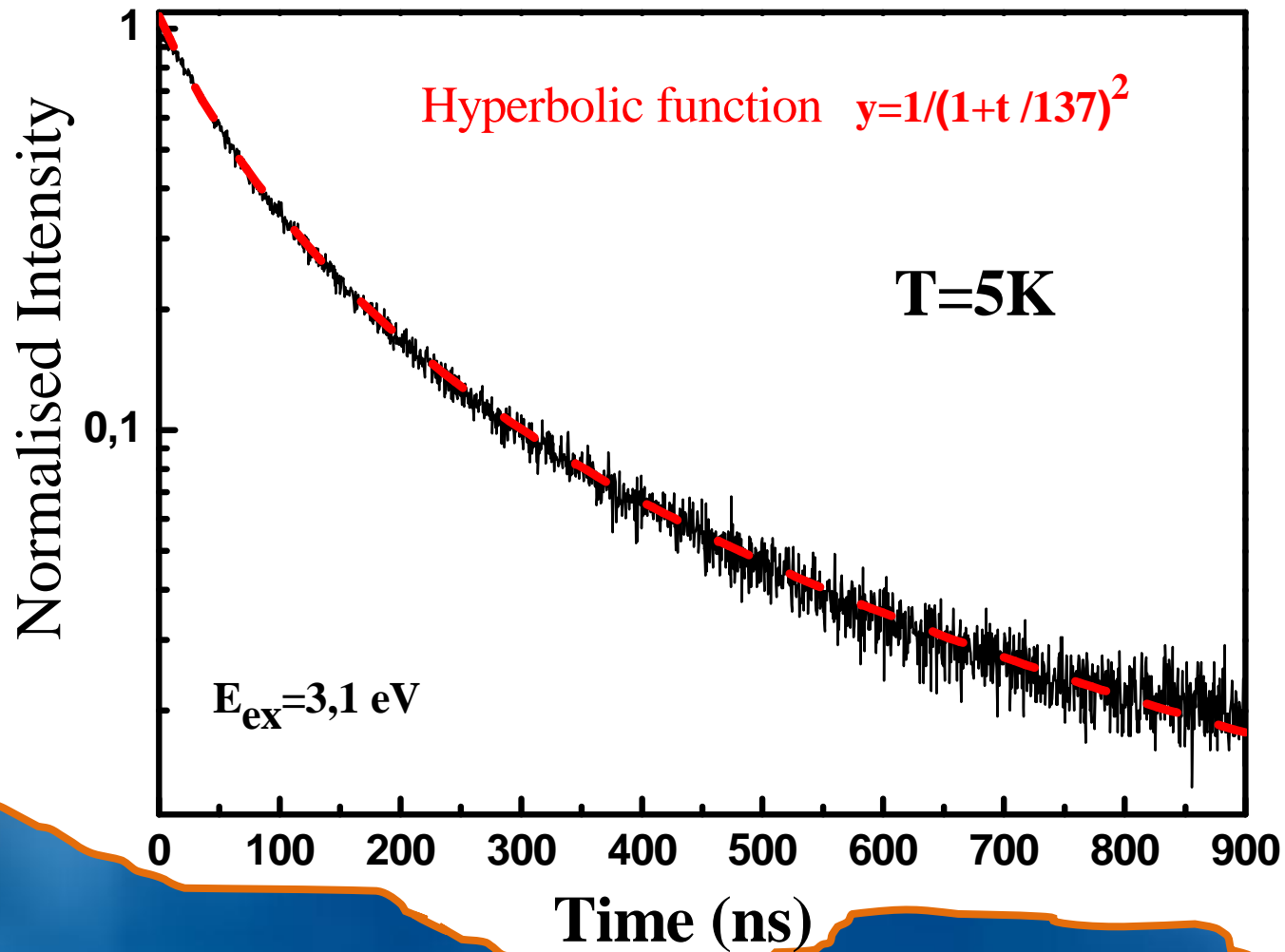
$$\frac{dn}{dt} = -\gamma n^2$$

$$n = \frac{n_0}{1 + \gamma n_0 t}$$

$$I_{emitted} \propto \left(\frac{n_0}{1 + \gamma n_0 t} \right)^2 \quad \text{Hyperbolic decay}$$

Photolumuminescence decay

QW ZnTe/ZnSe

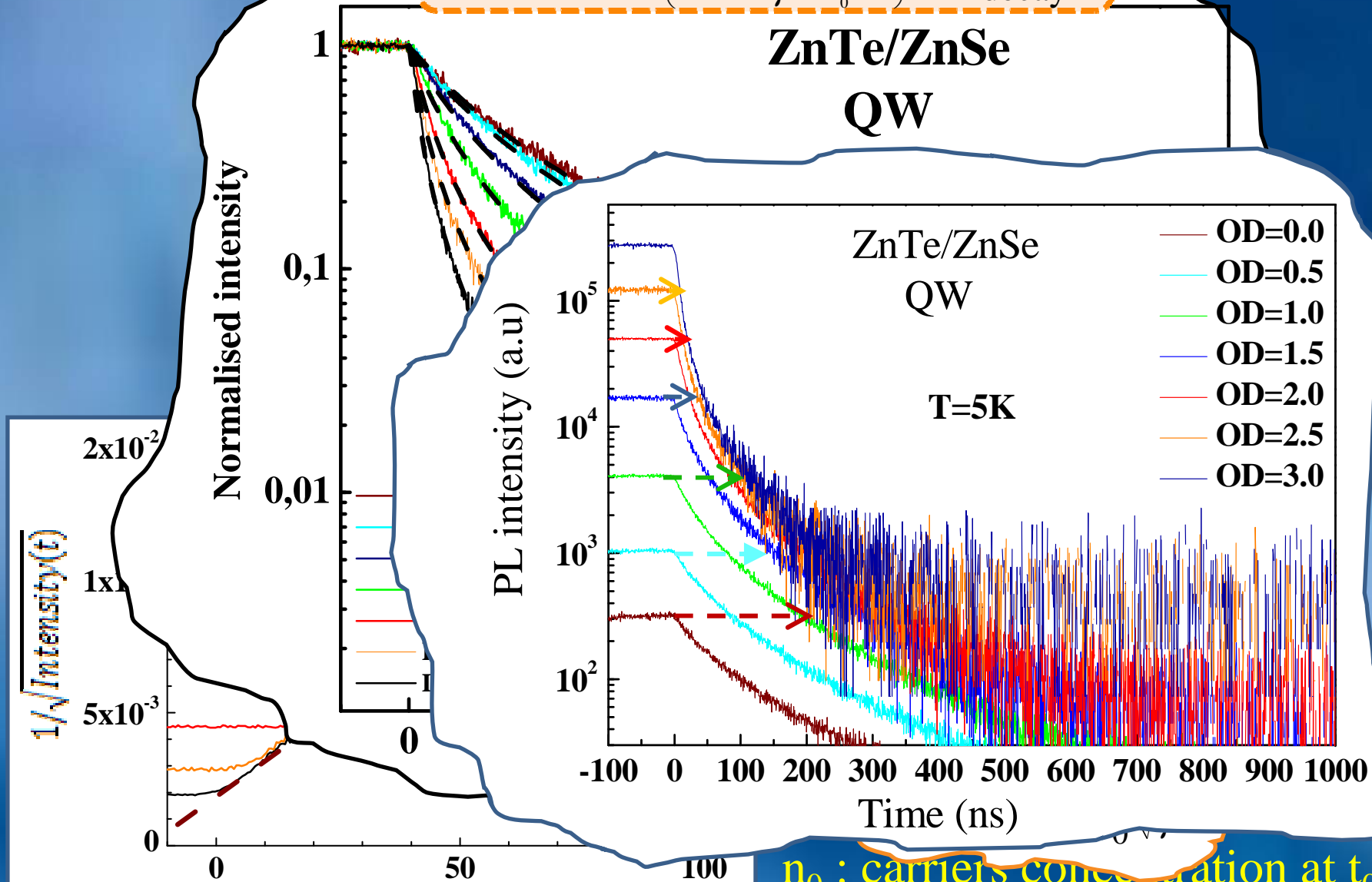


$$I_{emitted} \propto \frac{1}{\left(1 + \gamma n_0 t\right)^2} \quad \text{Hyperbolic decay}$$

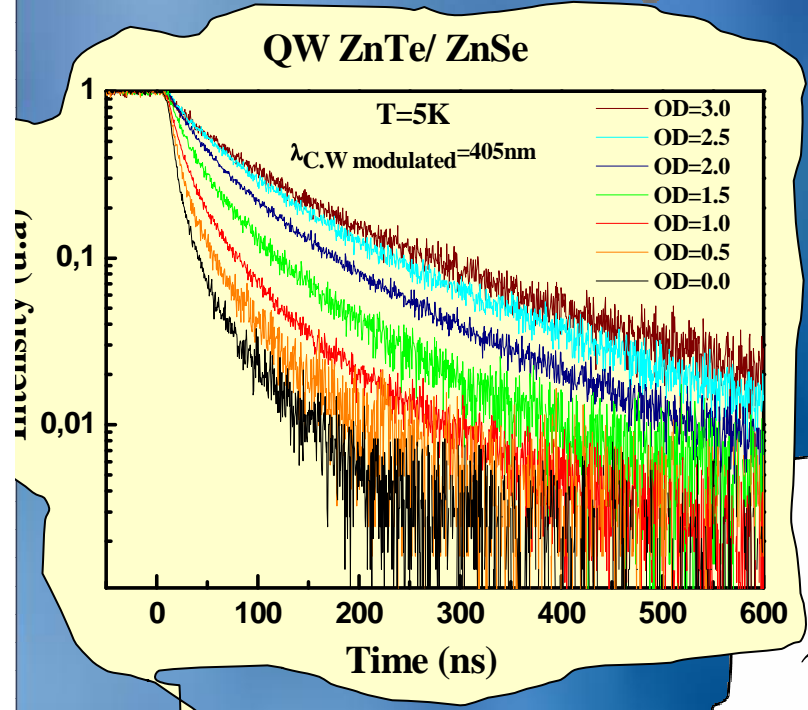
Time decay : Excitation power dependence

$$I_{\text{emitted}} \propto \left(\frac{n_0}{1 + \gamma n_0 t} \right)^2 \text{ Hyperbolic decay}$$

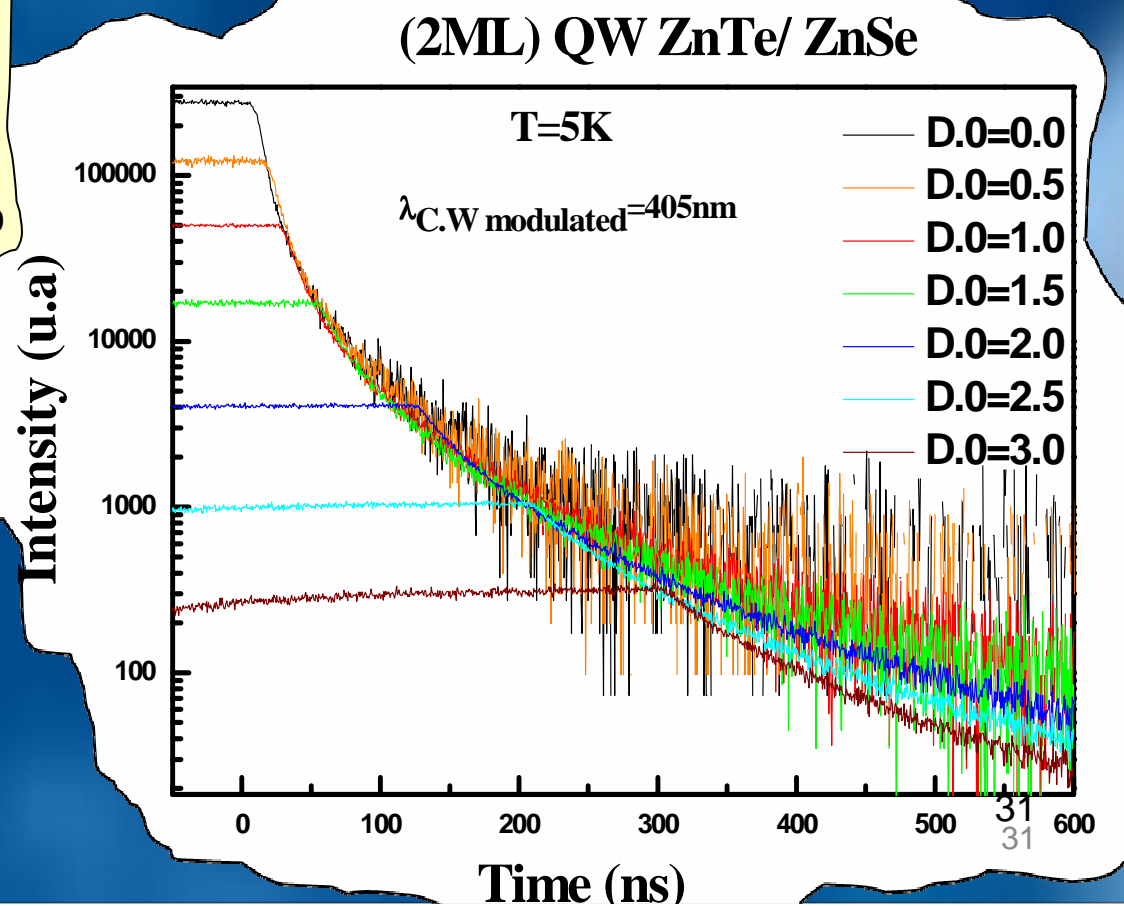
ZnTe/ZnSe
QW



Time decay : Excitation power dependence



n_0 : carriers concentration at t_0



QW

-PL decay (~100ns)

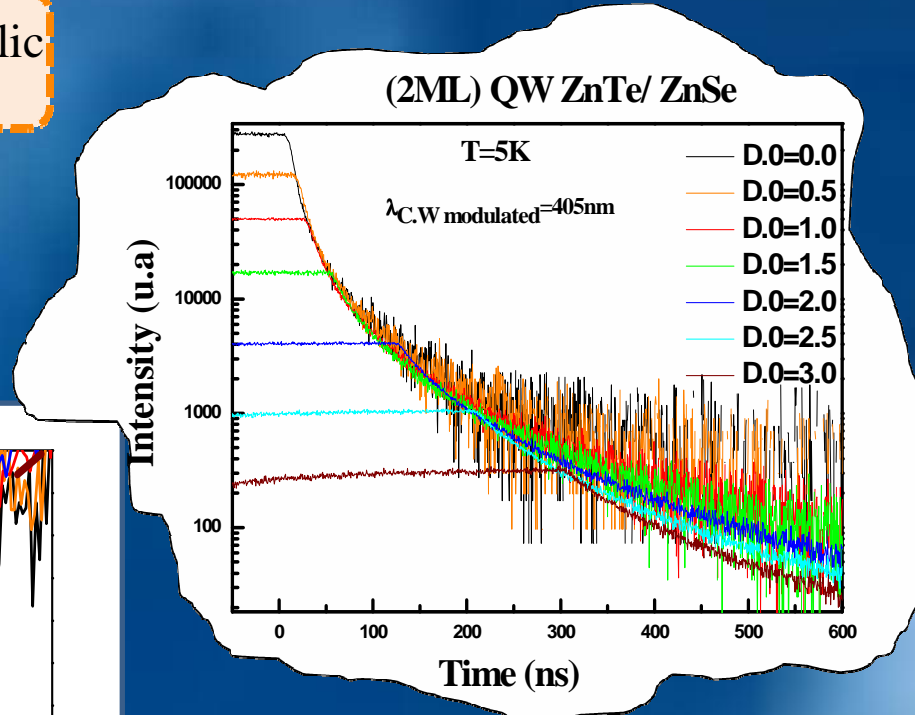
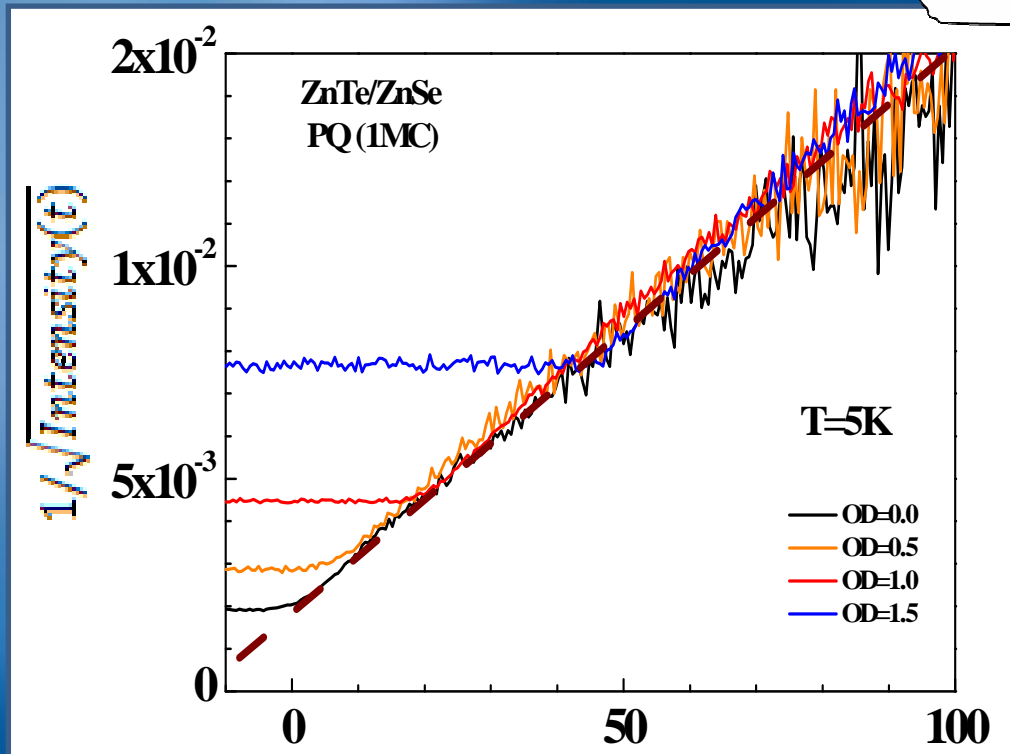
-strongly time-stretched with respect to an exponential decay

-highly sensitive to the excitation density

Time decay : Excitation power dependence

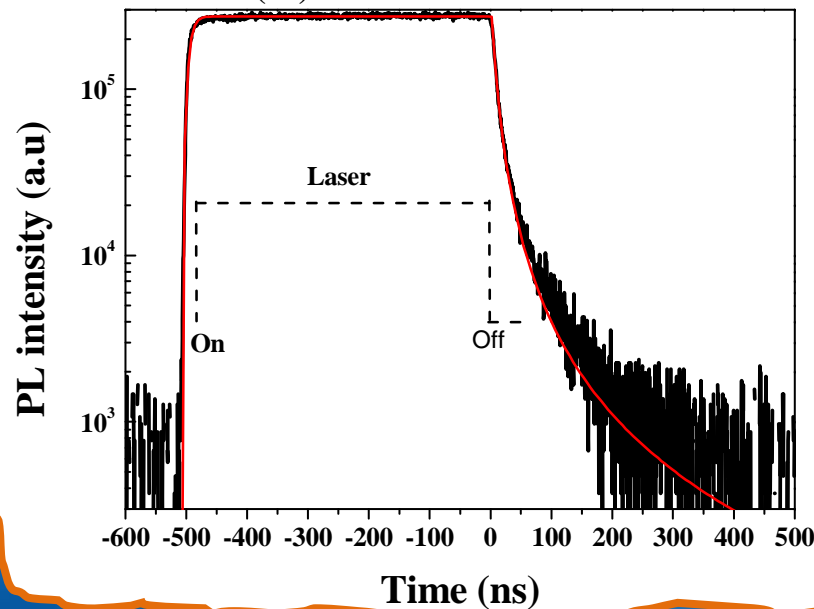
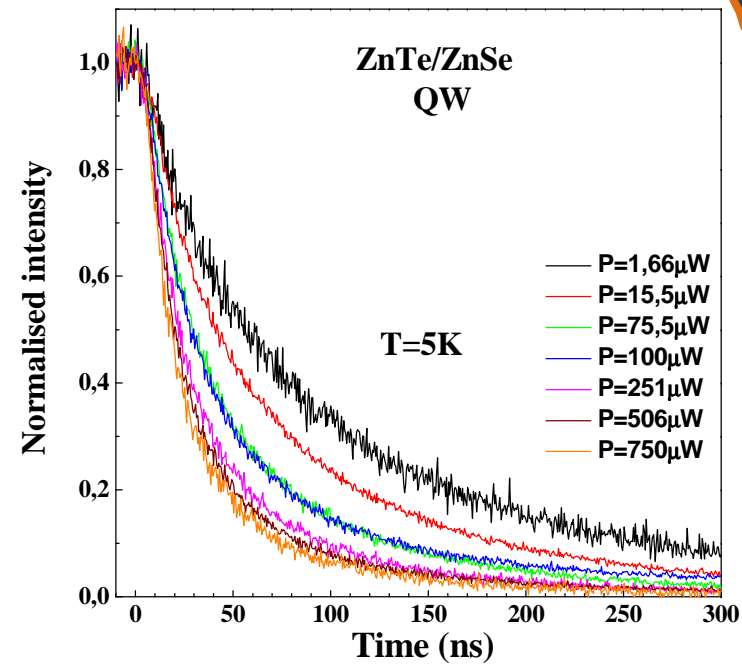
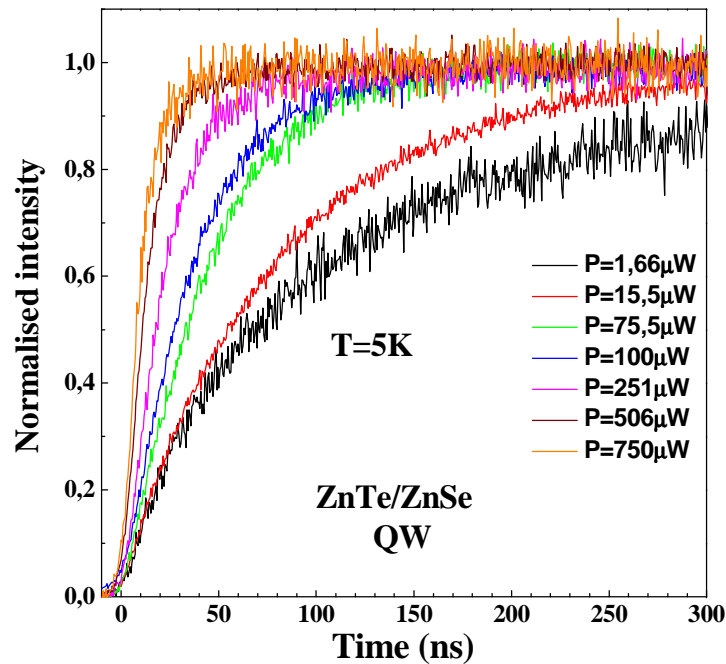
$$I_{\text{emitted}} \propto \left(\frac{n_0}{1 + \gamma n_0 t} \right)^2 \text{ Hyperbolic decay}$$

n_0 : carriers concentration at t_0



$$\frac{1}{\sqrt{I}} = \sqrt{\gamma t} + \frac{1}{n_0 \sqrt{\gamma}}$$

Raise & decay Times : Excitation power dependence



$$\frac{dn}{dt} = AP - \gamma n^2$$

$$\Rightarrow I(t) \propto AP [\tanh(\sqrt{AP\gamma}t)]^2$$

Summary – Part 2

Photoluminescence of type-II ZnTe/ZnSe heterostructures

- QWs: PL blue shift following $P^{1/3}$
 - consequence of separated 2D *electron* and *hole* planes
- Non-excitonic PL dynamics
 - hyperbolic decay governed by a single parameter γn_0
- QDs : 0D localization preserves excitons
 - exponential PL decay

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PL & Time Resolved PL Studies

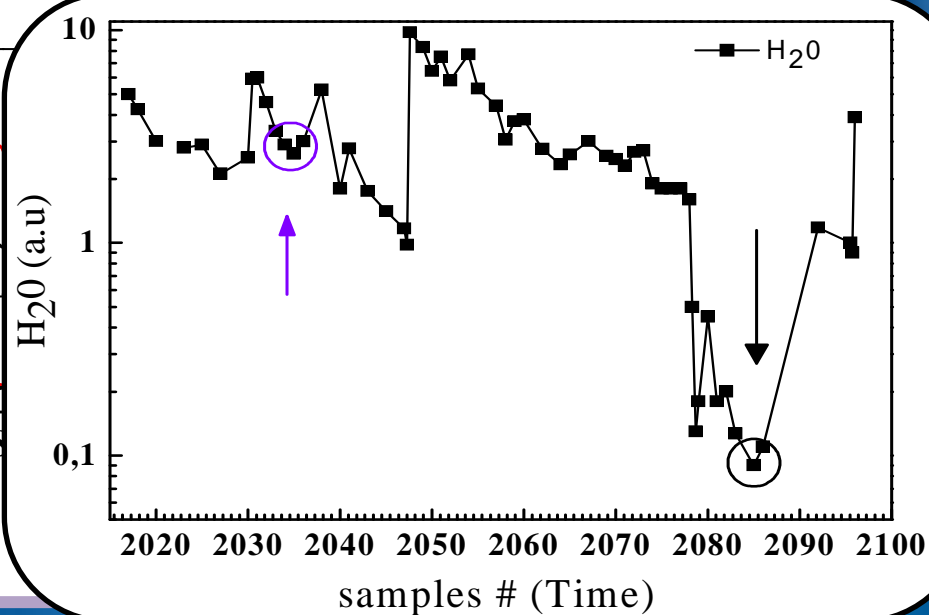
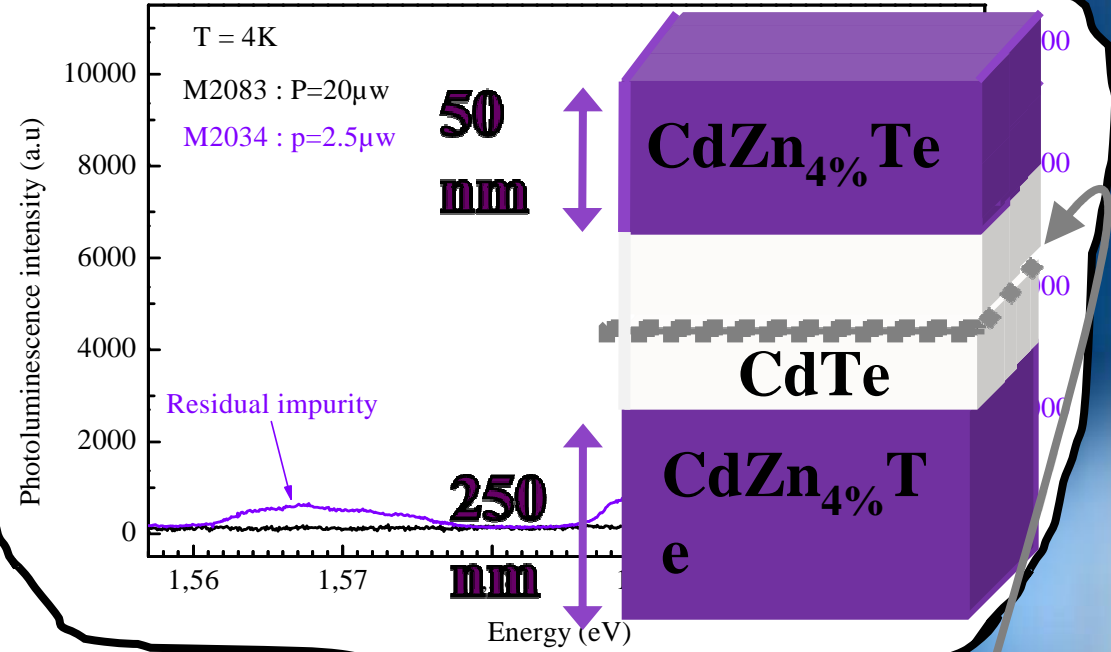
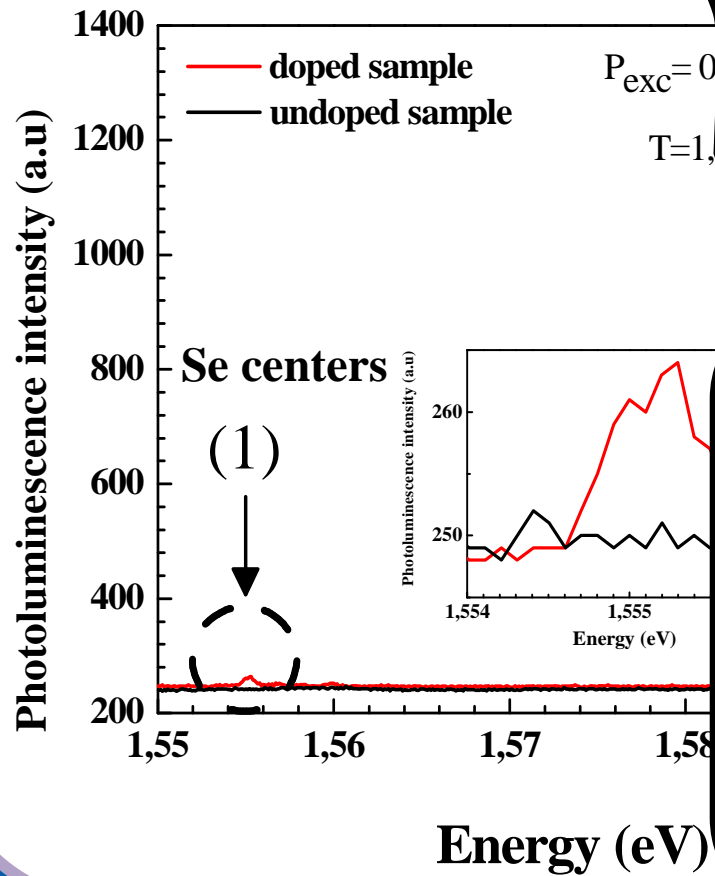
3- Isoelectronic doping CdTe:Se.

High purity samples

Optical studies

❖ Conclusion & Perspectives

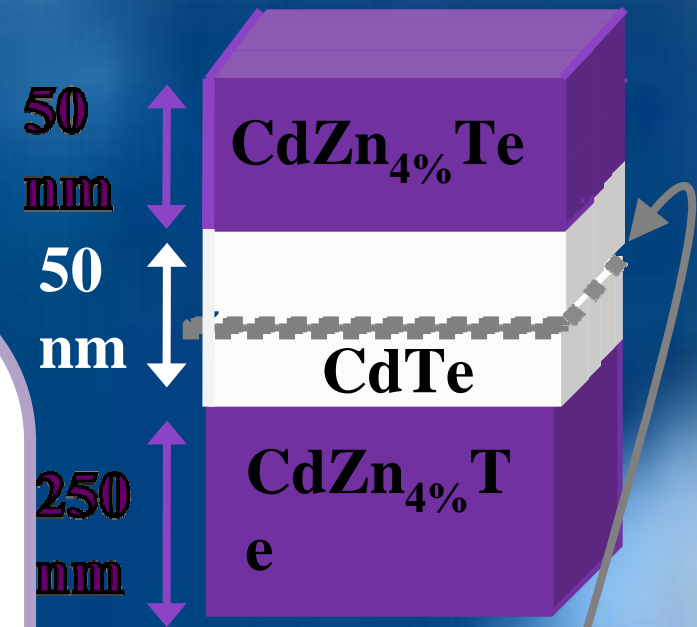
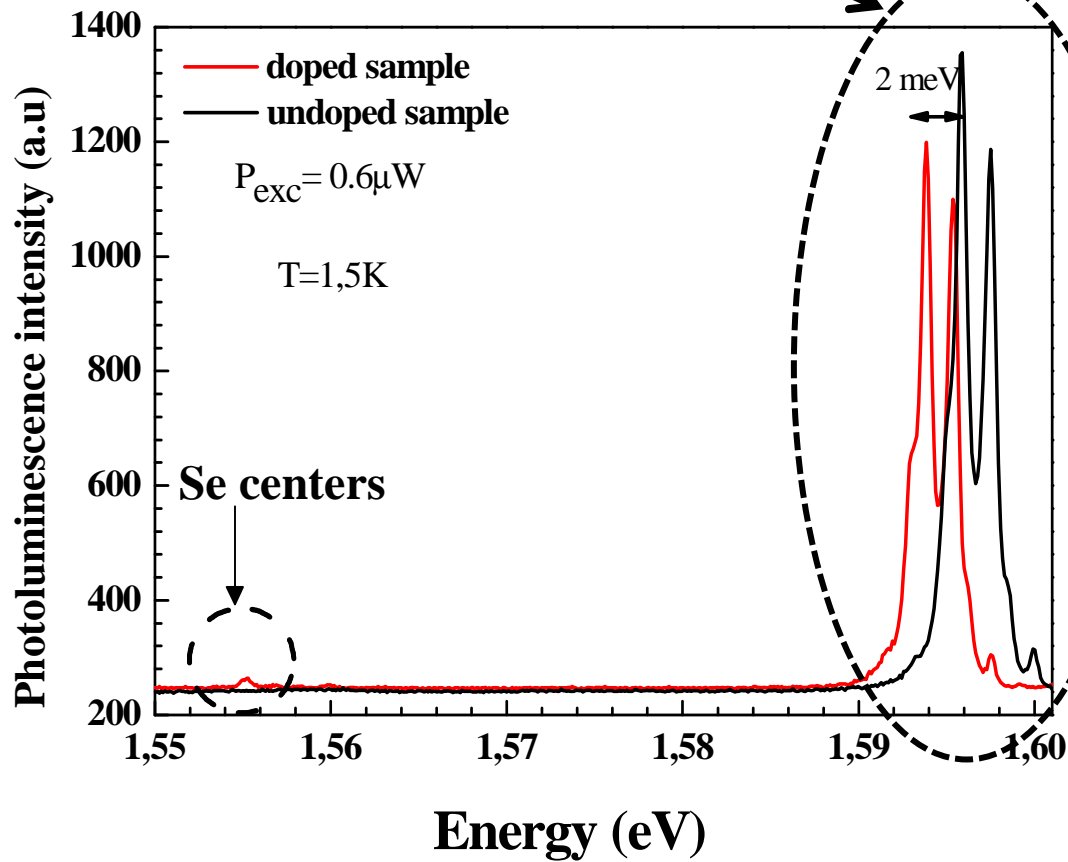
Effect of Selenium delta doping



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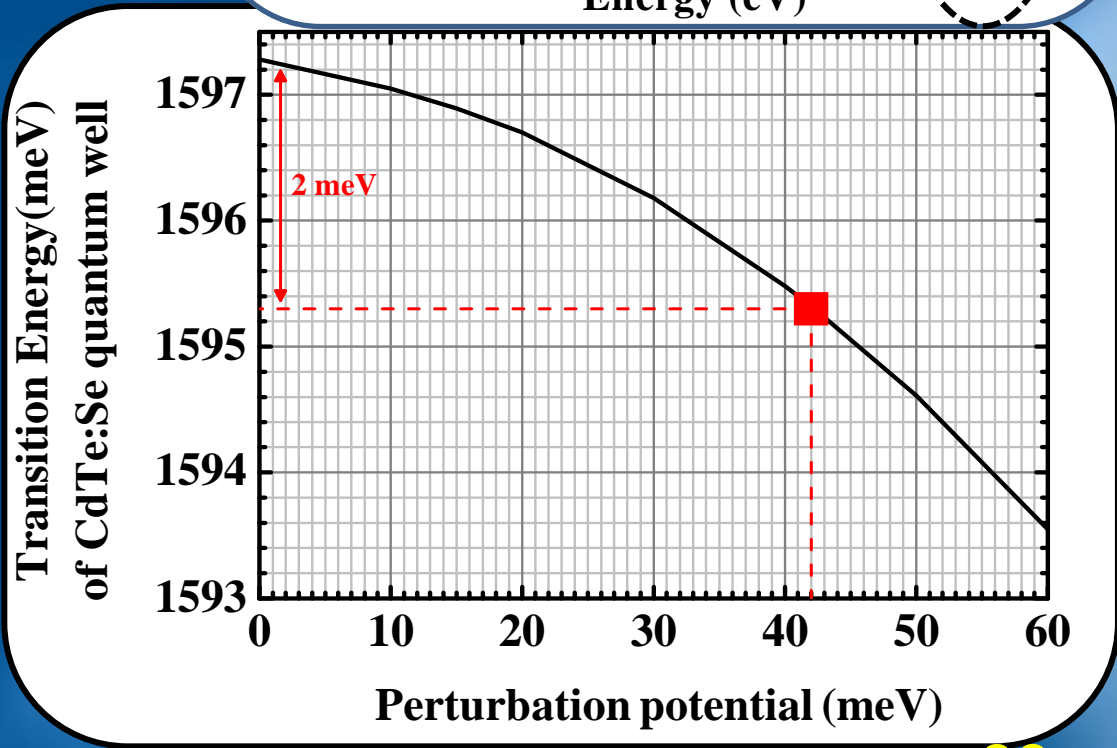
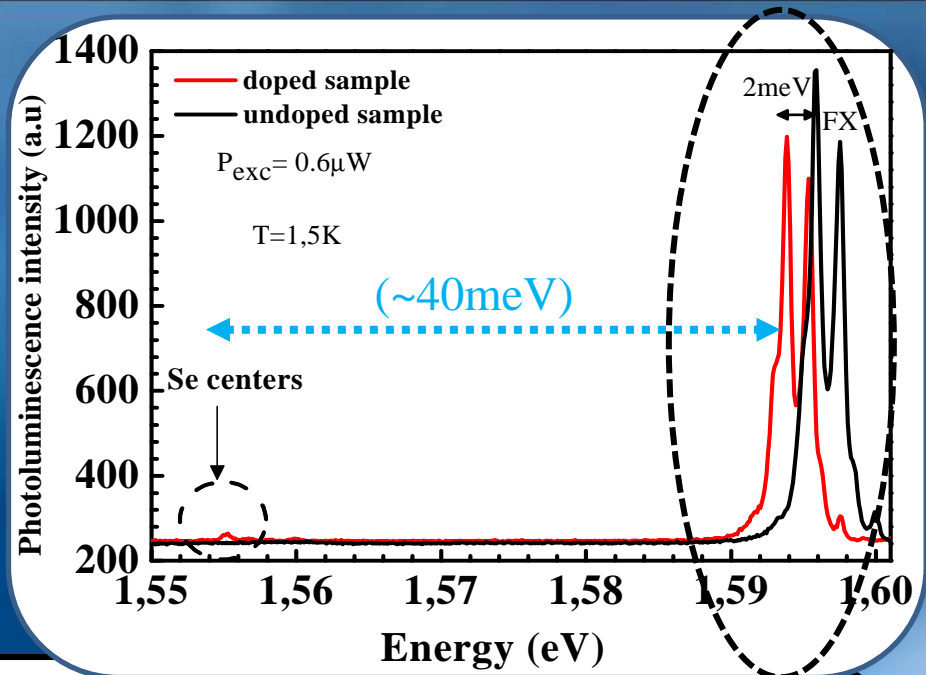
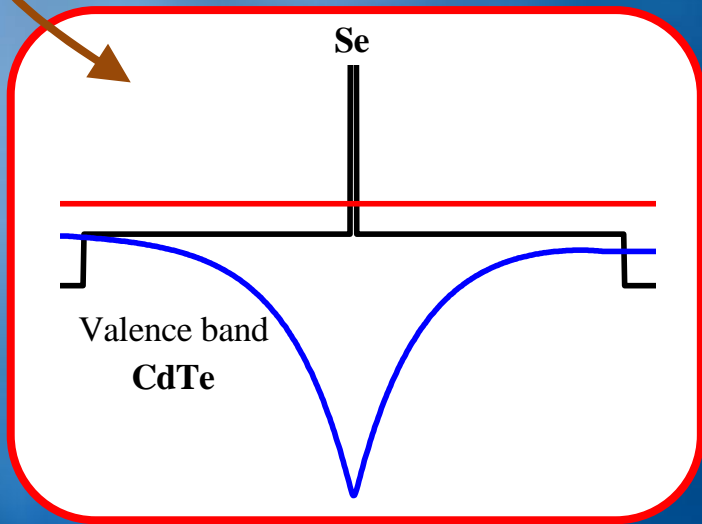
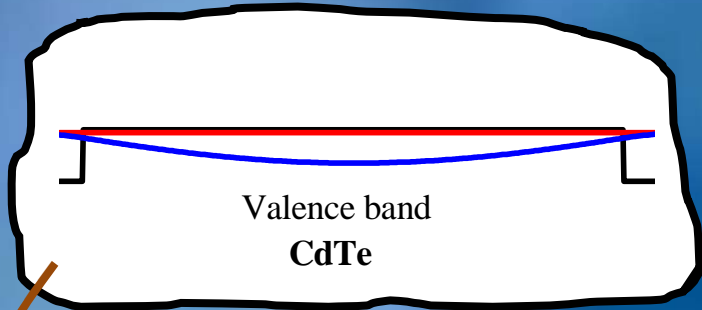
WARSAW)

Effect of Selenium delta doping



Selenium delta doping

Shift of main PL line

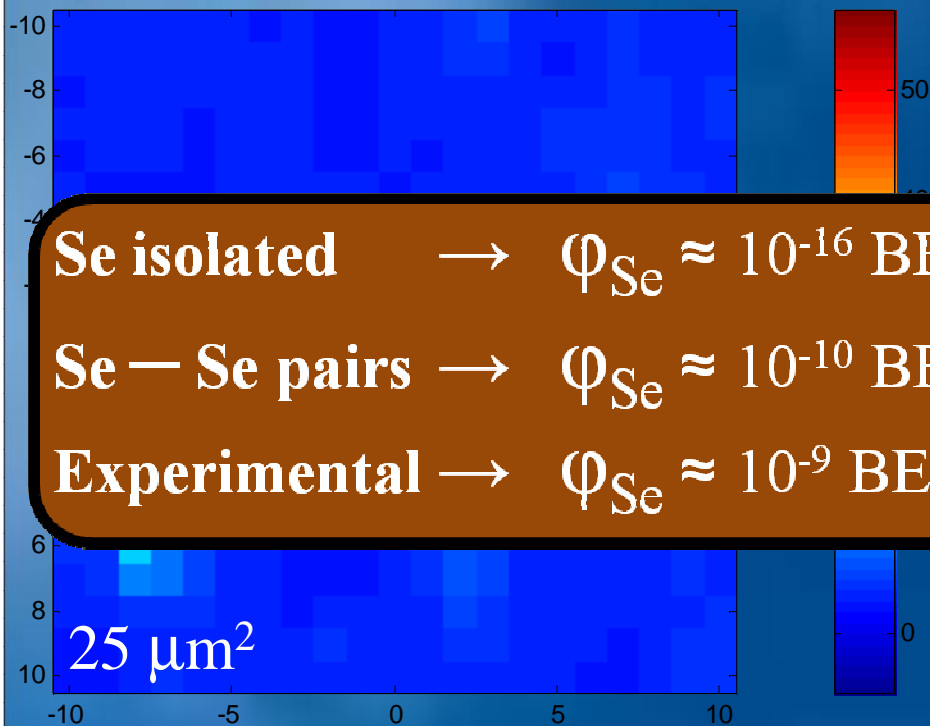


Photolumuminescence mapping

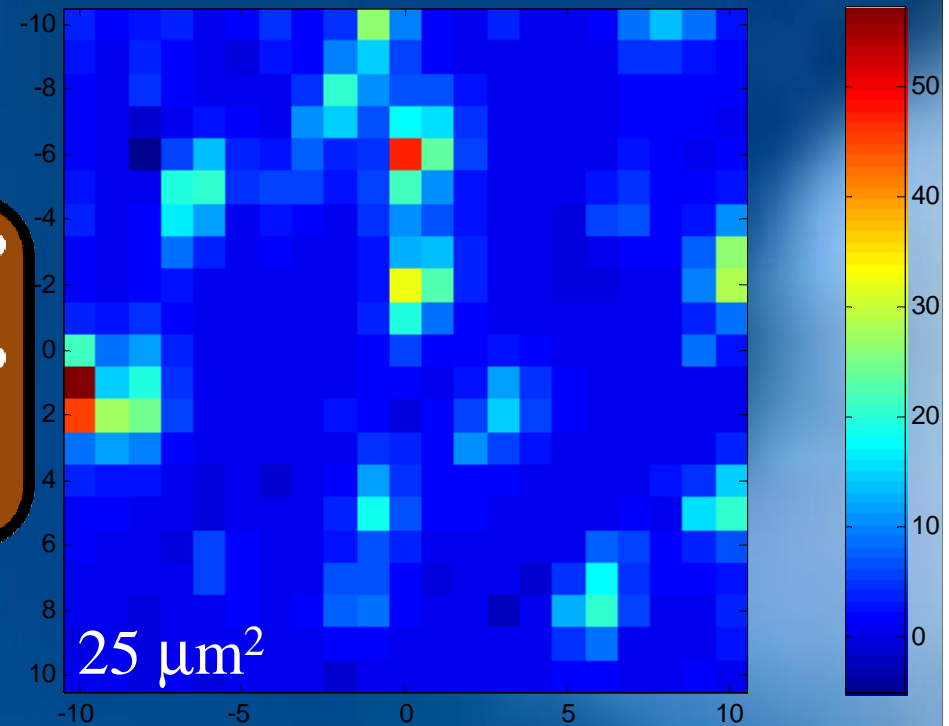
1558 – 1564 meV

Undoped sample

Doped sample



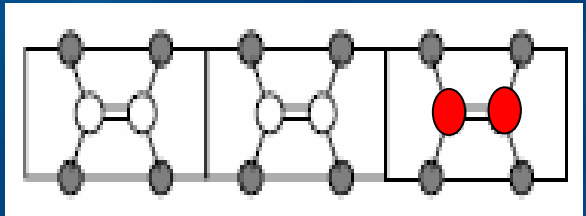
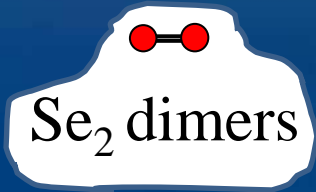
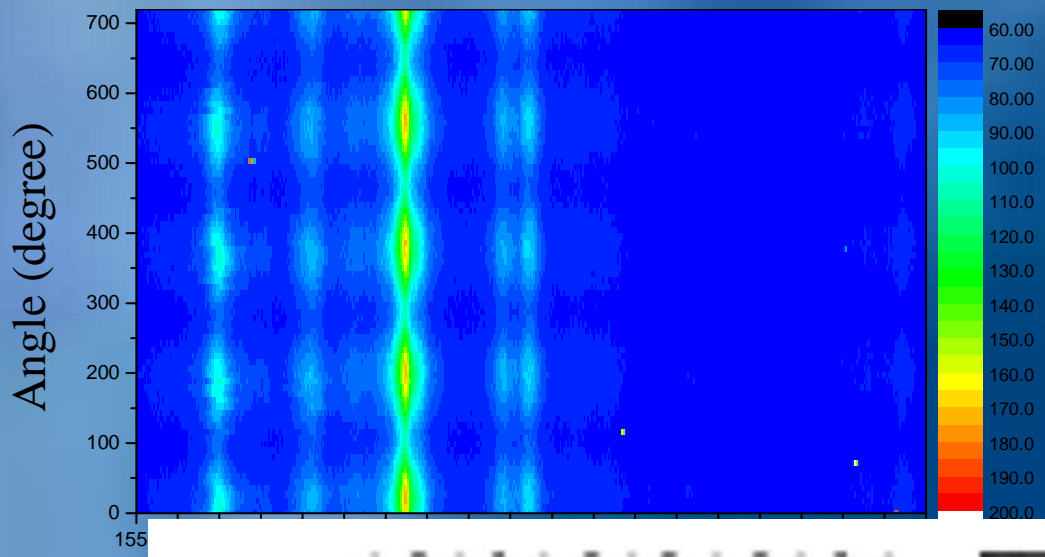
No emitters



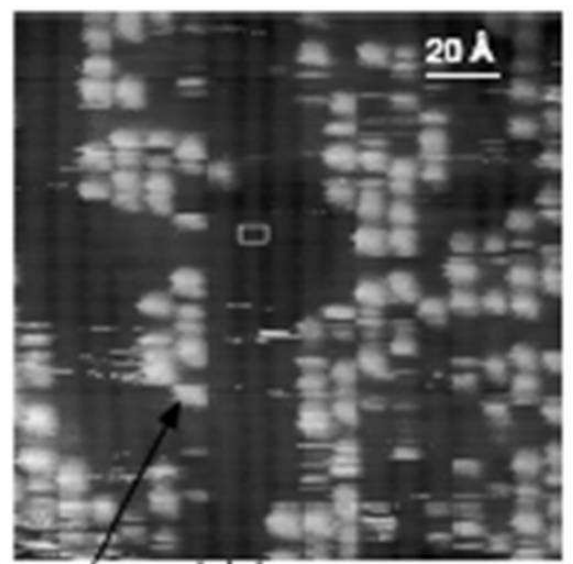
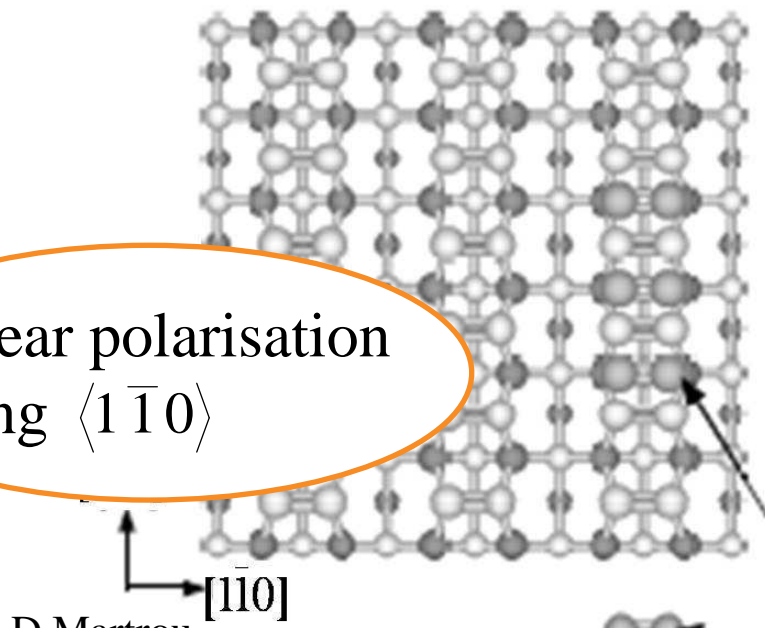
Low density of emitters $\sim 1 \mu\text{m}^{-2}$

Se – Se pairs ? 39

Same polarisation for all centers



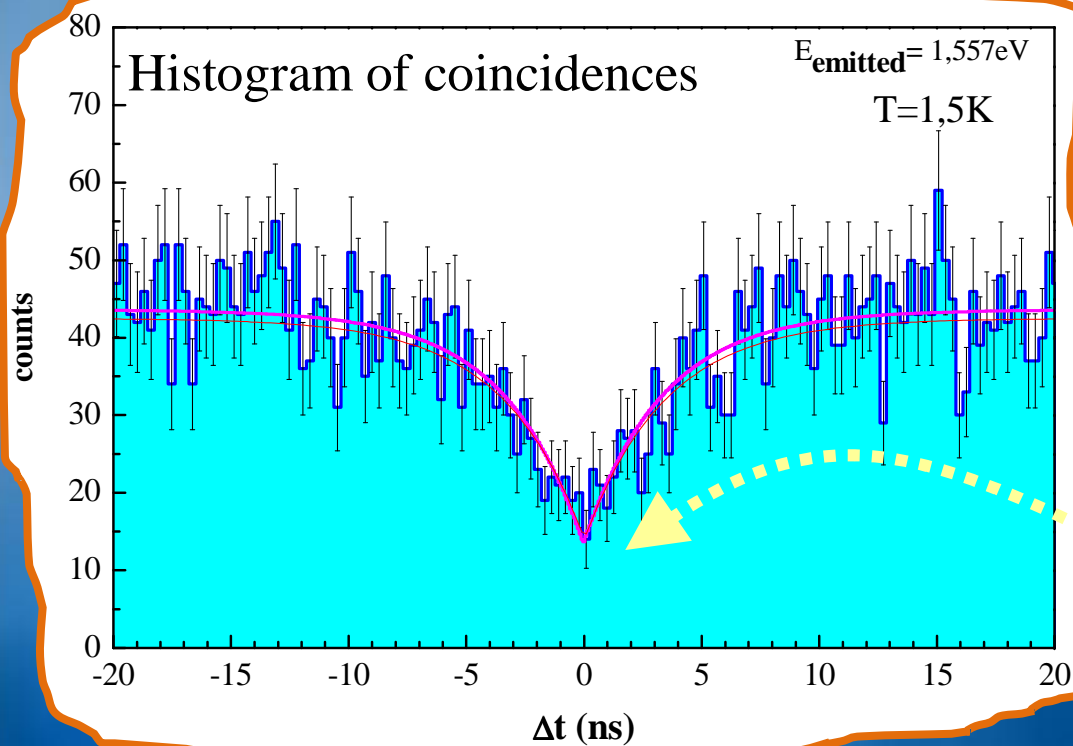
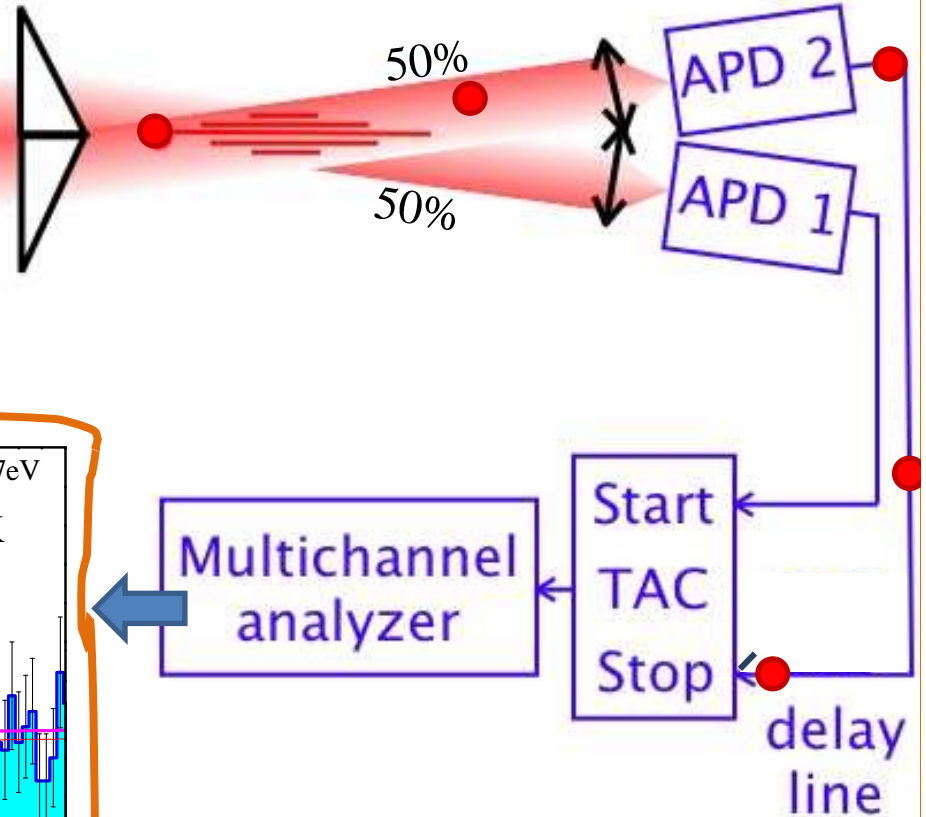
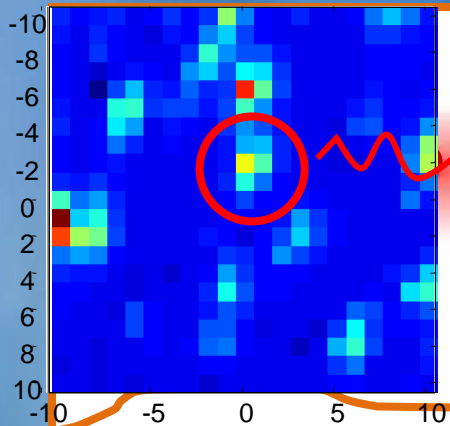
Linear polarisation along $\langle 1 \bar{1} 0 \rangle$



Te₂ dimers (2x1)

D.Martrou
Thèse U.J.F Grenoble (2000)

Anti-bunching effect



Single photon emission

Summary – Part 3

- Se δ -doping in high purity CdTe
- Localization on Se-Se pairs
 - very low density of emitters
- PL linearly polarized along $[1\bar{1}0]$
 - possibly related to Se dimers
- Se localization centers behave as single photon emitters
 - alternative to QD

OUTLINE

❖ Introduction :

Tellurium & Selenium based Semiconductor?

1- Growth Mechanism of ZnTe/ZnSe QDs:

Islands formation ?

Capping difficulties & solutions ?

2- Optical Properties of Type-II QWs & QDs.

PL & Time Resolved PL Studies

3- Isoelectronic doping CdTe:Se.

High purity samples

Optical studies

❖ Conclusion & Perspectives

Conclusion

Key points of my work:

- 1- Mastering of ZnTe/ZnSe QDs by MBE
→ Limitation of Te/Se segregation
- 2- PL dynamics of type-II QWs
→ Unusual hyperbolic behavior
- 3- Single isoelectronic centers in high purity CdTe
→ PL anti-bunching from a isolated Se-pair

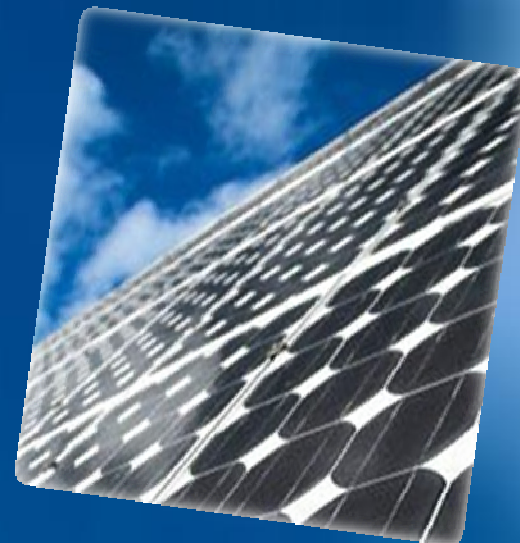
Perspectives

❖ Further developements :

- Better quantitative understanding of the segregation & ordered alloy formation :
 - MEIS
 - STM (cross sectional)
- Additional optical studies :
 - temperature behavior of type- II confinement
 - Study of *single* type-II QD

❖ Beyond fundamental effects :

- New design for photovoltaic cells
 - type-II interfaces
 - long life times carriers
- Well adapted band gap materials CdSe, CdTe ...



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*Thanks for your
attention*

Merry Christmas

