# Optical Properties of Solids: Lecture 12

**Stefan Zollner**
New Mexico State University, Las Cruces, NM, USA
*and* Institute of Physics, CAS, Prague, CZR (Room 335)
zollner@nmsu.edu or zollner@fzu.cz

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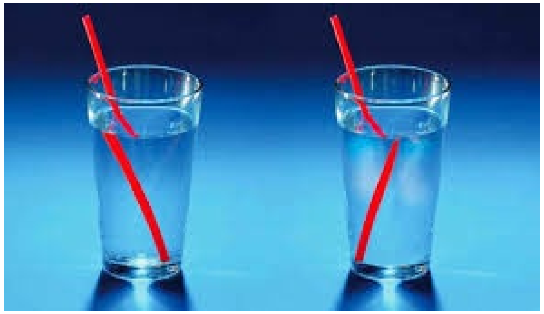
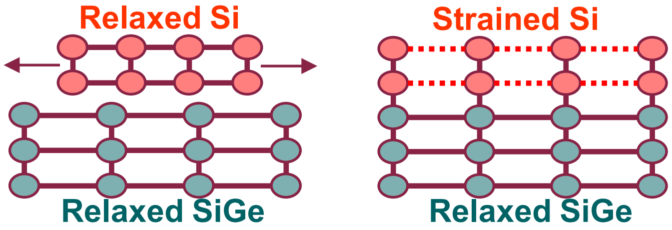
# Optical Properties of Solids: Lecture 12

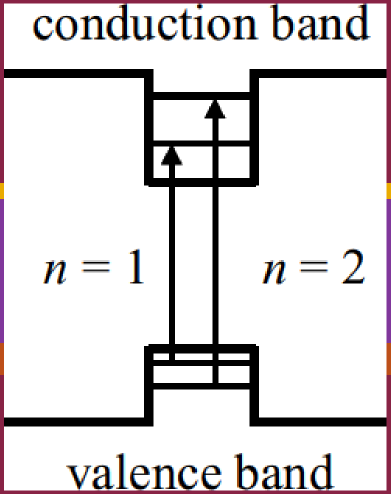
Quantum structures: wells, wires, dots
Absorption and emission of quantum wells
Intersubband absorption
Quantum cascade lasers

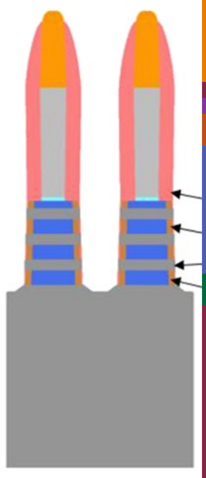
Defects (deep, shallow)

Stress and strain









# References: Band Structure and Optical Properties

## Solid-State Theory and Semiconductor Band Structures:

- Mark Fox, Optical Properties of Solids (6,8,9)
- Ashcroft and Mermin, Solid-State Physics
- Yu and Cardona, Fundamentals of Semiconductors
- Dresselhaus/Dresselhaus/Cronin/Gomes, Solid State Properties
- Cohen and Chelikowsky, Electronic Structure and Optical Properties
- Klingshirn, Semiconductor Optics
- Grundmann, Physics of Semiconductors
- Ioffe Institute web site: NSM Archive
  http://www.ioffe.ru/SVA/NSM/Semicond/index.html

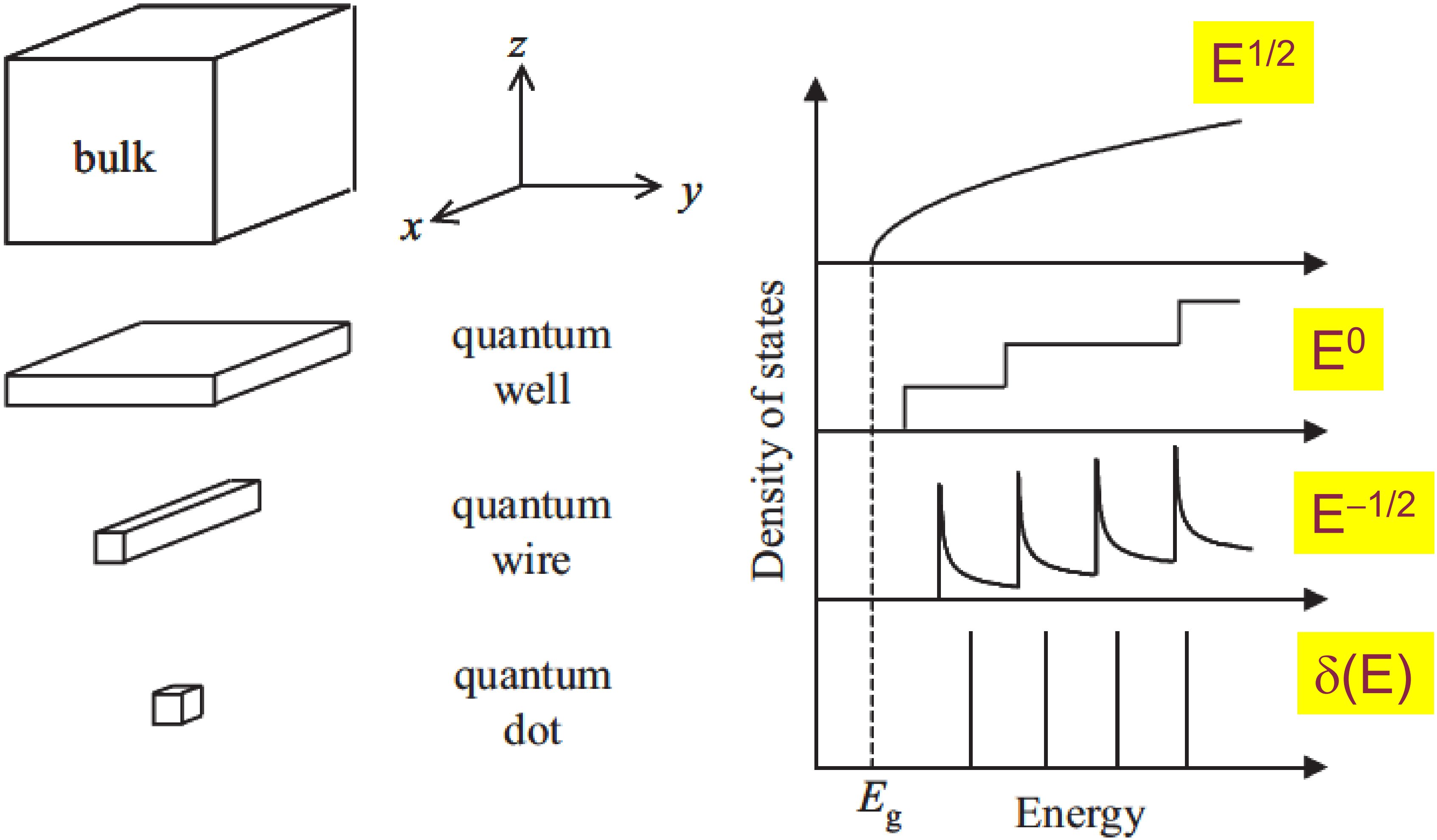
# Outline

Quantum confinement and Heisenberg uncertainty principle
Growth of quantum structures
**Carbon nanostructures, two-dimensional materials**
**Electronic states, quantum well absorption and emission**
**Intersubband transitions**
**Metamaterials and metasurfaces**

**Defects**
**Transition metal and rare earth impurities in insulators**
**Shallow defects in semiconductors**

**Stress and strain, deformation potentials**

# Quantum structures and density of states



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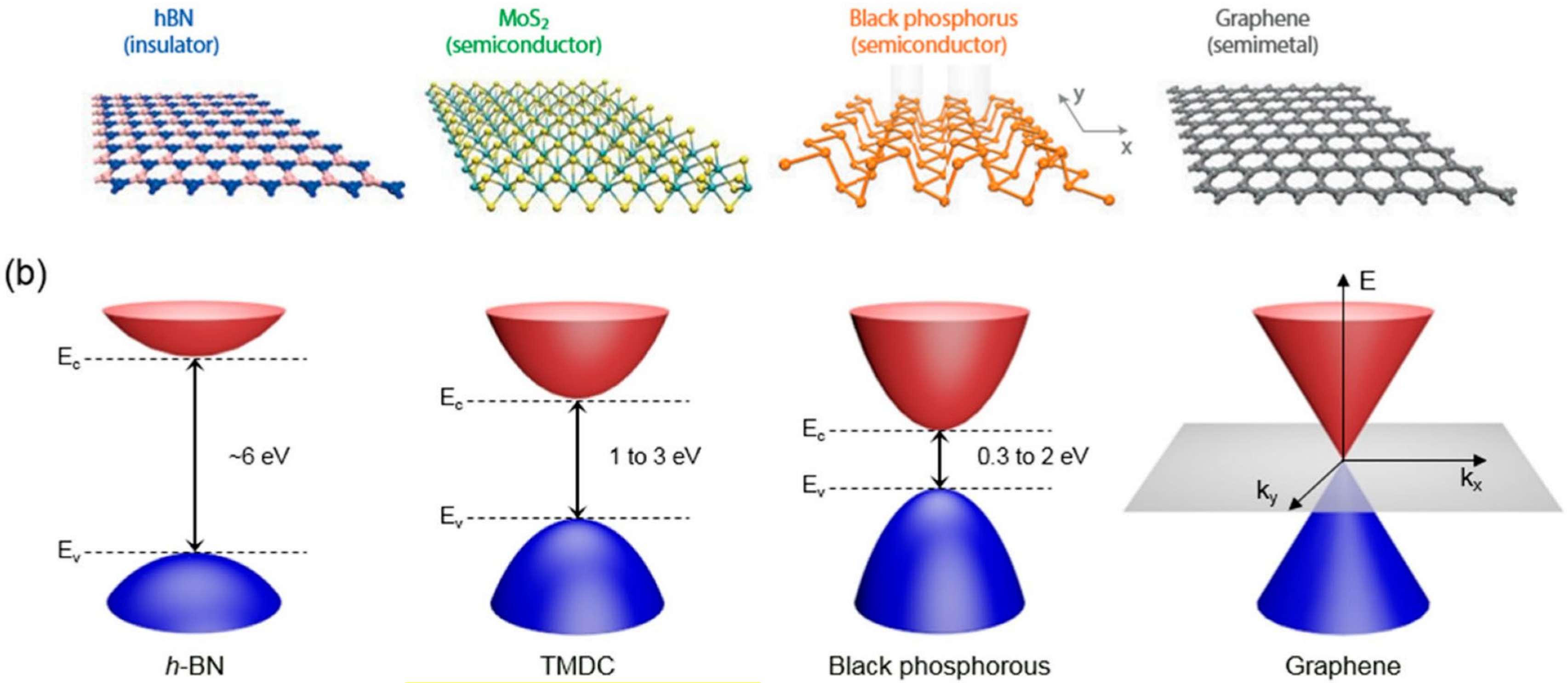
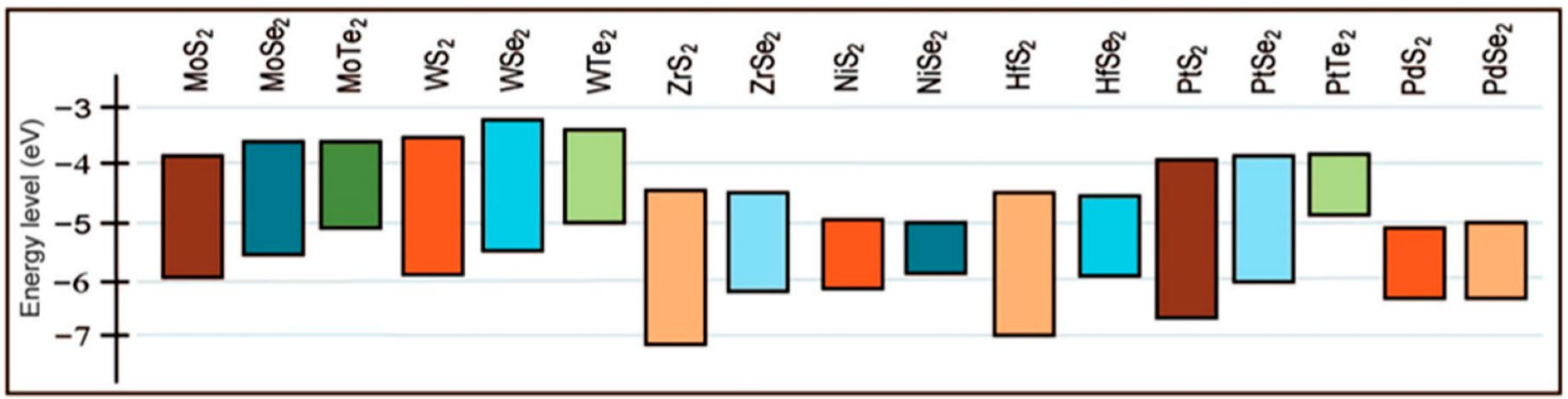
# Two-dimensional semiconductors

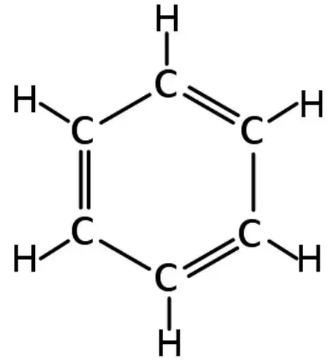


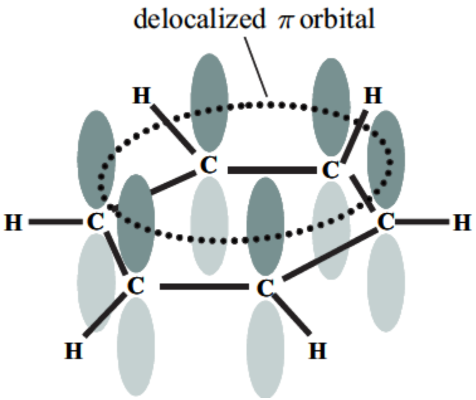
dichalcogenides

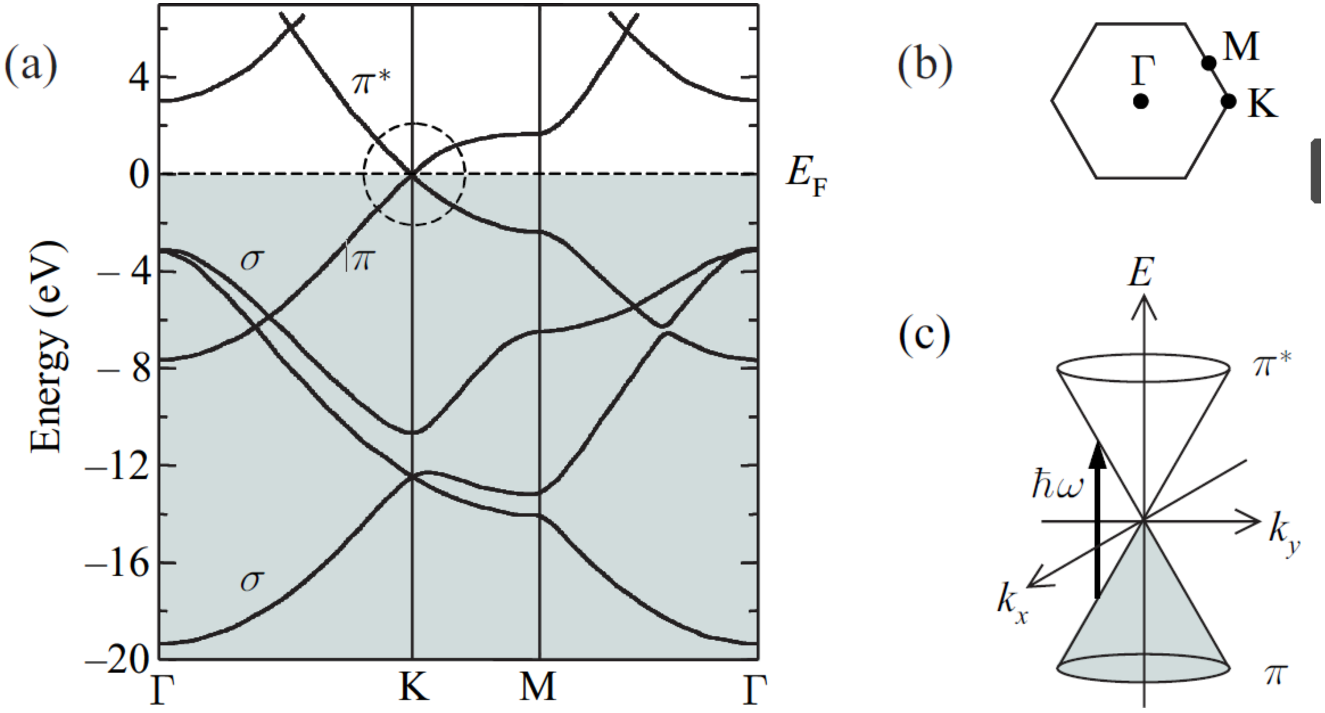
(c)



# Dirac point in graphene







Graphite: Strong bond in the graphene plane, weak bond between planes. Remove single graphene plane.

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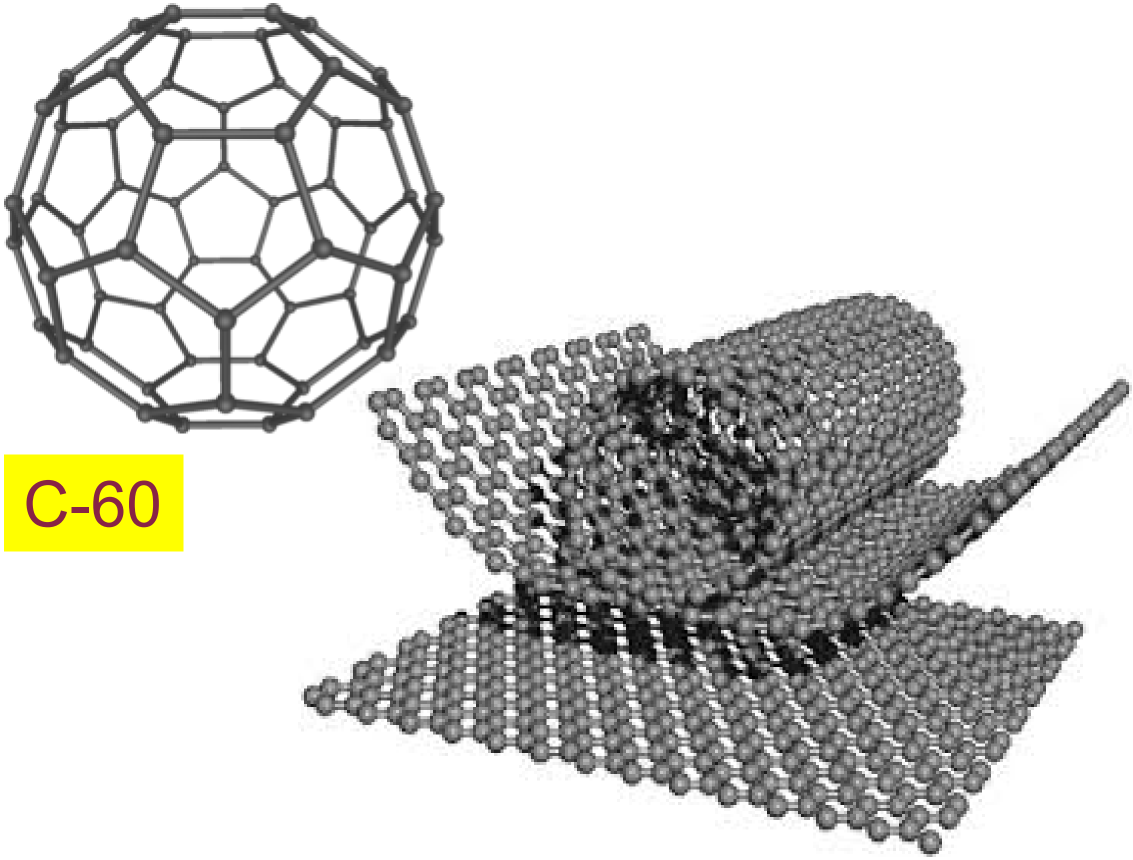
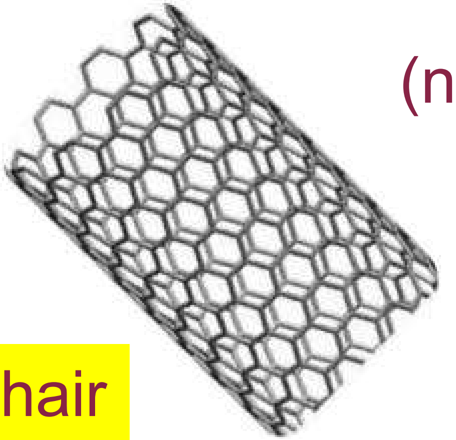
# Carbon nanotubes and fullerenes

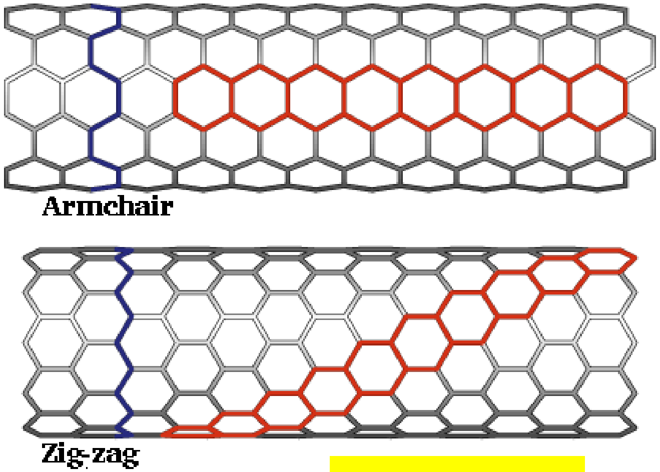
(n,m)



C-60



armchair



Zig-zag

Graphene sheets are rolled up to form tubes.
Many Raman studies, doping with defects.

Jorio, Dresselhaus, Dresselhaus
Carbon Nanotubes

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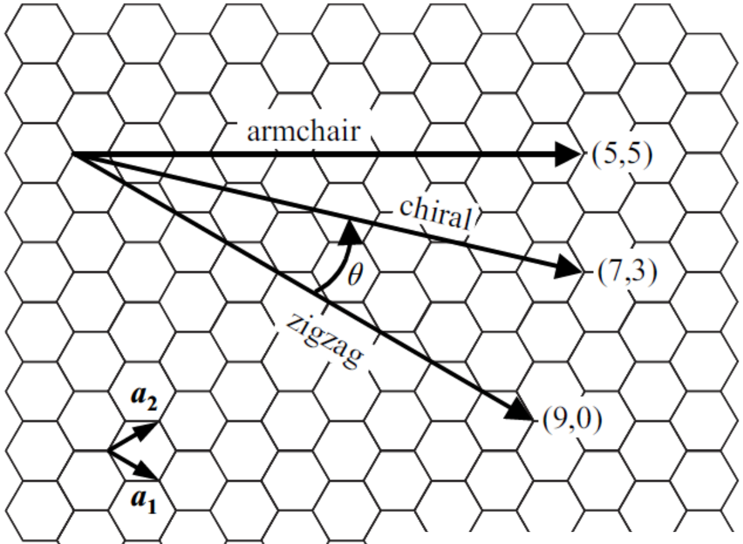
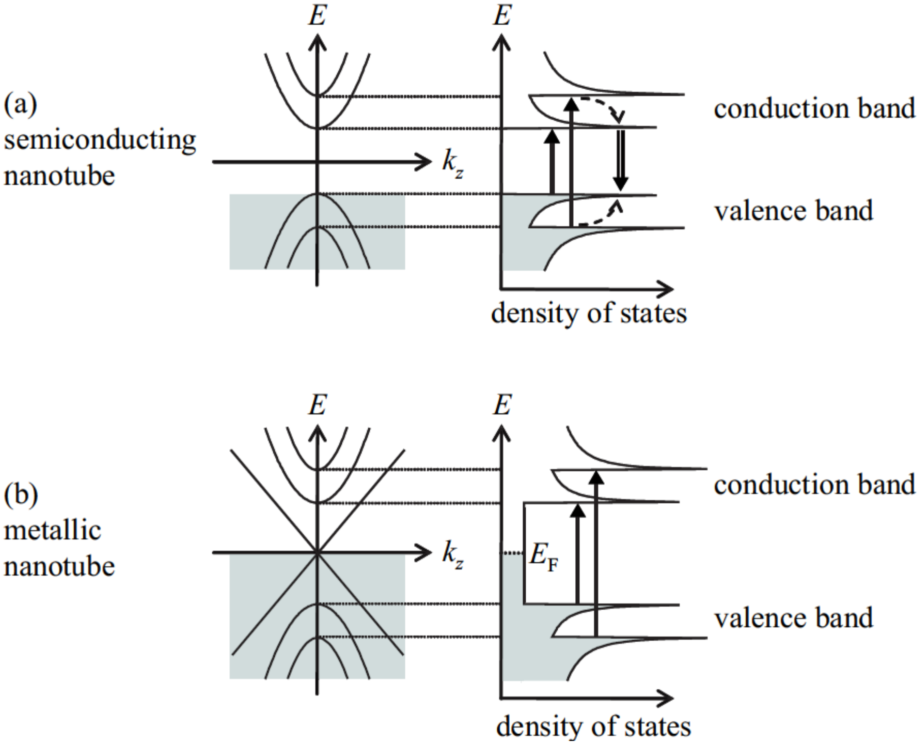
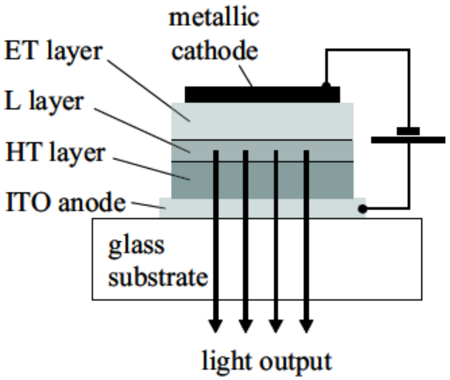
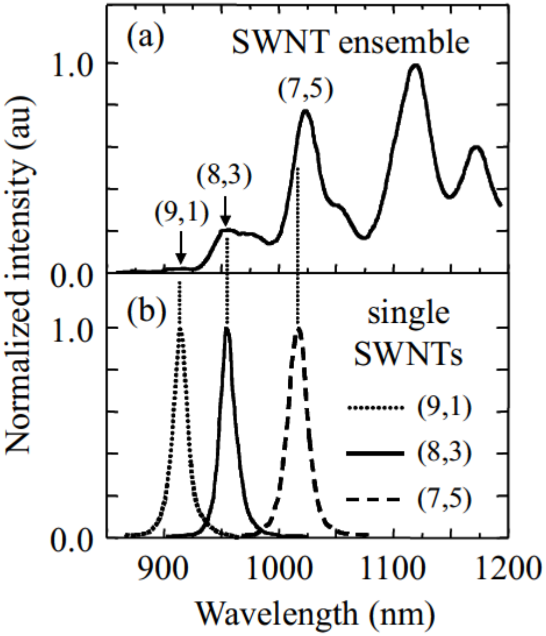
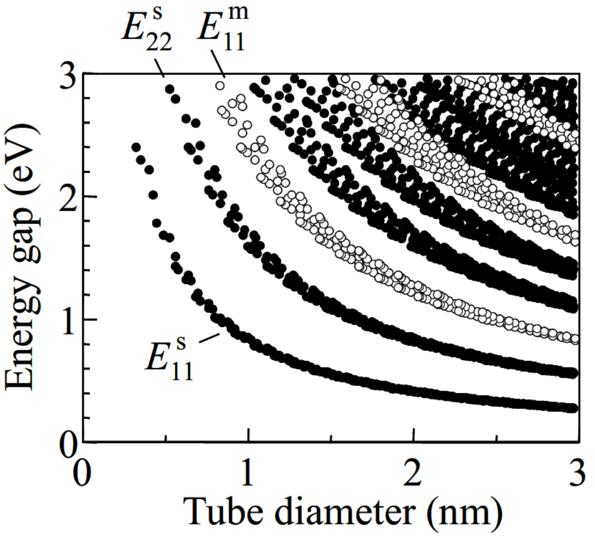
# (n,m) Carbon nanotubes: electrical properties











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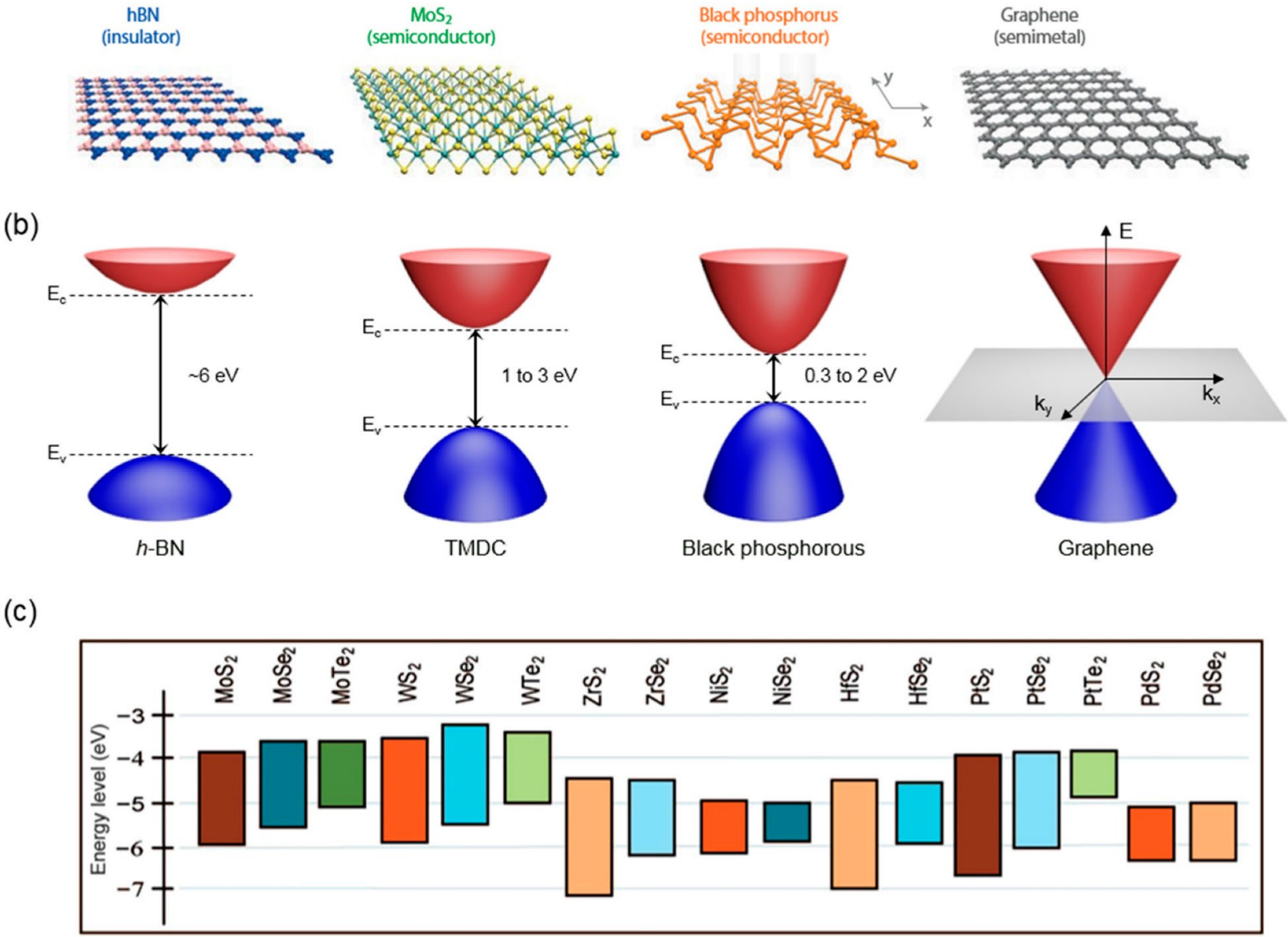
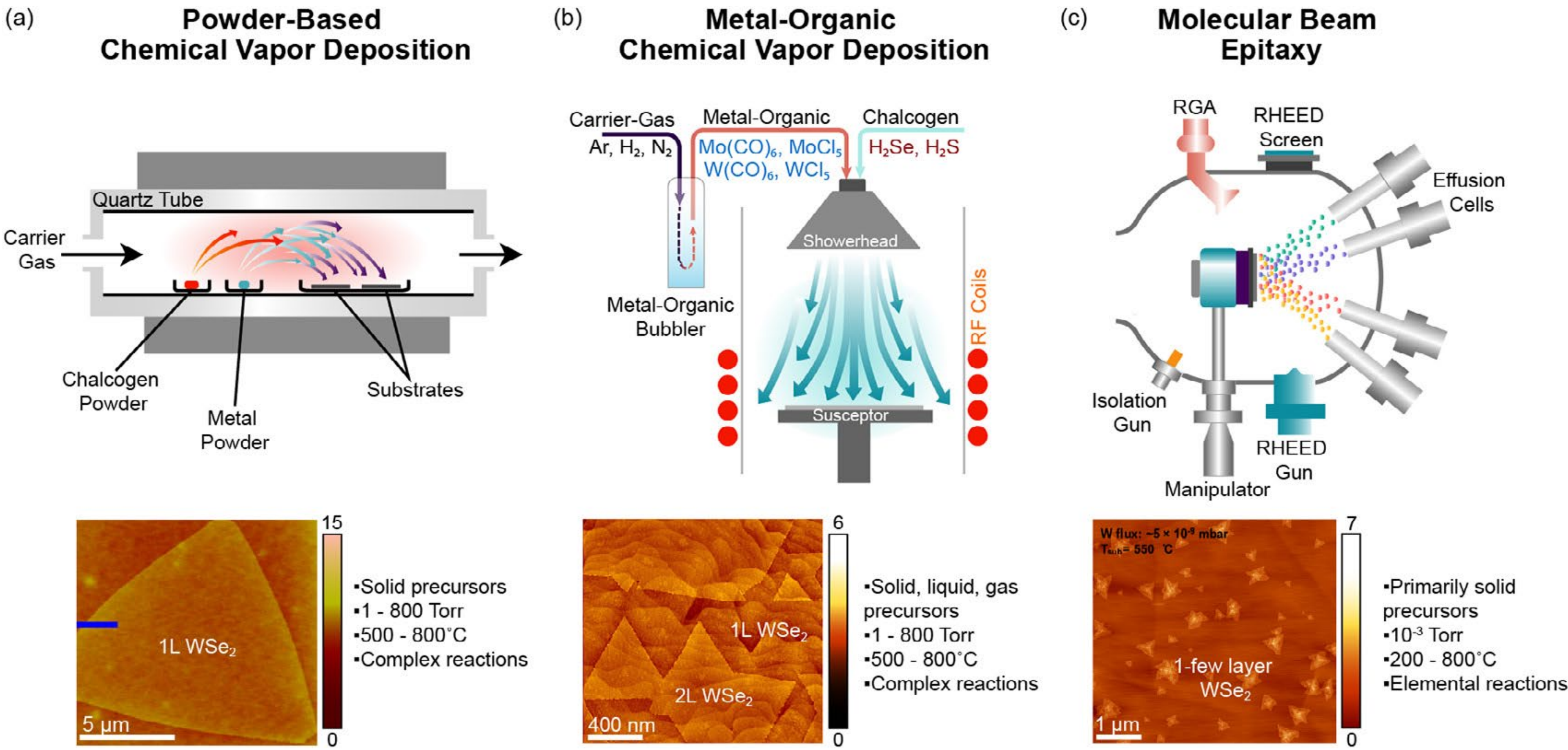
# Two-dimensional semiconductors



# Two-dimensional semiconductors: $WSe_2$, $MoSe_2$



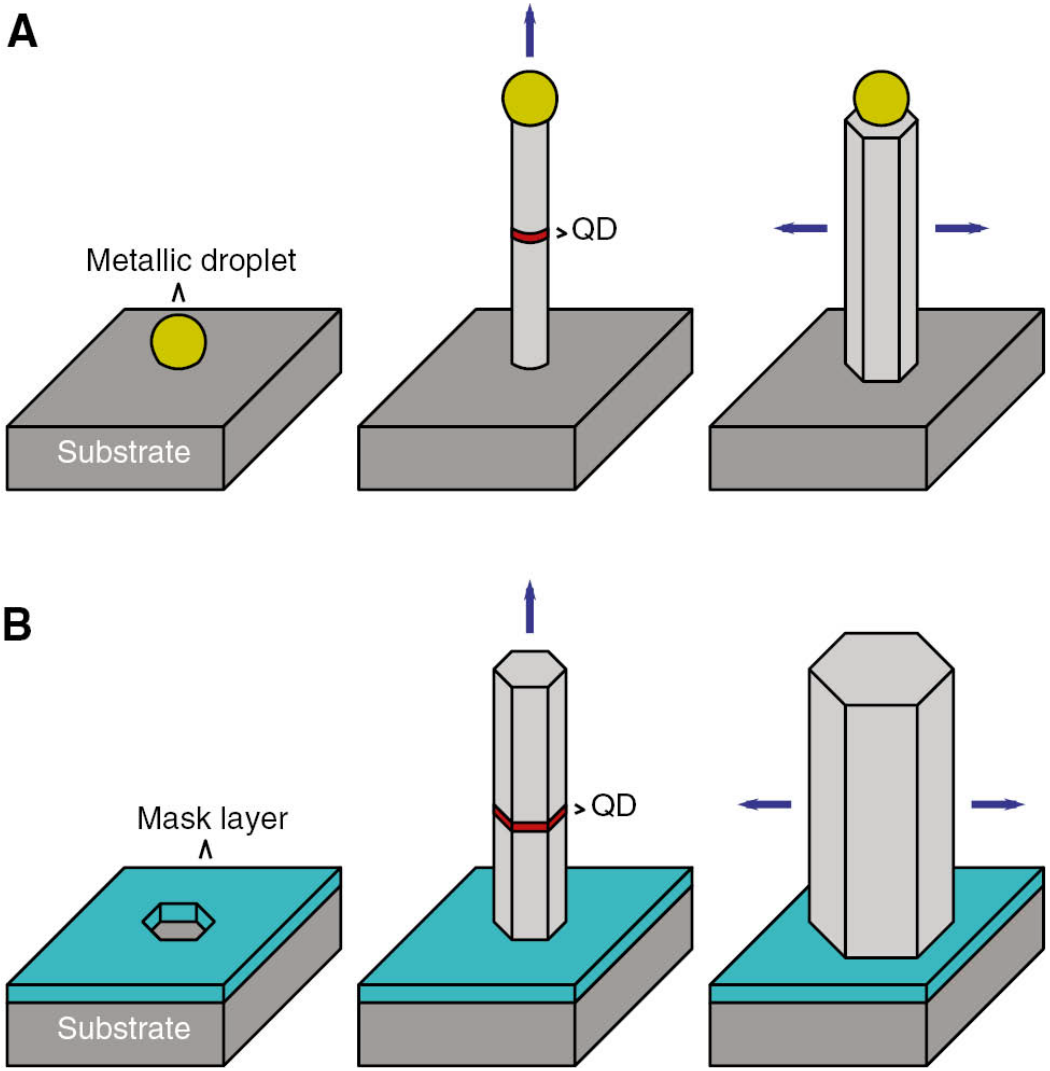
- Solid precursors
- 1 - 800 Torr
- 500 - 800°C
- Complex reactions

- Solid, liquid, gas precursors
- 1 - 800 Torr
- 500 - 800°C
- Complex reactions

- Primarily solid precursors
- $10^{-3}$ Torr
- 200 - 800°C
- Elemental reactions

N. Briggs, 2D Materials **6**, 022001 (2019)

# Growth of vertical quantum wires

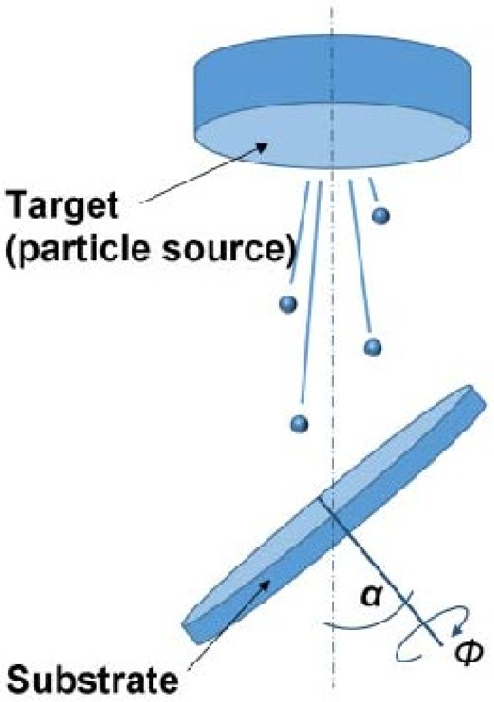


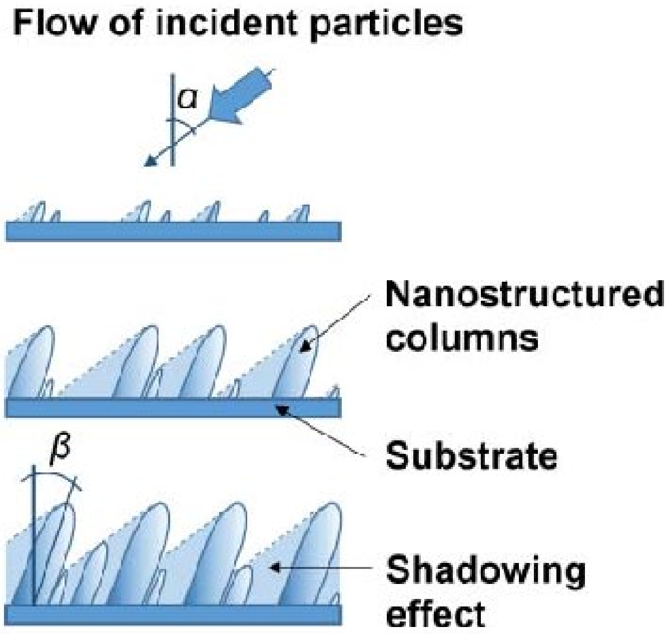
Vapor-liquid-solid

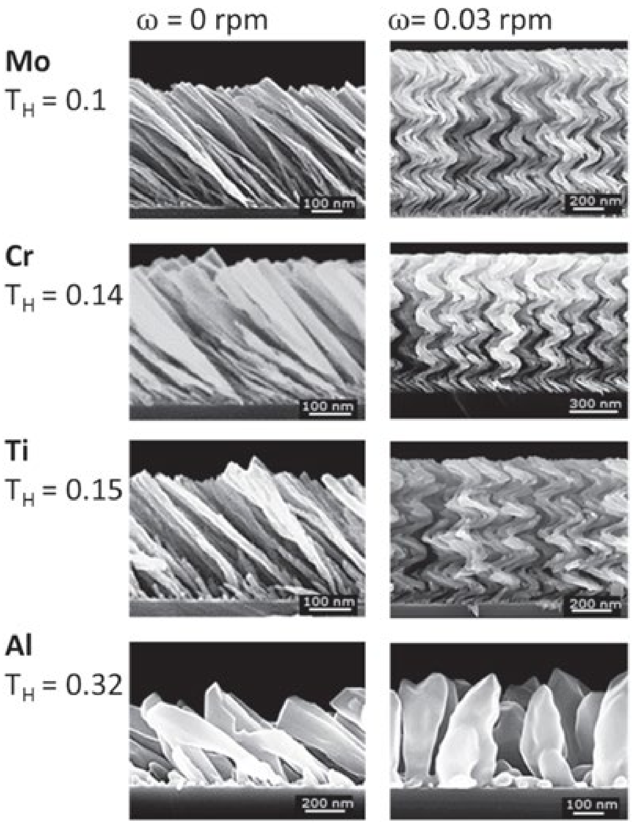
Selective area epitaxy

Mäntynen, Nanophotonics **8**, 747 (2019)

# Glancing angle deposition (GLAD) of quantum wires

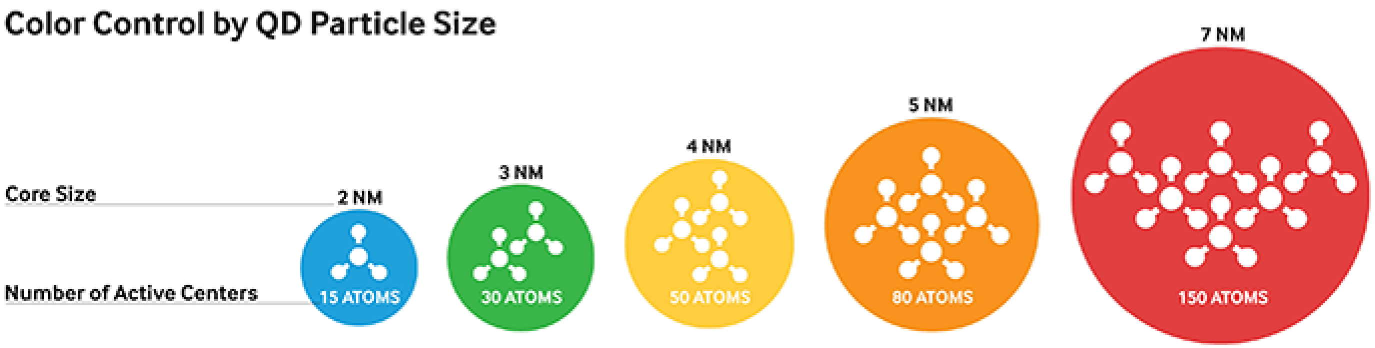


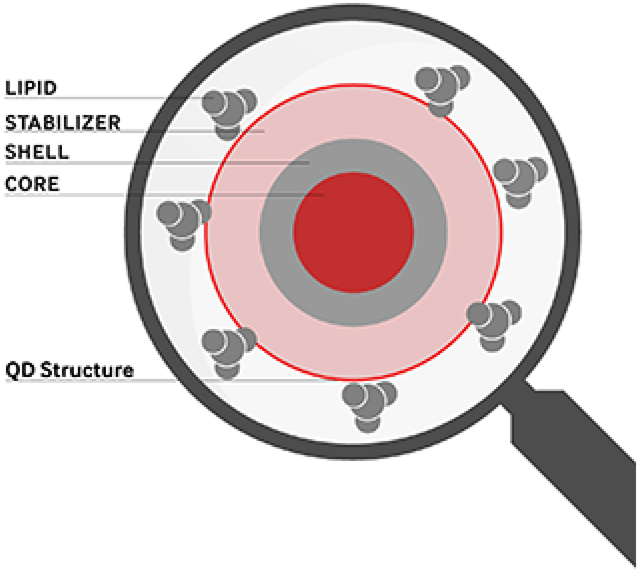




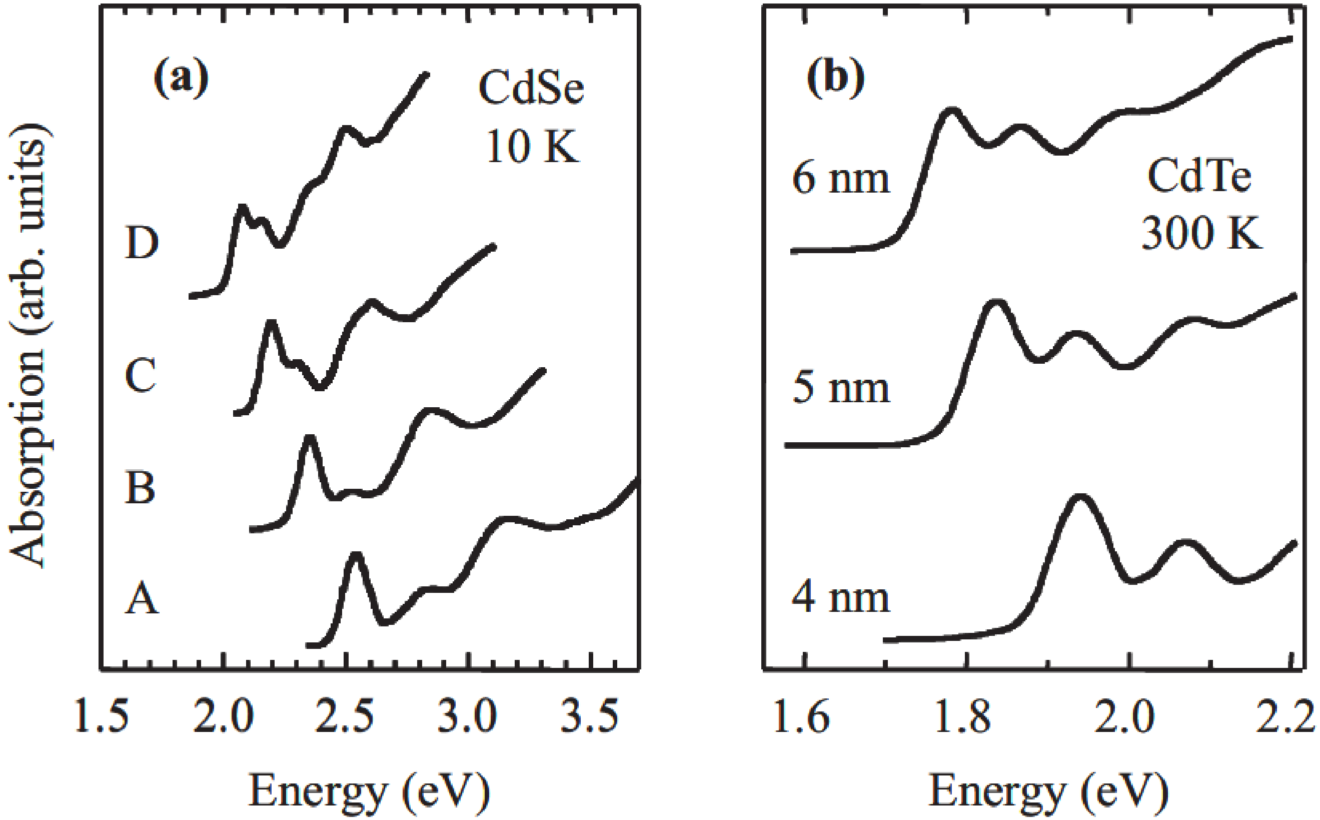
Initial imperfections on the substrate
Shadow effect leads to tilted column growth.

# Colloidal quantum dots





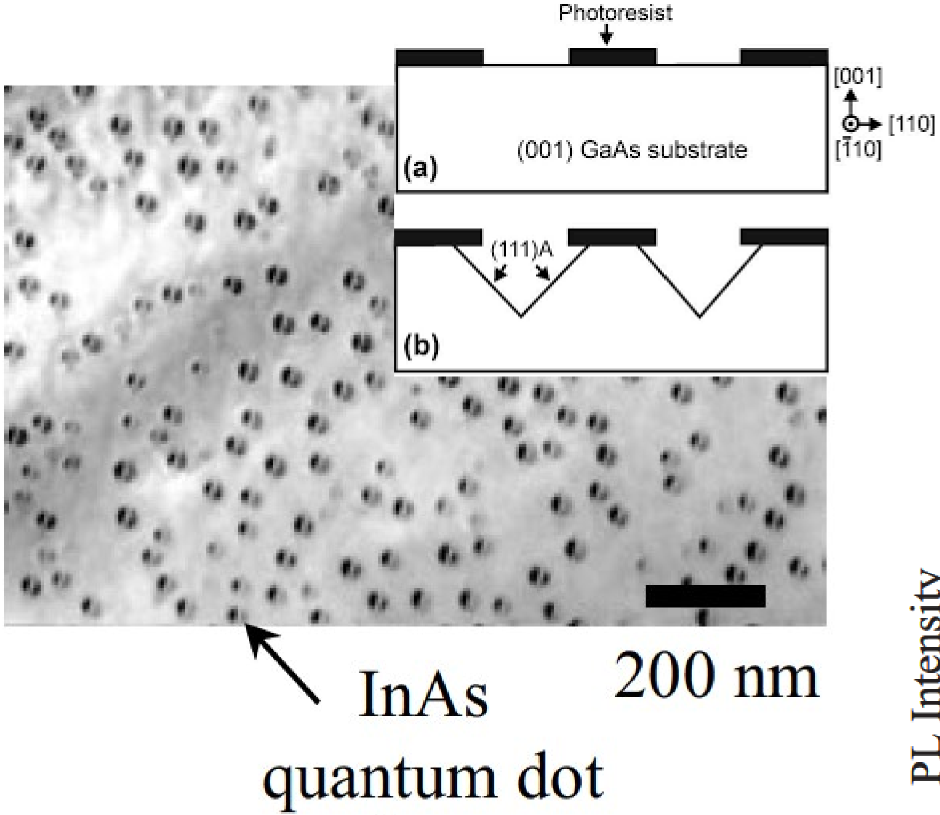
# Colloidal quantum dots

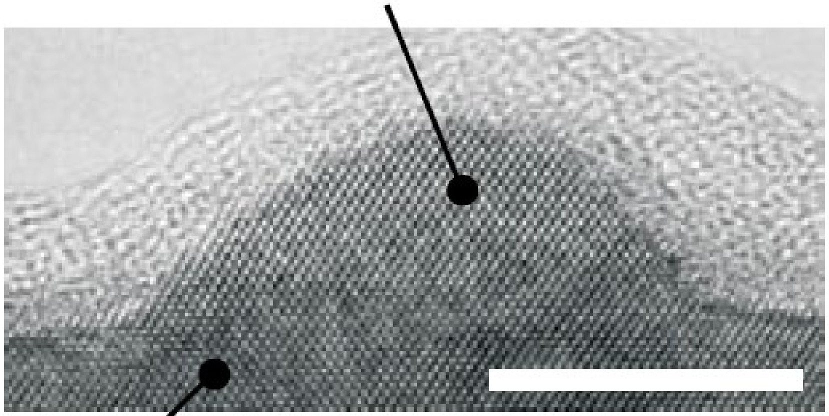


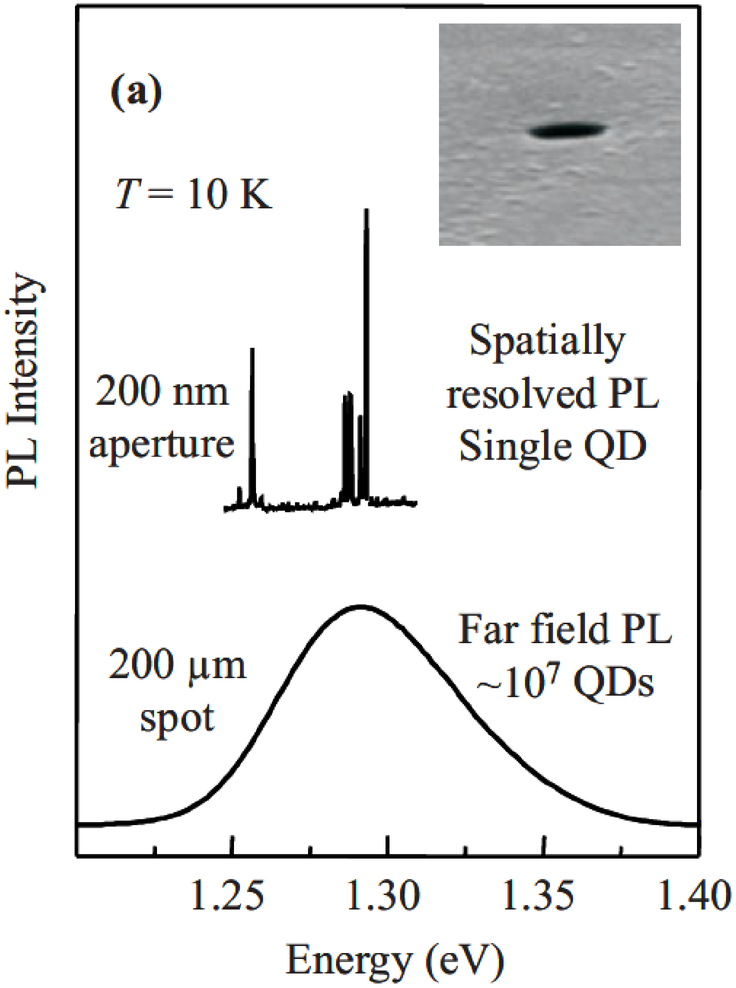
Fox, Chapter 6
C.R. Kagan, C.B. Murray, M.G. Bawendi, PRB **54**, 8633 (1996)

# Epitaxial quantum dots

## Stranski-Krastanov growth of semiconductor islands by MBE







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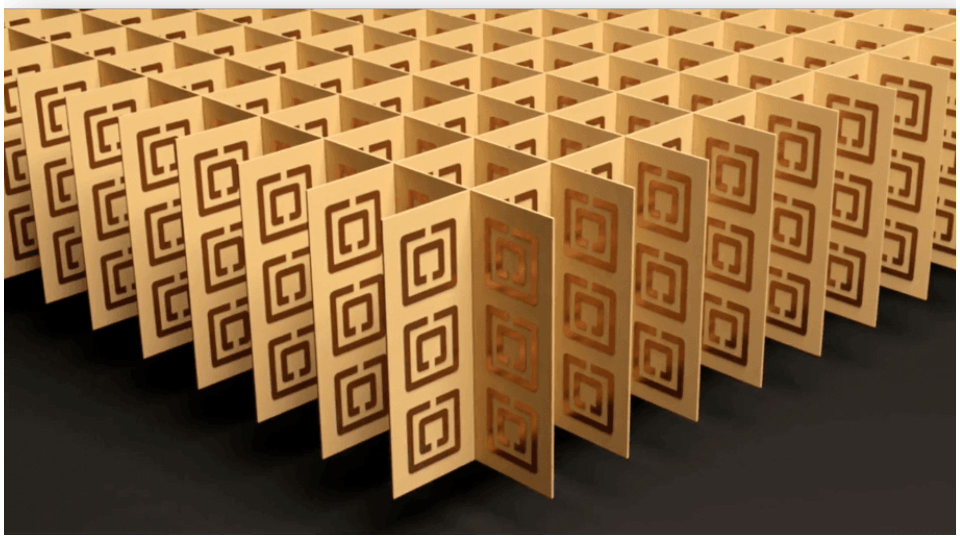
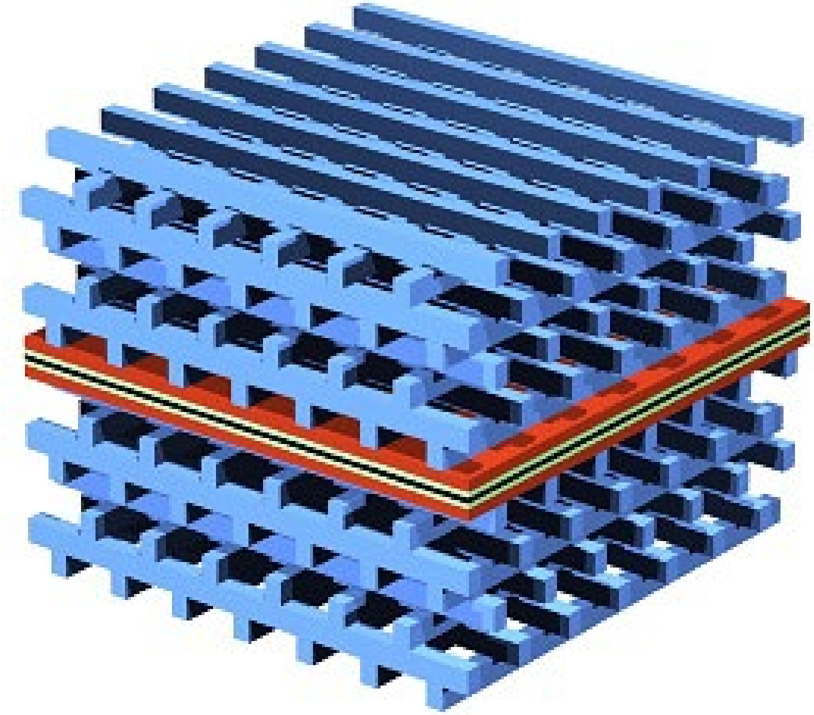
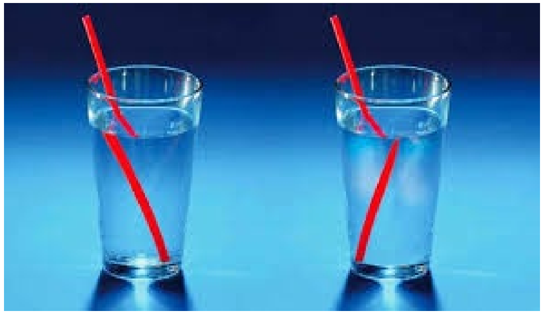
# Metamaterials







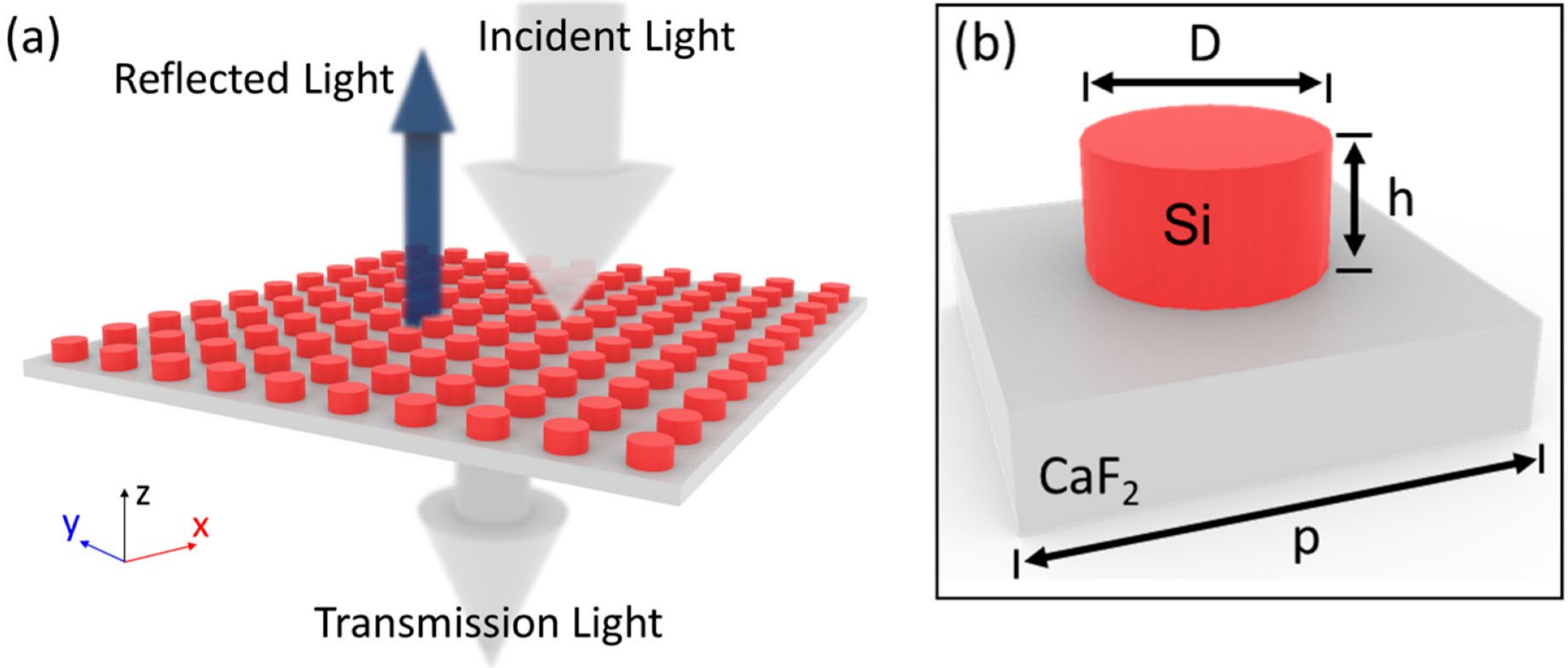
Faraday: $\vec{k} \times \vec{E}_0 = \omega\mu\mu_0\vec{H}_0$

Metamaterials are artificially structured three-dimensional materials with feature size less than a wavelength. They have unusual properties:

**Photonic band gaps, left-handed materials, negative index.**

Sajeev John
Shelby, APL **78**, 489 (2001)

# Metasurfaces

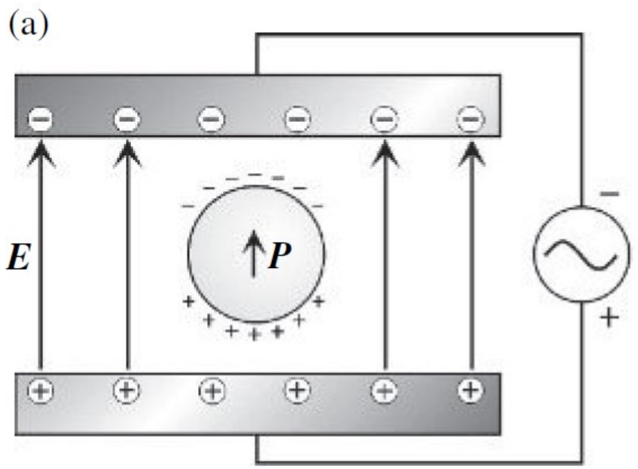


Metasurfaces can be designed to have reflection, absorption, and emission properties not possible in homogeneous materials. Especially useful for sensors and antennas.

# Modeling Metamaterials and Metasurfaces

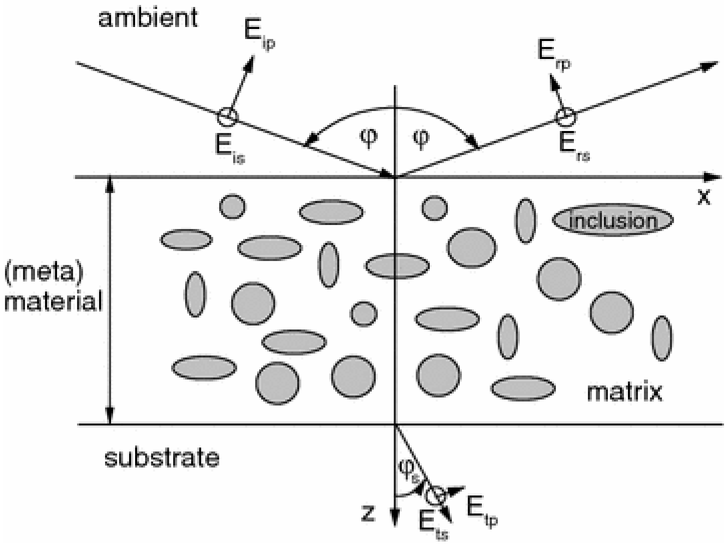
## Bruggeman effective medium approximation (BEMA)

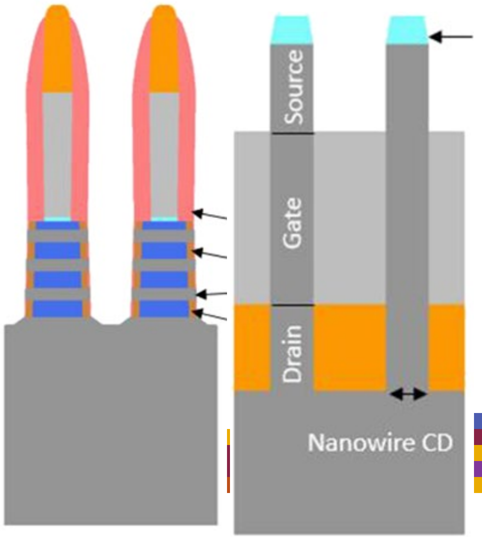
$$\sum_{i=1}^{n} f_i \frac{\varepsilon_i - \varepsilon}{\varepsilon_i + 2\varepsilon} = 0$$

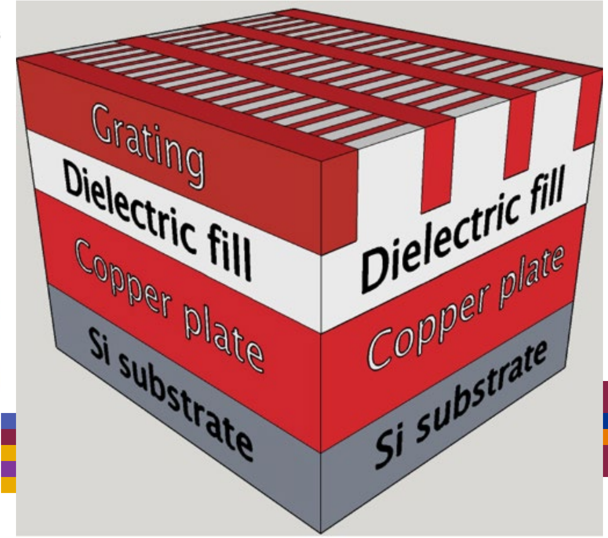


## Rigorous coupled wave approximation:

- Fourier method for periodic structures
- Numerical solution of Maxwell's equations

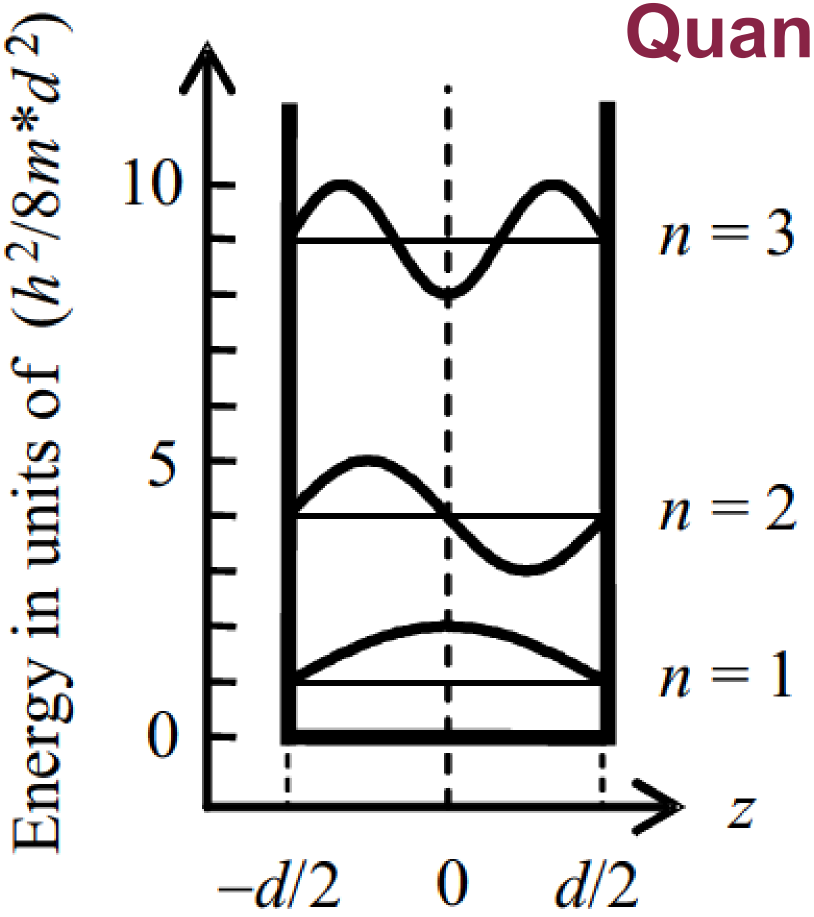






Schmidt, JAP **114**083519 (2013)
Diebold, APL Mater. **6**, 058201 (2018)

# Quantum well with infinite barriers

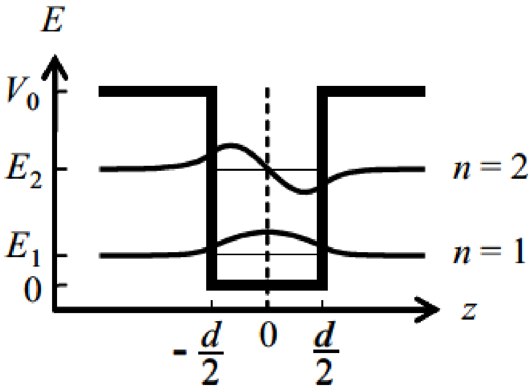


$$\Psi(x,y,z) = \psi(x,y)\varphi(z)$$

$$E\left(\vec{k},n\right) = \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{2m}\left(\frac{n\pi}{d}\right)^2$$

Use carrier effective mass.
(Electrons more affected than holes).

**Finite barrier:**
Confinement energies are lower.
Wave function leaks into barrier.
Finite number of bound states.
Solve numerically.



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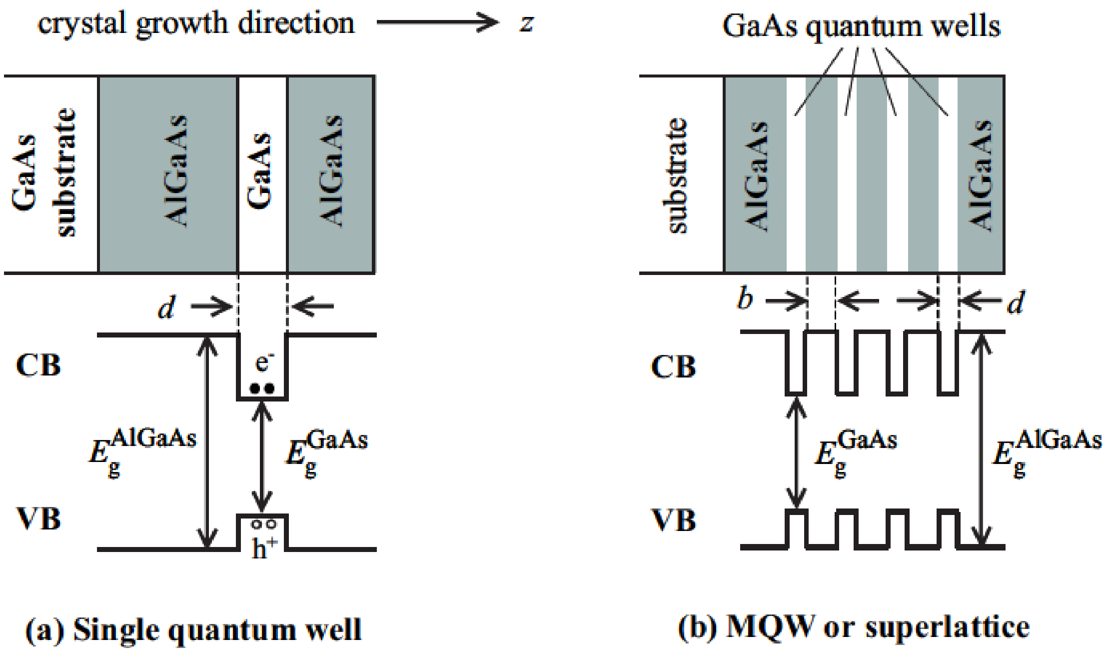
# Quantum wells and superlattices (or MQW)



(a) Single quantum well (b) MQW or superlattice

Quantum well: wave function entirely contained in one well.

Superlattice: wave function leaks through the barrier into the next well (barrier thin or low).

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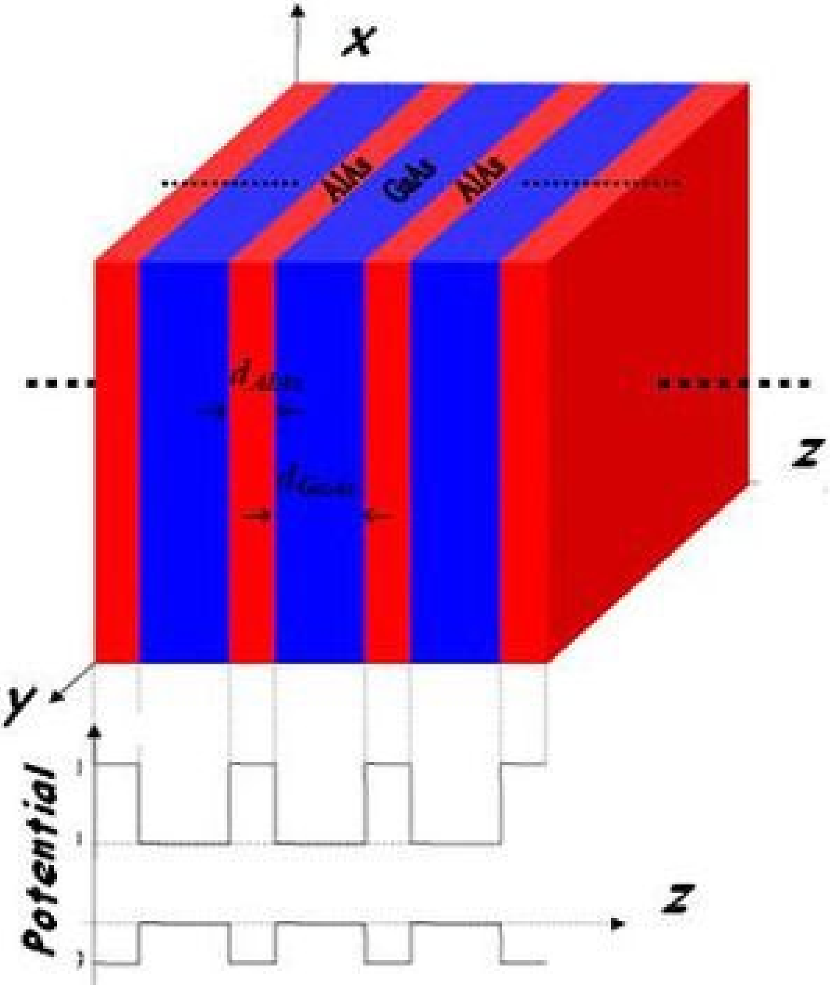
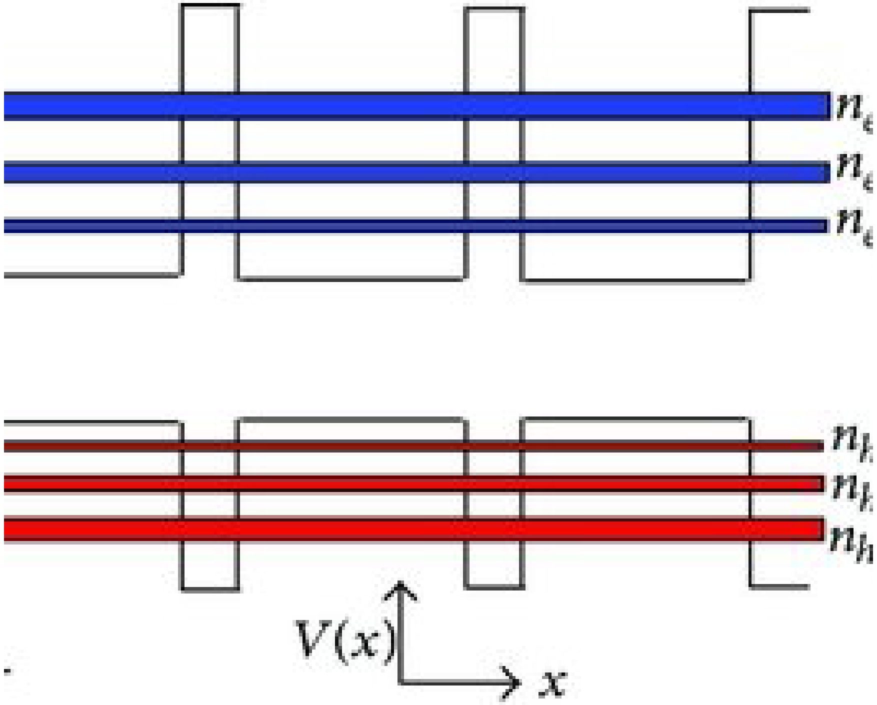
# Superlattice minibands



CB

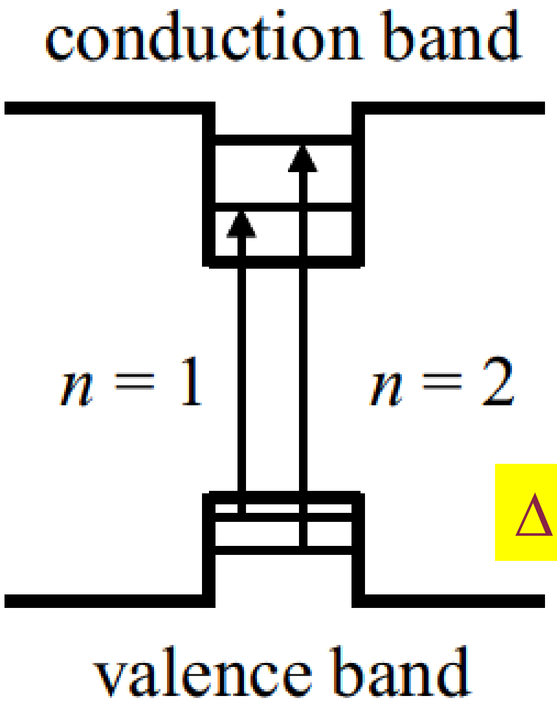


VB

# Enhanced absorption/emission in quantum structures

$$\frac{1}{\tau} = \frac{2\pi}{\hbar}|\langle f|H_{eR}|i\rangle|^2 g_{fi}(\hbar\omega)$$

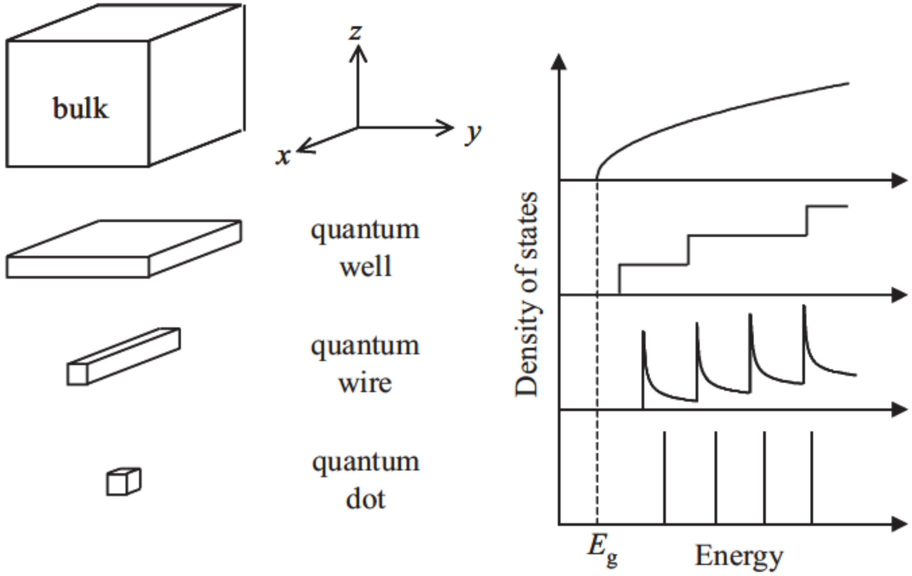
Confinement enhances overlap matrix element



(l=0)

Δn=0

(l=1)



Modified density of states

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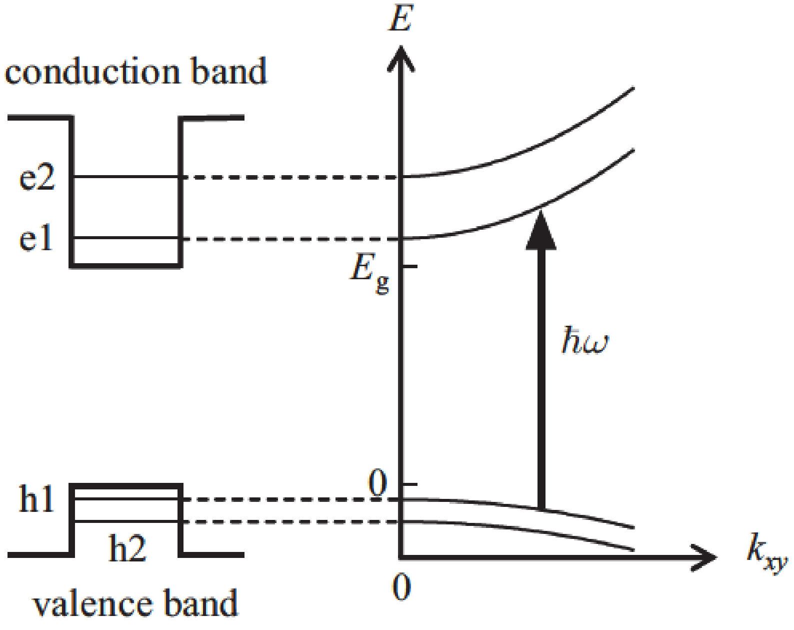
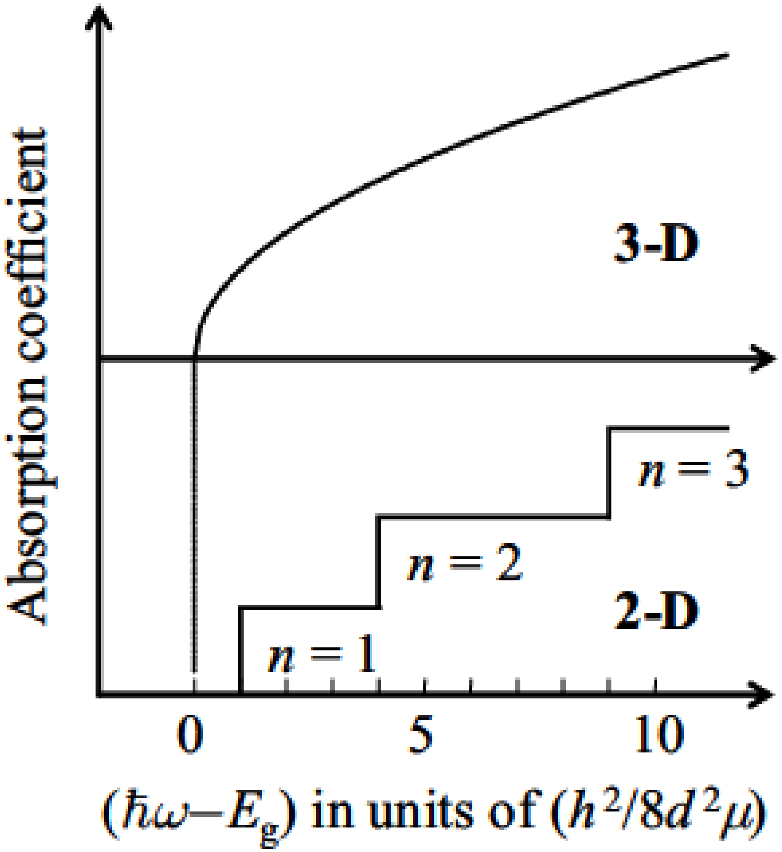
# Quantum well absorption



Electron and hole subbands



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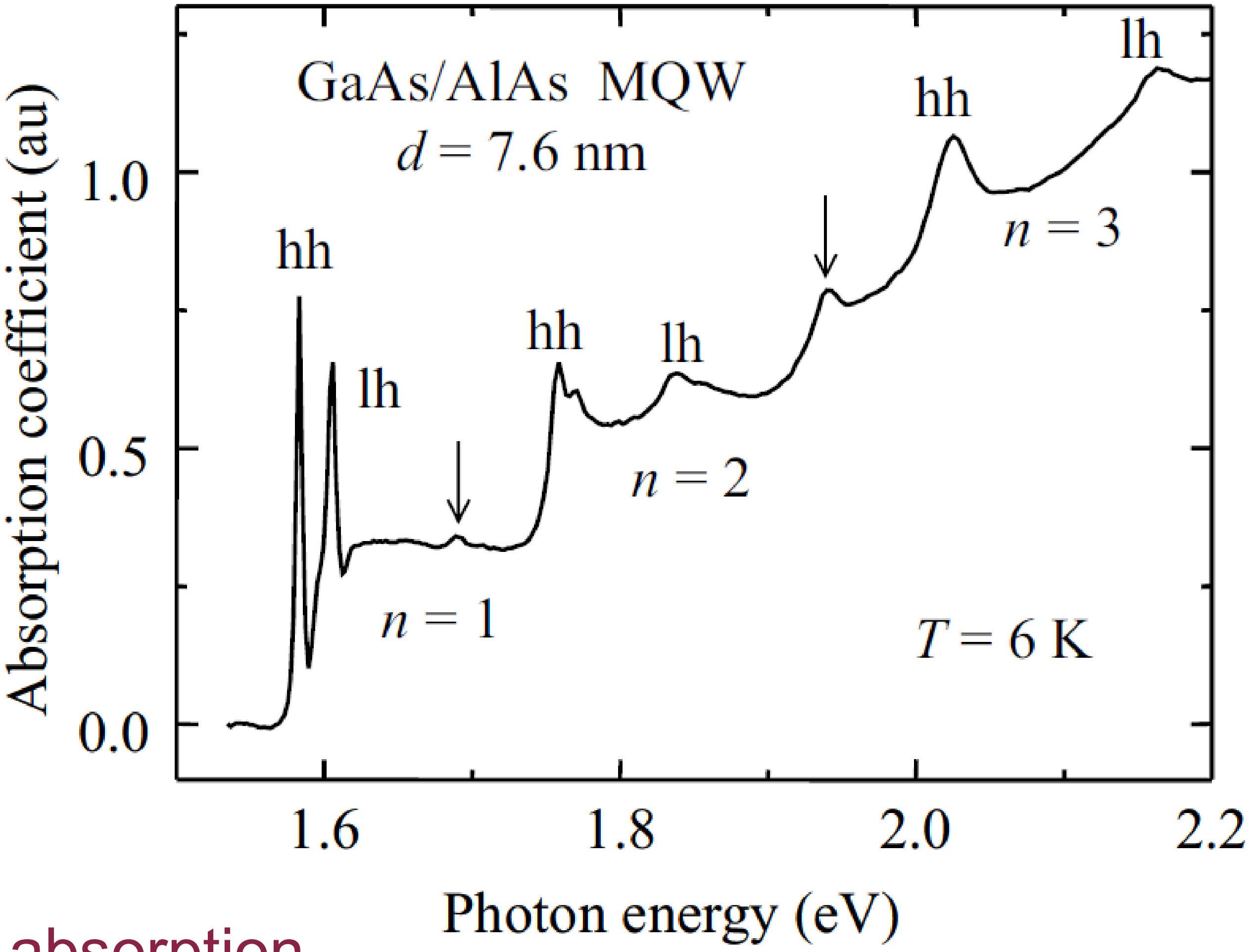
# Quantum well absorption in GaAs/AlAs MQW



Steps: 2-D absorption

Peaks: Discrete excitons (arrows show forbidden transitions)

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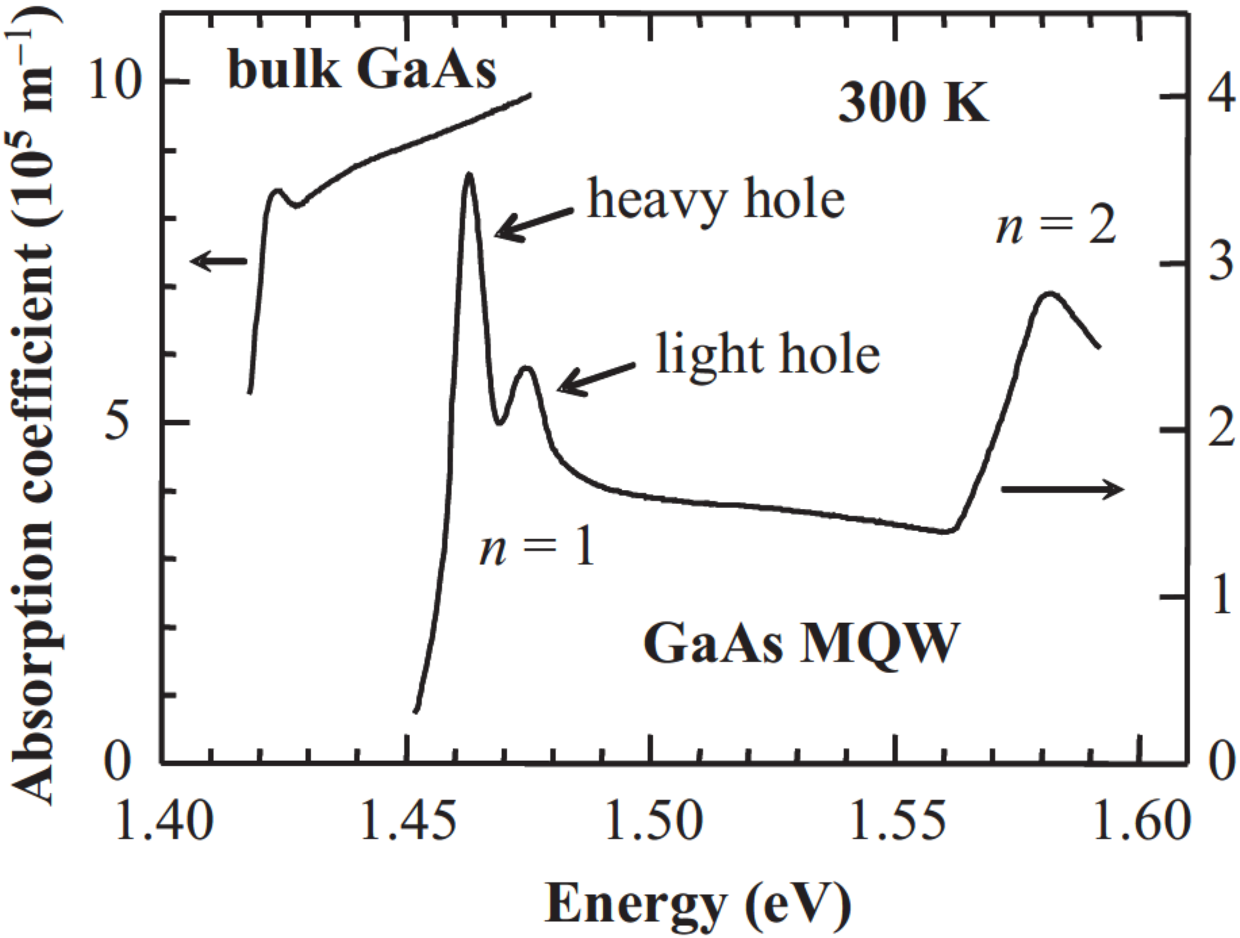
# Excitonic effects are enhanced in quantum wells



Bulk GaAs:
$R_X$=4.2 meV

Here (d=10 nm):
$R_X$=10 meV
Increased overlap integral

hh/lh splitting:
Confinement or strain ???

$$E\left(\vec{k},n\right)=\frac{\hbar^2k^2}{2m}+\frac{\hbar^2}{2m}\left(\frac{n\pi}{d}\right)^2$$

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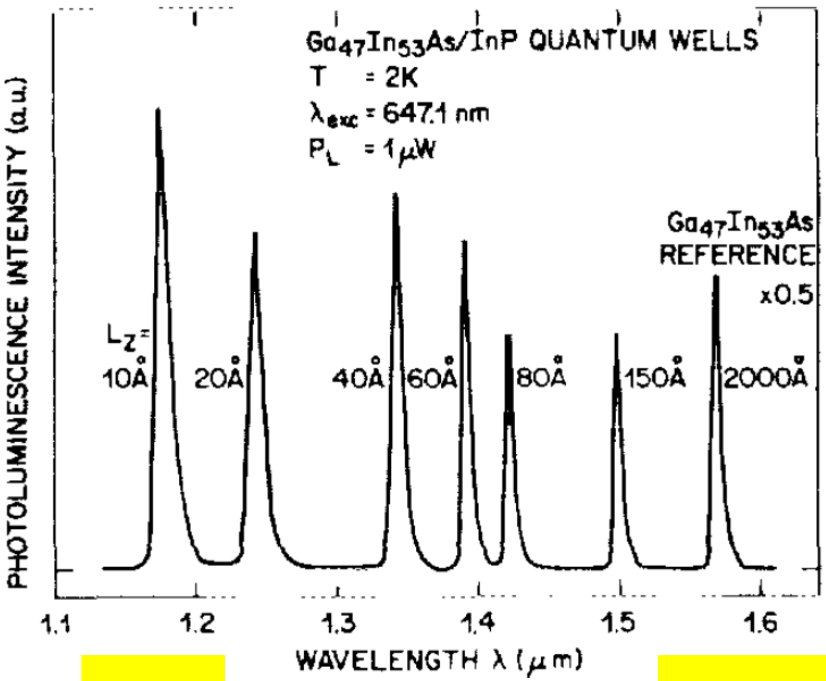
# Confinement shifts in quantum wells

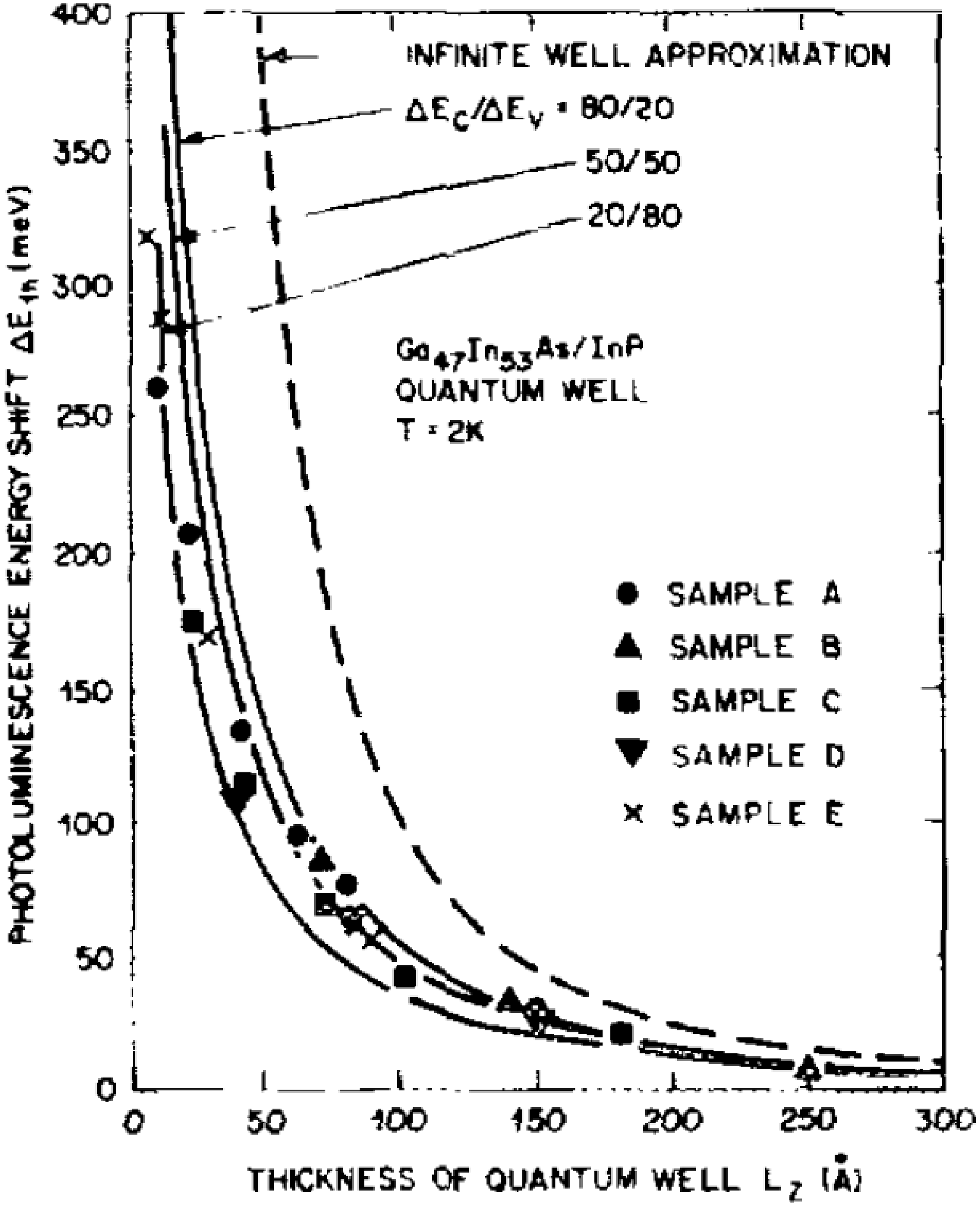
$$\hbar\omega = E_g + E_{hh1} + E_{e1}$$



thin

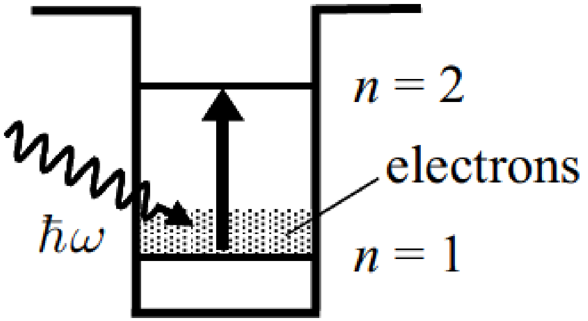
thick

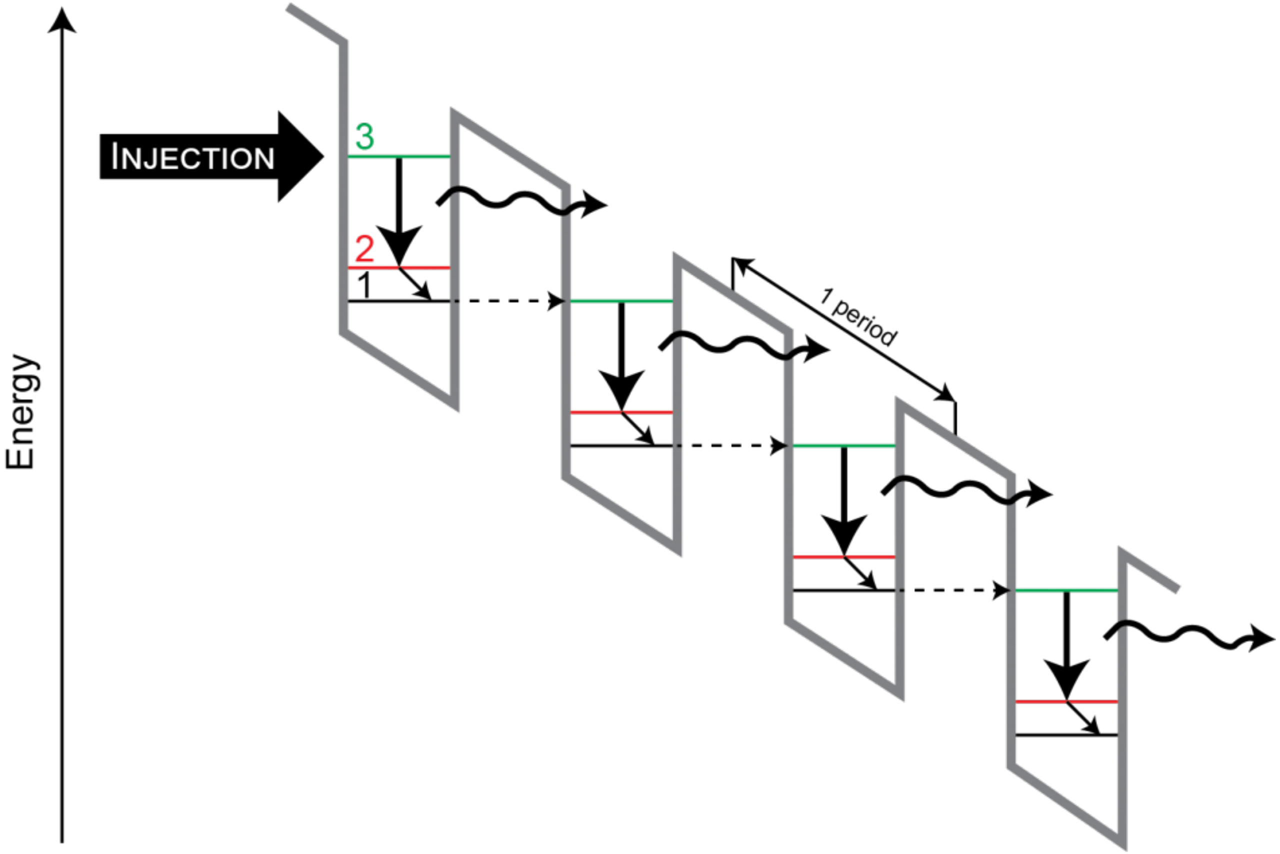
$$\Delta E = \frac{\hbar^2}{2m}\left(\frac{n\pi}{d}\right)^2$$



W.T. Tsang & E.F. Schubert,
Appl. Phys. Lett. **49**, 220 (1986)

# Intersubband transitions, quantum cascade lasers





Δn odd

Infrared detectors and lasers
Light polarized along z (beam in quantum well plane)

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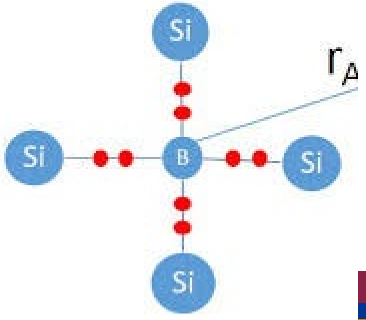
# Defects

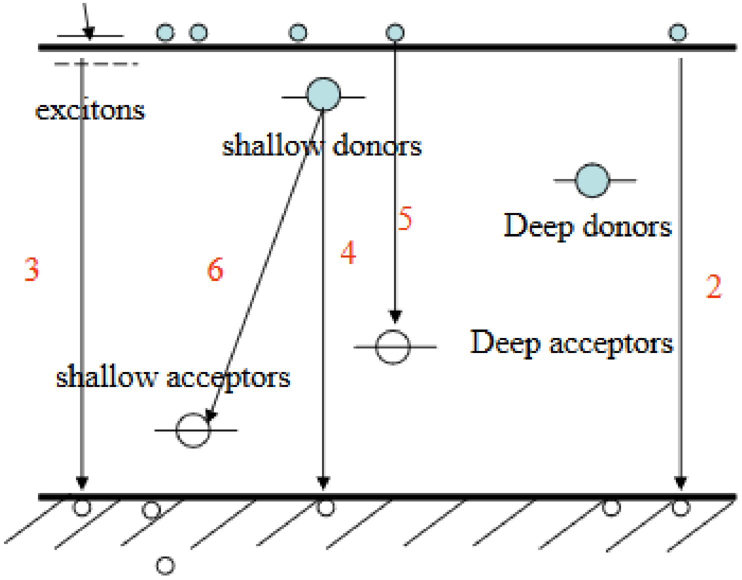
| | | |
|---|---|---|
| **Vacancy** | $V_A$ | missing atom |
| **Interstitial** | $I_A$ | extra atom between lattice sites |
| **Substitutional** | $C_A$ | defect atom replaces host atom |
| **Antisite** | | atoms are switched |
| Frenkel defect pair | $V_A$-$I_A$ | atom moved to interstitial site |

More complex defects (combinations)

**Donor**: Substitutional defect, adds an electron
**Acceptor**: Substitutional defect, adds a hole
**Isoelectronic**: Impurity has same number of electrons as host

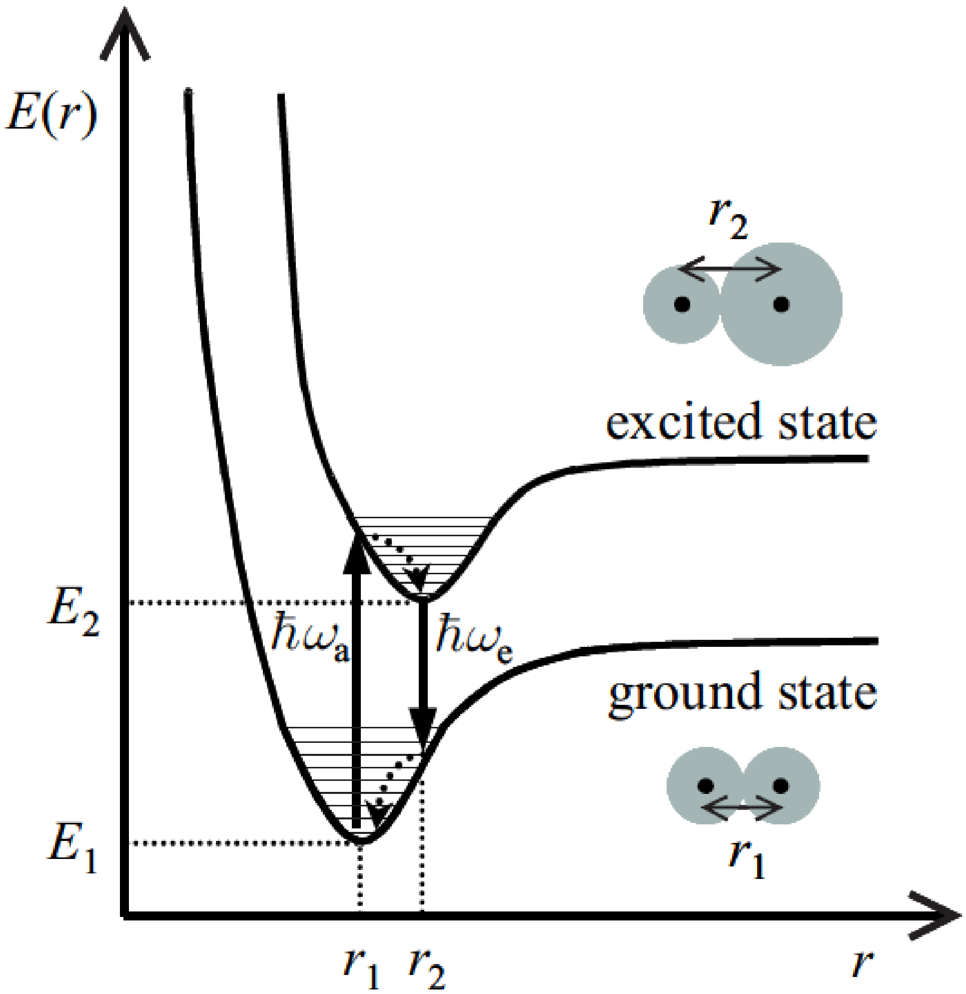
**Shallow** and **deep** defects.

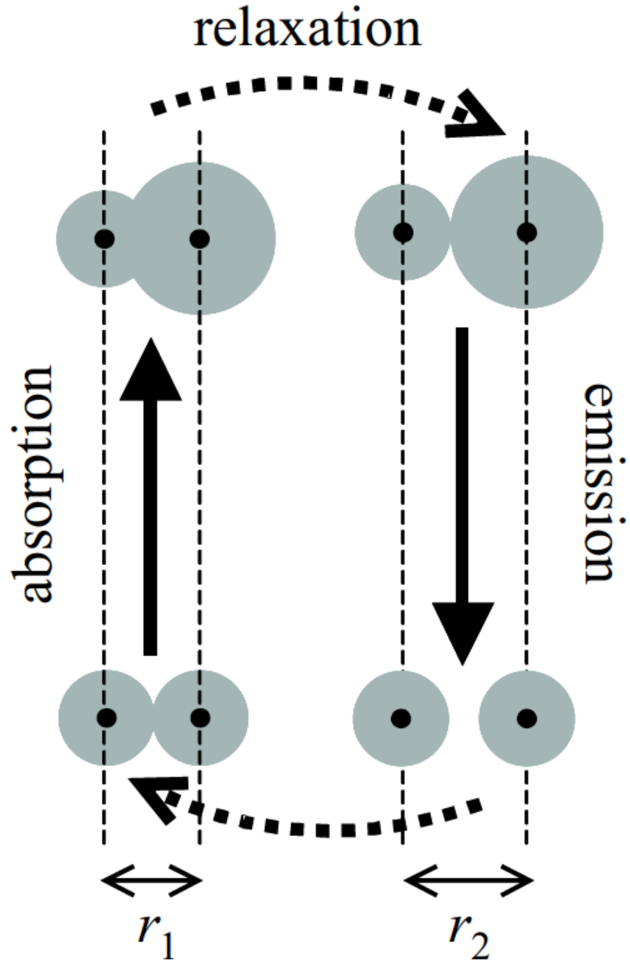




Yu & Cardona

# Defects: Frank-Condon principle

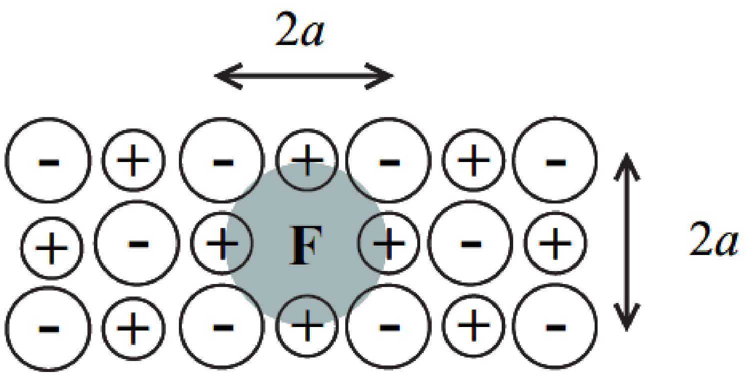


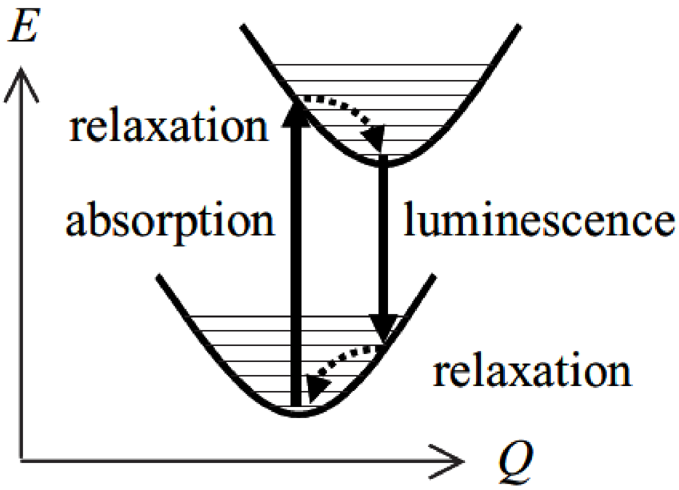


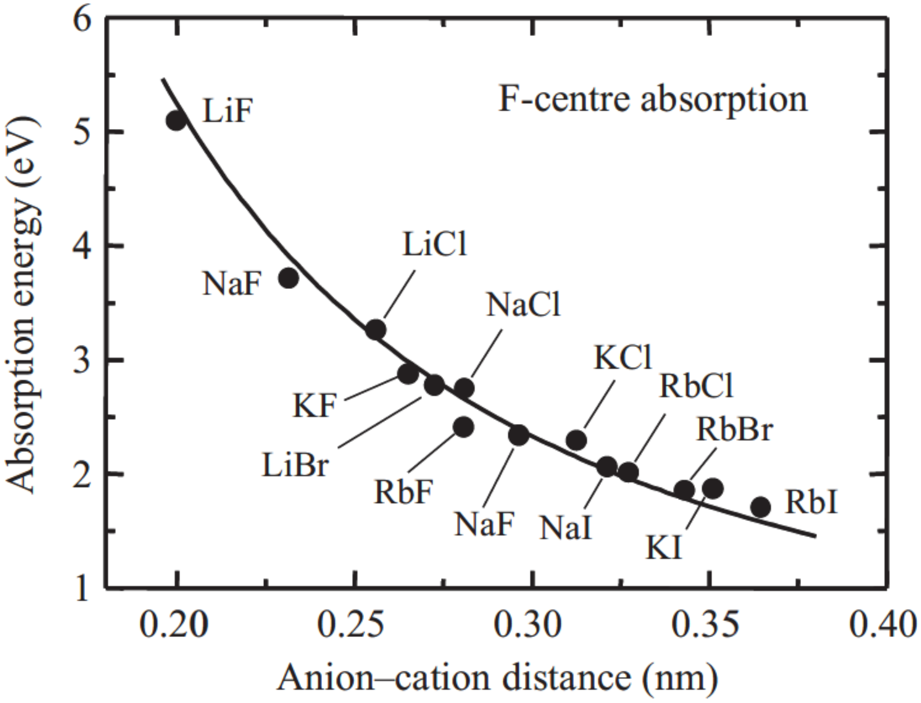
Born-Oppenheimer approximation

Fox, Chapter 8

# Defects: Color centers (F-centers)





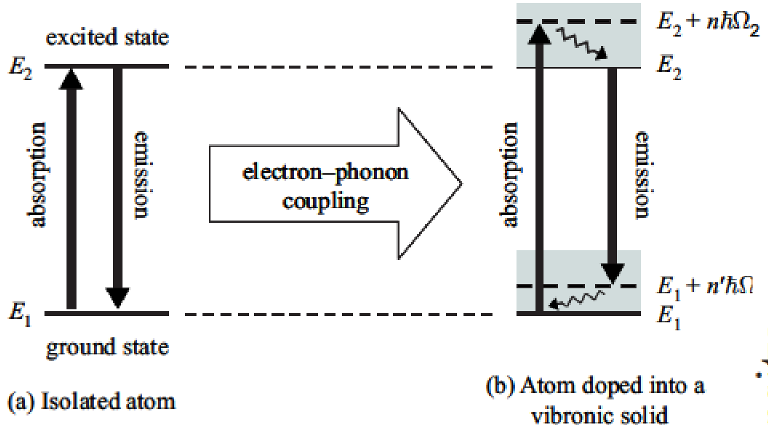


Alkali halide: large-gap insulator
Vacancy: positively charged hole

F-center: electron trapped at anion vacancy.

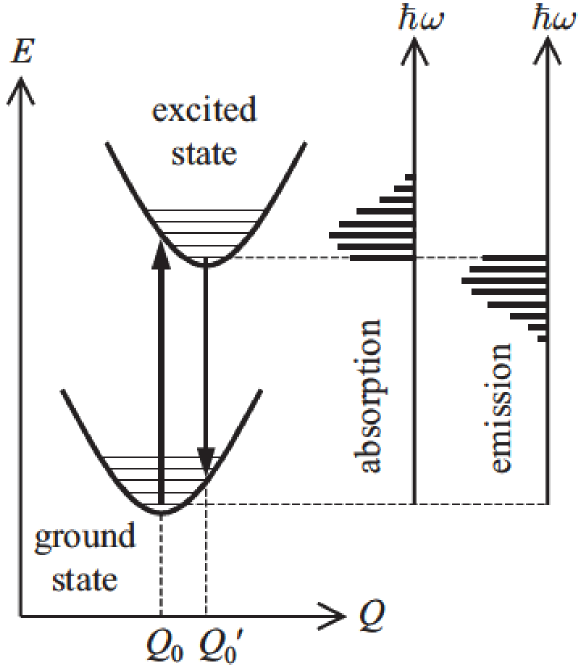
Fox, Chapter 9

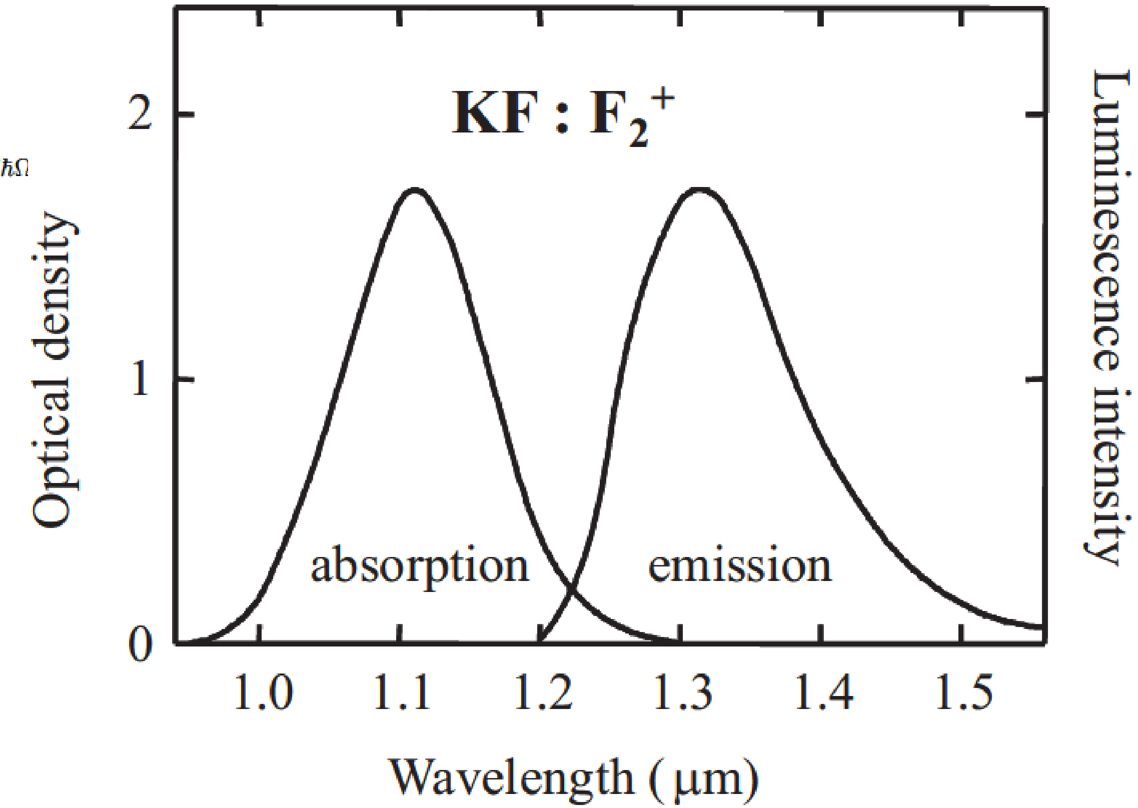
# Defects: Shift between absorption and emission



(a) Isolated atom

(b) Atom doped into a vibronic solid





Two vacancies, one electron
Color-center lasers

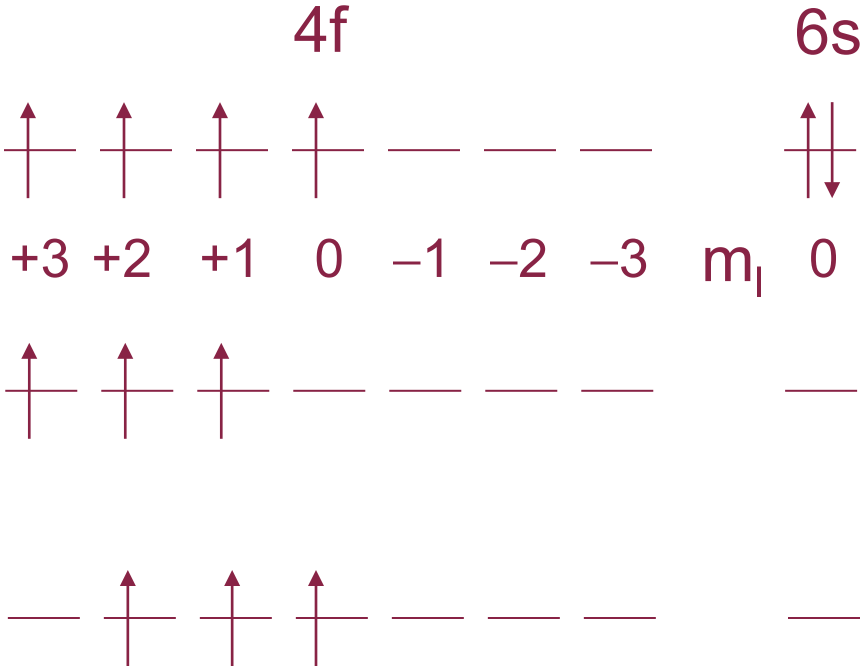
Fox, Chapter 8,9

# Hund's Rules (applied to Neodymium, Z=60)

1. Maximize S
2. Maximize L
3. If shell is less than half full, J=L–S
   If shell is more than half full, J=L+S.

$^{2S+1}L_J$

Russell-Saunders
(LS) coupling



atom: $^5I_4$

Nd: $4f^4\ 6s^2$ S=2, L=6, J=4

3+ ion ground state: $^4I_{9/2}$

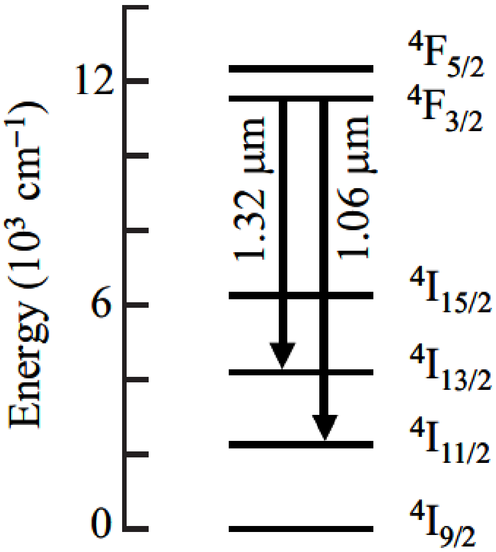
$Nd^{3+}$: $4f^3\ 6s^0$ S=3/2, L=6, J=9/2

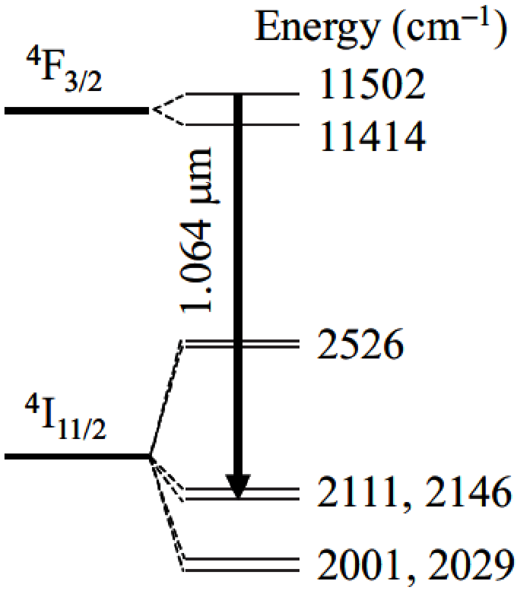
3+ ion excited state: $^4F_{3/2}$

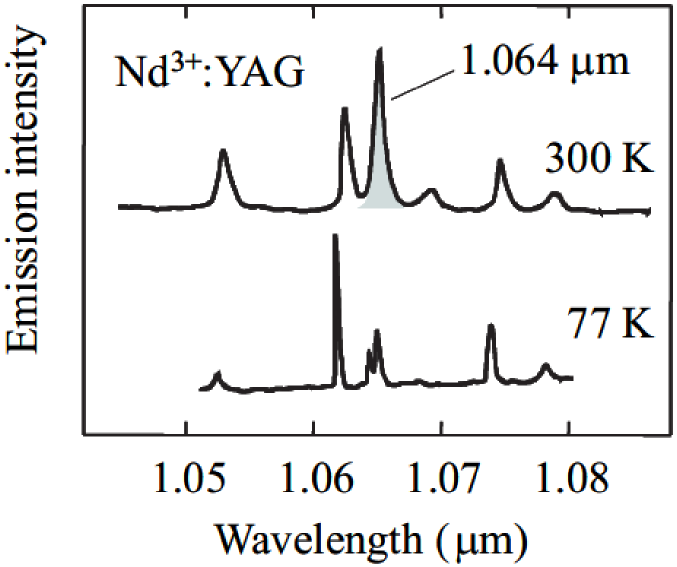
$Nd^{3+}$: $4f^3\ 6s^0$ S=3/2, **L=3**, J=3/2

Fox, Chapter 9

# Defects: Rare earth metal ions in insulator (Nd:YAG)







Atomic configuration

Weak crystal-field splitting

YAG: $Y_3Al_5O_{12}$

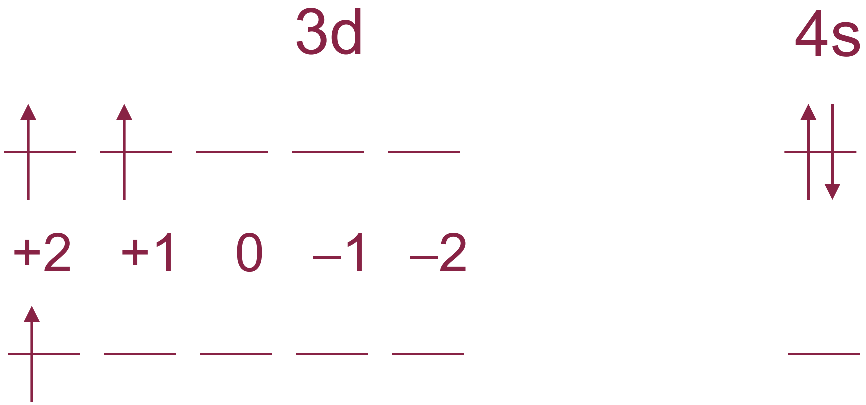
ΔJ=4 or 5 forbidden

Transition weakly allowed with crystal-field splitting

Nd:YAG lasers
YAG: 1064 nm
$YLiF_4$: 1053 nm
Broad (120 GHz)

Fox, Chapter 9

# Defects: Transition metal ions (Ti:sapphire)



3d

4s

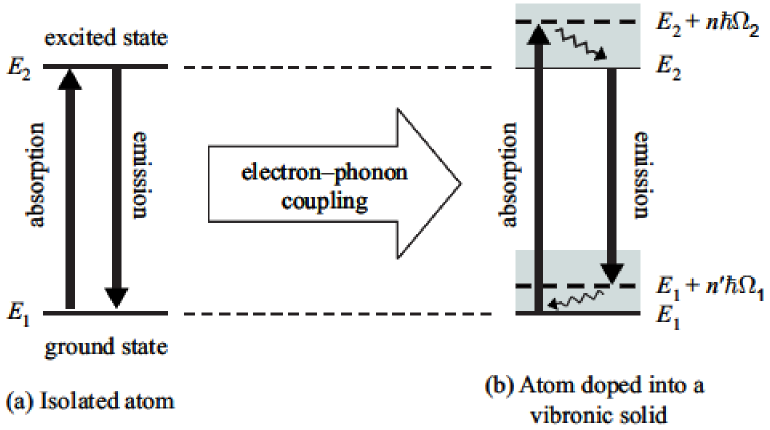
+2 +1 0 −1 −2

atom: $^3F_2$

Ti: $3d^2\ 4s^2$ S=1, L=3, J=2

ion: $^2D_{3/2}$

$Ti^{3+}$: $3d^1\ 4s^0$ S=1/2, L=2, J=3/2



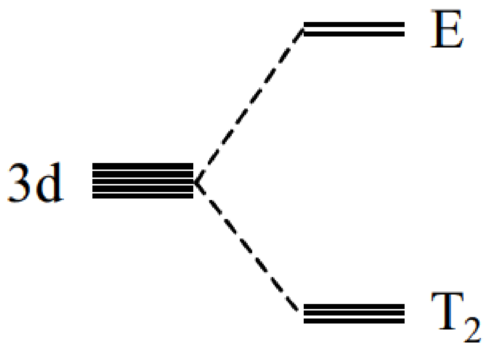
(a) Isolated atom

(b) Atom doped into a vibronic solid

Strong vibronic coupling

Broad lines (gain spectrum)

Good for ultrafast lasers

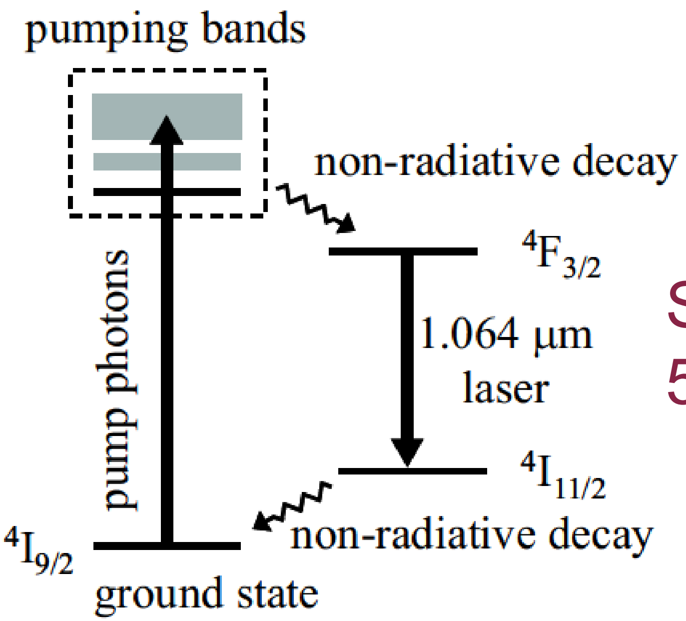


Strong crystal-field splitting

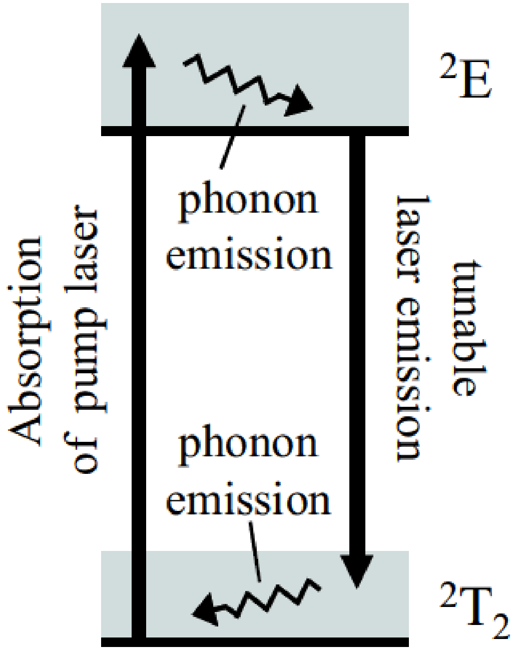
Depends on crystal environment

Fox, Chapter 9

# Solid-State Lasers: Ti:sapphire and Nd:YAG

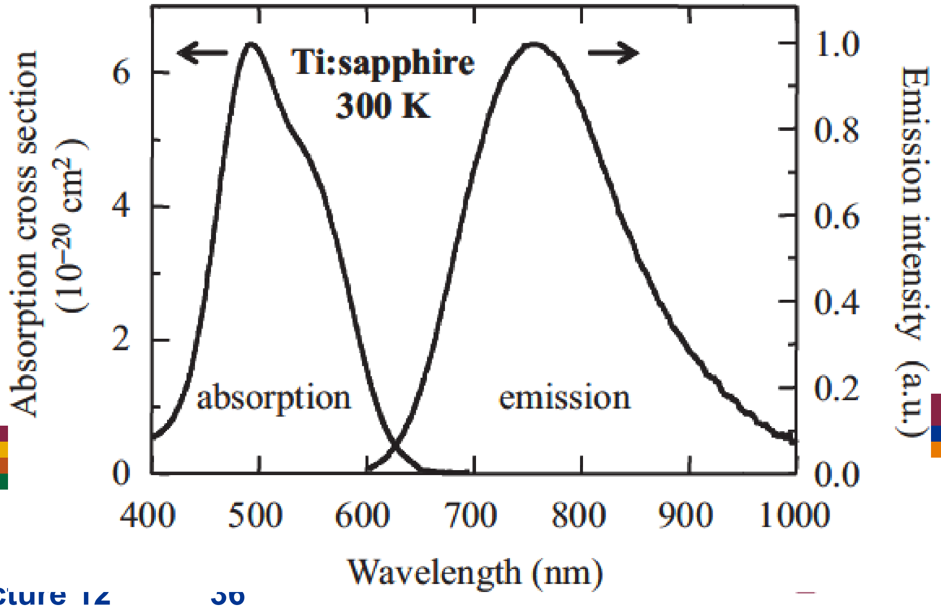


SHG
532 nm

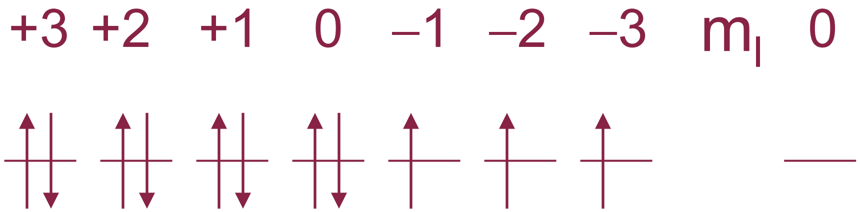


Pumping with
- Flash lamp (pulsed)
- Xe lamp (CW)
- GaAs diode (efficient)

Fox, Chapter 9

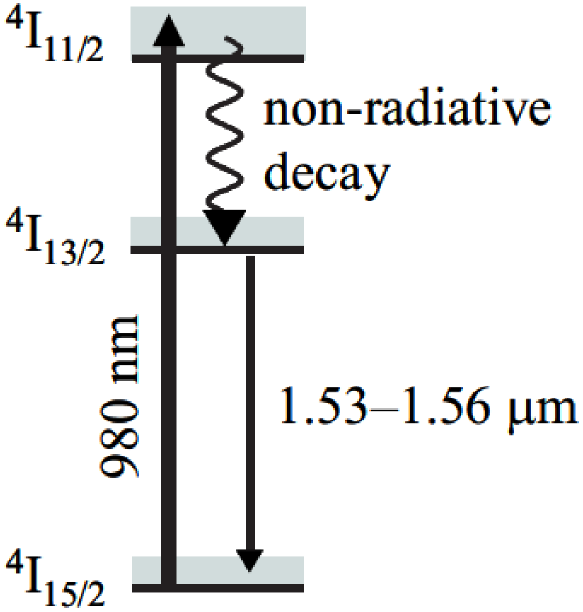


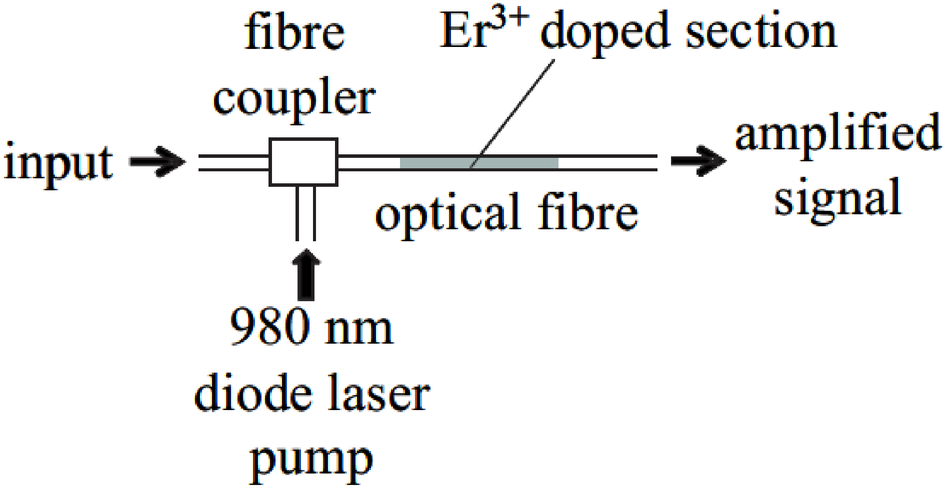
# Erbium fiber laser



3+ ion ground state: $^4I_{15/2}$

Er$^{3+}$: 4f$^{11}$ 6s$^0$ S=3/2, L=6, J=15/2



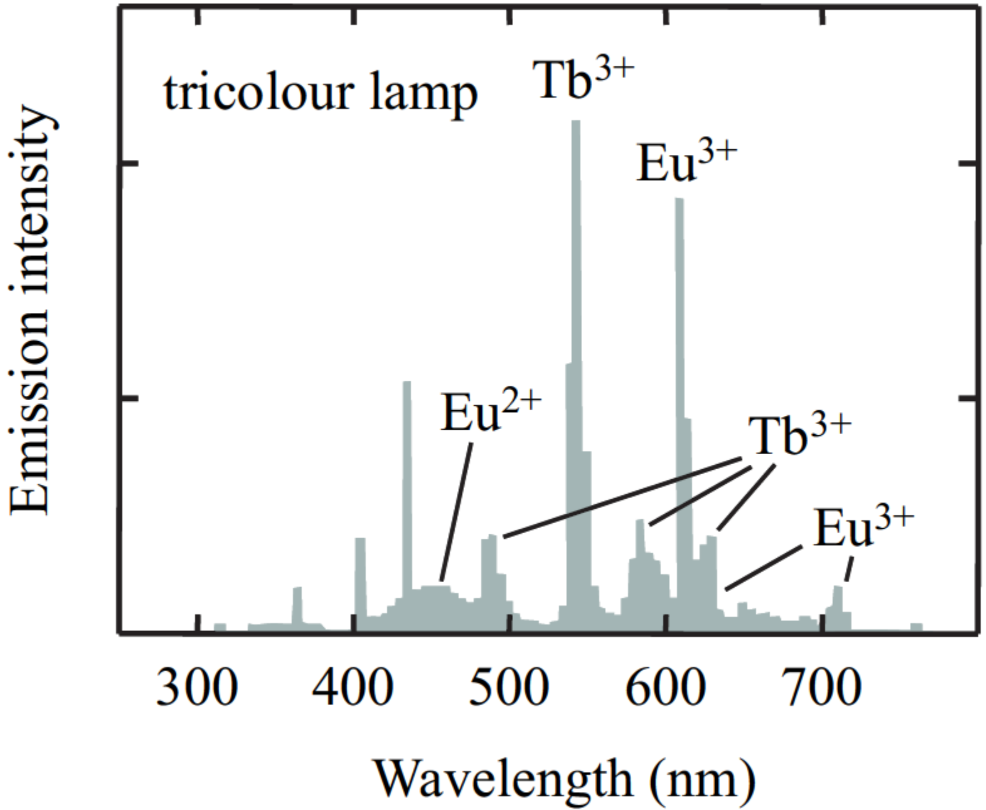


Pumped with 980 nm diode laser.
Important for telecommunications.

Fox, Chapter 9

# Phosphors

Obsolete: Cathode ray tubes (TV, oscilloscope)
Fluorescent tubes.
Convert discrete LED (or Hg) emission into white light.



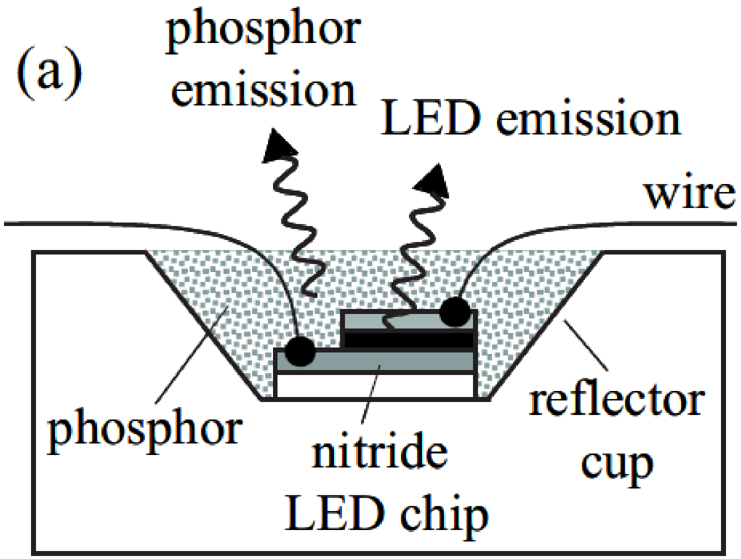
$BaMgAl_{10}O_{17}$:$Eu^{2+}$ ($4f^7$)
450 nm (blue)

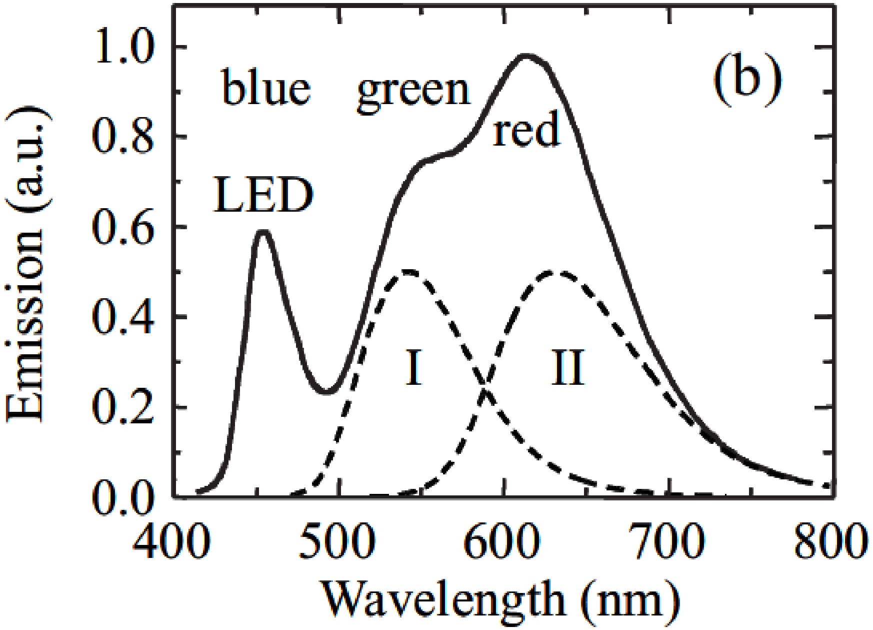
$CeMgAl_{11}O_{19}$:$Tb^{3+}$ ($4f^8$)
550 nm (green)

$Y_2O_3$:$Eu^{3+}$ ($4f^6$)
610 nm (red)

Fox, Chapter 9

# White light emitting diodes (white LEDs)





Blue InGaN LED with green and red phosphors

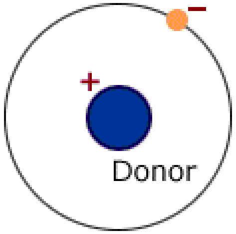
I: $SrSi_2O_2N_2:Eu^{2+}$

II: $Sr_2Si_5N_8:Eu^{2+}$

Color temperature: 3200 K

Fox, Chapter 9

# Shallow (hydrogenic) defect: Si donor in GaAs

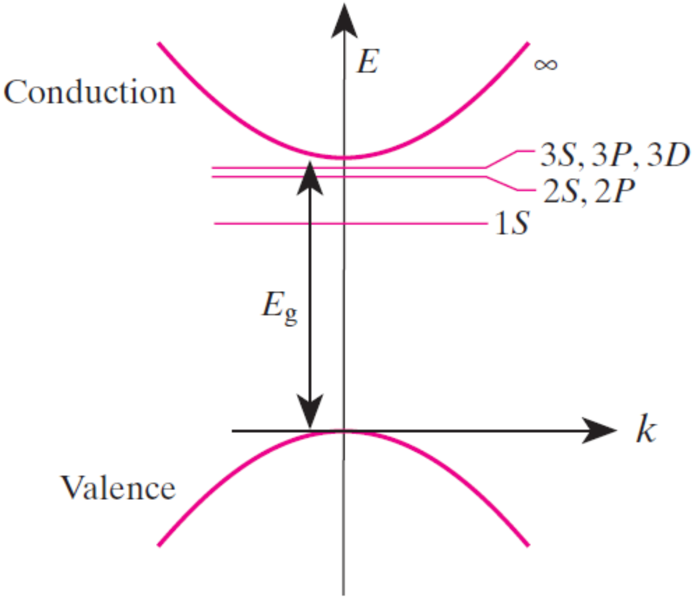


Extra valence electron
P nucleus positively charged (but screened in crystal)
Hydrogen-like energy spectrum (screened, heavy)

Extra potential: $V_S = +\frac{|e|}{4\pi\varepsilon_0 r}$

Rydberg series: $E = E_{CBM} - \frac{R}{n^2}$

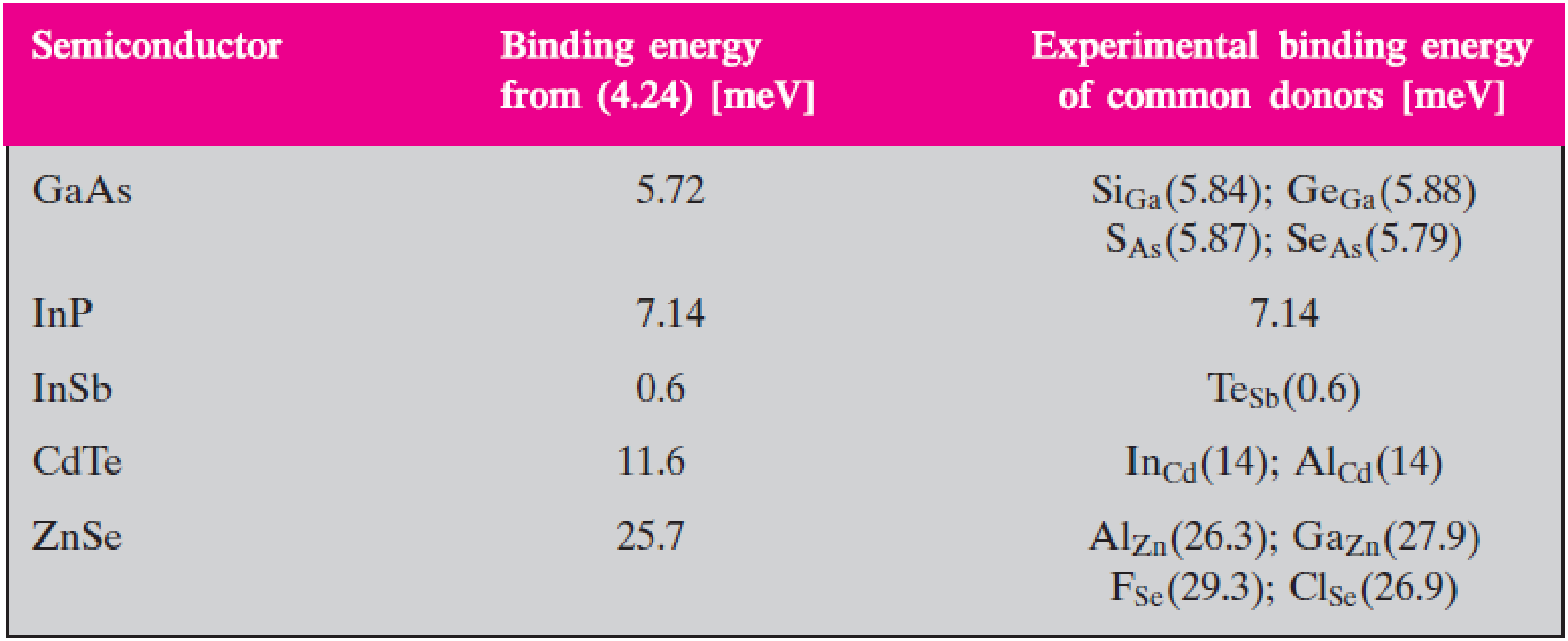
Binding energy: $\boxed{R = \frac{m^*}{m_0}\frac{1}{\varepsilon_s^2}\frac{e^4 m_0}{2\hbar^2(4\pi\varepsilon_0)^2}}$



Bohr radius.
Similar to exciton problem.

Yu & Cardona

# Shallow (hydrogenic) defect: Si donor in GaAs

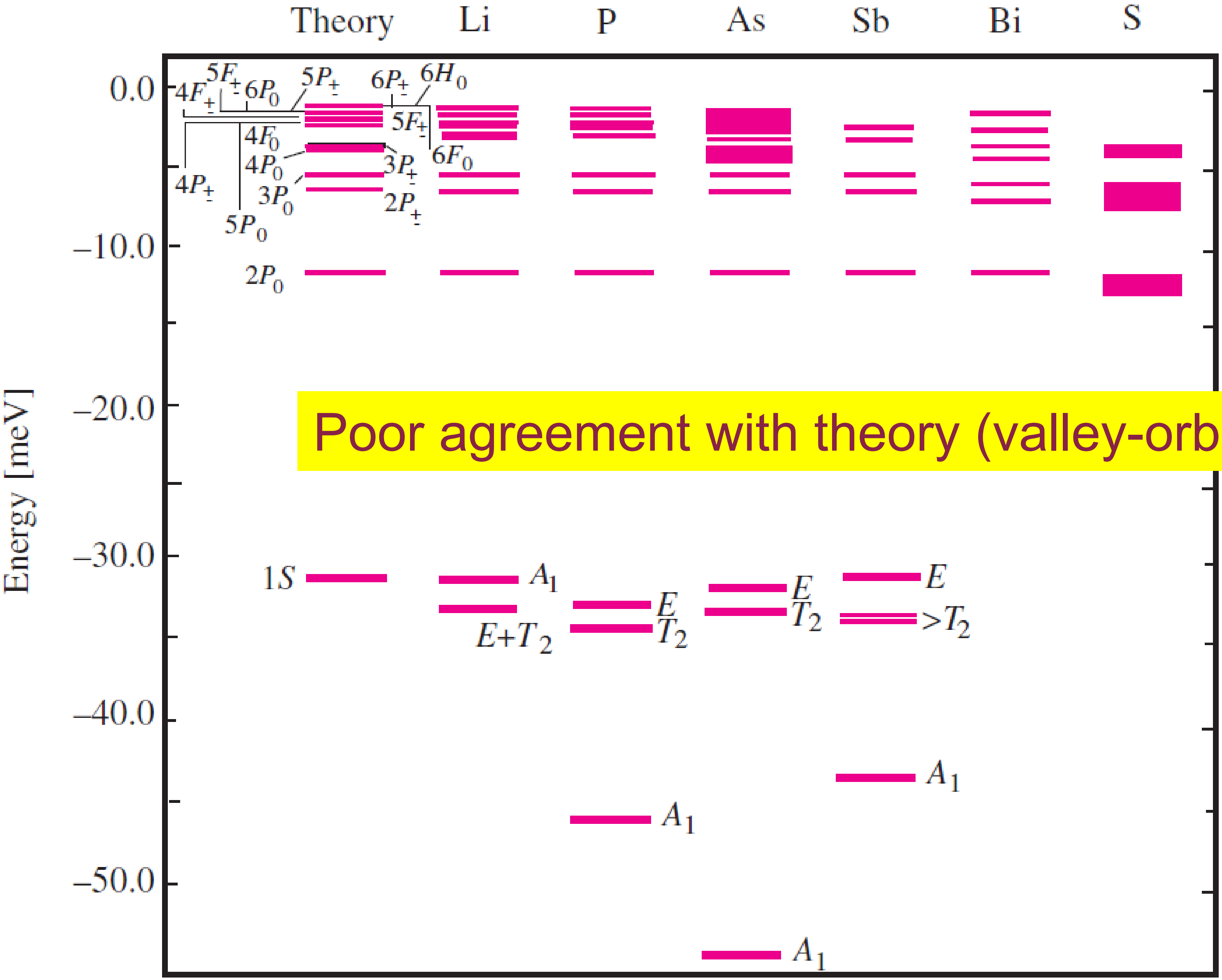


| Semiconductor | Binding energy from (4.24) [meV] | Experimental binding energy of common donors [meV] |
|---|---|---|
| GaAs | 5.72 | $Si_{Ga}$(5.84); $Ge_{Ga}$(5.88)<br>$S_{As}$(5.87); $Se_{As}$(5.79) |
| InP | 7.14 | 7.14 |
| InSb | 0.6 | $Te_{Sb}$(0.6) |
| CdTe | 11.6 | $In_{Cd}$(14); $Al_{Cd}$(14) |
| ZnSe | 25.7 | $Al_{Zn}$(26.3); $Ga_{Zn}$(27.9)<br>$F_{Se}$(29.3); $Cl_{Se}$(26.9) |

Works quite well for s-like conduction bands.
Complications due to p-like VB, anisotropic bands (Ge, Si, GaP)

Yu & Cardona

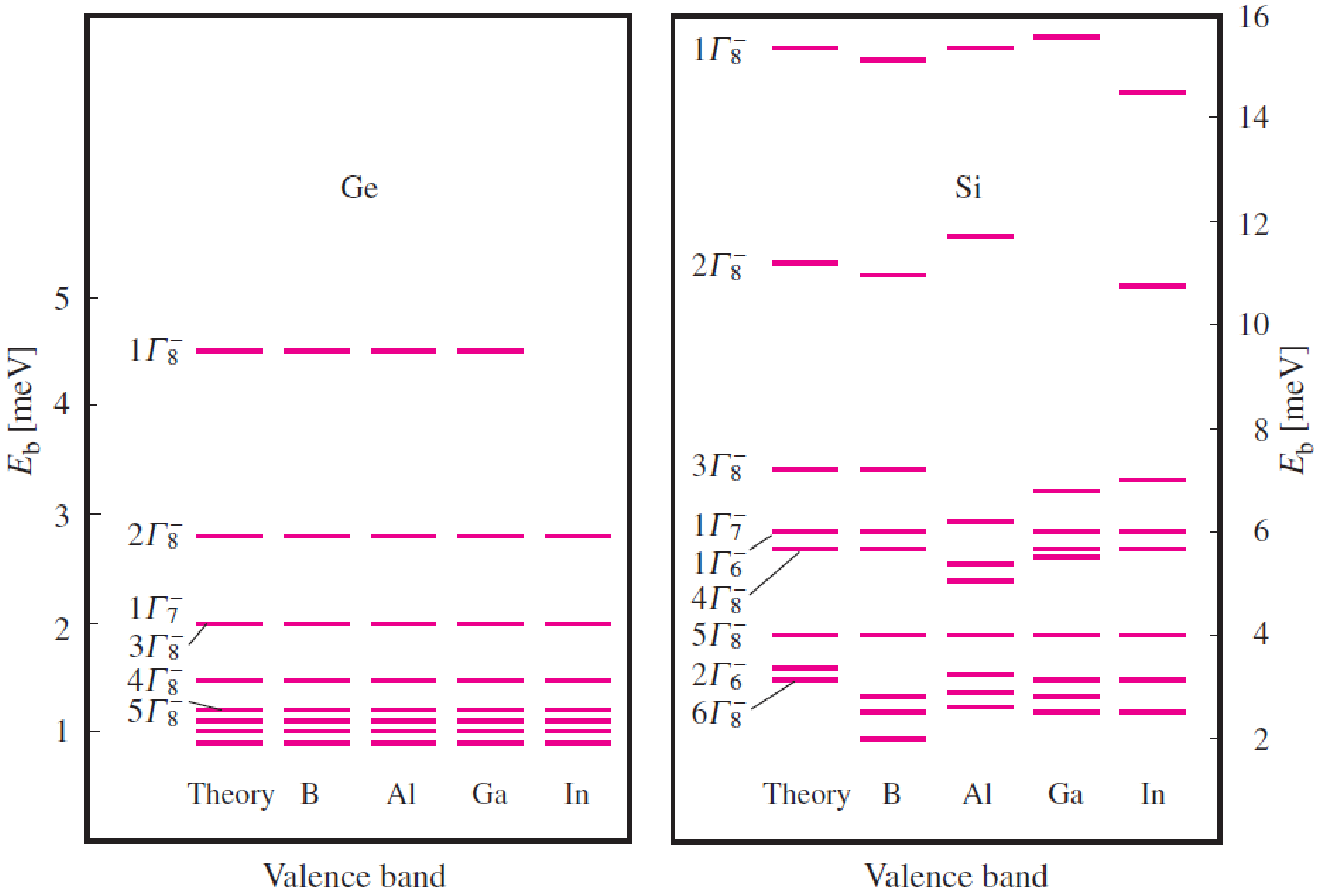
# Shallow (hydrogenic) defect: Donors in Si and Ge



Poor agreement with theory (valley-orbit coupling)

Yu & Cardona

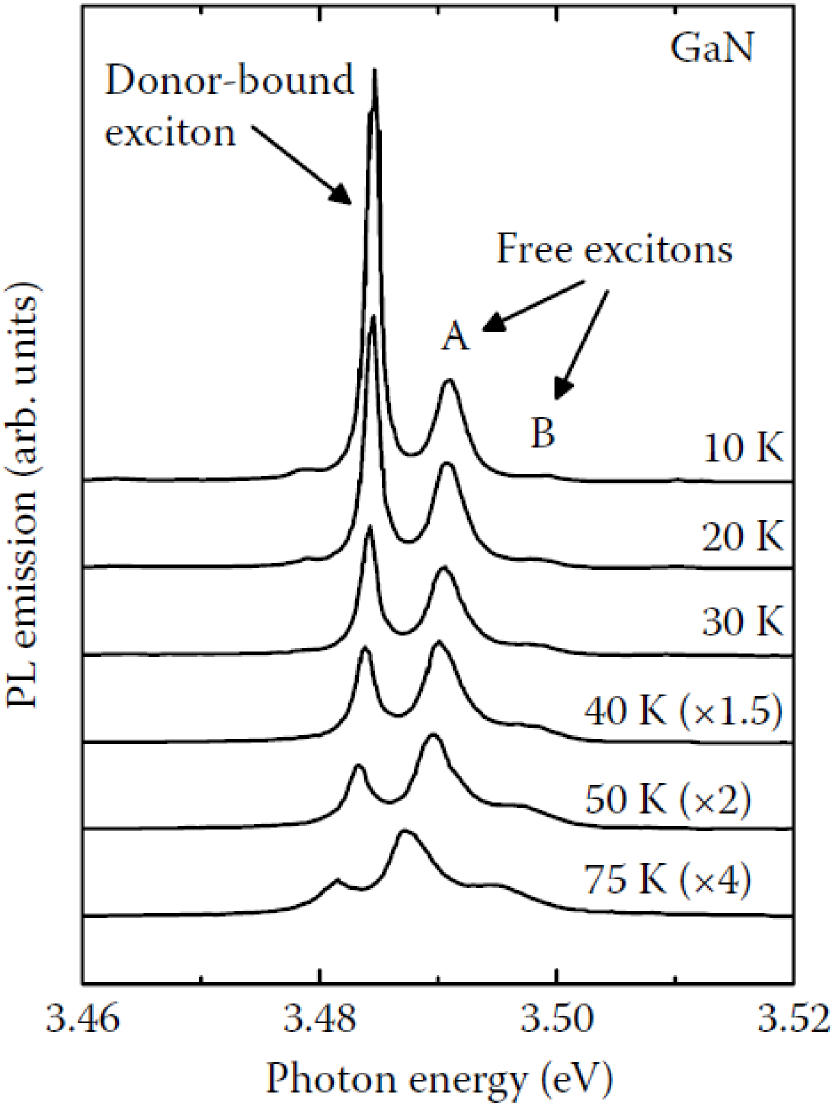
# Shallow (hydrogenic) defect: Acceptors in Si and Ge

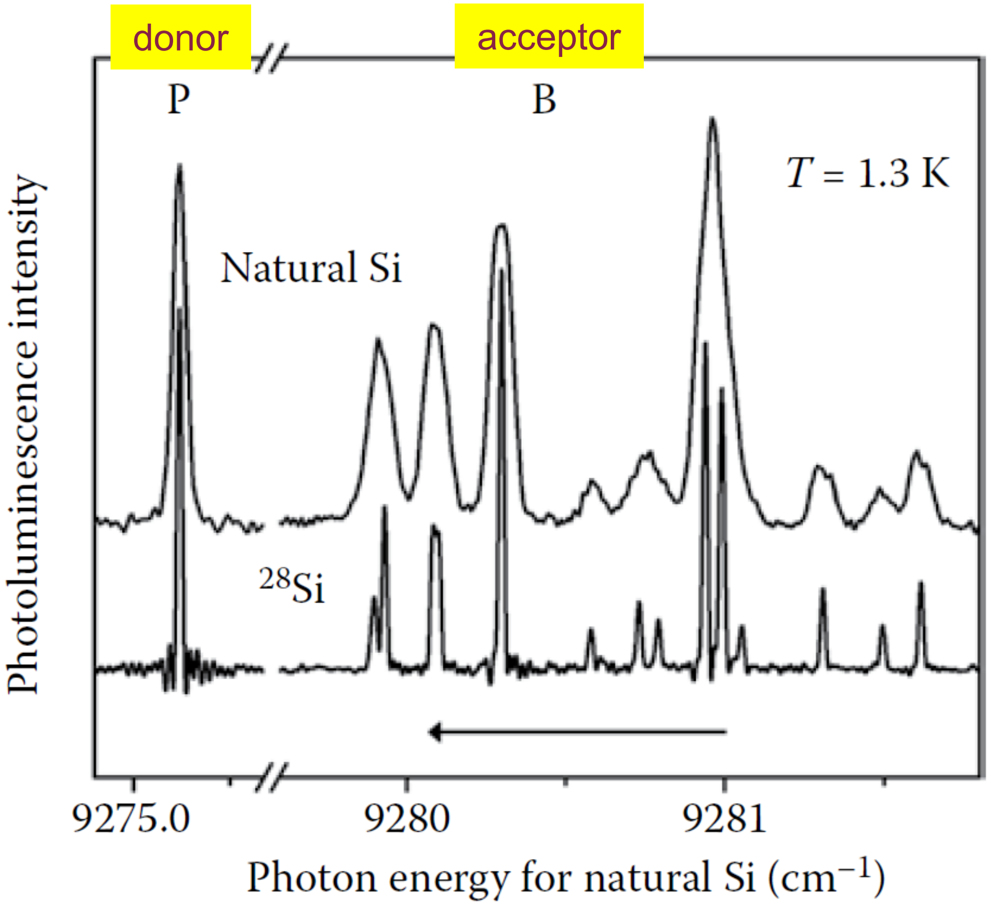


Need to include valence band warping (Luttinger theory) and other corrections.

Yu & Cardona

# Free and bound excitons (photoluminescence)



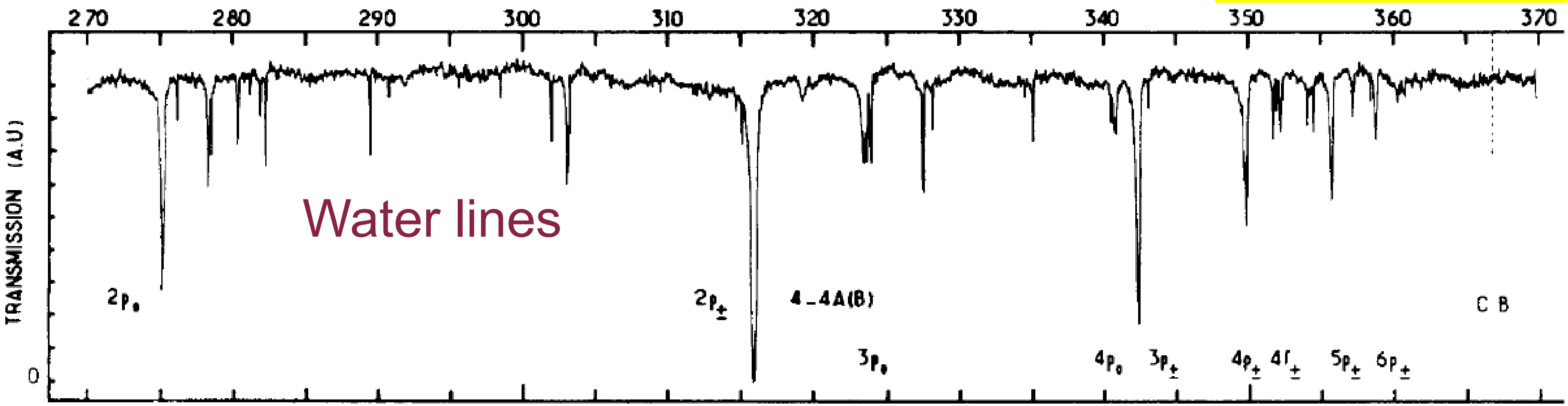


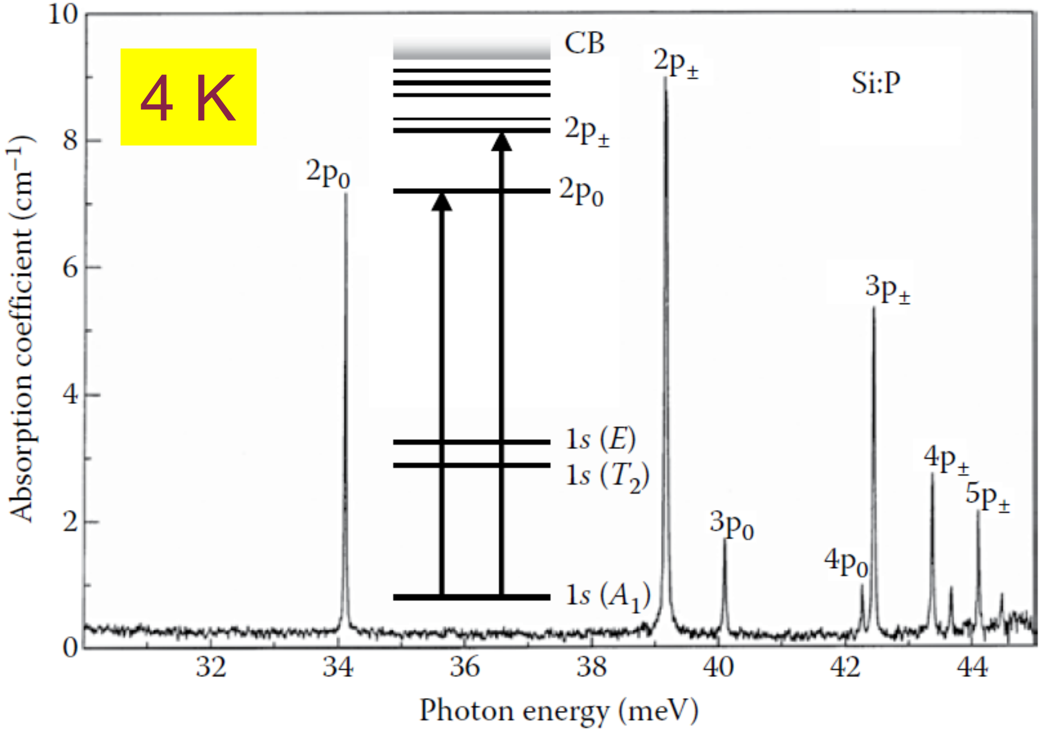
Band to defect recombination shifted from free exciton energy.

McClusky & Haller, Dopants and Defects

# Infrared defect spectroscopy: P donor in Si

Energy ($cm^{-1}$)



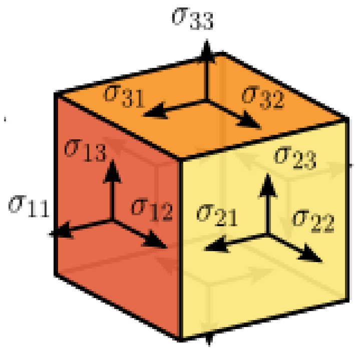


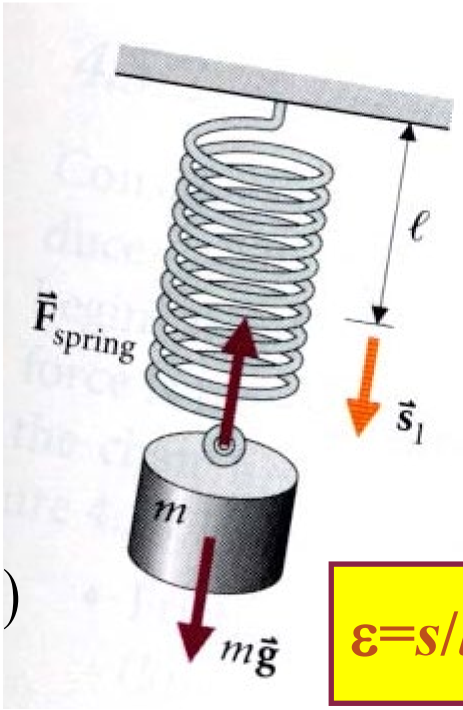
McClusky & Haller, Dopants and Defects
A.K. Ramdas, PRB **23**, 2082 (1981)
Pajot, Solid State Commun. **31**, 759 (1979)

# Stress and Strain: Hooke’s Law

- Stress: Force per unit area (GPa), (1st rank tensor)

$$\mathbf{X} = \begin{pmatrix} X_{11} & X_{12} & X_{13} \\ X_{21} & X_{22} & X_{23} \\ X_{31} & X_{32} & X_{33} \end{pmatrix}$$





ε=s/*l*

- Strain: Describes the response to the stress, (1st rank tensor)

$$\varepsilon = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} \end{pmatrix} = \vec{\nabla} \otimes \left( \vec{a}_{\text{strained}} - \vec{a}_{\text{unstrained}} \right)$$

- Constituent relation (Hooke’s law) between stress and strain: compliance tensor $\mathbf{S}$, stiffness tensor $\mathbf{c}$ (6x6 2nd rank tensors)

$$\varepsilon = \mathbf{SX}$$

$$\mathbf{X} = \mathbf{c}\varepsilon$$

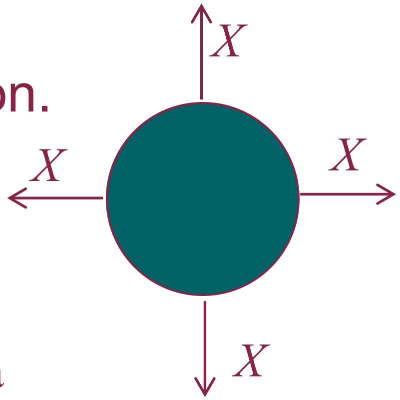
Spring: Strain is ε=s/*l*, Relative change in length.

Landau & Lifshiftz, *Elasticity Theory*
Yu & Cardona, *Fundamentals of Semiconductors.*

# Biaxial Stress in Epitaxial Film on (001) substrate

- Stress:
  Forces act along the wafer, but not along the growth direction.
  - SiGe on Si: Compressive stress (X<0)
  - Si on SiGe: Tensile stress (X>0)

$$\mathbf{X}_{\text{biaxial}} = \begin{pmatrix} X & 0 & 0 \\ 0 & X & 0 \\ 0 & 0 & 0 \end{pmatrix}$$



- Resulting Strain:

$$\boldsymbol{\varepsilon}_{\text{biaxial}} = \begin{pmatrix} (S_{11}+S_{12})X & 0 & 0 \\ 0 & (S_{11}+S_{12})X & 0 \\ 0 & 0 & 2S_{12}X \end{pmatrix} = \begin{pmatrix} \varepsilon_{\parallel} & 0 & 0 \\ 0 & \varepsilon_{\parallel} & 0 \\ 0 & 0 & \varepsilon_{\perp} \end{pmatrix}$$

$\varepsilon_{\parallel} = 0.553\ X/10^{11}\ \text{Pa}$

tensile in-plane strain

$\varepsilon_{\perp} = -0.979\ X/10^{11}\ \text{Pa}$

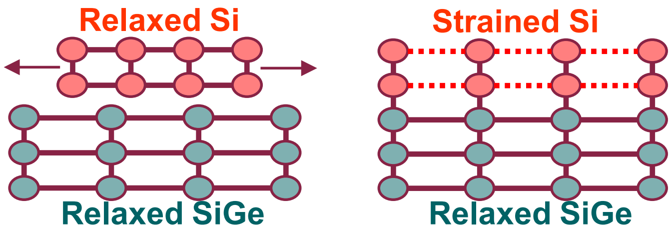
compressive vertical strain

- Hydrostatic strain component: tensile (>0), softens phonons, gap decreases

$$\varepsilon_{\mathrm{H}} = \left(2\varepsilon_{\perp} + \varepsilon_{||}\right)/3$$

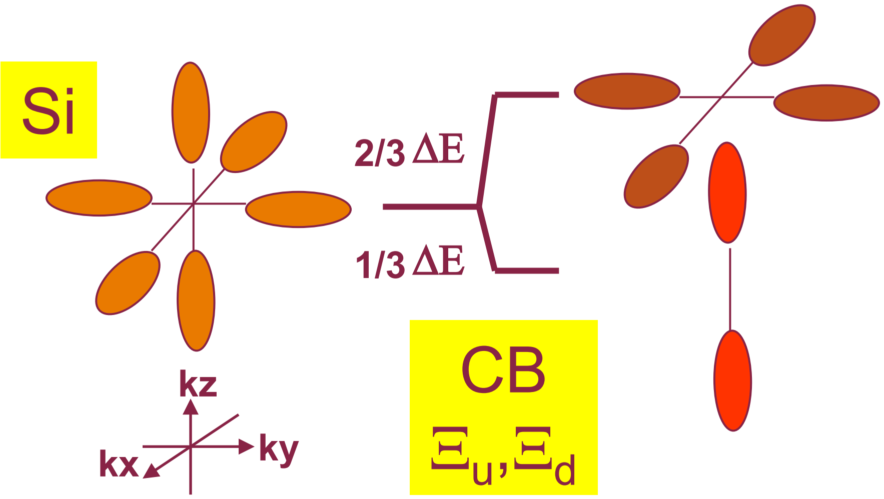
- (100) Shear strain component: compressive (<0),
  Splits phonons and bands into singlet/doublet. Selection rules!

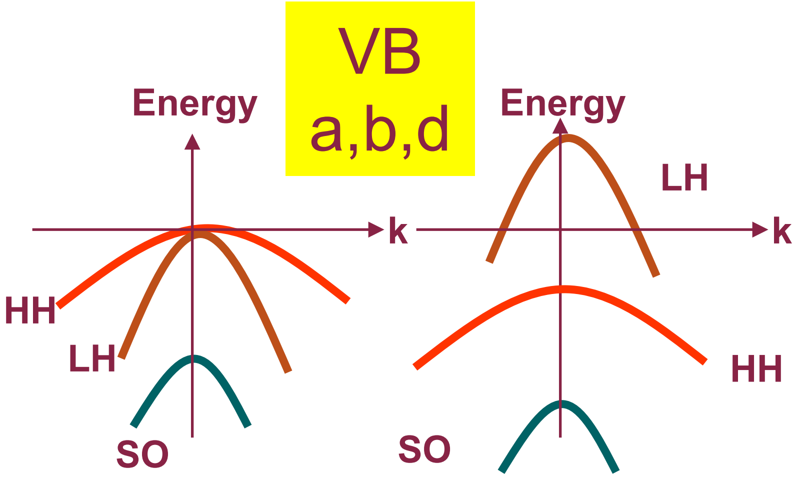
$$\varepsilon_{\mathrm{S}} = \left(\varepsilon_{||} - \varepsilon_{\perp}\right)/3$$



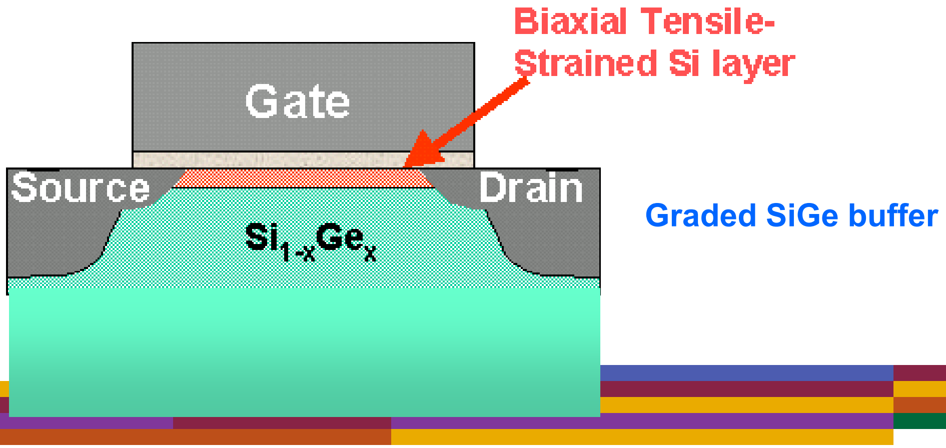
S. Zollner, *Properties of Silicon-Germanium-Carbon Alloys: Growth, Properties, Applications*

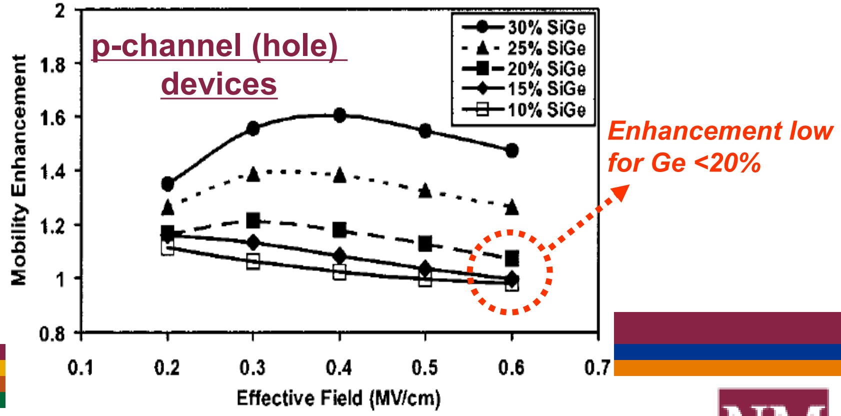
# Thin Strained Silicon Layers for CMOS



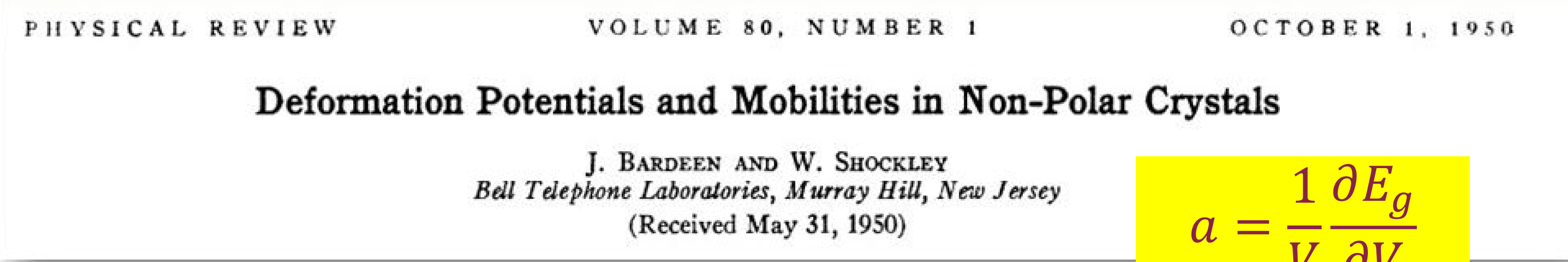


- Biaxial tension lowers band gaps, reduces effective masses, and splits bands/valleys (reduced intervalley and inter-valence band scattering).
- Silicon under biaxial tension has higher electron and hole mobilities and therefore offers better transport properties than bulk silicon.





# Deformation potentials



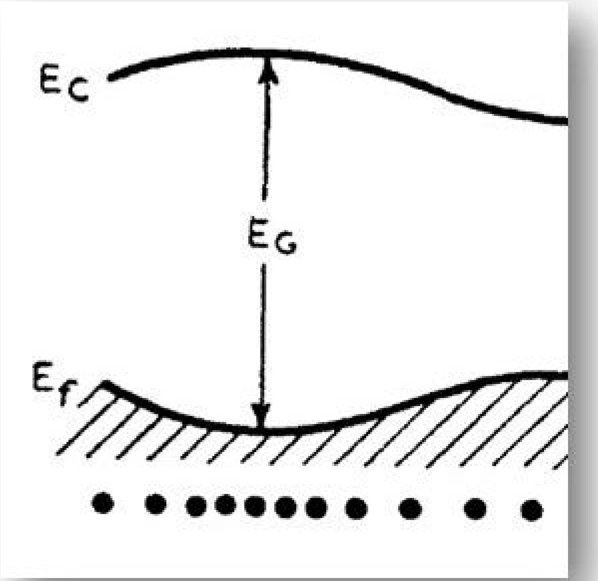
PHYSICAL REVIEW VOLUME 80, NUMBER 1 OCTOBER 1, 1950

**Deformation Potentials and Mobilities in Non-Polar Crystals**

J. BARDEEN AND W. SHOCKLEY
*Bell Telephone Laboratories, Murray Hill, New Jersey*
(Received May 31, 1950)

$$a = \frac{1}{V}\frac{\partial E_g}{\partial V}$$

$$\Delta E_g = a\,\mathrm{Tr}(\varepsilon)$$



$$a_V^{\Gamma\text{-}\Gamma} = \frac{\partial E_g^{\Gamma\text{-}\Gamma}}{\partial \ln V}$$

$$a_P^{\Gamma\text{-}\Gamma} = -\left(\frac{1}{B}\right) a_V^{\Gamma\text{-}\Gamma}$$

# Summary

- Quantum confinement and Heisenberg uncertainty principle
- Growth of quantum structures
- **Carbon nanostructures, two-dimensional materials**
- **Electronic states, quantum well absorption and emission**
- **Intersubband transitions**
- **Metamaterials and metasurfaces**

- **Defects**
- **Transition metal and rare earth impurities in insulators**
- **Shallow defects in semiconductors**

- **Stress and strain, deformation potentials**