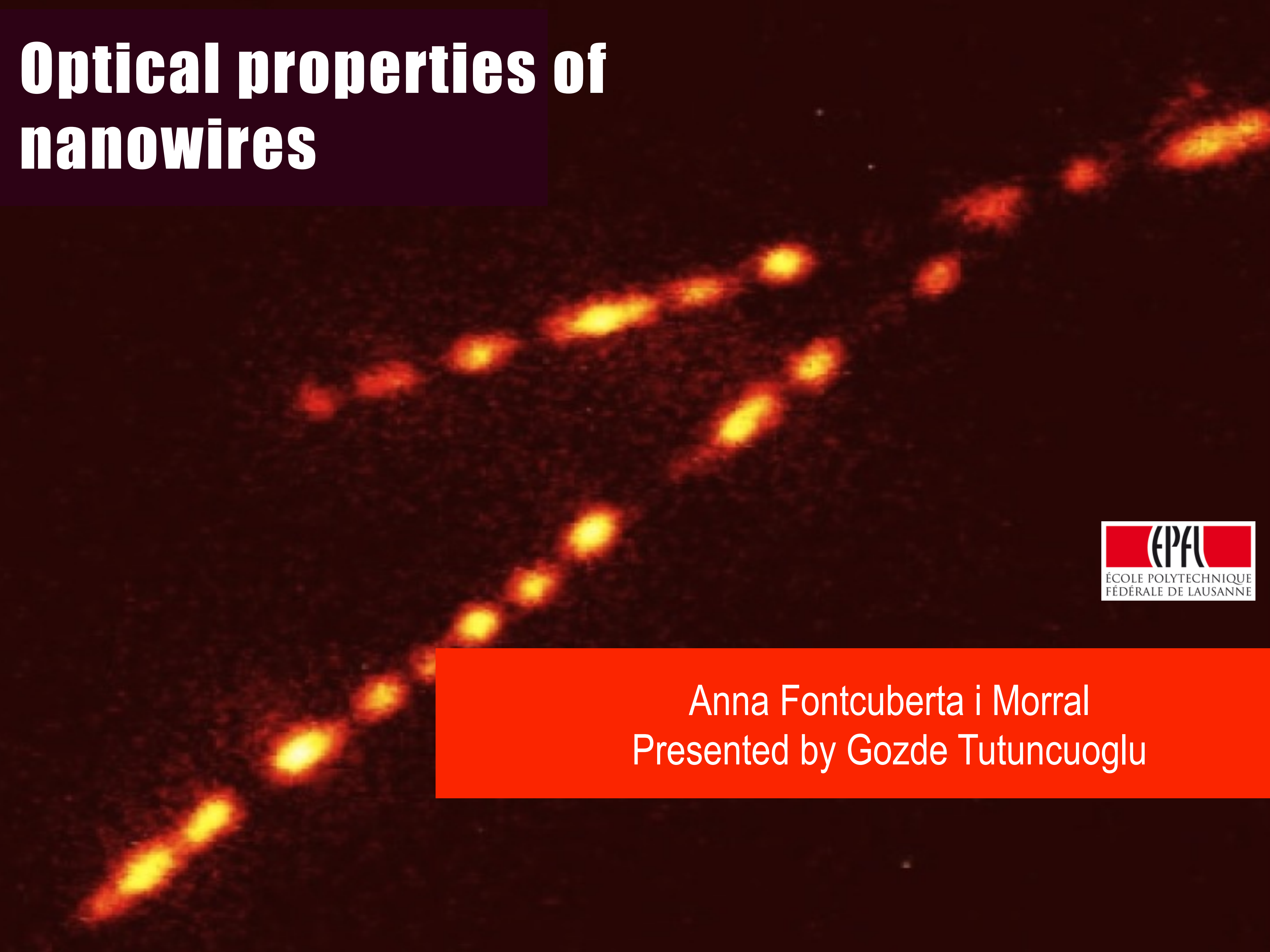
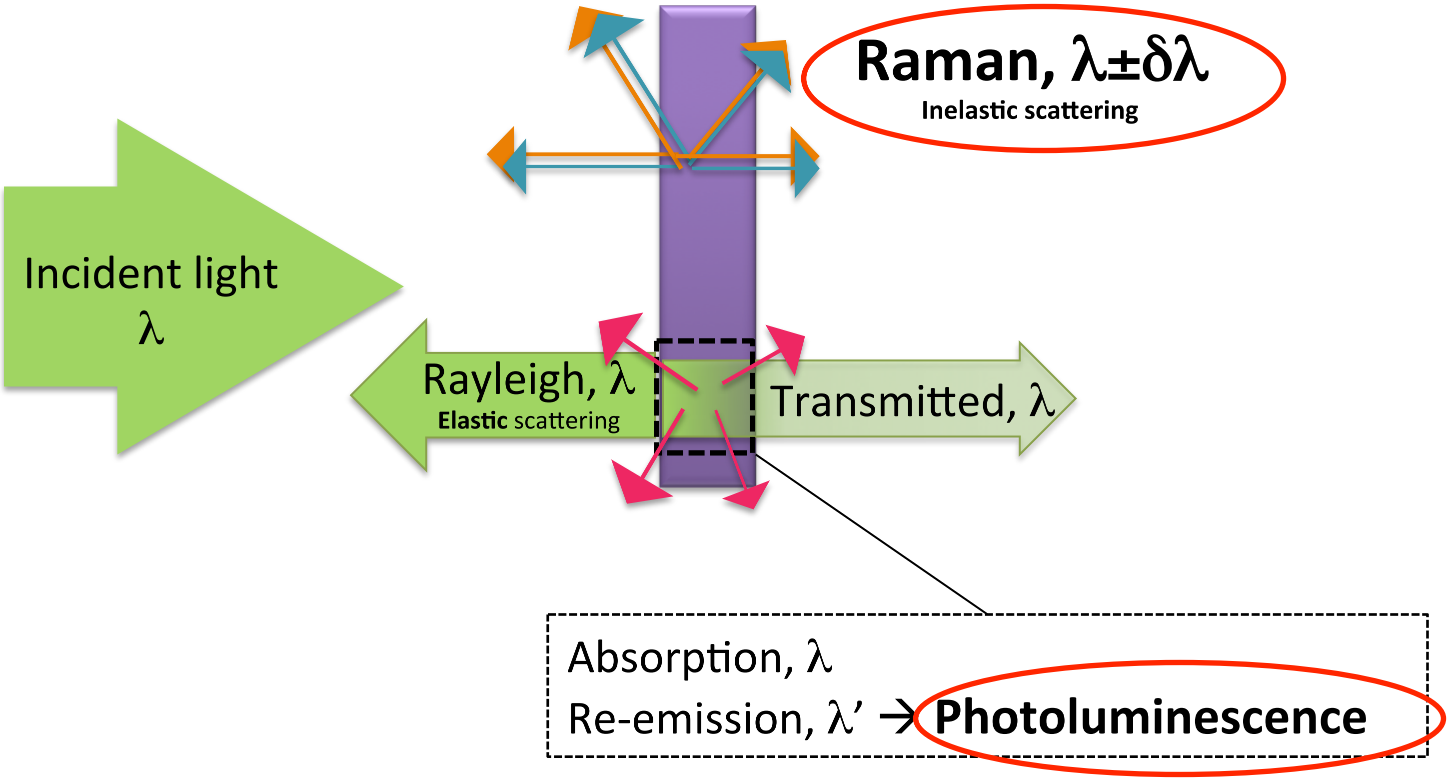
Optical properties of nanowires



Anna Fontcuberta i Morral
Presented by Gozde Tutuncuoglu

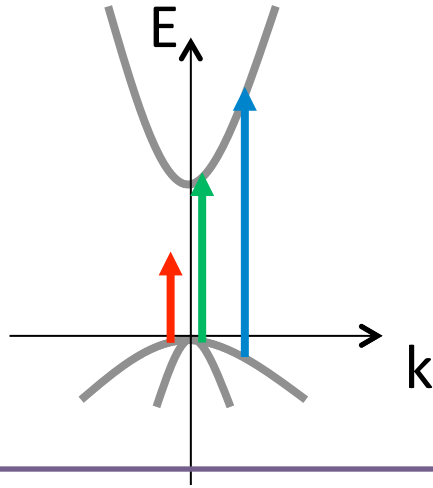
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Light-matter interaction



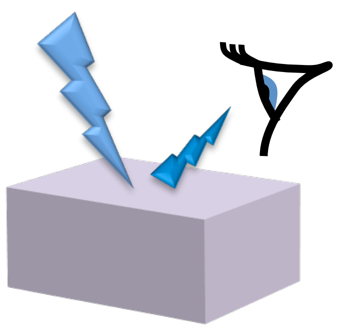
Light-matter interaction

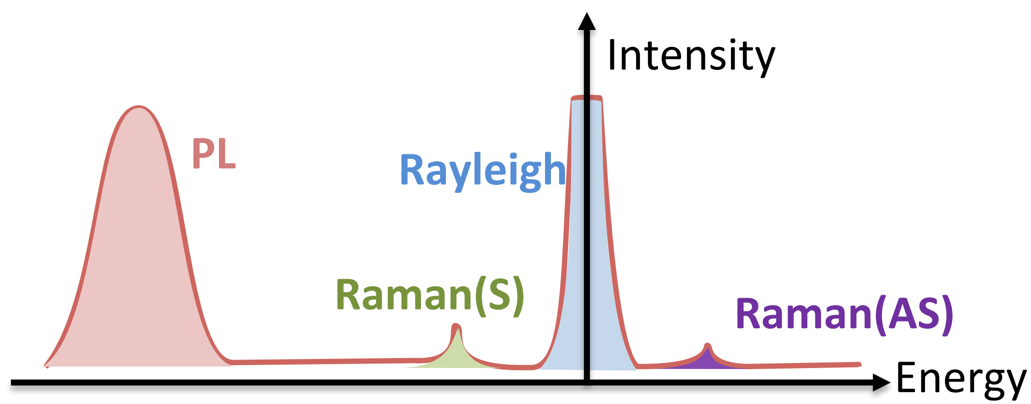
Optical excitation



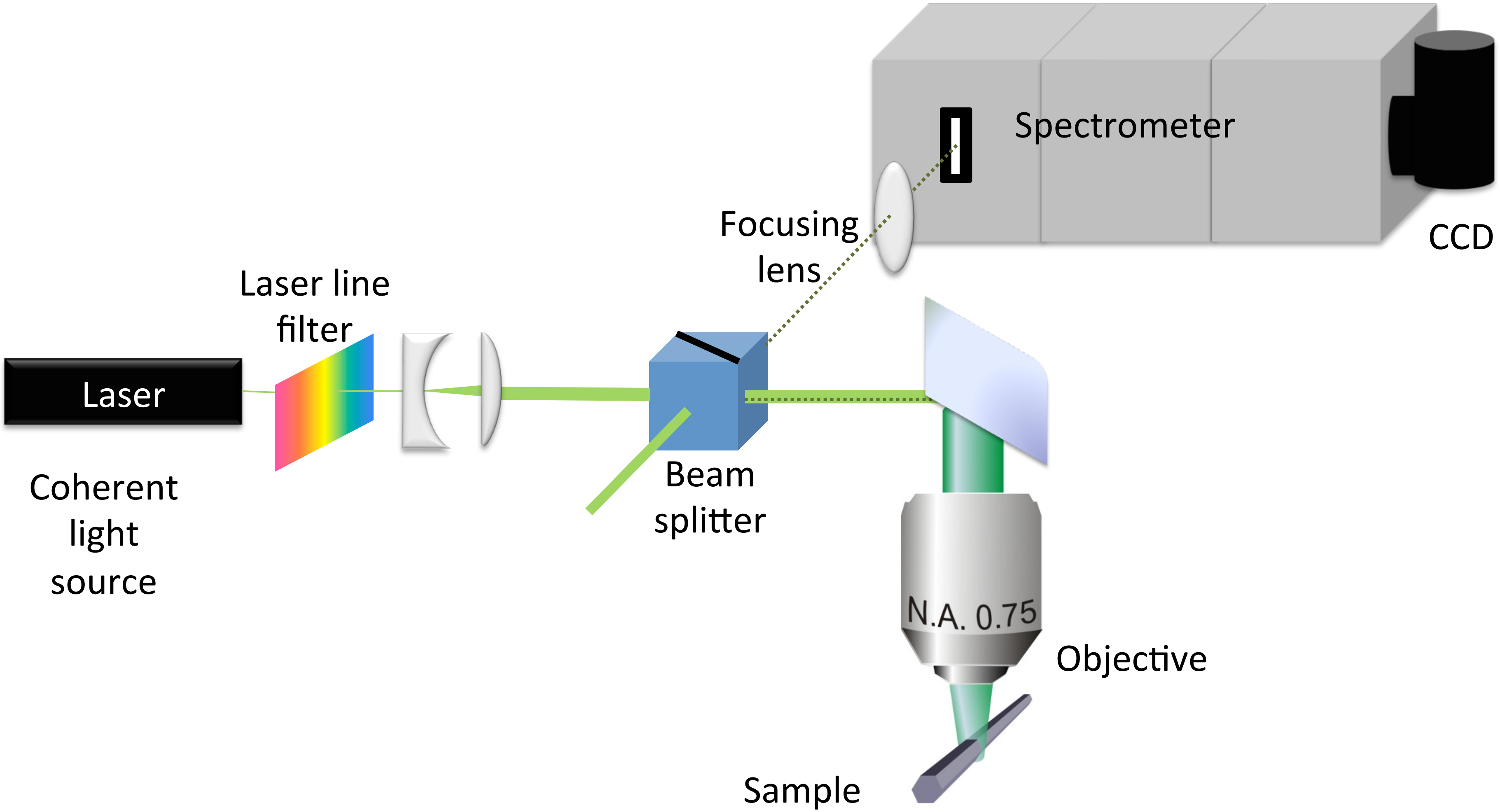
Optical signal:

- Raman
- Resonant Raman, PL (very close to laser)
- Raman, PL





Experimental set-up for PL and Raman spectroscopy



Components of the set-up

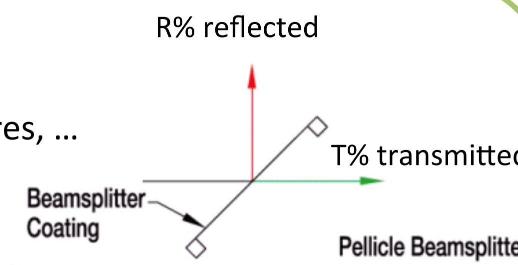
Coherent Light sources

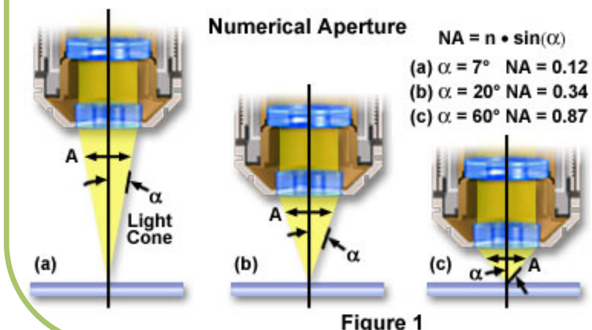
Light Amplification by Stimulated Emission of Radiation

Laser diodes
Gas ionization lasers
Crystal lasers
…

Optics

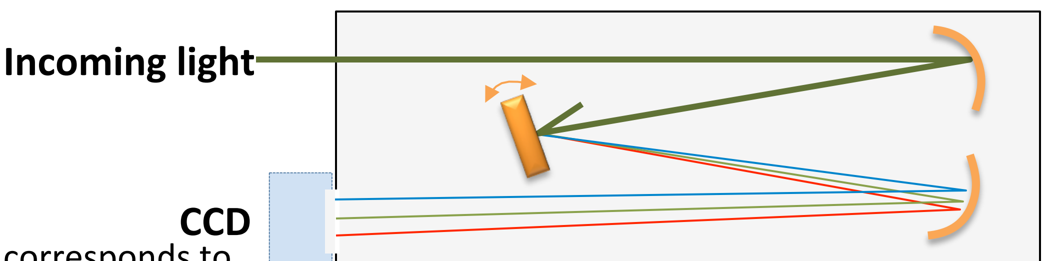
Lenses, mirrors, apertures, …
Beam splitter
Objective





Spot size,
d=1.22 λ/NA

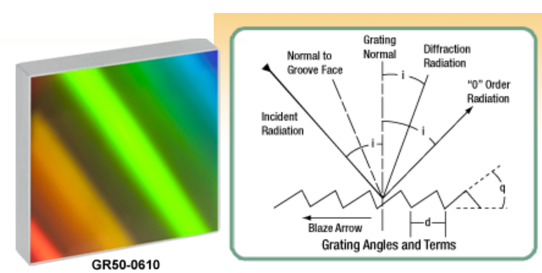
Light analysis



Each pixel corresponds to a different wavelength

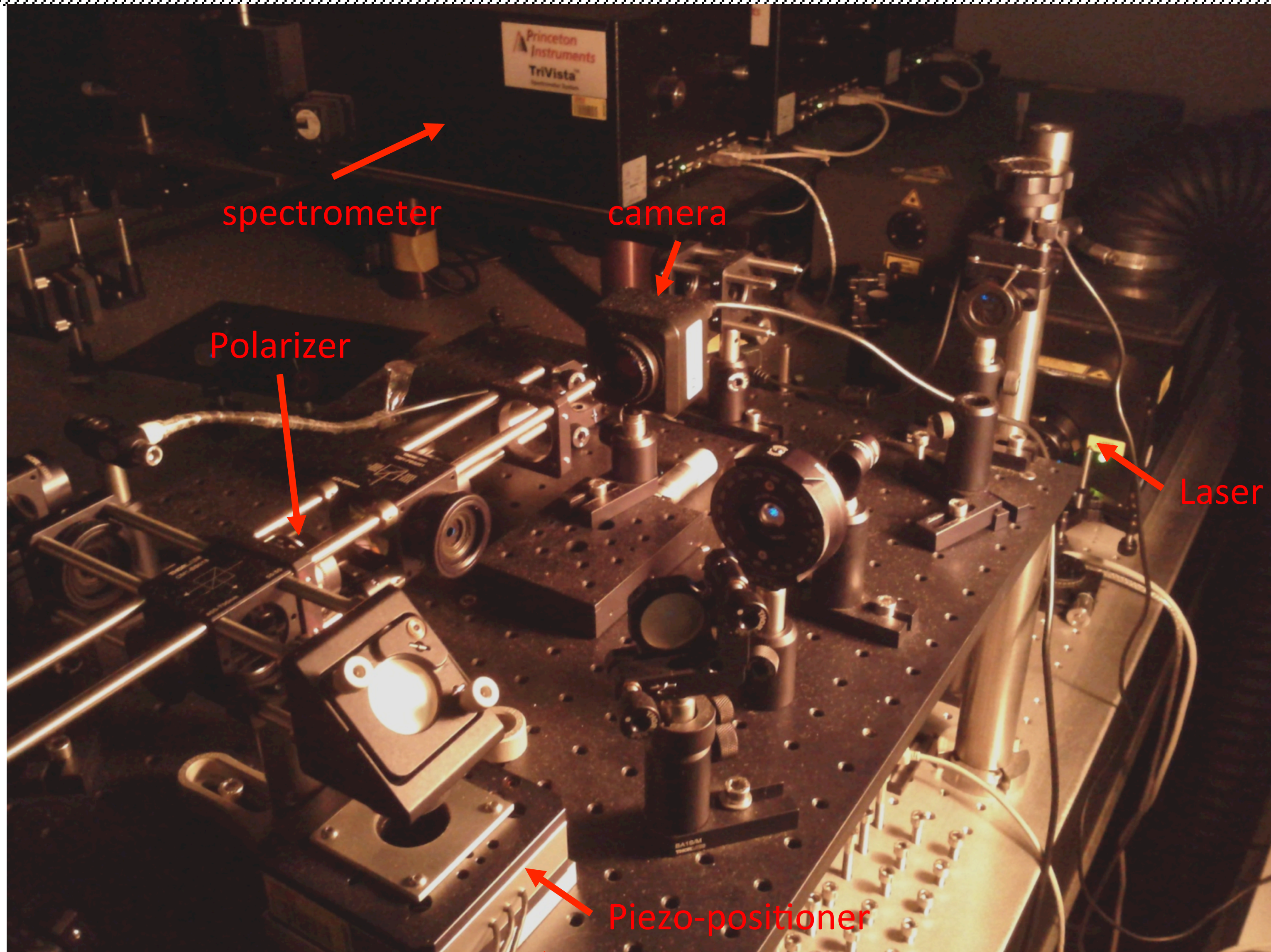
Grating

Grating type (lines/mm) and angle determine the range of wavelengths to be detected

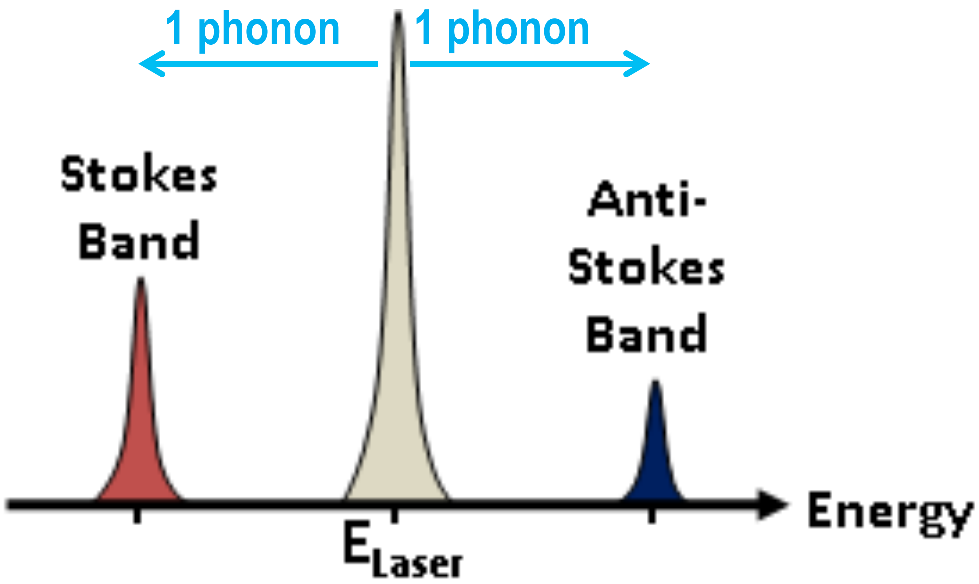


Sources: www.thorlabs.de, www.microscopyu.com

Our set-up @ EPFL for PL and Raman



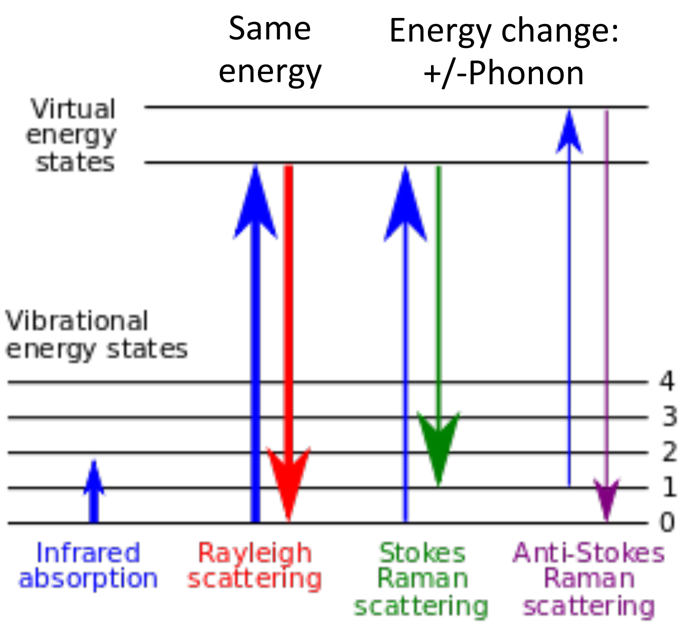
① The Raman effect

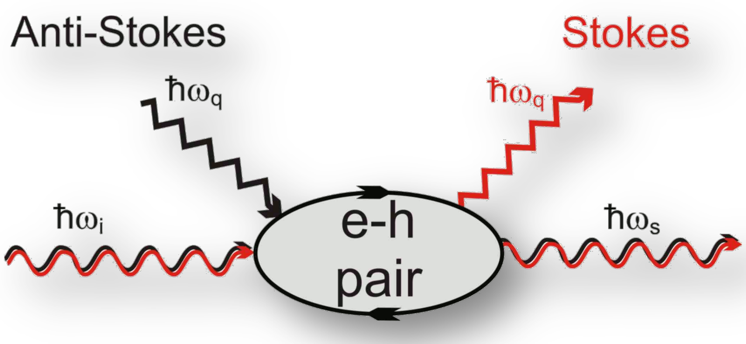


The Raman effect

Sir Chandrasekhara Venkata Rāman (1888-1970)

Nobel Prize in Physics (1930) for the discovery of what is now called Raman effect

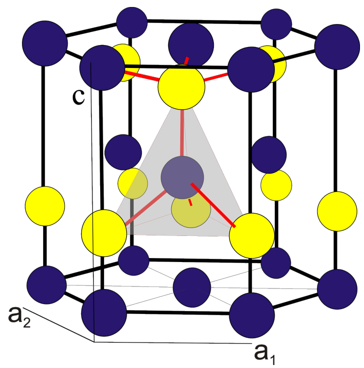




(*e-h* pair is generally virtual
if real → Resonant Raman)

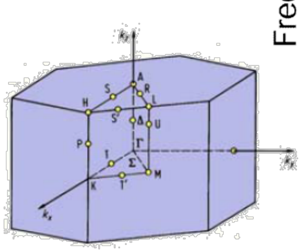
Phonons in crystals

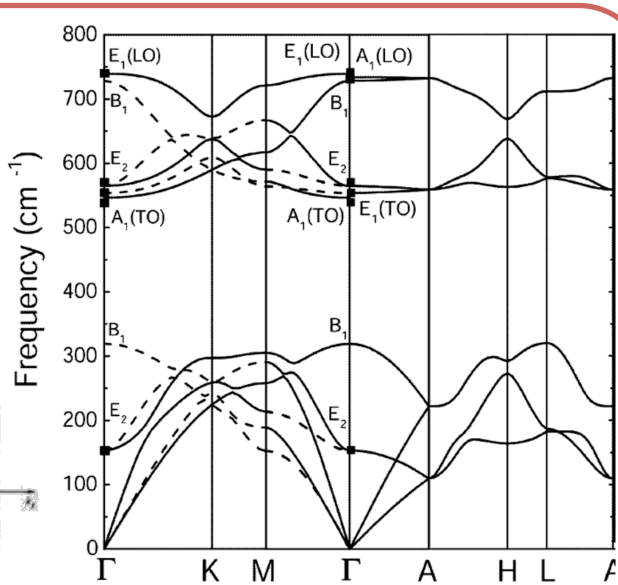
Example: Wurtzite hexagonal structure
(In,Al,Ga)N, Zn(O,S), CdSe, …



Due to crystal symmetry, collective vibrations have specific atomic motions and symmetries

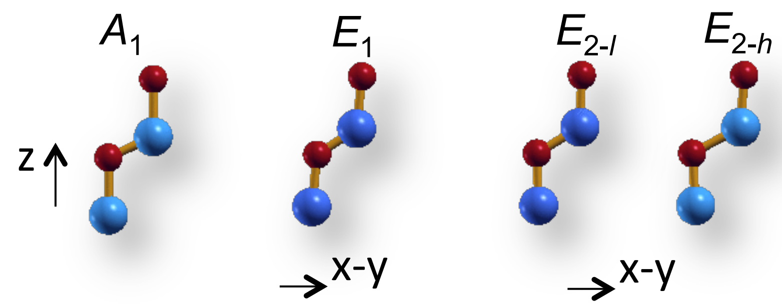
Frequency depends on propagation wavevector
$\omega(q)$





H.-L. Liu et al. / Chemical Physics Letters 345 (2001) 245–251

$$\Gamma_{opt} = A_1 + E_1^{(2)} + 2E_2^{(2)} + 2B_1$$

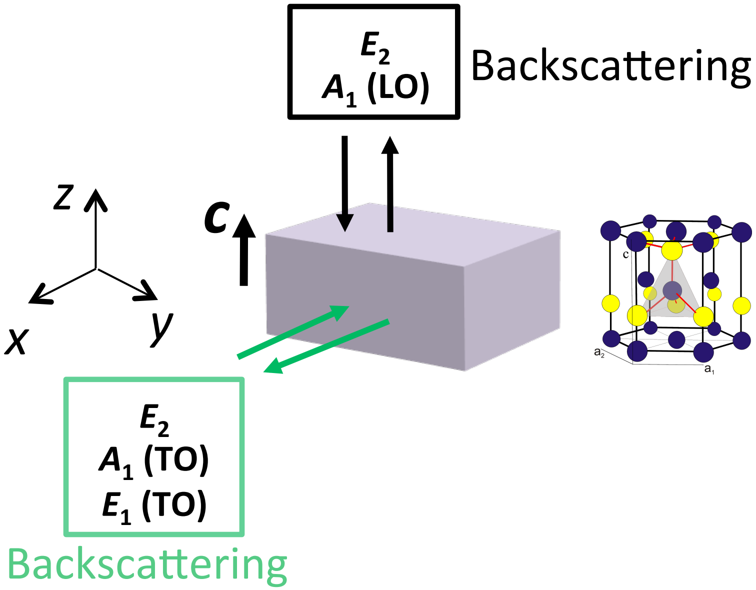


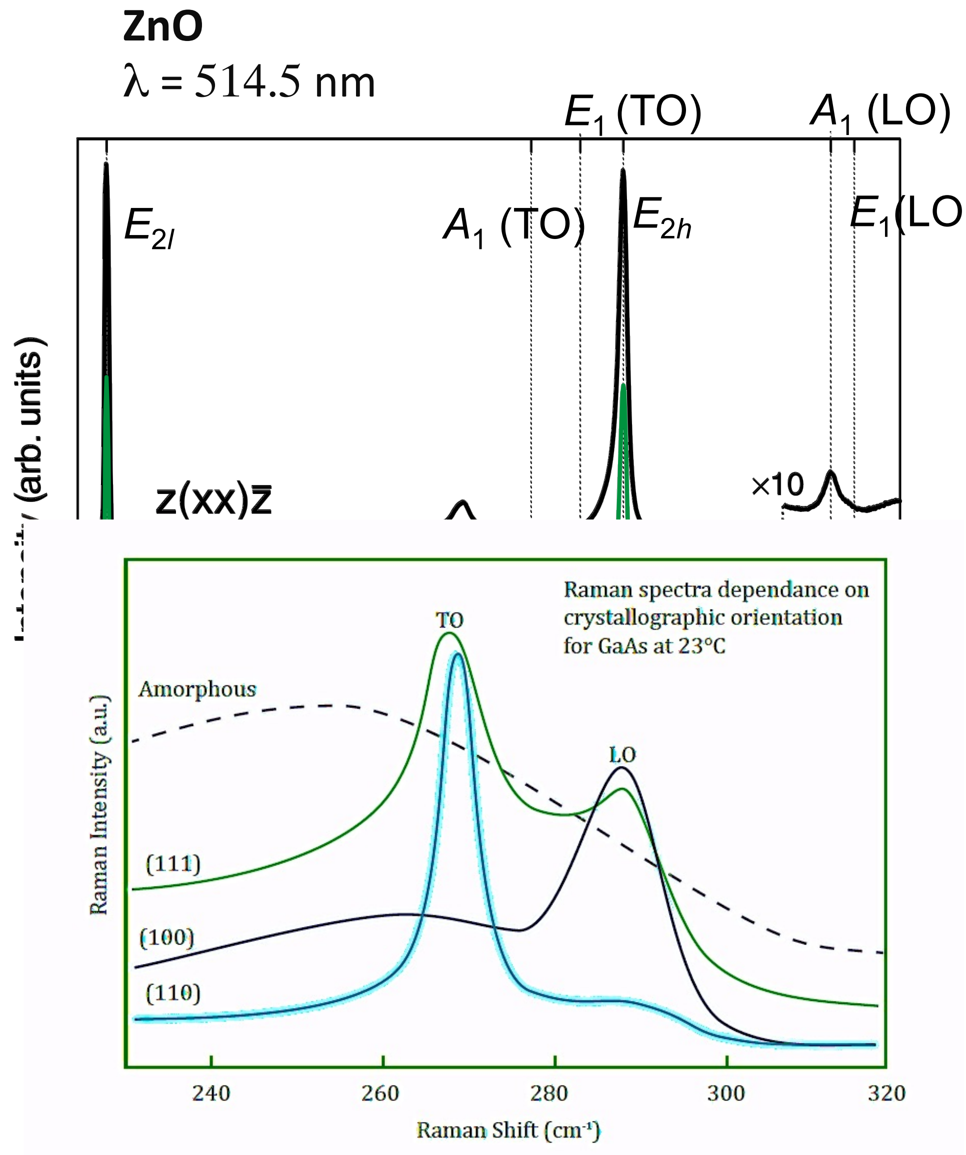
Polar
(TO-LO)

Non-Polar

TO: Transverse Optical mode
LO: Longitudinal Optical mode

Raman selection rules (non-resonant)





Porto's notation

Incident light — Scattered light

z(xy)z̄

polarization direction — propagation direction

R. Cusco et. al., Phys. Rev. B 75, 165202 (2007)

The Raman effect

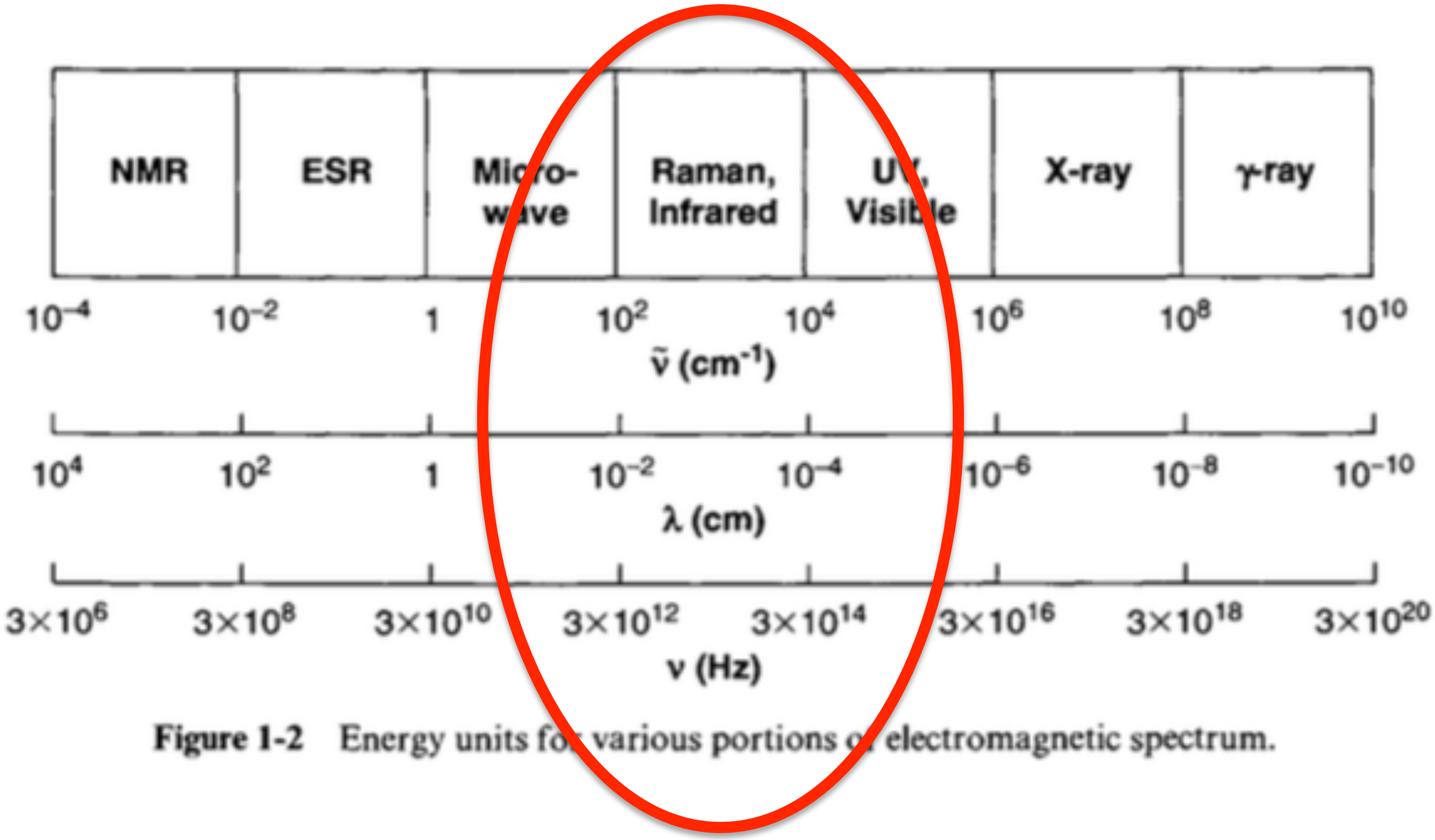
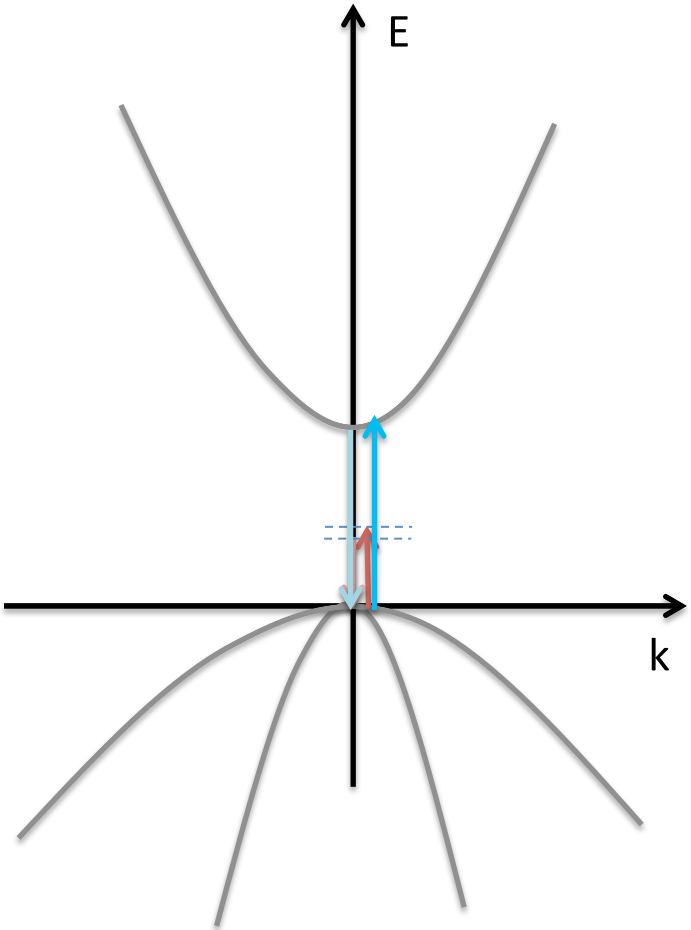
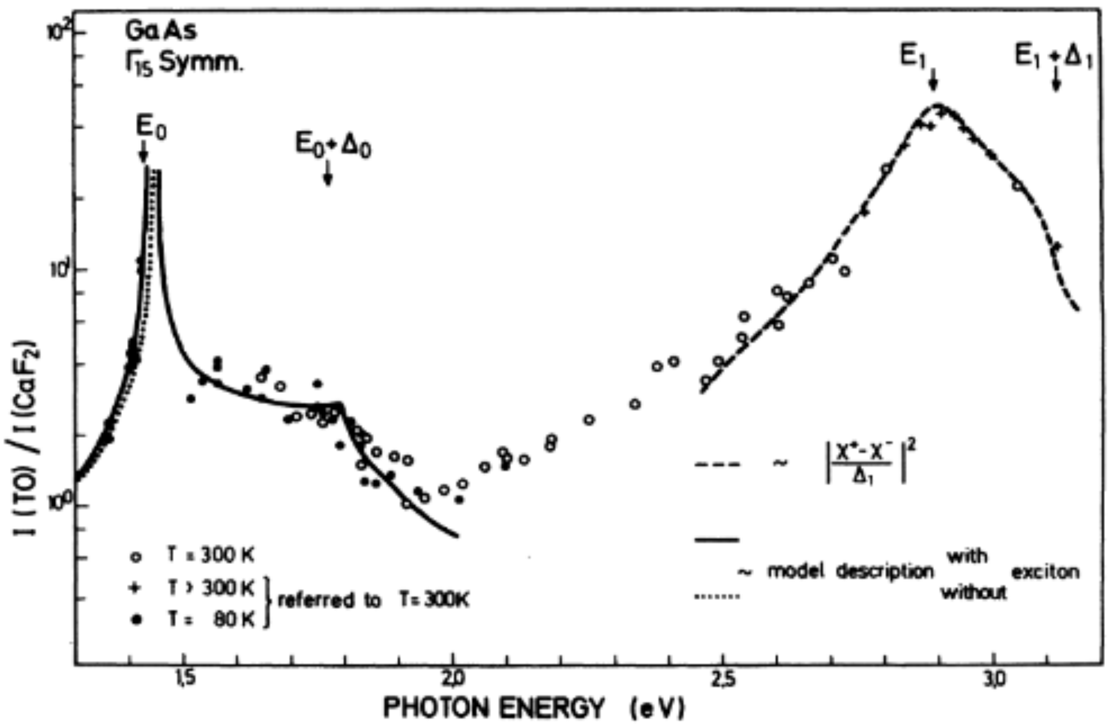


Figure 1-2 Energy units for various portions of electromagnetic spectrum.

Introductory Raman Spectroscopy, 2003
Author: John R. Ferraro, Kazuo Nakamoto and Chris W. Brown

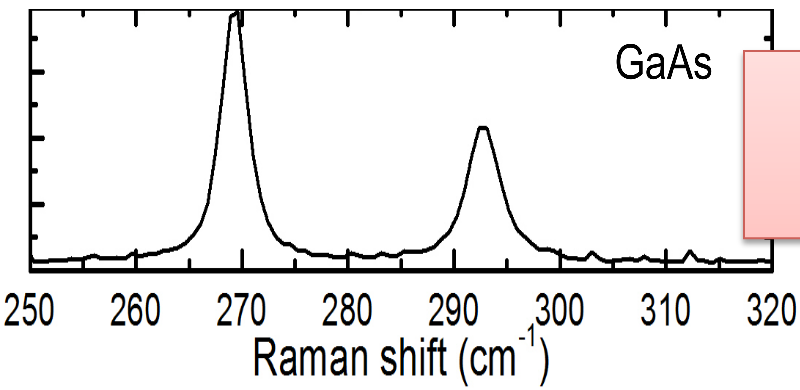
Resonant Raman: determination of band structure





R.Trommer and M. Cardona,
PRB 17, 1865 (1978)

The use of Raman spectroscopy in materials science



Strain

Crystal structure

Substitutional impurities

Alloy composition

Free carriers

Temperature

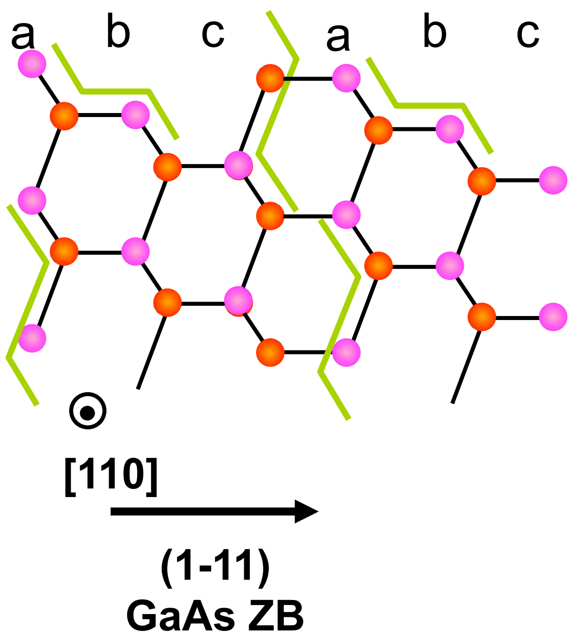
Band structure

GaAs and related materials

Case study: crystal structure of GaAs

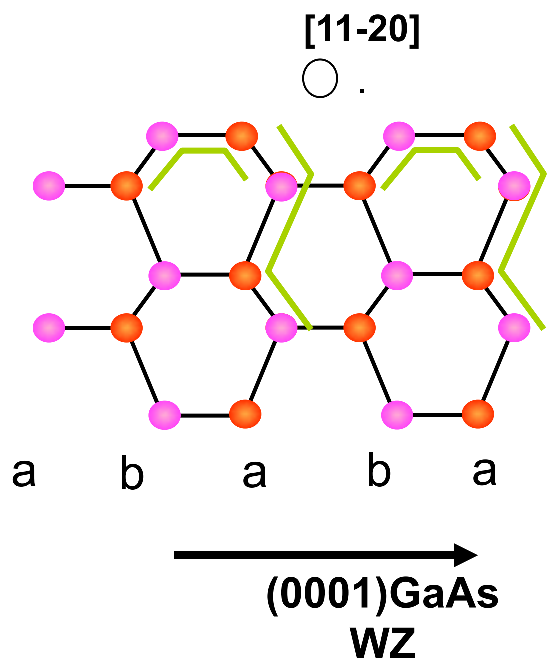
Zinc Blende

E_g (ZB)= 1.517 eV

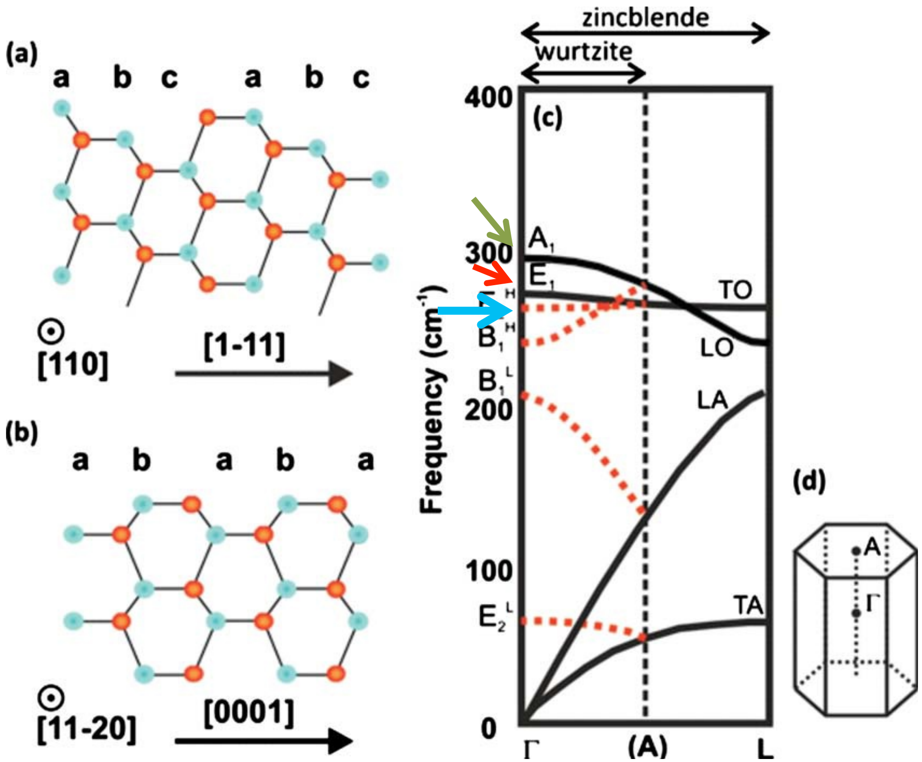


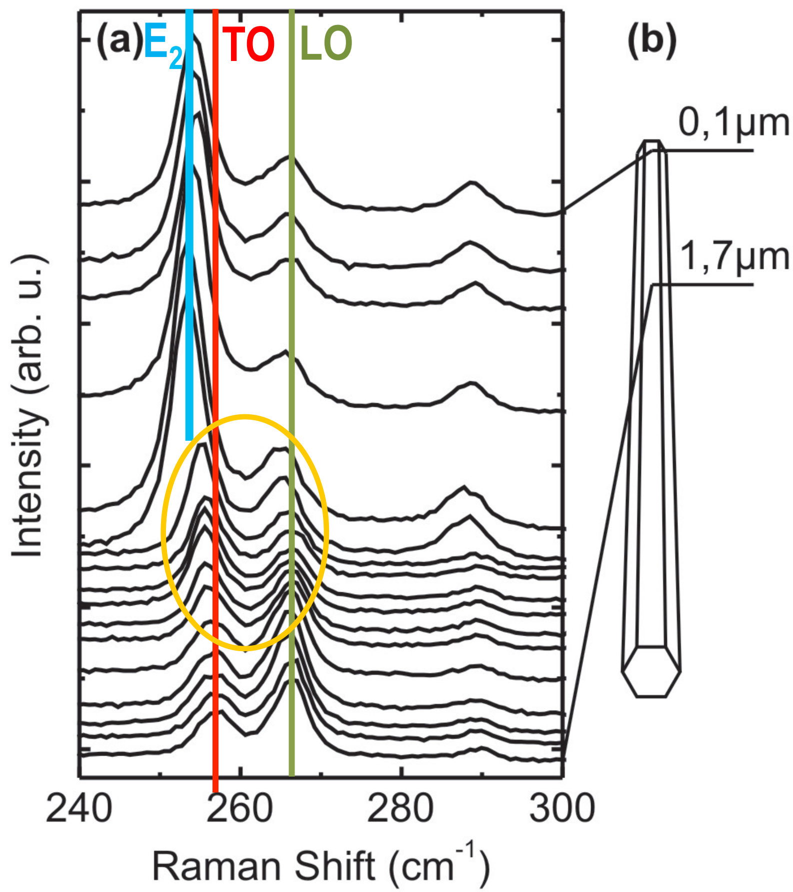
Wurtzite

E_g (WZ)= 1.550 eV



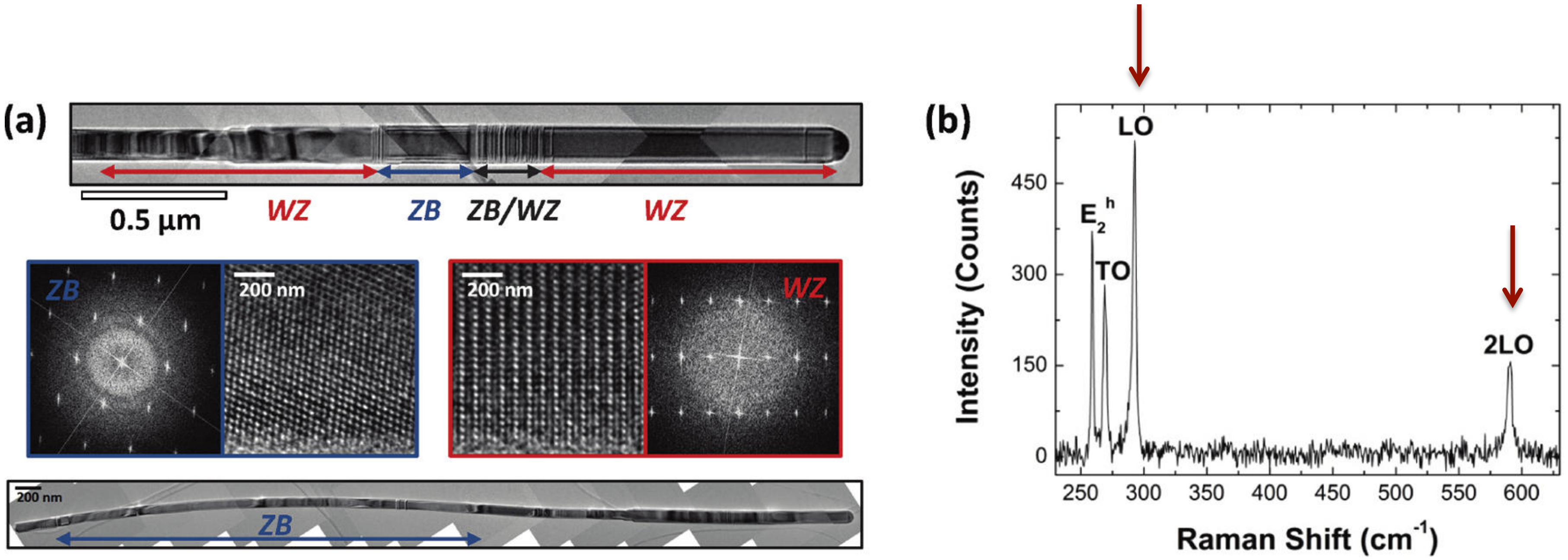
Can we identify the structures by Raman spectroscopy?





I. Zardo et al PRB (2009)

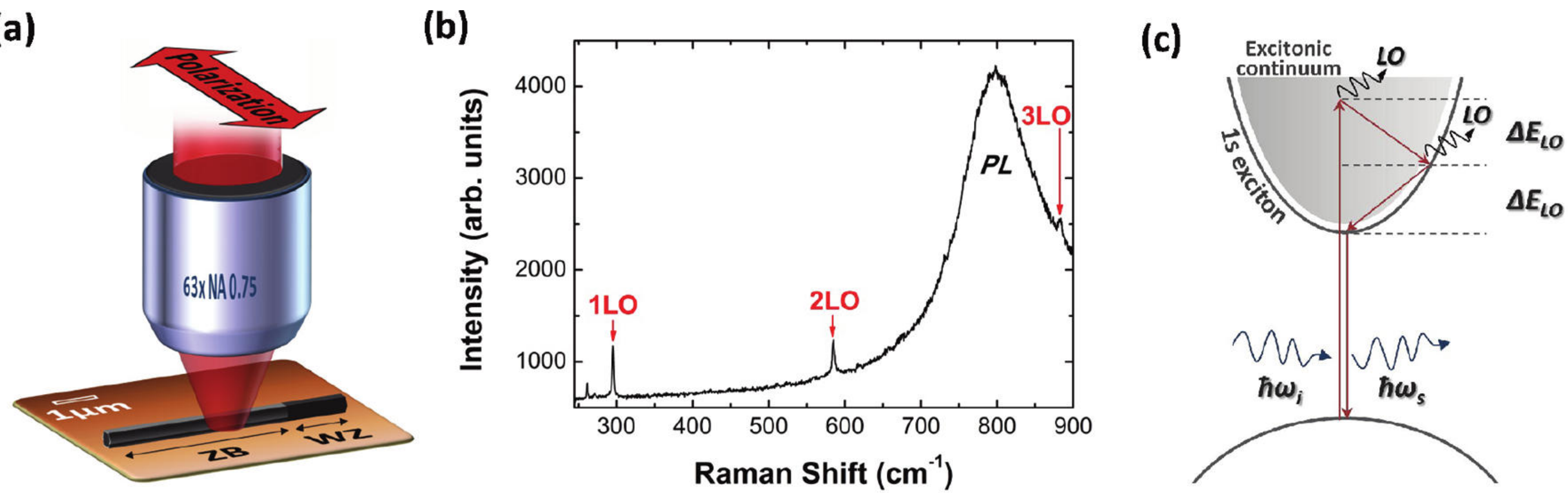
Light-matter interaction



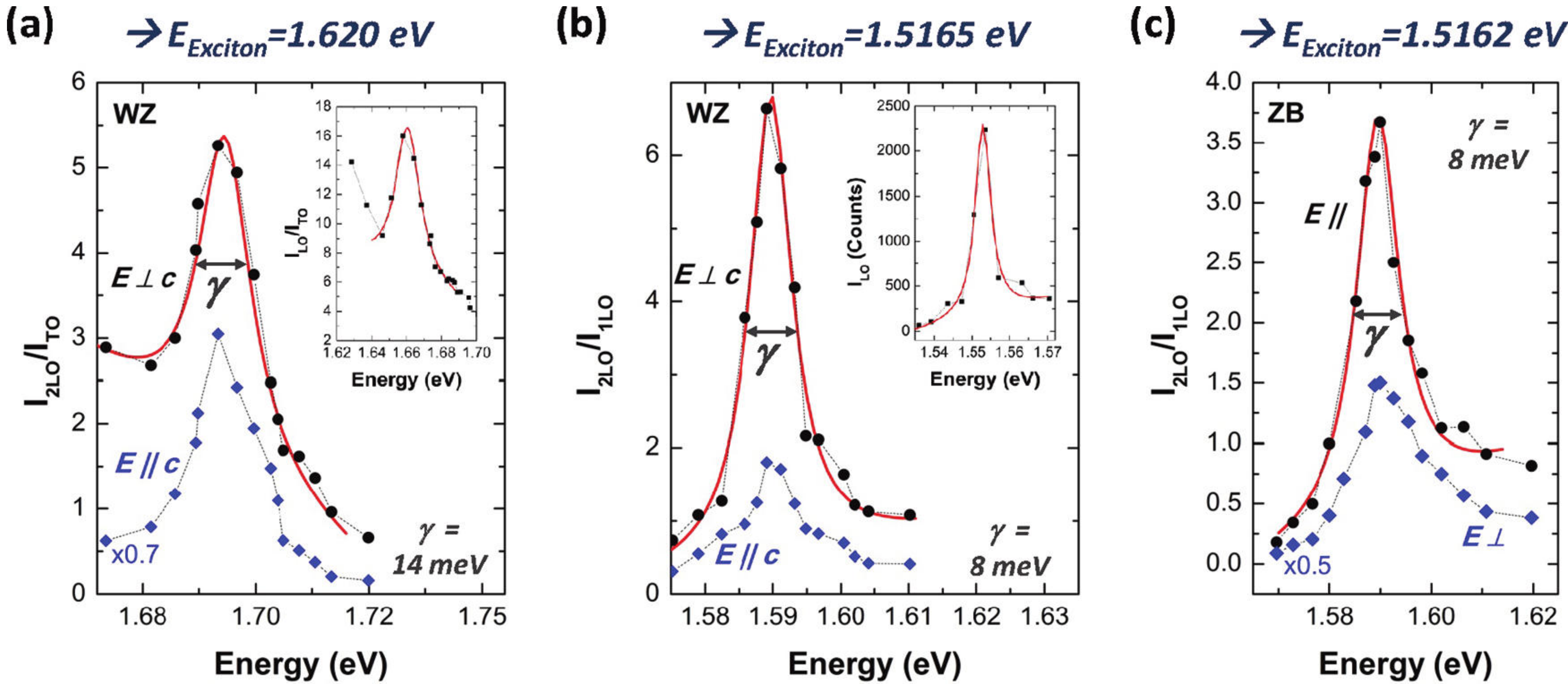
Near-resonant micro raman spectrum of WZ NW part exhibiting E_2^h mode of the WZ structure

B. Ketterer et al ACS Nano (2011)

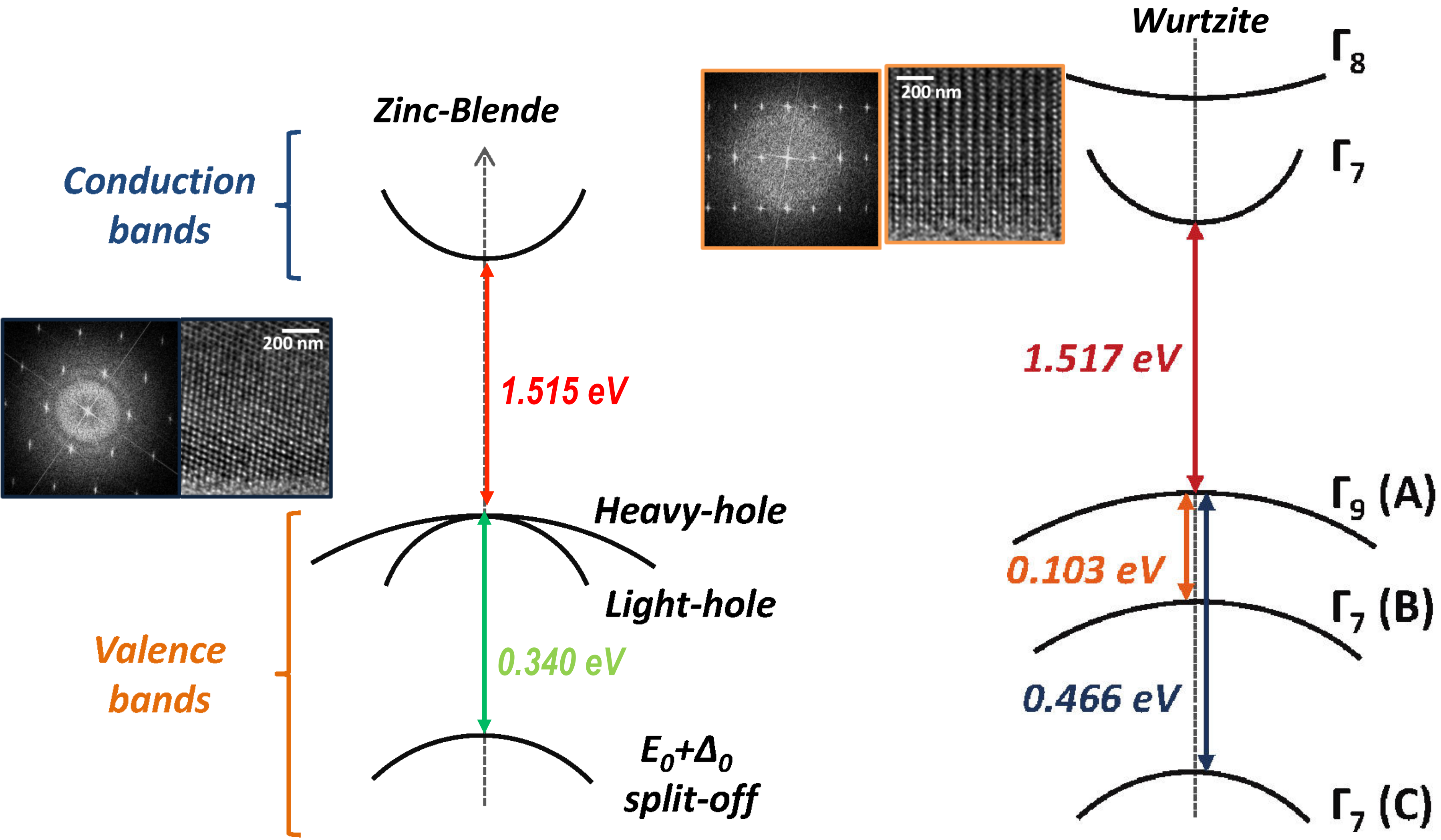
Using resonant Raman to obtain the band structure



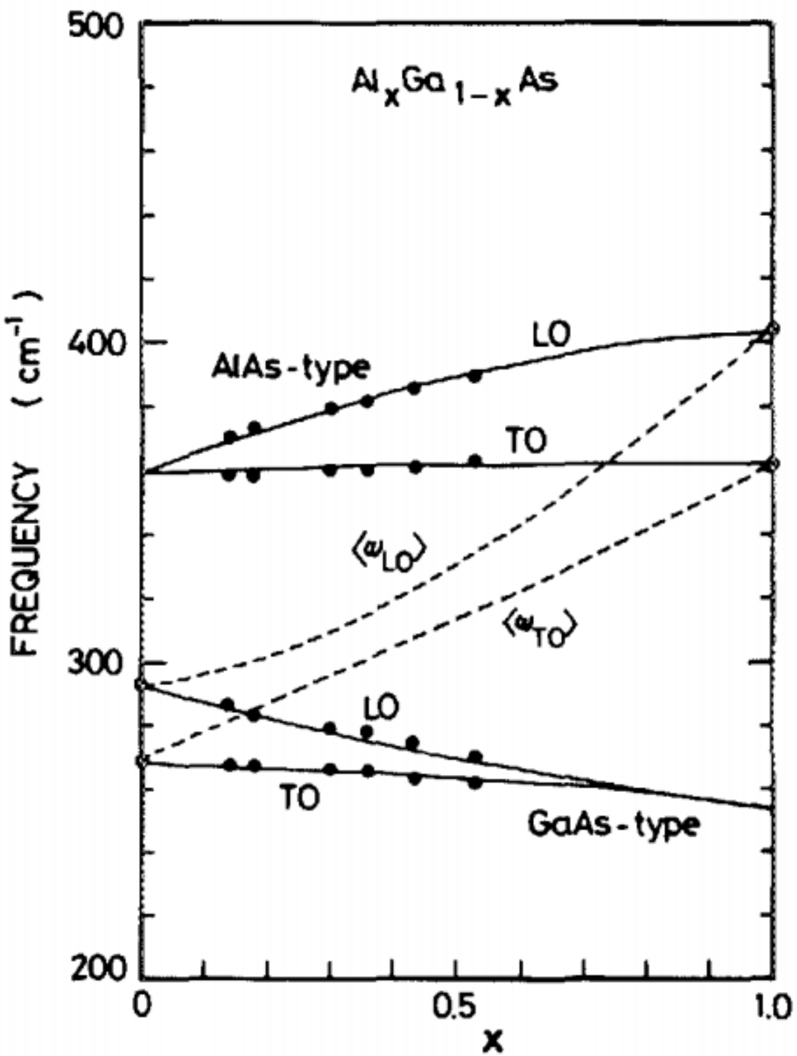
Using resonant Raman to obtain the band structure



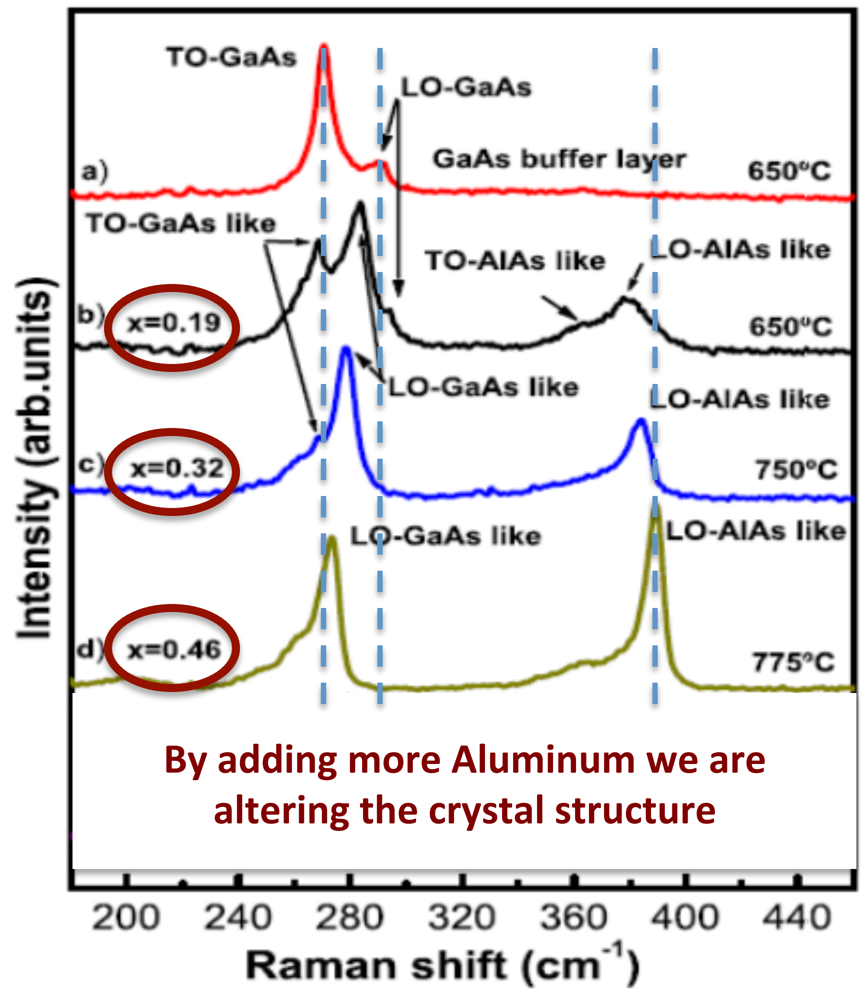
Light-matter interaction



Alloy composition: $Al_xGa_{1-x}As$



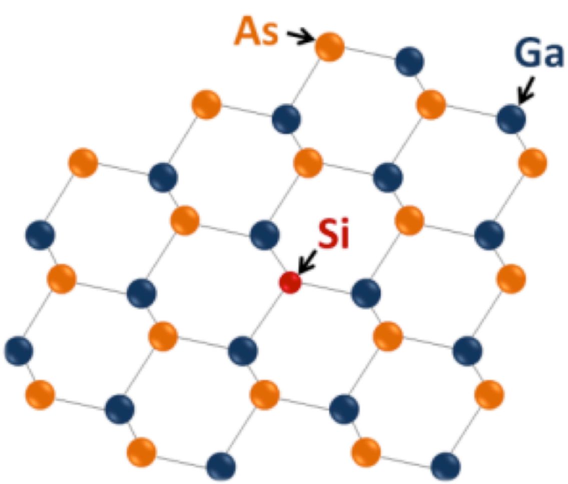
S. Adachi et al JAP (1985)

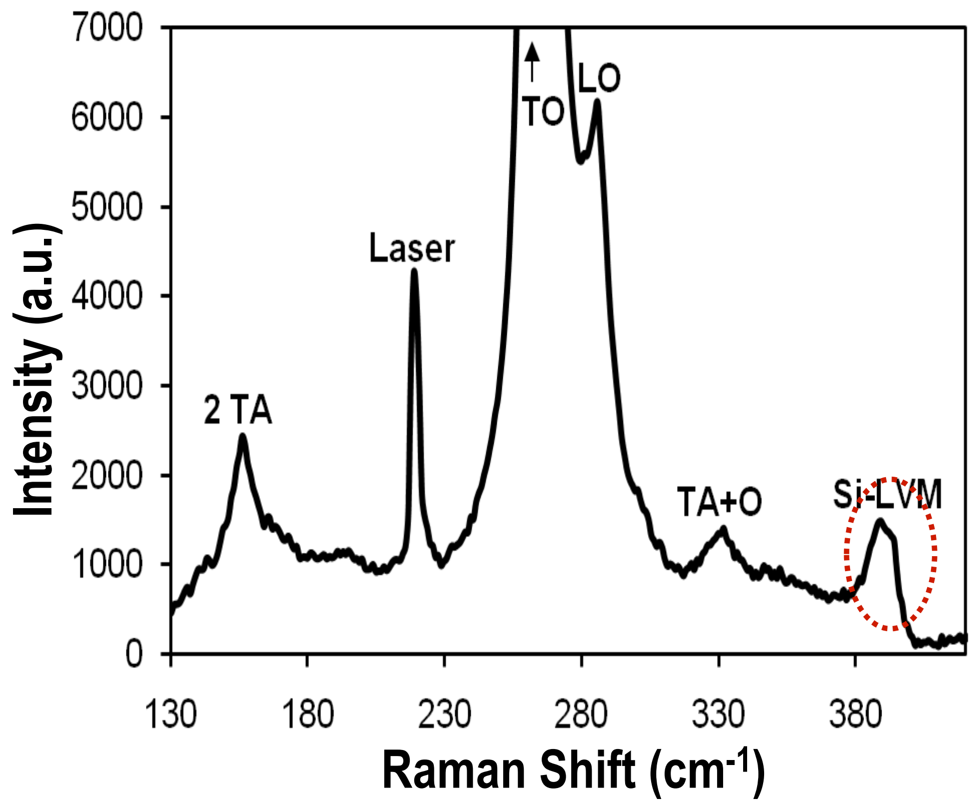


J. Diaz-Reyes Superficies y Vacio (2010)

Alloy composition: doping (<<0.1%)

GaAs doped with Si

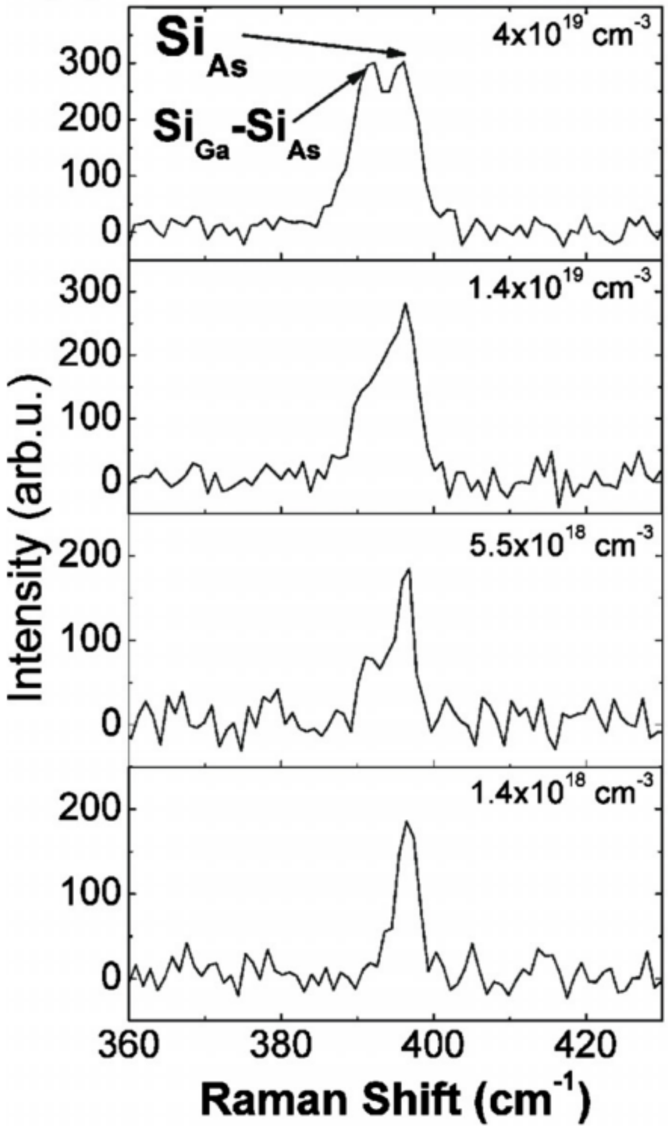




- The local vibrational mode (LVM) corresponds to Si in the site of AS
- The intensity of the local vibrational mode is proportional to the concentration of dopants.

B. Ketterer APL (2010)

Alloy composition: doping (<<0.1%)



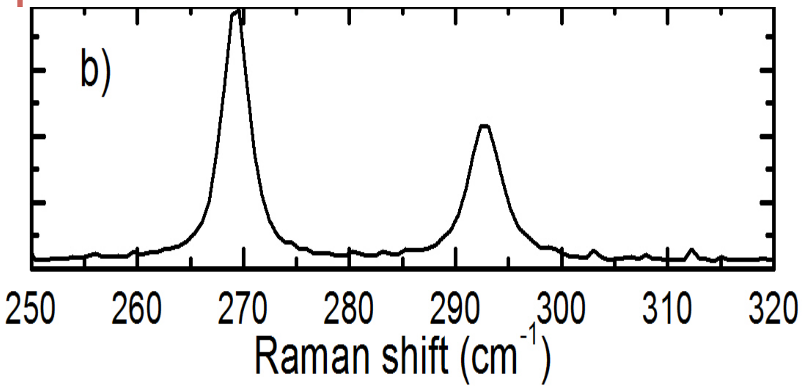
Silicon mainly incorporated as an acceptor on arsenic sites

Neutral Si-Si pairs form when the total silicon concentration increases

B. Ketterer APL (2010)

From bulk to nano

In Bulk & NWs



Strain

Crystal structure

Substitutional impurities

Alloy composition

Free carriers

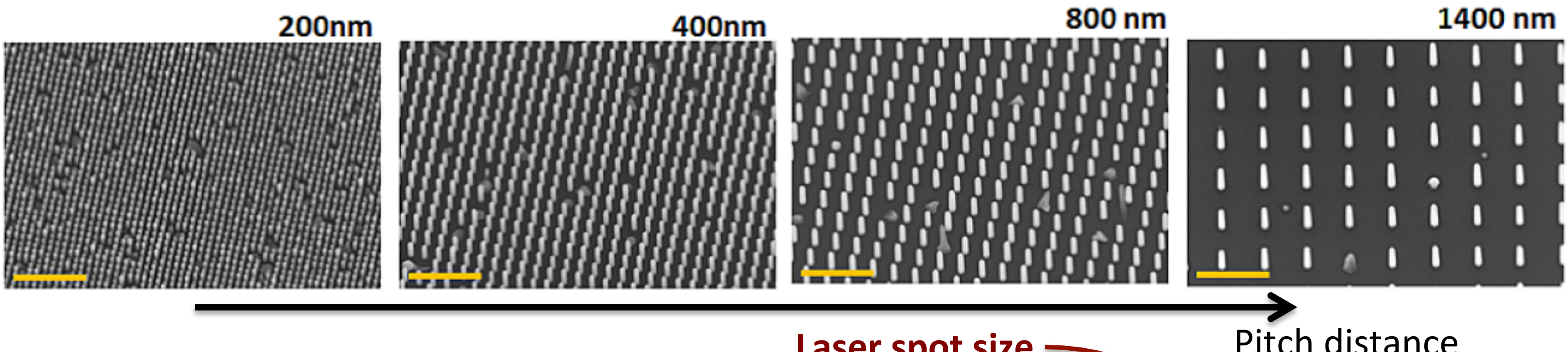
Temperature

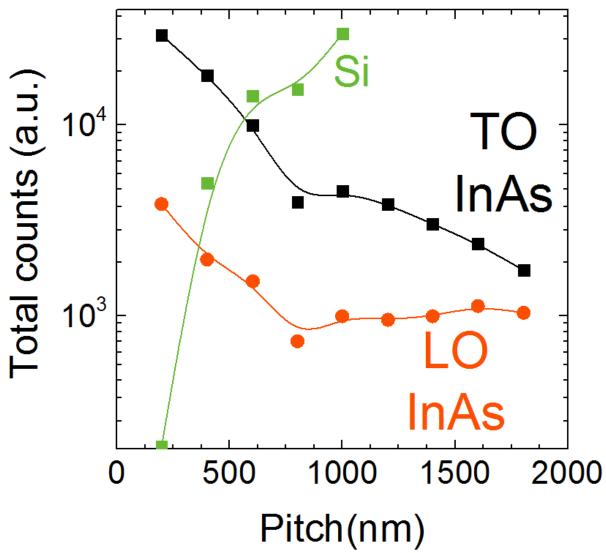
Band structure

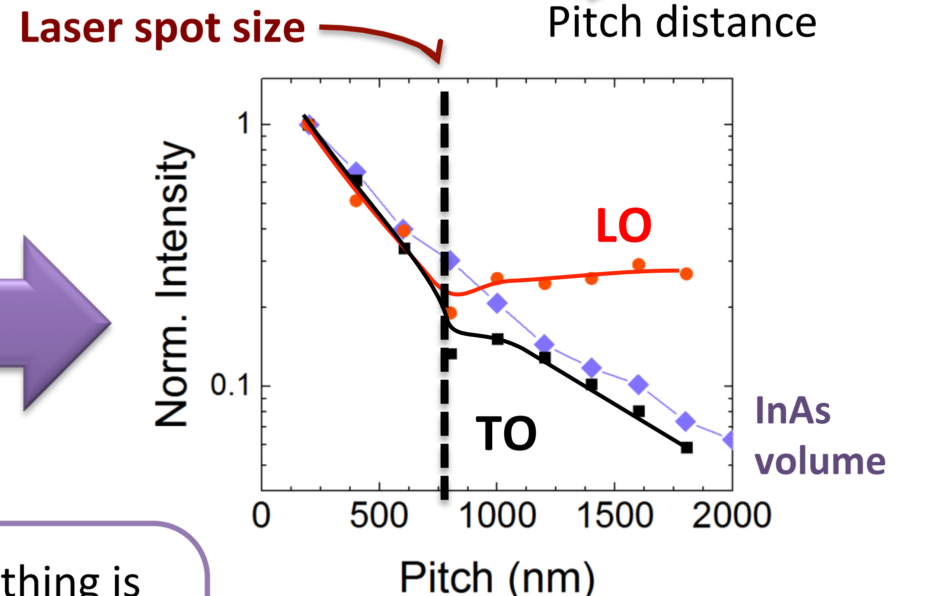
Anything additional in nanostructures?

From bulk to nano: the role of photonic resonances

InAs NWs on patterned Silicon



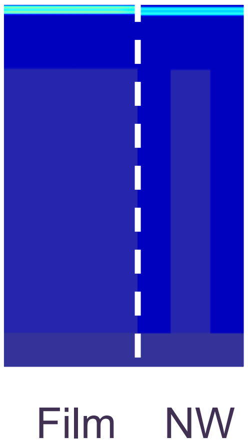




Something is changing the selection rules!

M. Heiss et al., Nanotech. 25 014015 (2014)

From bulk to nano: the role of photonic resonances

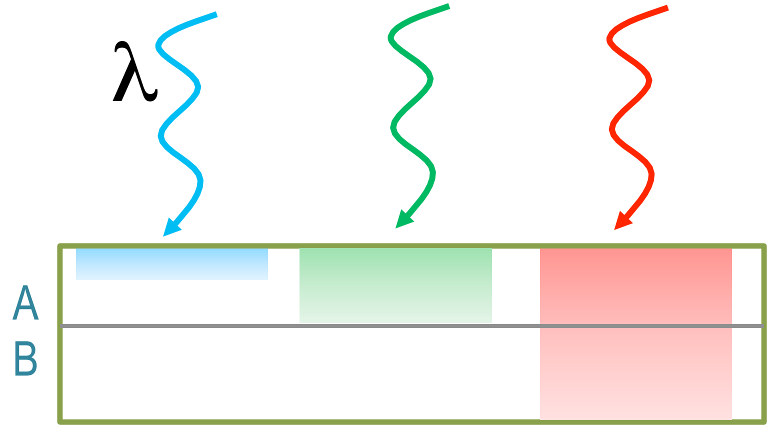


Due to sub-wavelength dimensions, the light inside the NW “bends”, “rotates” and “is localized”

Simulations from Esther Alarcon-Lladó

From bulk to nano: the role of photonic resonances

$$I(\lambda) = I\downarrow o \exp(-\alpha z)$$

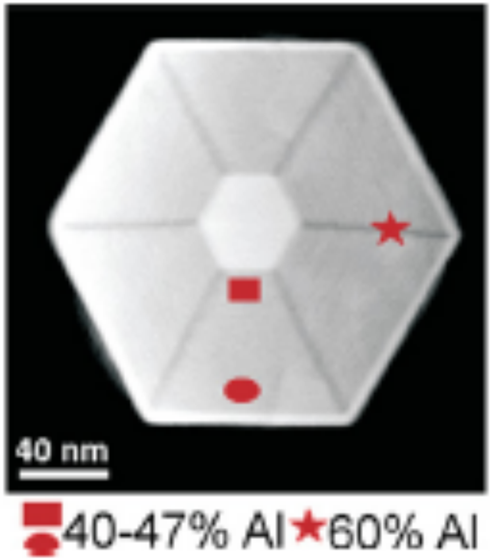


In general: as the coefficient t of absorption a is higher for shorter wavelengths, light with shorter wavelengths is absorbed more towards the surface and longer wavelengths more towards the bulk of the material.

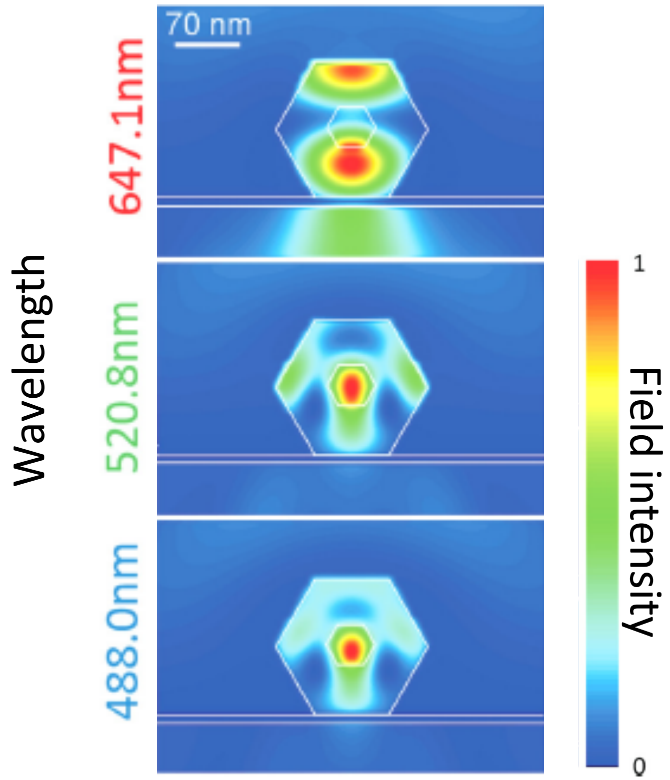
From bulk to nano: the role of photonic resonances

- Spatial distribution of the e-m field depends on:
  - NW morphology (size and shape)
  - Light wavelength

GaAs/AlGaAs core-shell NW



FDTD simulation

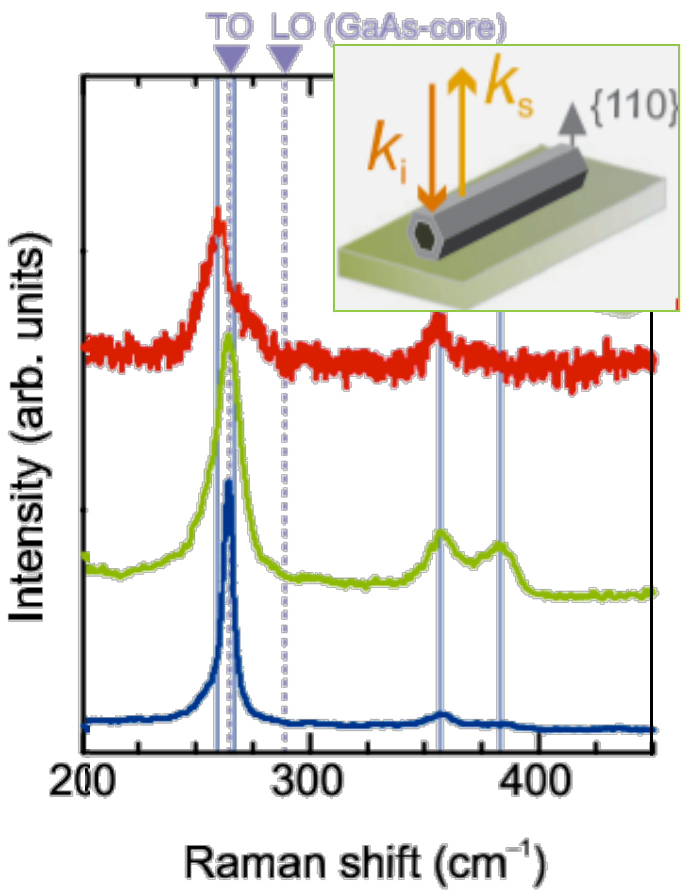


Short λ light is enhanced around the core, while longer λ light resonates around the shell

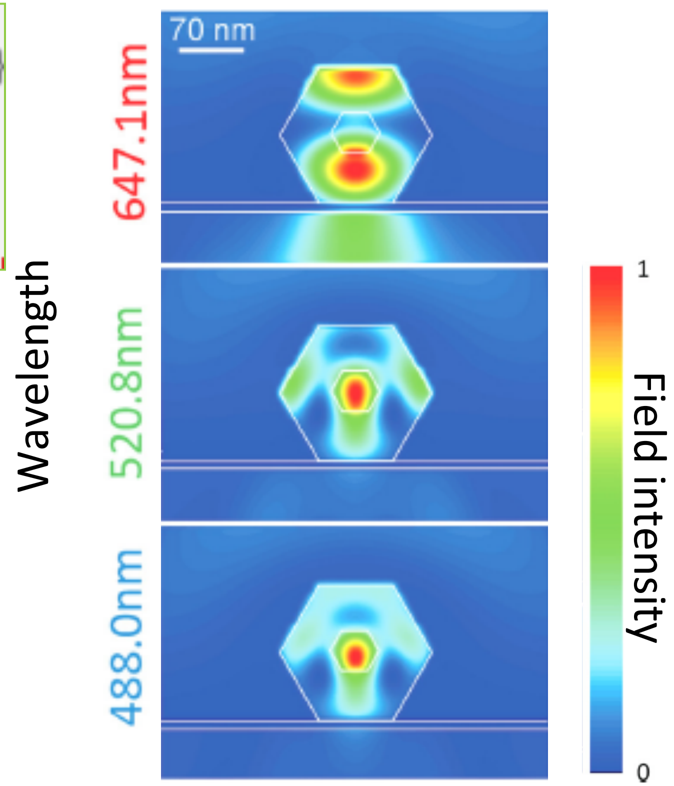
F. Amaduzzi et al., J. Appl. Phys. 116, 184303 (2014)

From bulk to nano: the role of photonic resonances

- Spatial distribution of the e-m field depends on:
  - NW morphology (size and shape)
  - Light wavelength



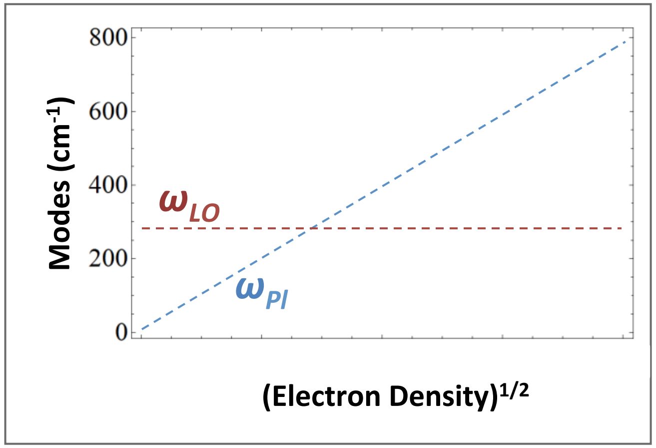
FDTD simulation



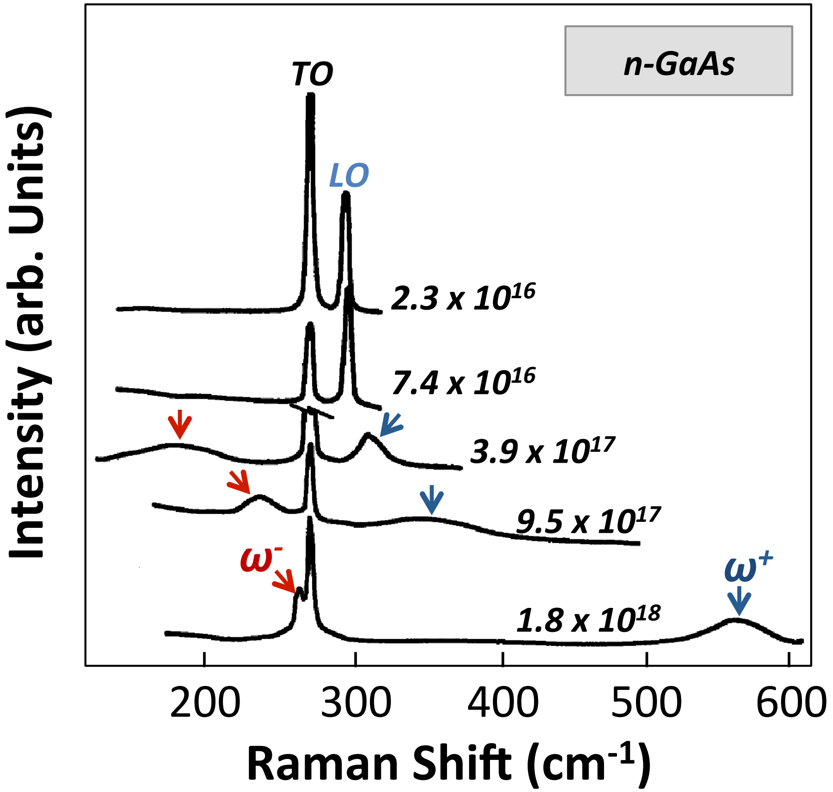
Short λ light is enhanced around the core, while longer λ light resonates around the shell

Why is it important to enhance unallowed modes?

Method:
LO-Phonon-Plasmon Coupling



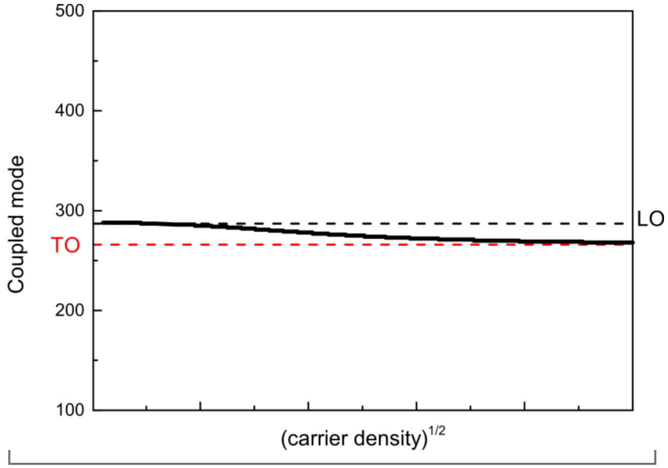
$$\epsilon(0,\omega) = \epsilon_\infty + \frac{\omega_{LO}^2 - \omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\gamma\omega} - \frac{\omega_p^2}{\omega^2 + i\Gamma_p\omega}$$



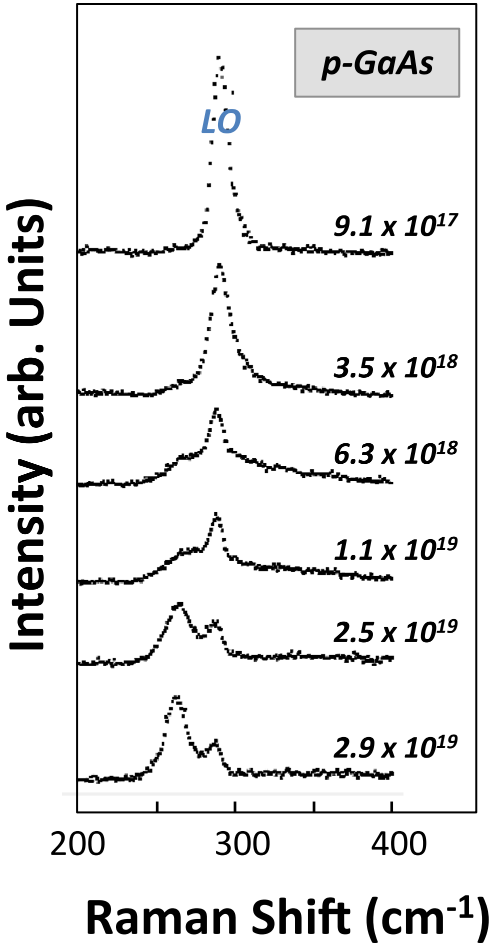
Phys. Rev. Lett., 16, 999 (1966)

Why is it important to enhance unallowed modes?

Method:
LO-Phonon-Plasmon Coupling

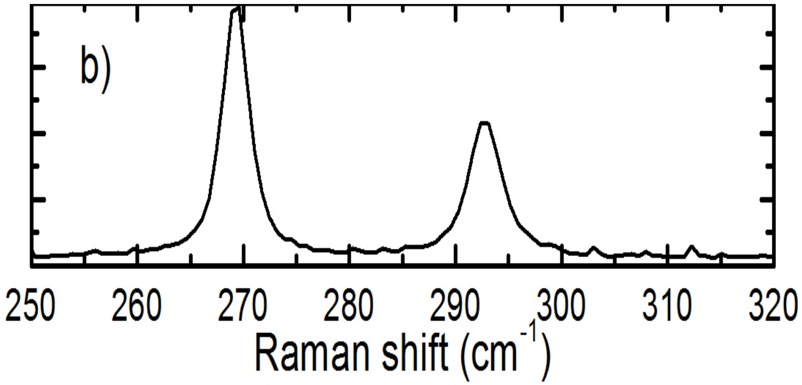


$$\epsilon(0,\omega) = \epsilon_\infty + \frac{\omega_{LO}^2 - \omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\gamma\omega} - \frac{\omega_p^2}{\omega^2 + i\Gamma_p\omega}$$



Jpn. J. Appl. Phys., 25, 652 (1986)

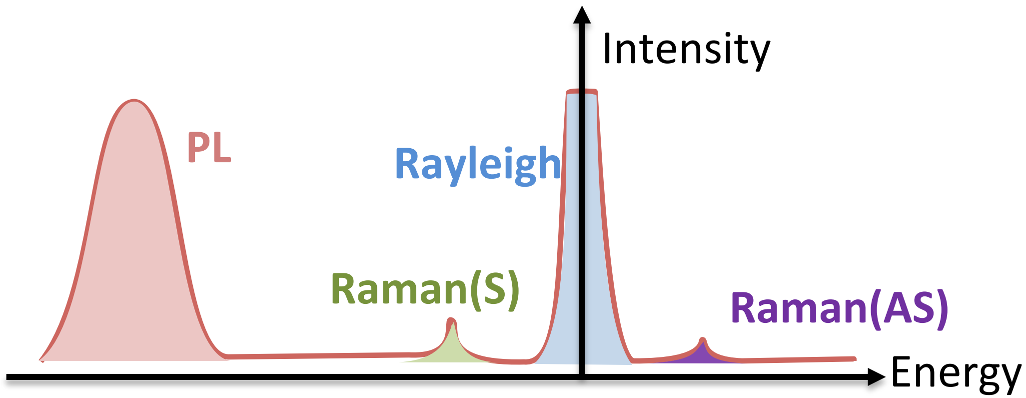
Conclusions on Raman spectroscopy



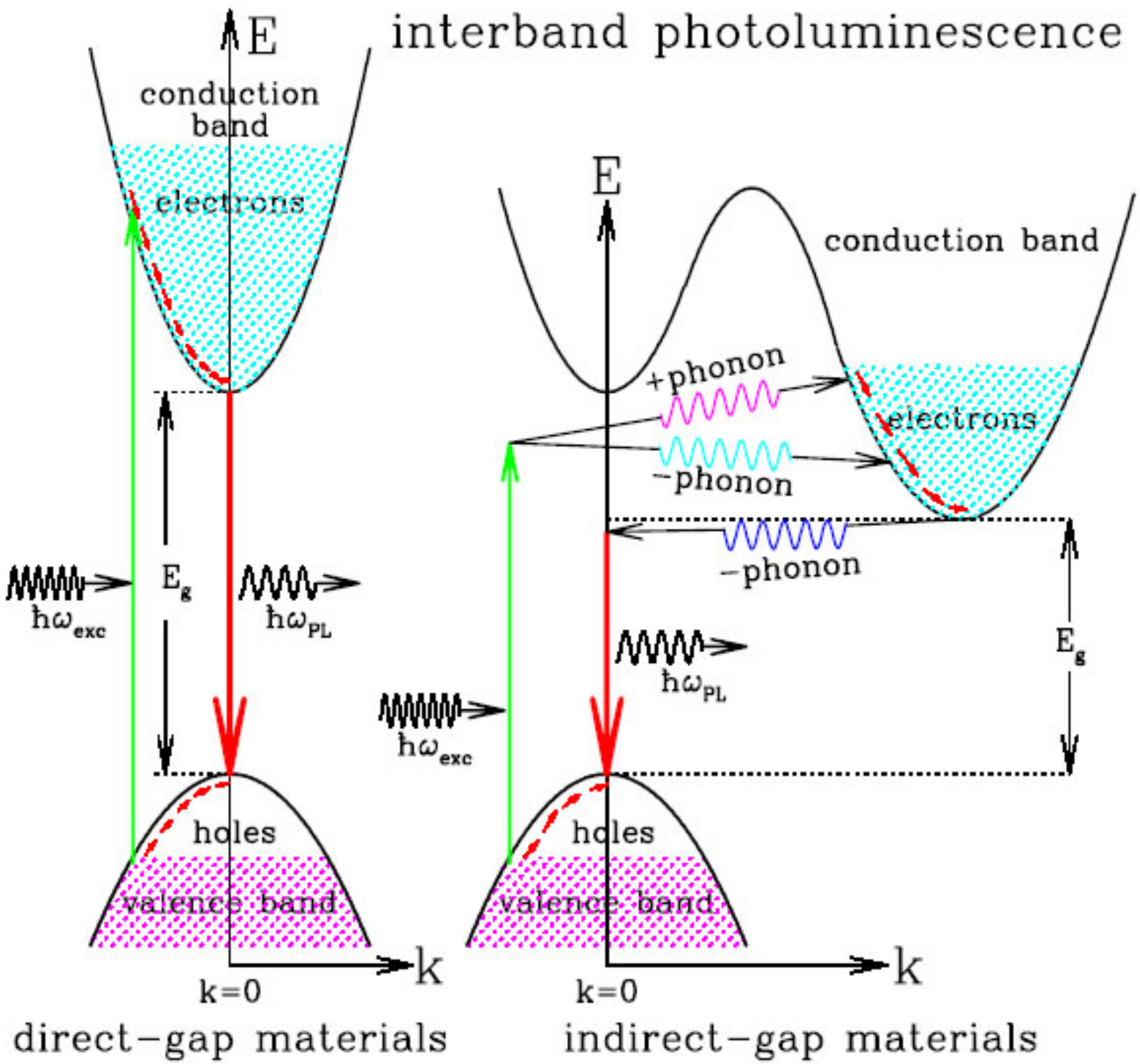
Strain
Crystal structure
Substitutional impurities
Alloy composition
Free carriers
Temperature
Band structure

In nanostructures one has an additional degree of freedom due to photonic effects.

② Luminescence

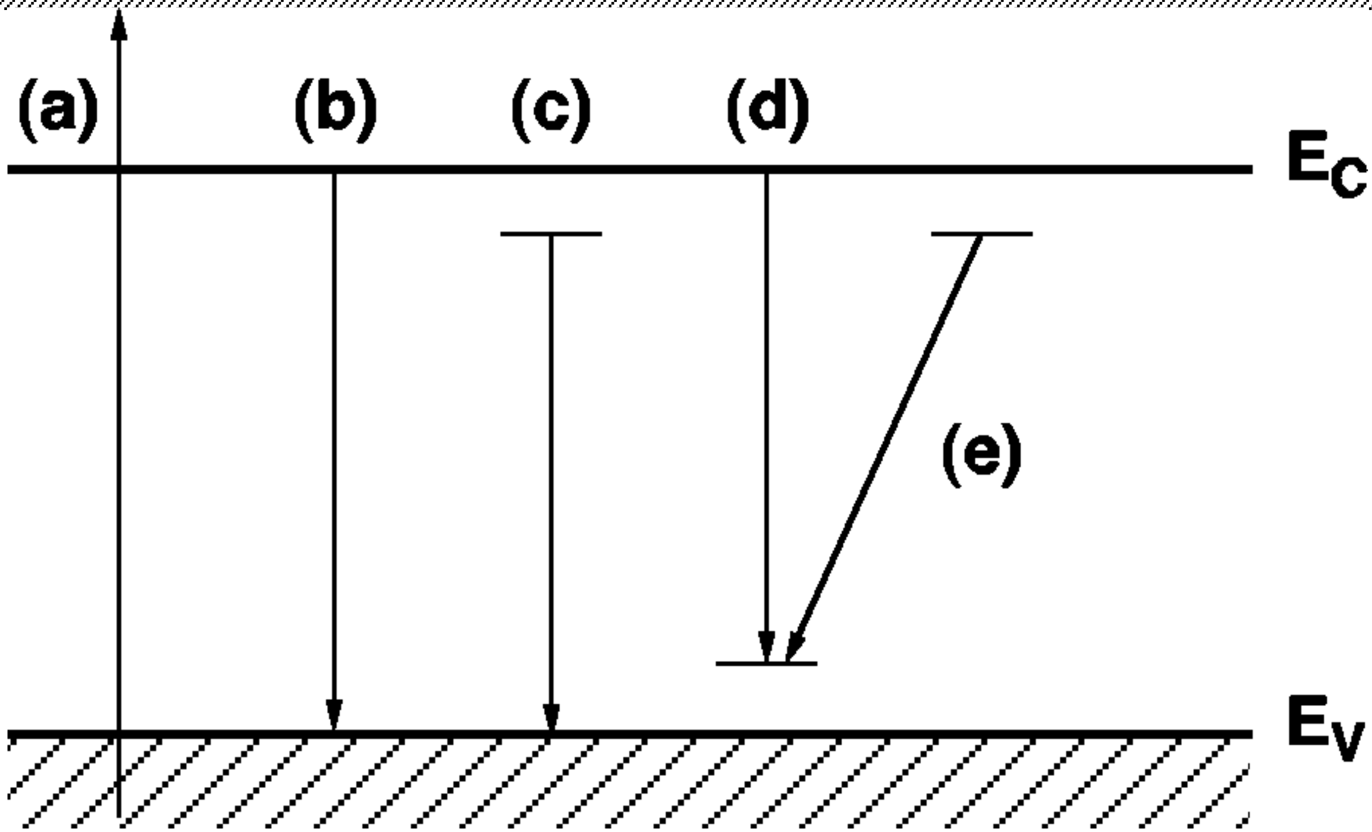


Interband luminescence



Source: ned.ipac.caltech.edu

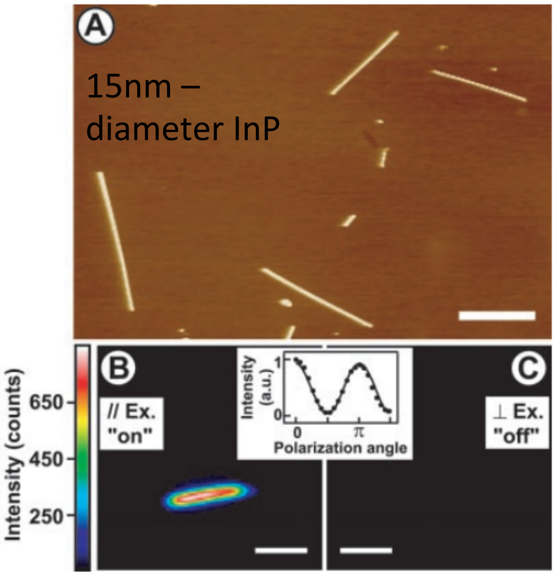
Interband luminescence



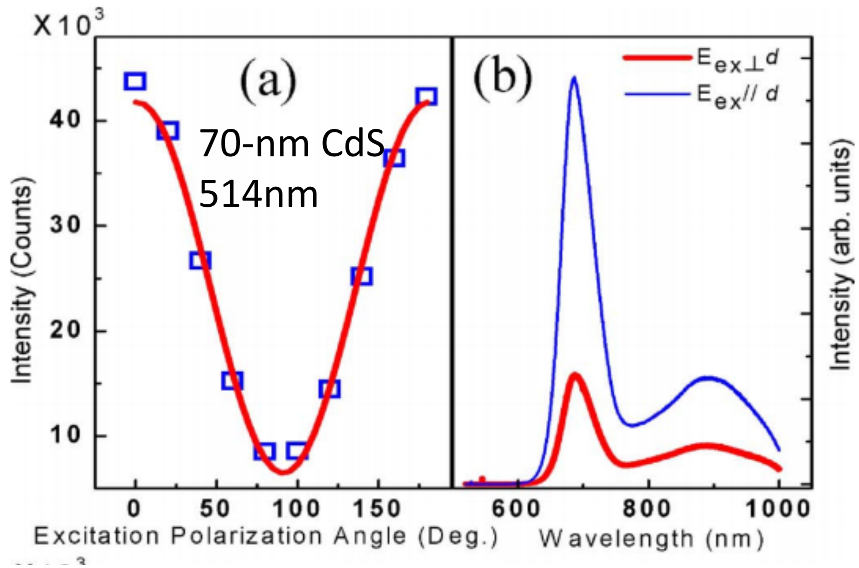
(a) Excitation
(b) Band-to-band recombination
(c) Donor-to-valence band recombination
(d) Conductionband-to-acceptor recombination
(e) Donor-to-acceptor recombination

From bulk to nano

Observation of strongly polarized PL excitation and emission along the NW axis

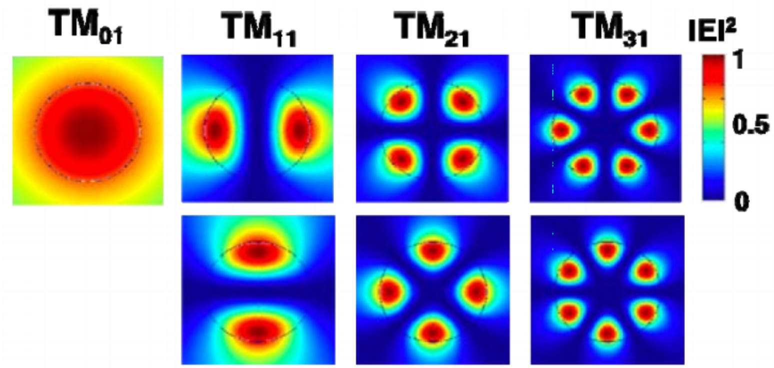


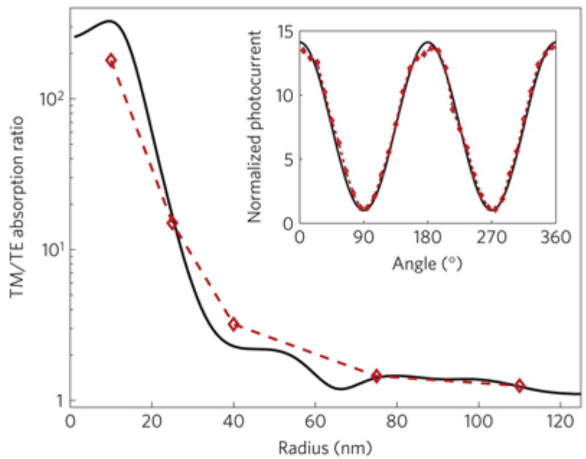
J. Wang et al., Science 293, 1455 (2001)



C. Shan et al., Phys. Rev. B **74**, 153402 (2006)

From bulk to nano: the role of photonic resonances



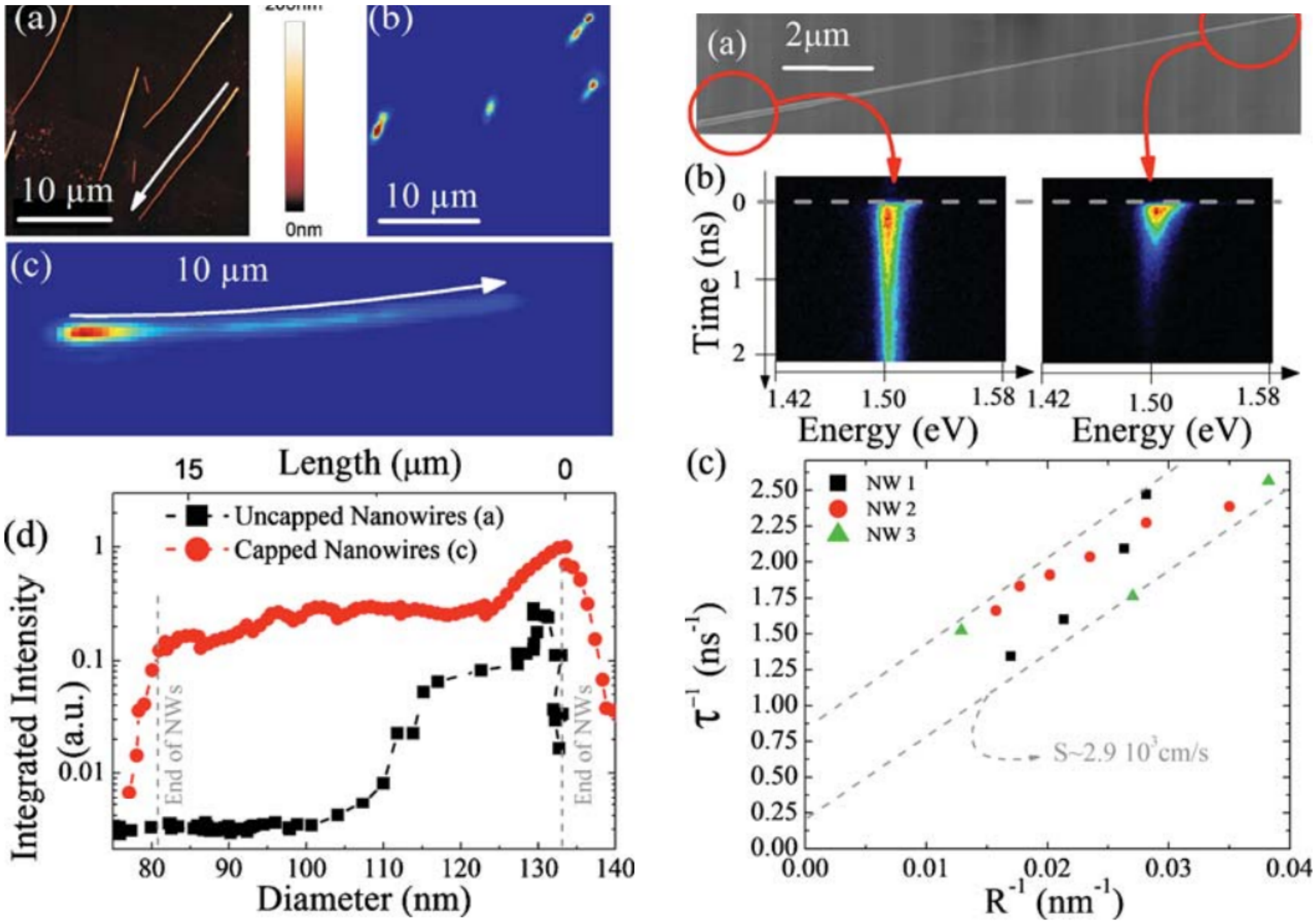


Theoretical/experimental light absorption anisotropy in Ge NWs (inset:25nm NW)

Small wires (d<<λ/4) can support single TM01 mode, for which light response is highly polarized ($I \sim \cos^2 \alpha$)

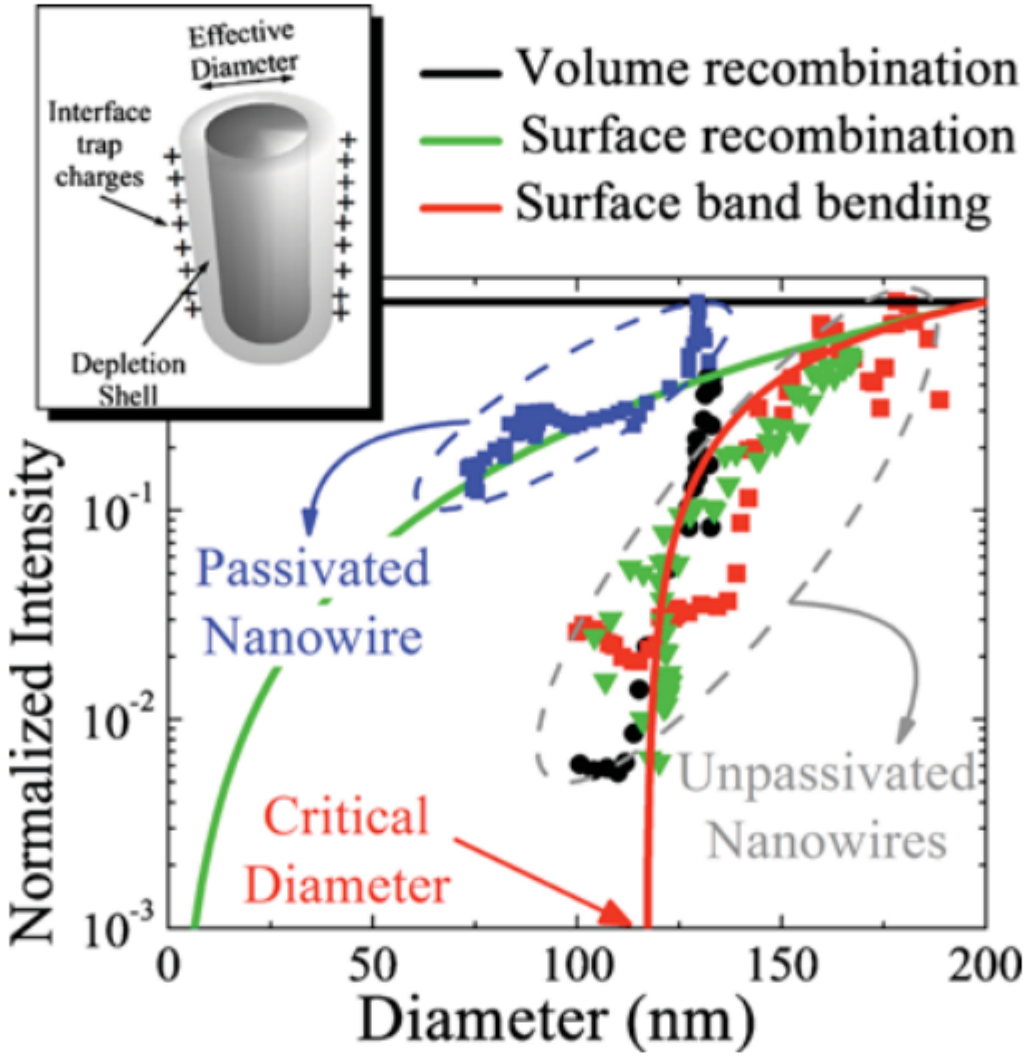
L. Cao et al., Nat. Mat. 8, 643 (2009)
Q. Xiong et al., Appl. Phys. A 85, 299 (2006)

Surface recombination in nanowires



O. Demichel et al Appl. Phys. Lett. 97, 201907(2010)

Surface recombination in nanowires

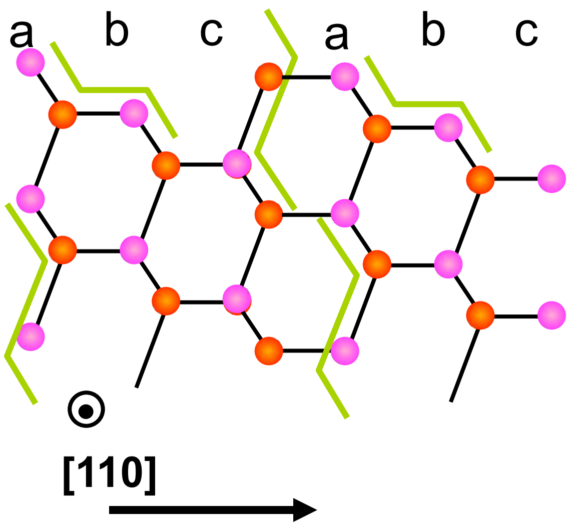


O. Demichel et al Appl. Phys. Lett. 97, 201907(2010)

Polytypism

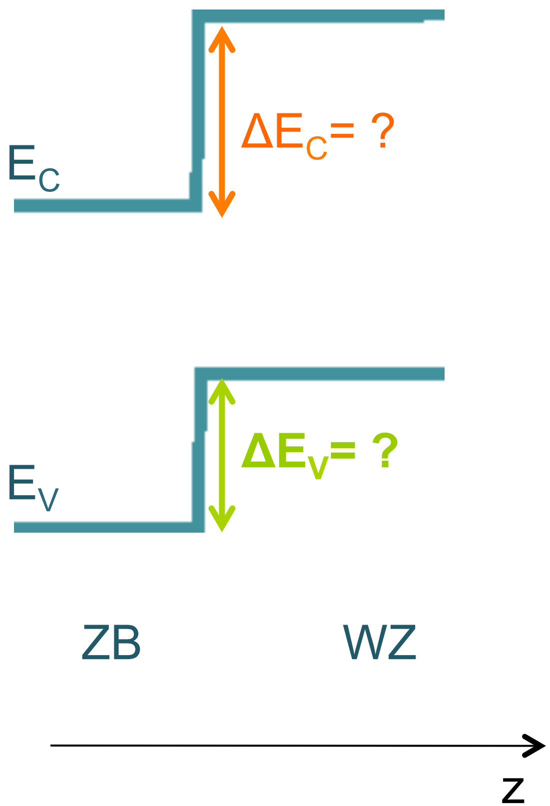
Zinc Blende

E_g (ZB)= 1.517 eV



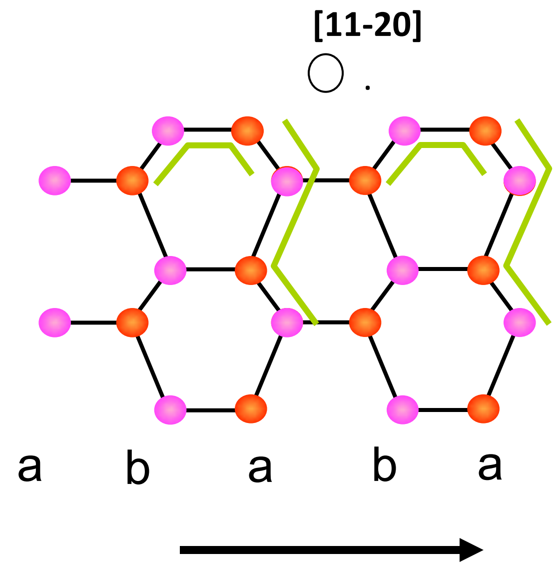
(1-11) GaAs ZB

Theoretical prediction at Γ point:



Wurtzite

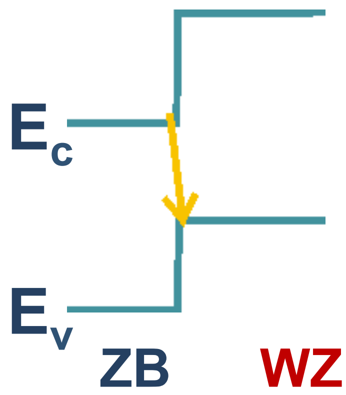
E_g (WZ)= 1.550 eV

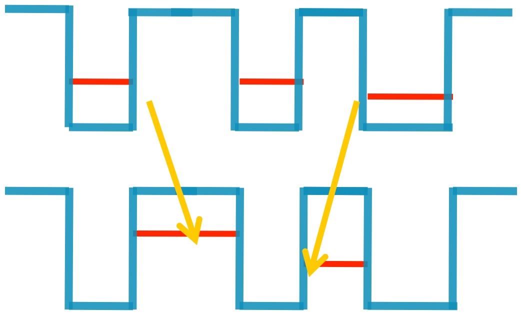


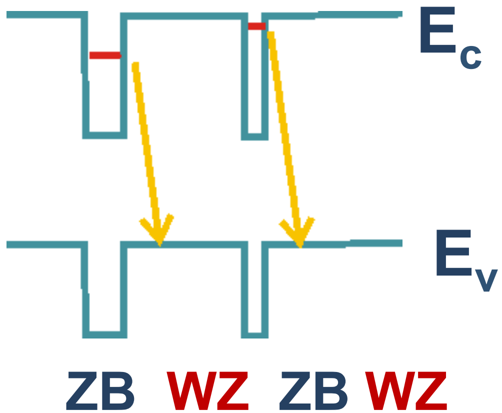
(0001)GaAs WZ

D. Spirkoska et al PRB (2009)

Polytypism (picture by 2009)







$$\hbar\omega = E_g(ZB) - \Delta E_V$$

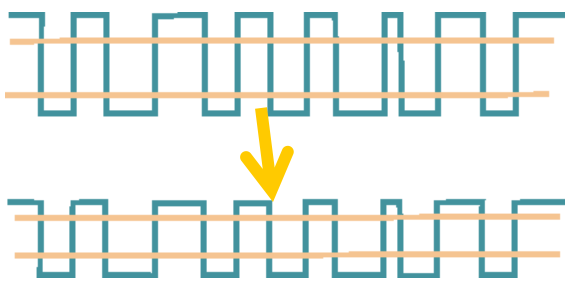
$$\hbar\omega \leq E_g(WZ)$$

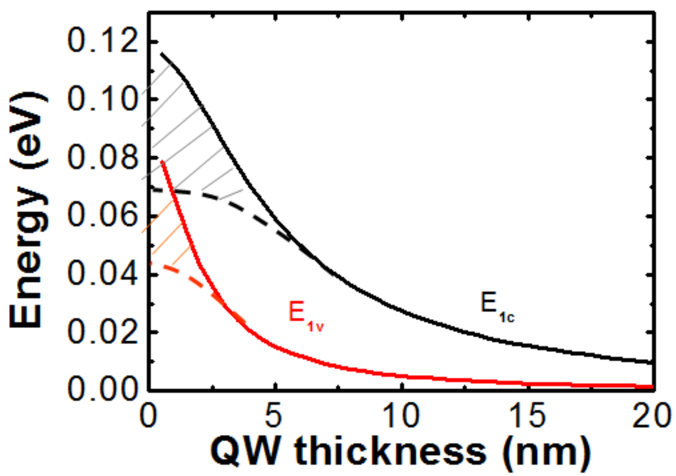
1.43 eV

1.44-1.48 eV

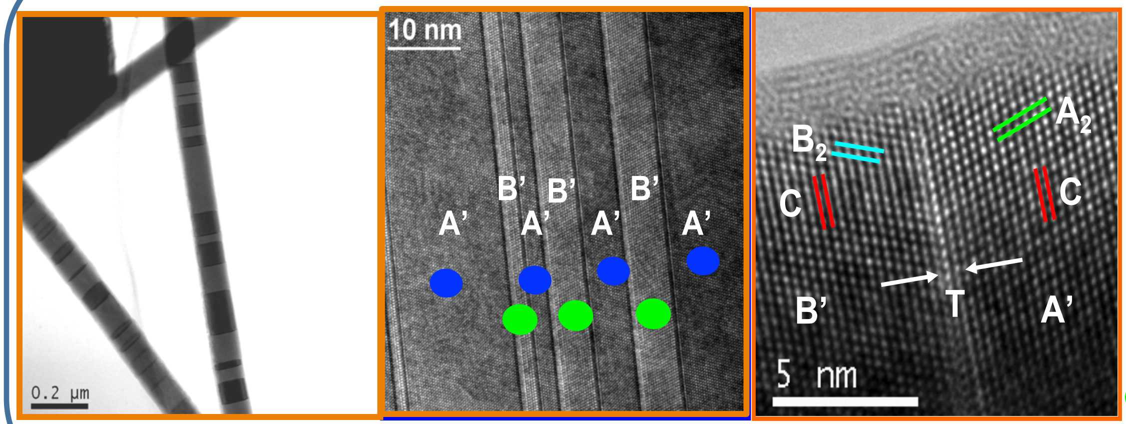
1.48-1.51 eV

1.42-1.46





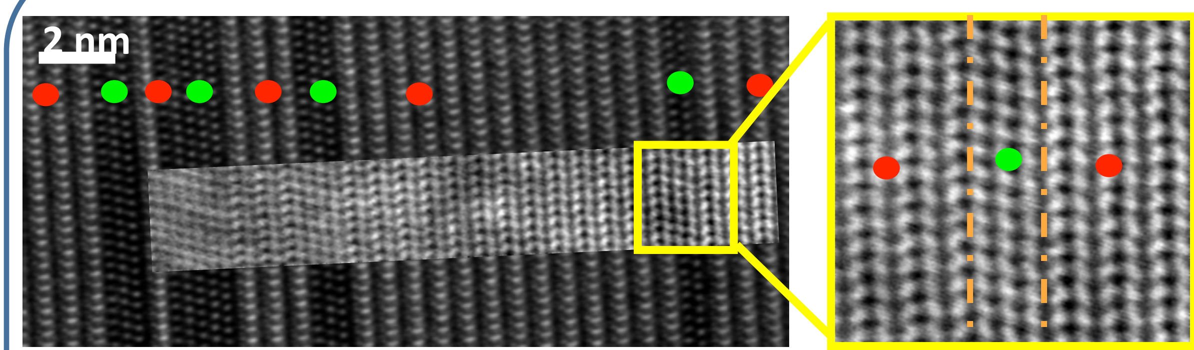
Polytypism



[110]
[011]

High growth rate conditions

→ Pure zinc-blende structure



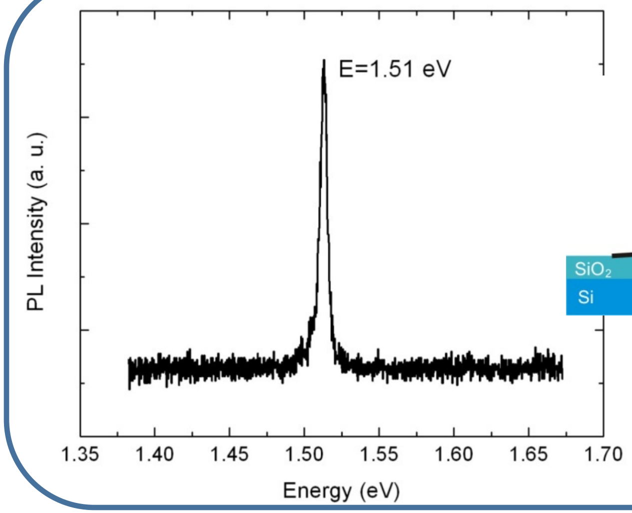
[11-20] GaAs WZ (**Wurtzite**)
[110] ZB (**Zinc Blende**)
[011] ZB

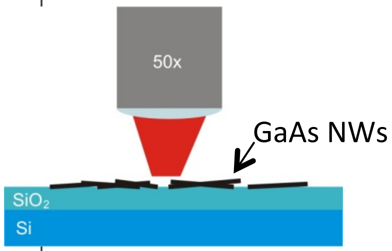
By decreasing the growth rate:

→ Percentage of wurtzite structure increases

D. Spirkoska et al PRB (2009)

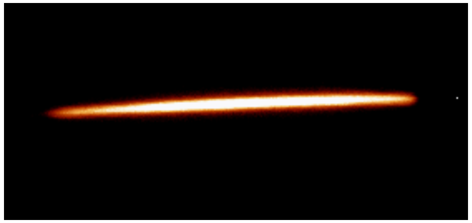
Polytypism



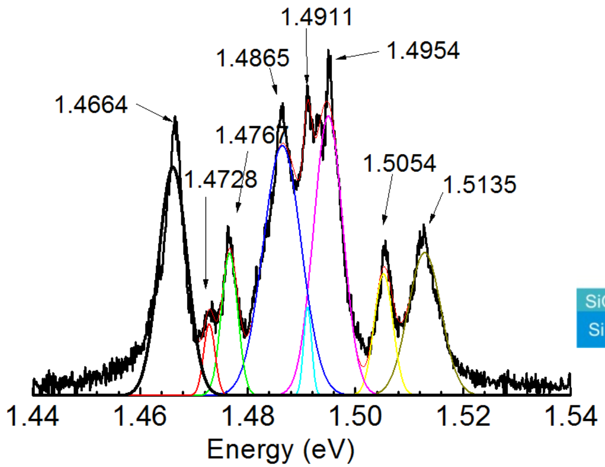


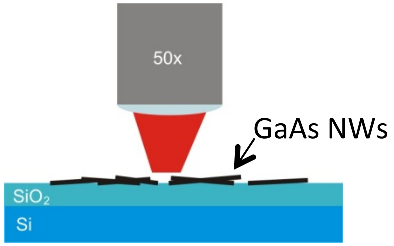
Micro-PL on a single ZB nanowire

Mapping with cathodoluminescence

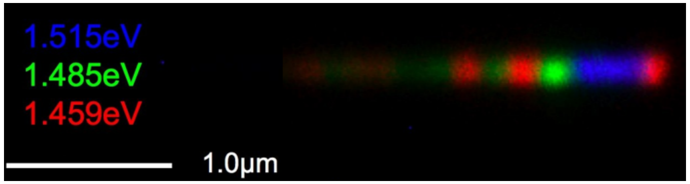


1.51 eV





The spectra become richer when wurtzite sections are intercalated in the structure



(in cooperation with Anders Gustafsson & Lars Samuelson)

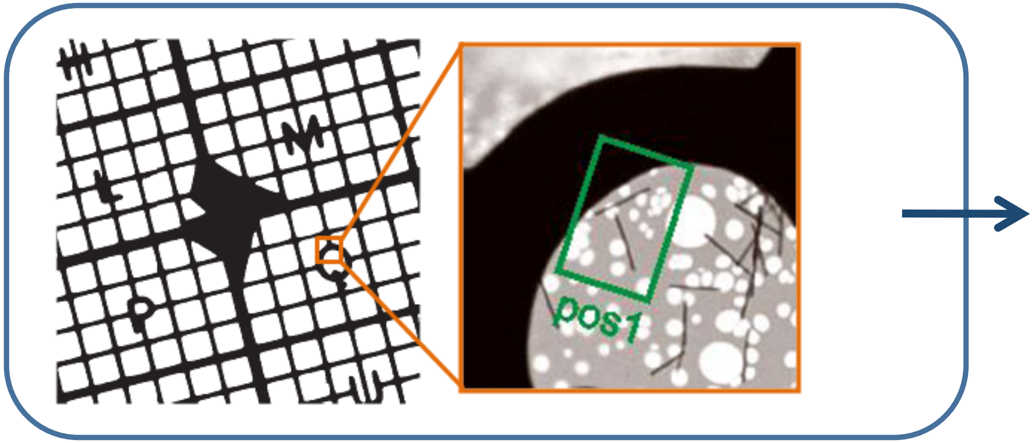
D. Spirkoska et al PRB (2009)

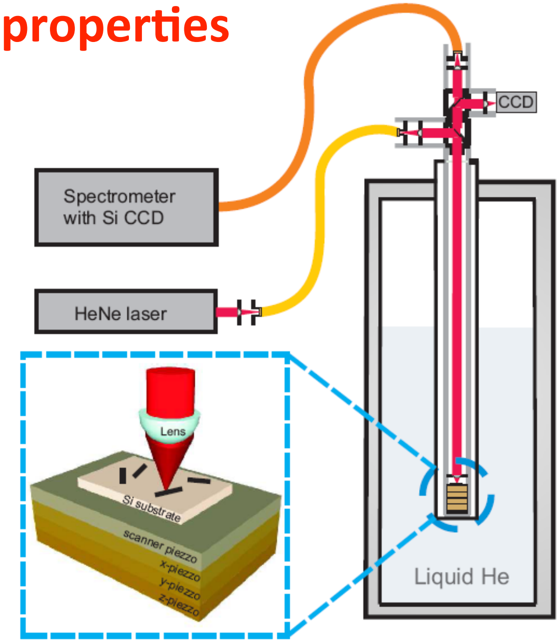
Direct correlation

M. Heiβ

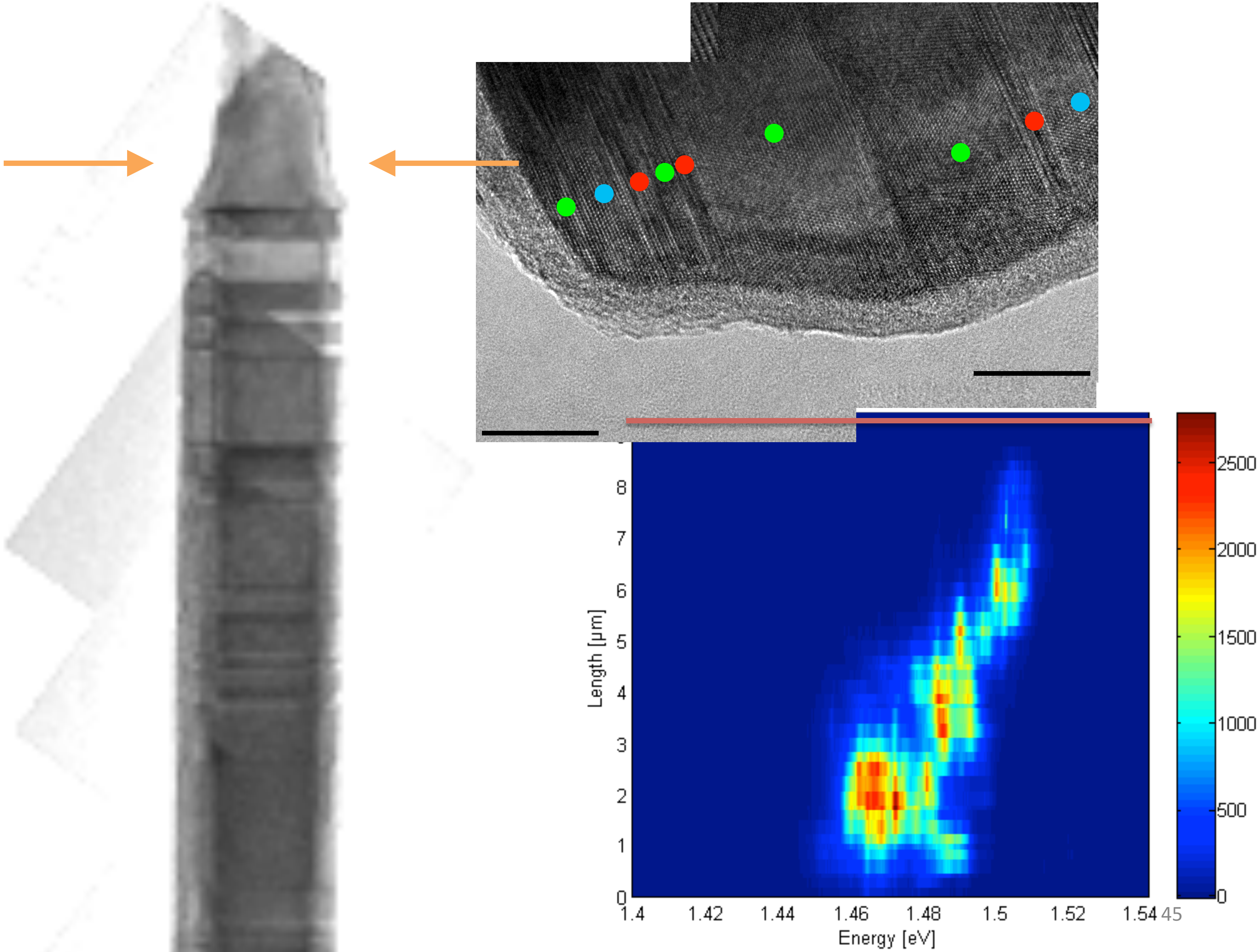
S. Conesa-Boj

Structure ←→ Optical properties

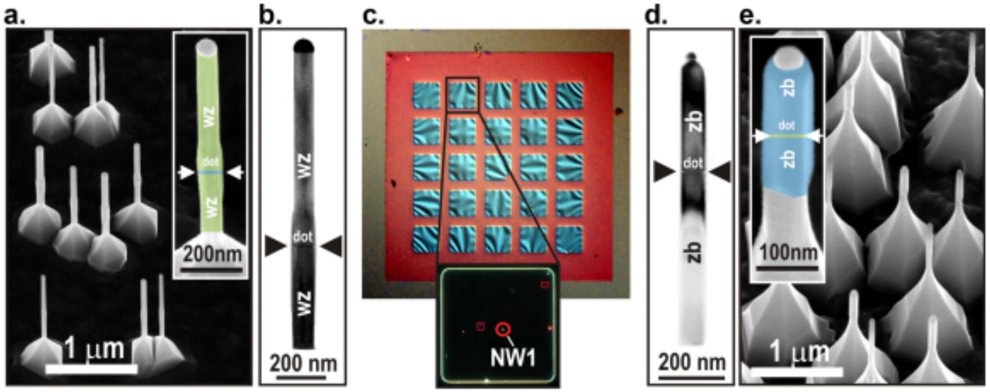




M. Heiss et al PRB (2010)

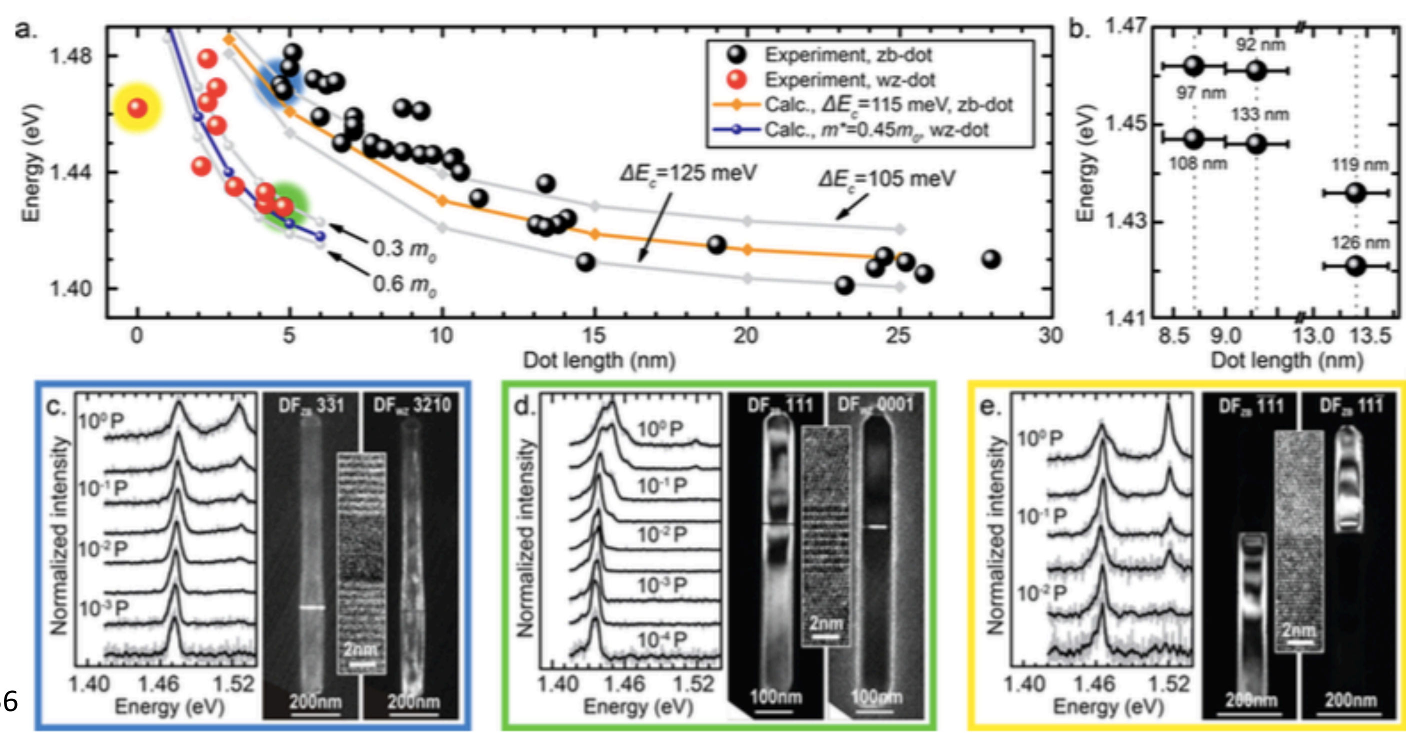

Length [µm]
0
1
2
3
4
5
6
7
8
Energy [eV]
1.4
1.42
1.44
1.46
1.48
1.5
1.52
1.54
0
500
1000
1500
2000
2500

High control on crystal phase quantum dots



4−20 nm zincblende GaAs segments/dots in wurtzite GaAs confine electrons and that the inverse system confines holes.

By varying the thickness of the nanodots strong quantum confinement effects are observed and effective mass of the carriers is extracted..



Nano Lett.
2015, 15, 2652−2656

Conclusions

Raman and PL are very powerful & non-destructive optical characterization tools.

We can access to several information about crystal structure, band structure, composition, doping, strain etc. thanks to Raman Spectroscopy.

The combination of micro-PL and TEM can bring valuable insights for the optical characterization of nanostructures.

Bulk characterization techniques should be applied with care in nanoscale since different selection rules, geometric & photonic effects are pronounced.

Special acknowledgements


Marie Heim-Vögtlin

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ERA.Net RUS

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StG

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