Optical Properties of Solids: Lecture 12

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Optical Properties of Solids: Lecture 12

Quantum structures: wells, wires, dots

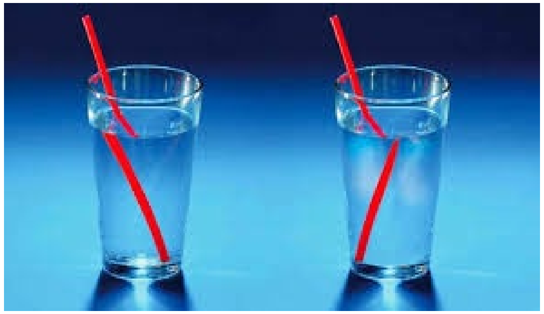
Absorption and emission of quantum wells

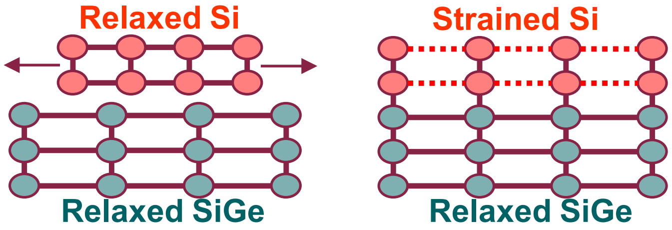
Intersubband absorption

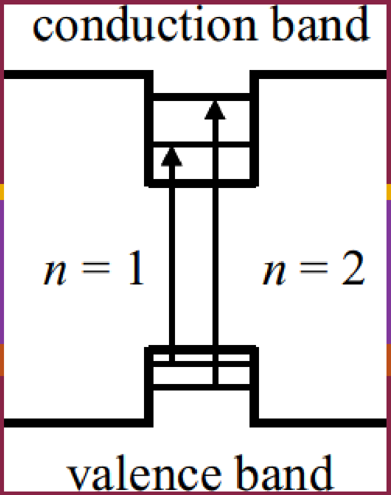
Quantum cascade lasers

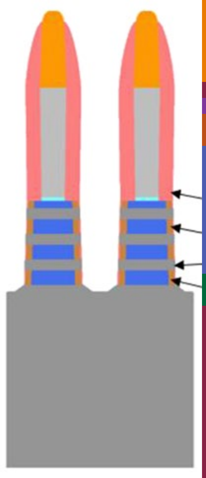
Defects (deep, shallow)

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

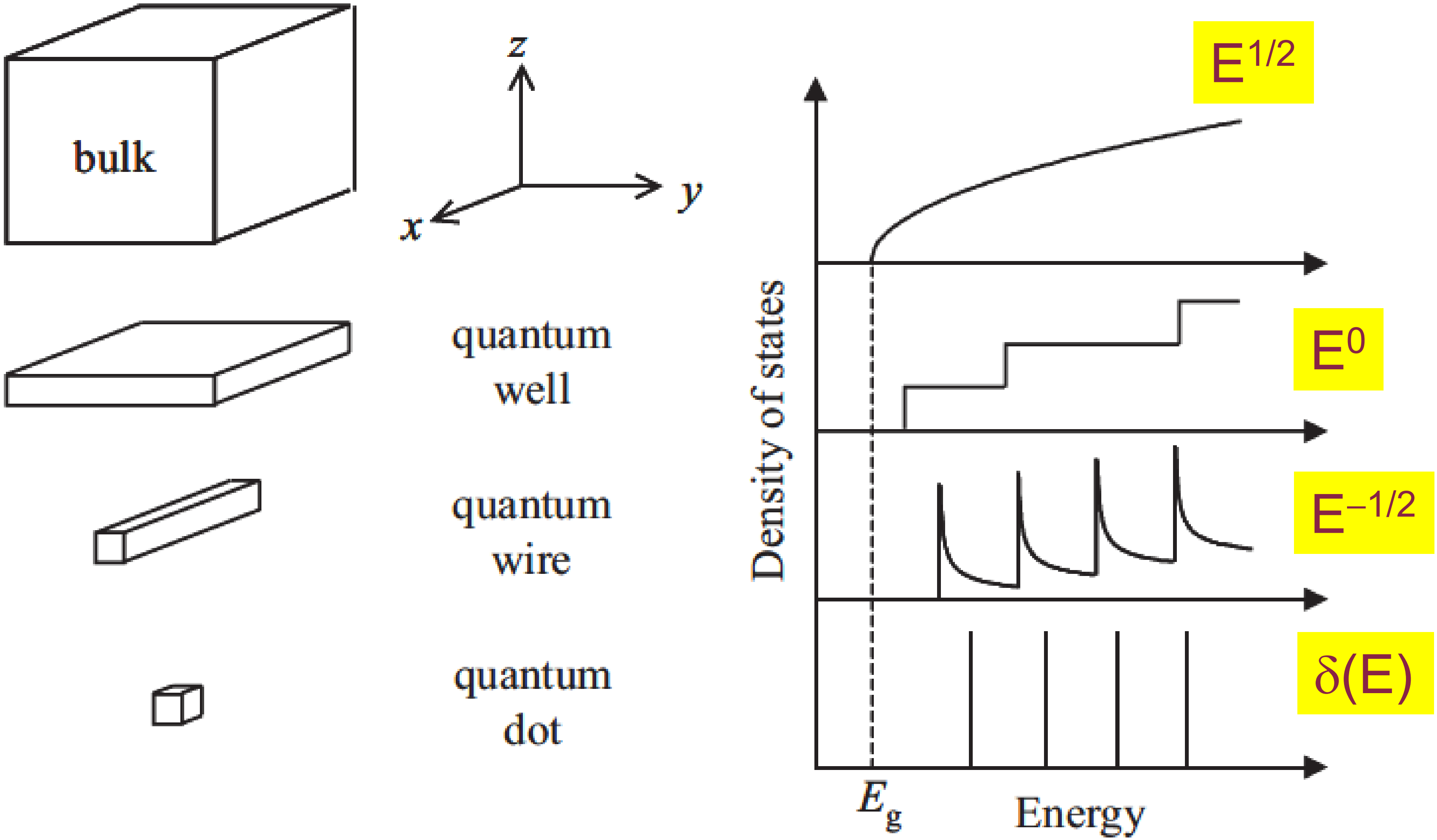
Outline

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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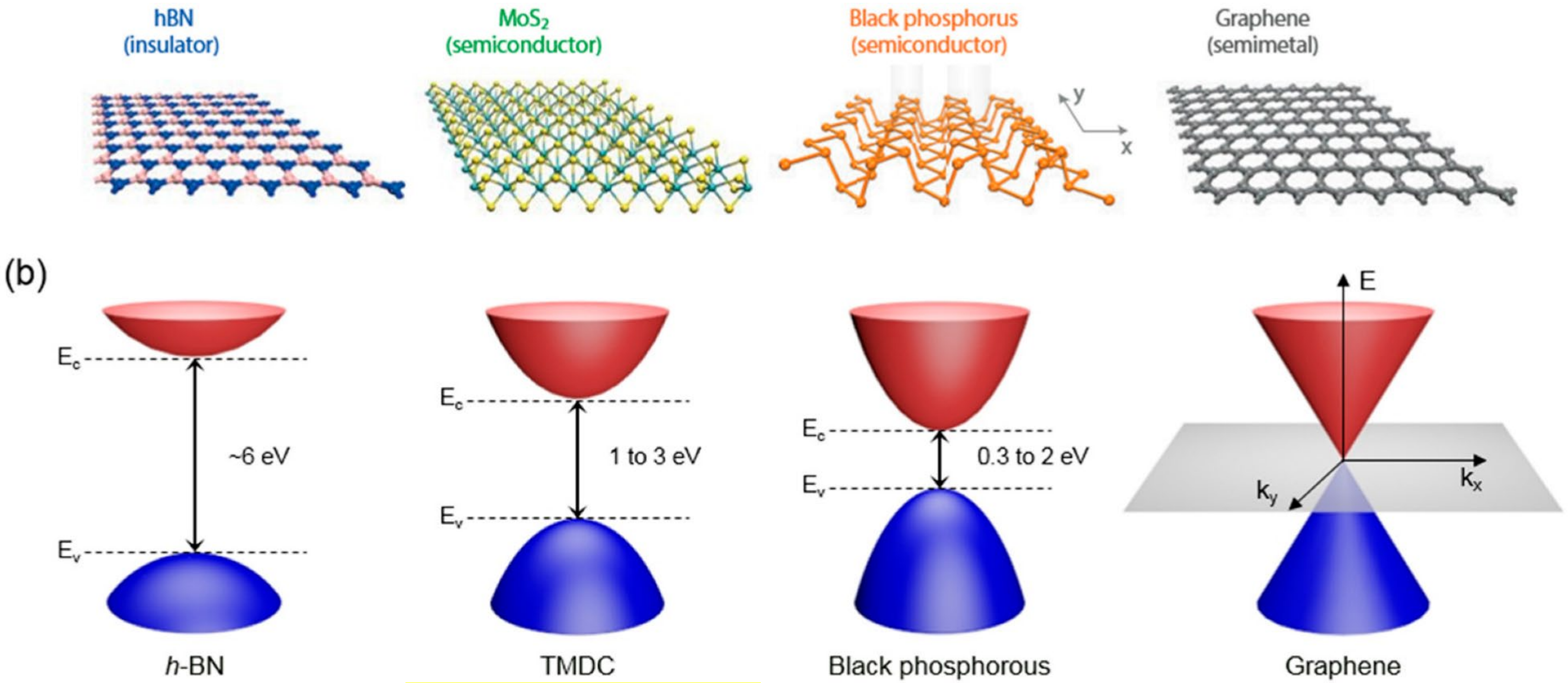
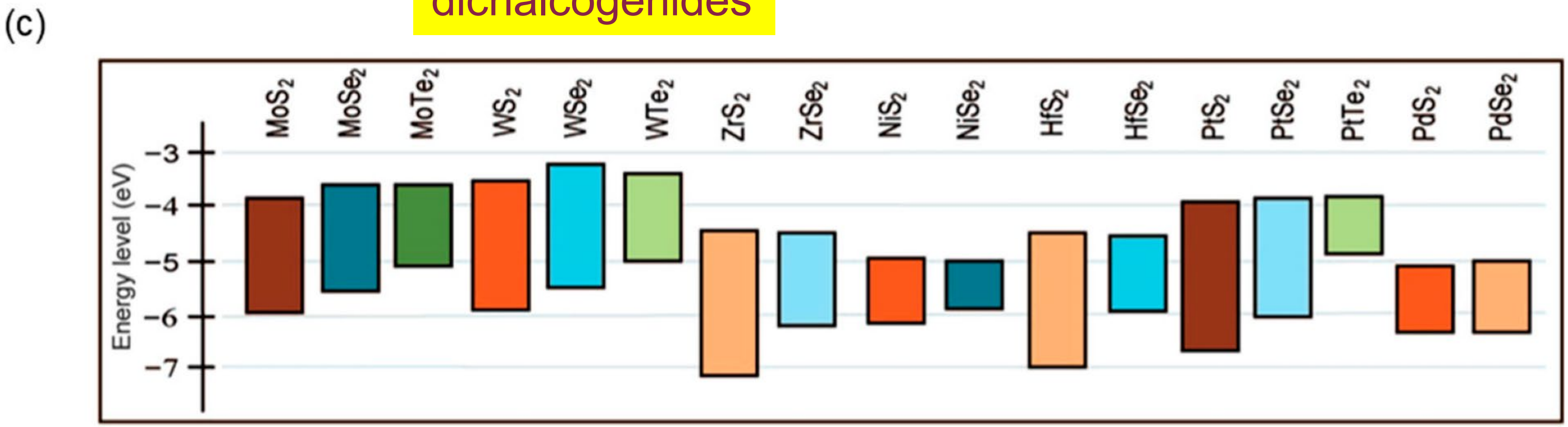
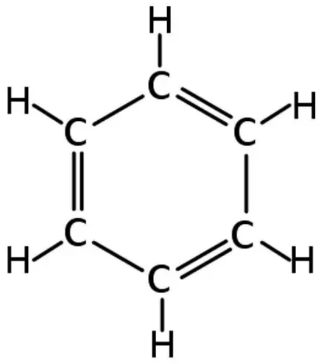
Two-dimensional semiconductors

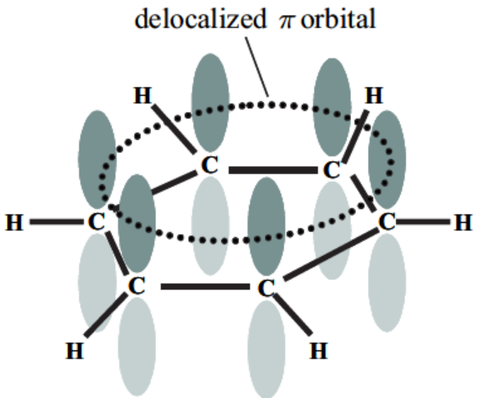


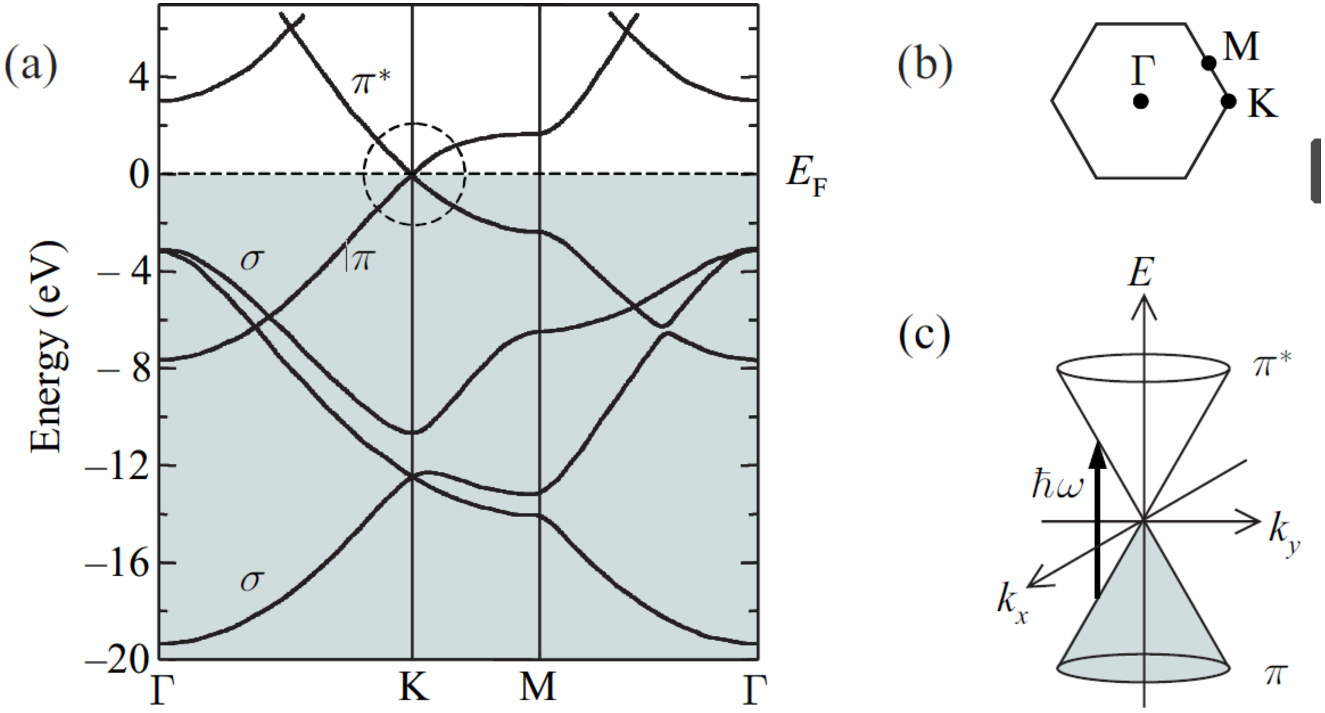
dichalcogenides



Dirac point in graphene







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

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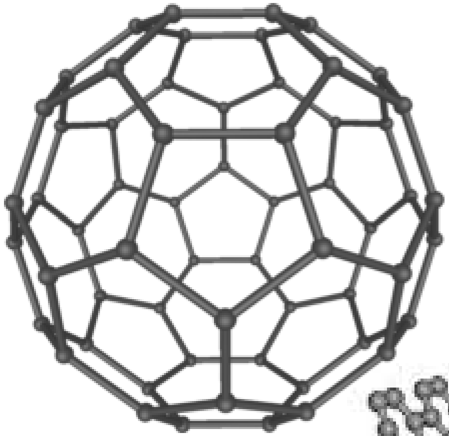
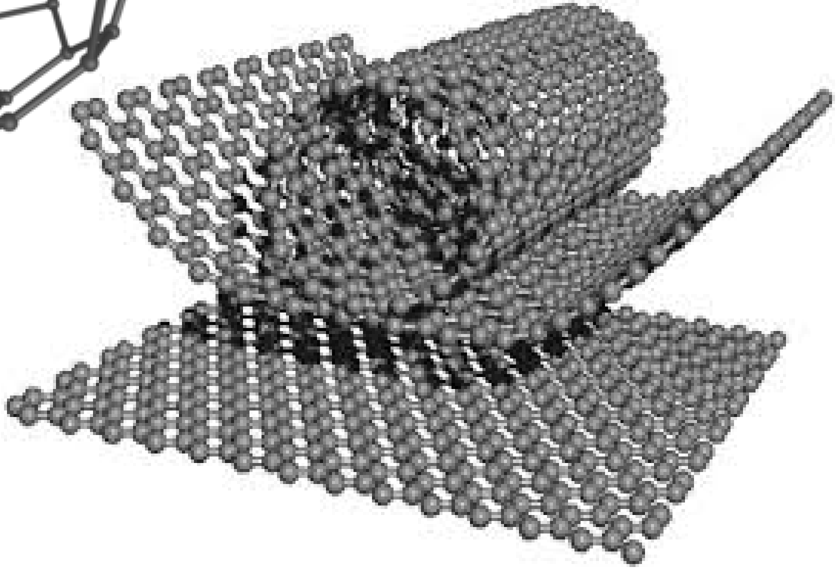
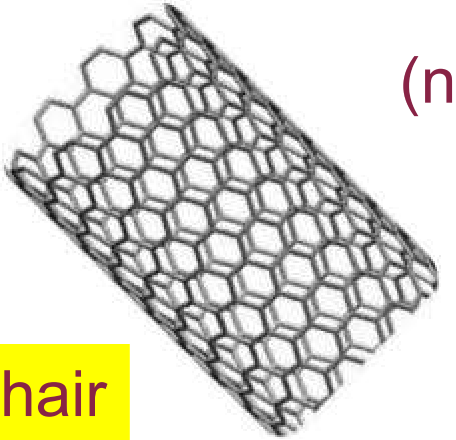
Carbon nanotubes and fullerenes

(n,m)

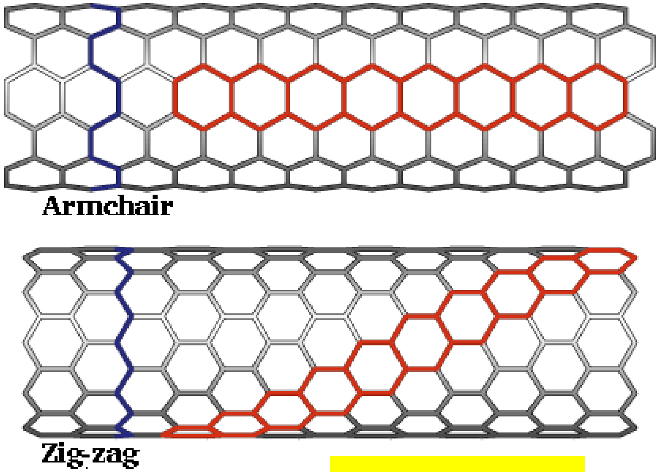


C-60





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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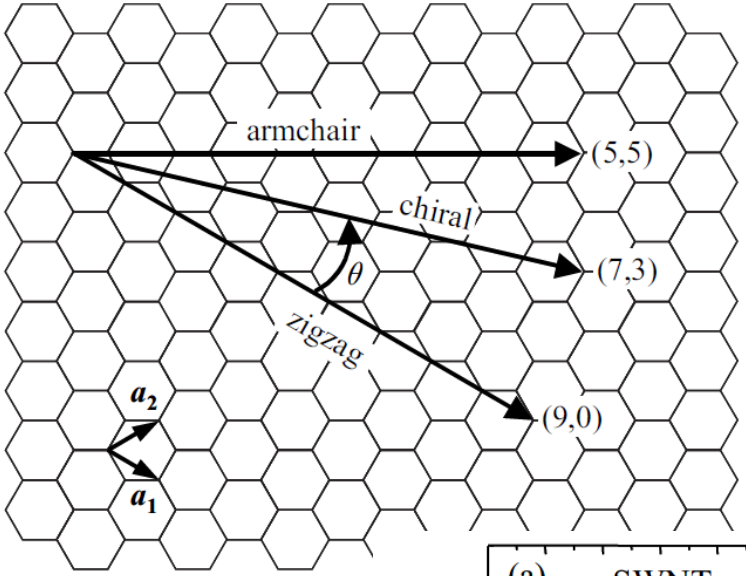
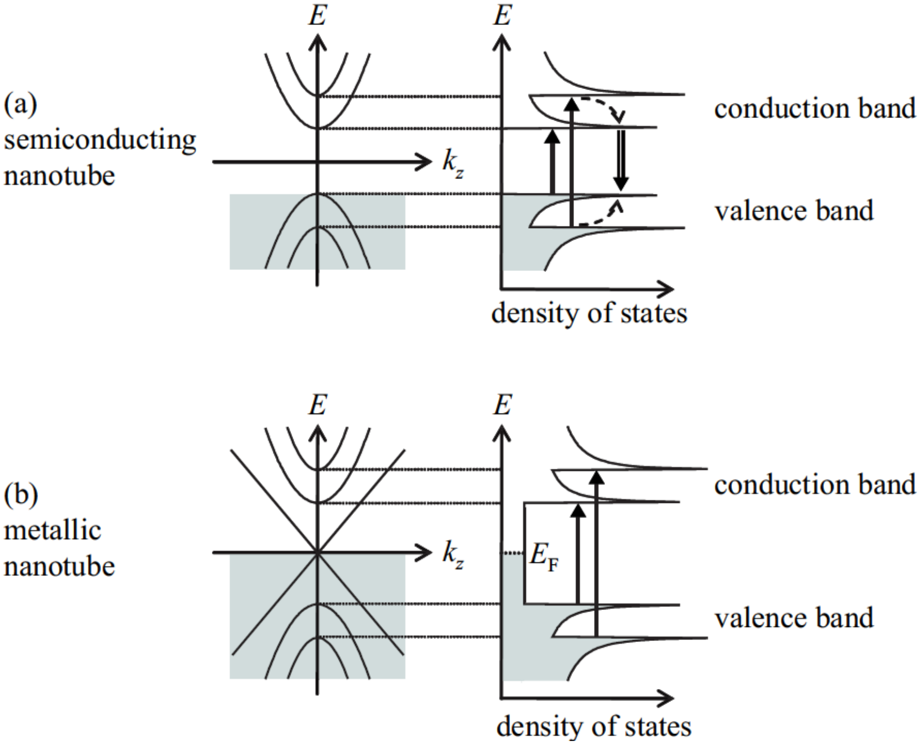
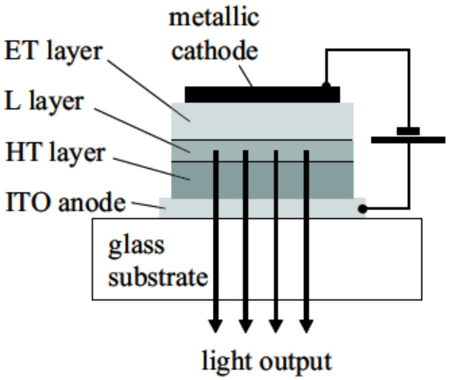
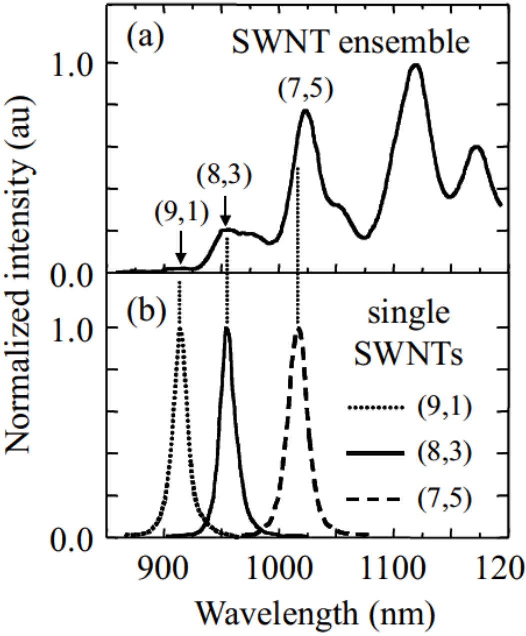
(n,m)

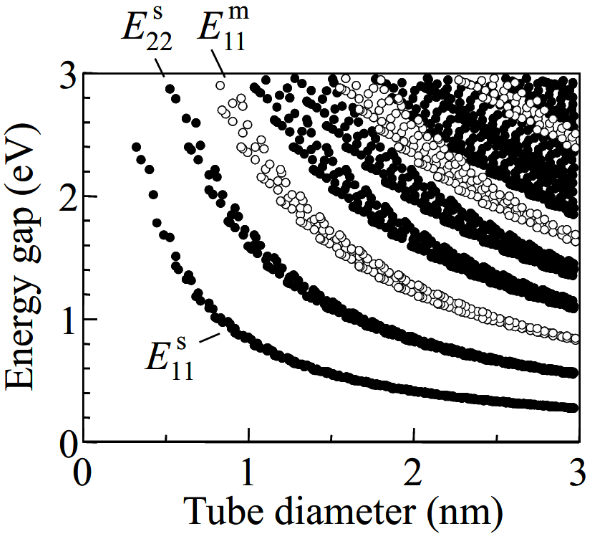
Carbon nanotubes: electrical properties











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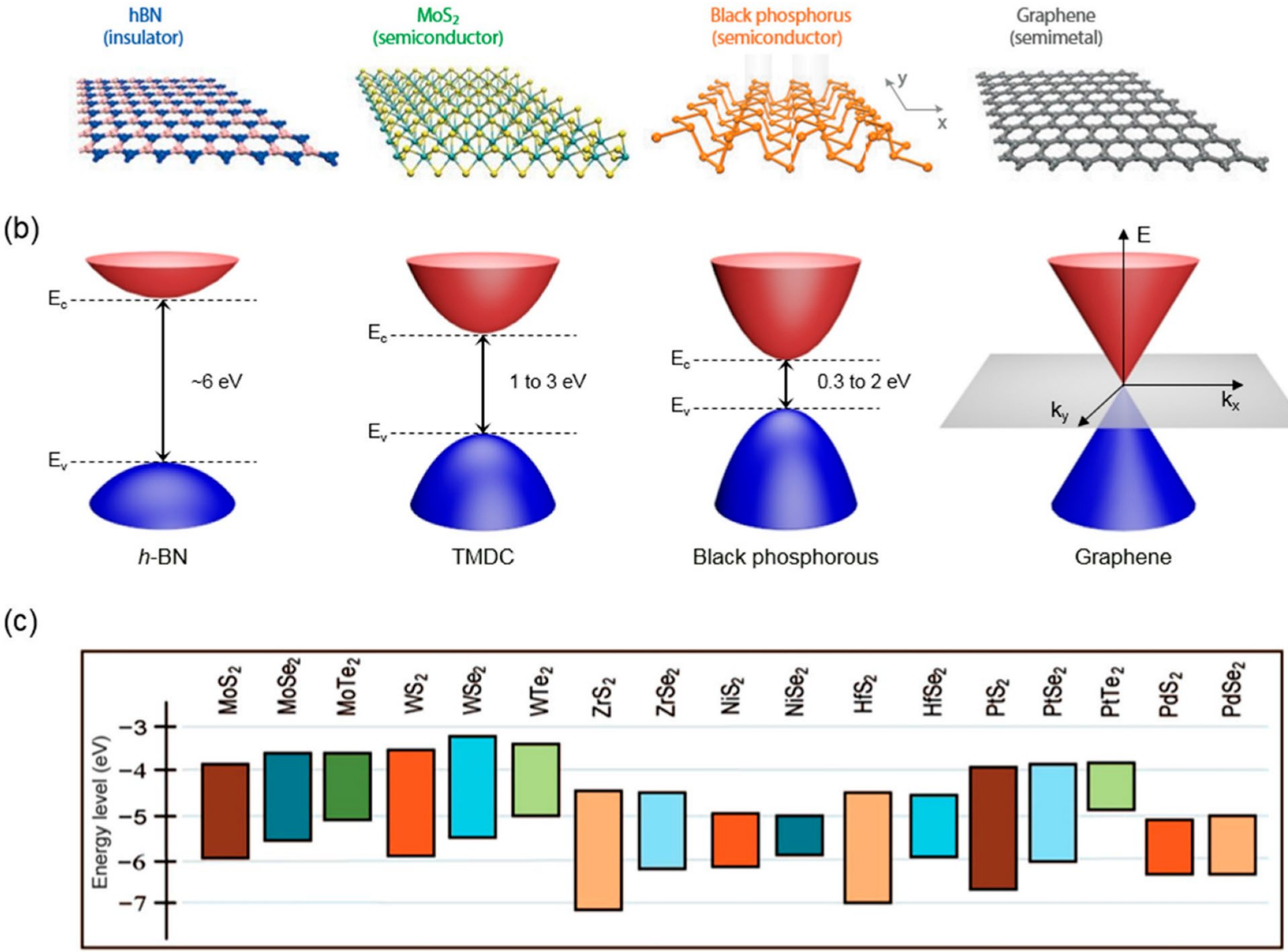
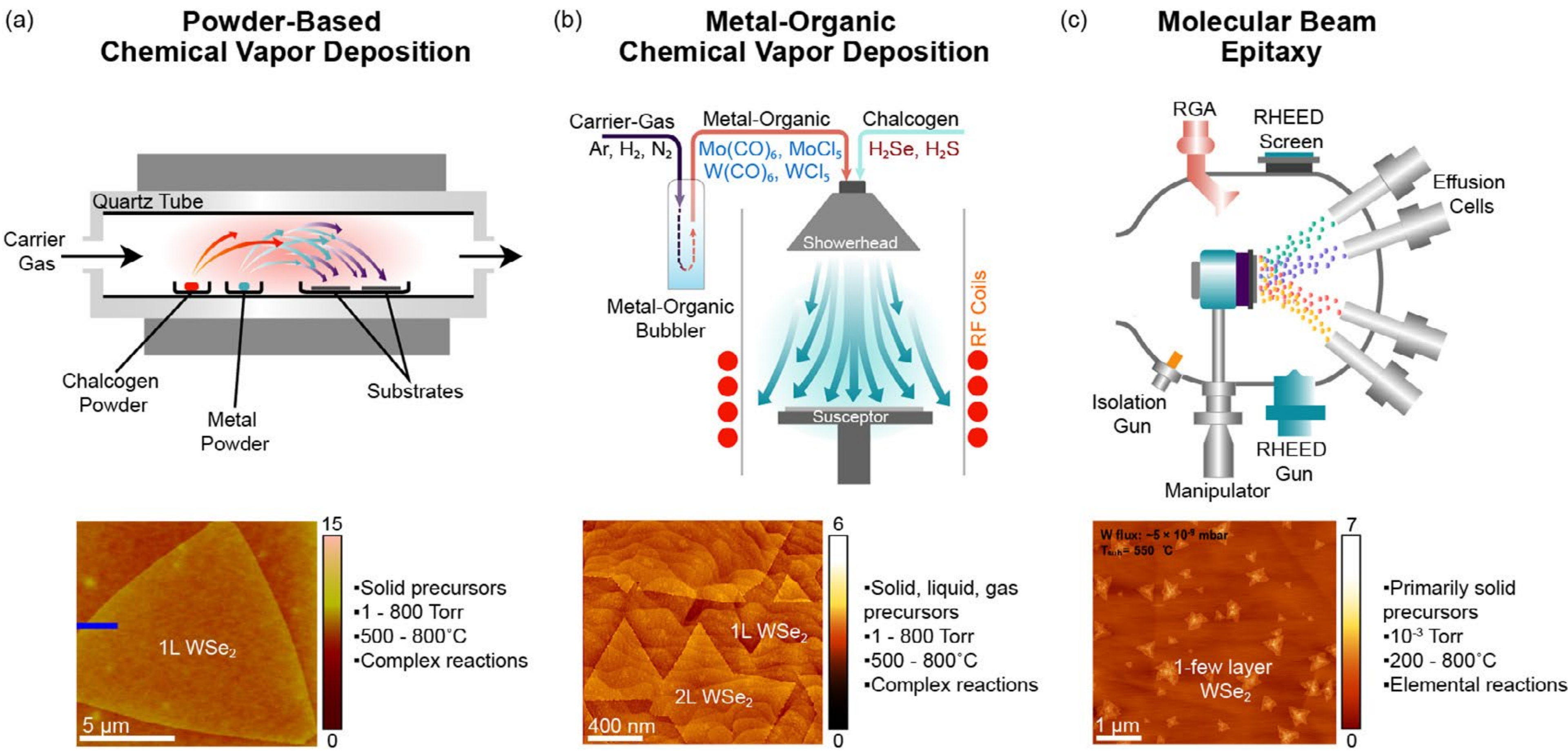
Two-dimensional semiconductors

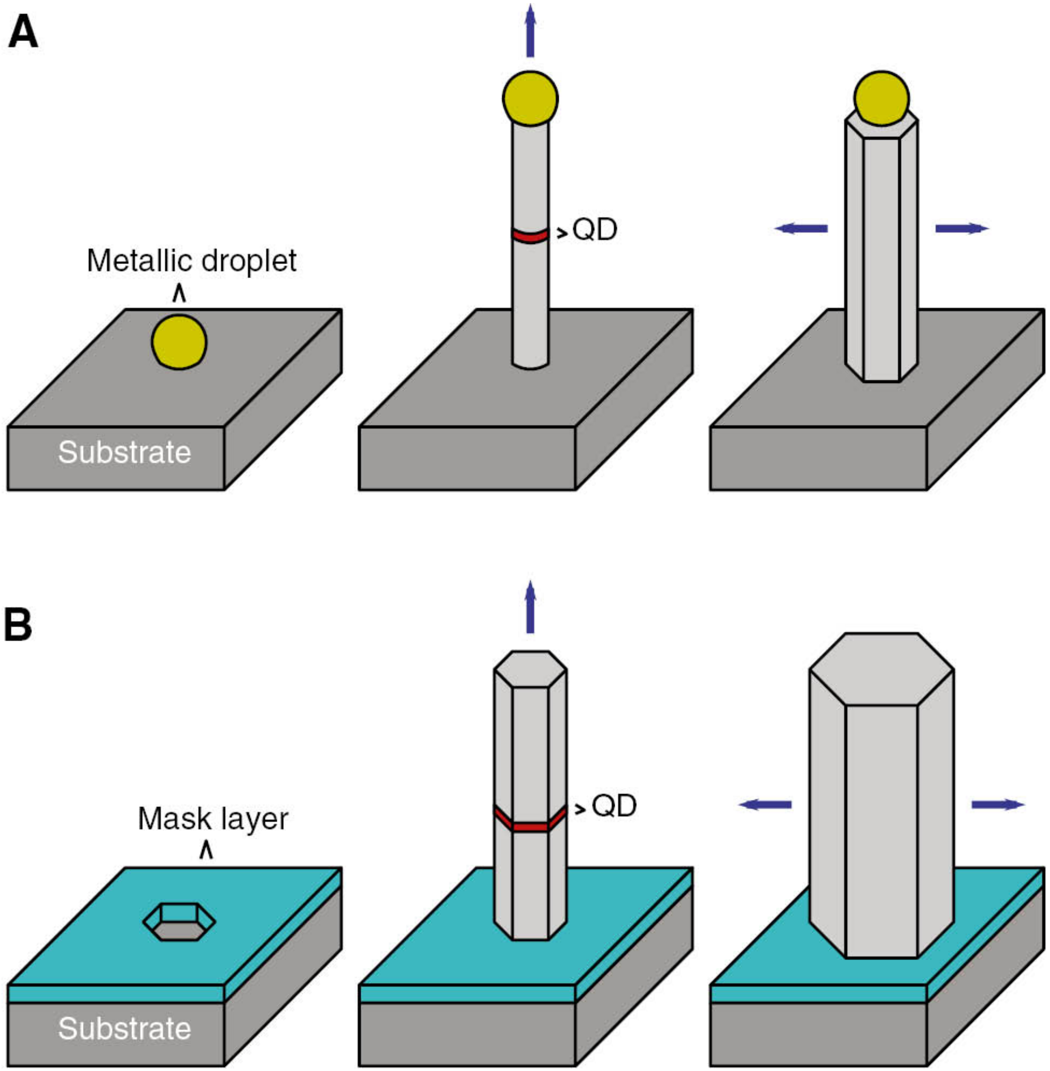


Two-dimensional semiconductors: WSe_2, $MoSe_2$



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

Growth of vertical quantum wires

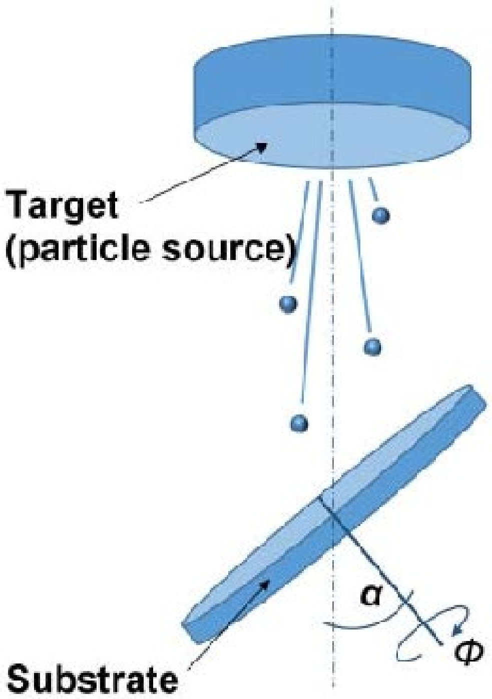


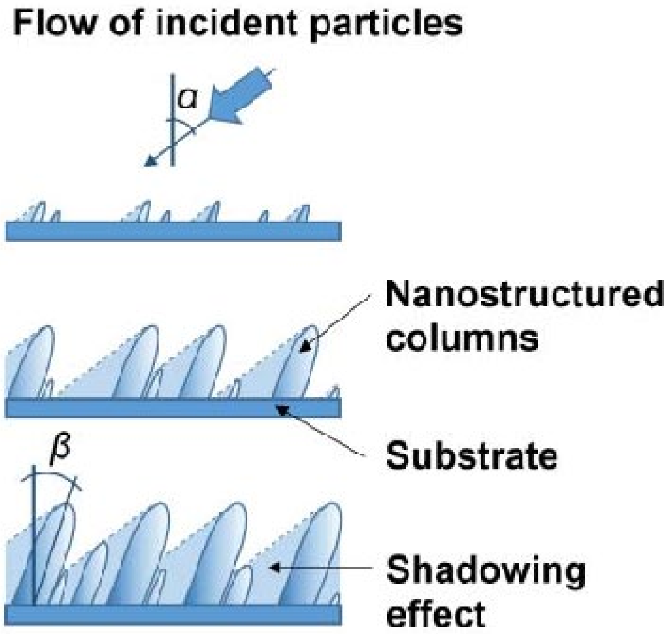
Vapor-liquid-solid

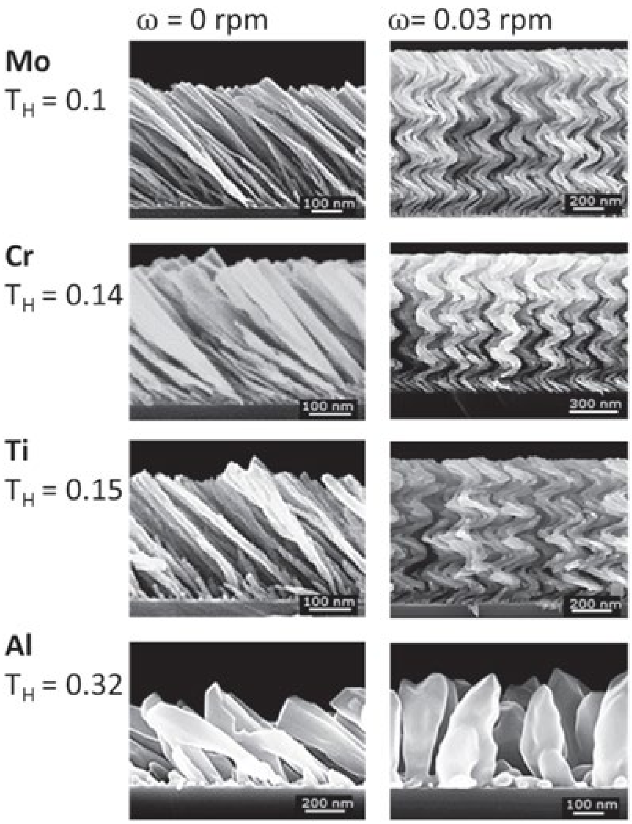
Selective area epitaxy

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

Glancing angle deposition (GLAD) of quantum wires



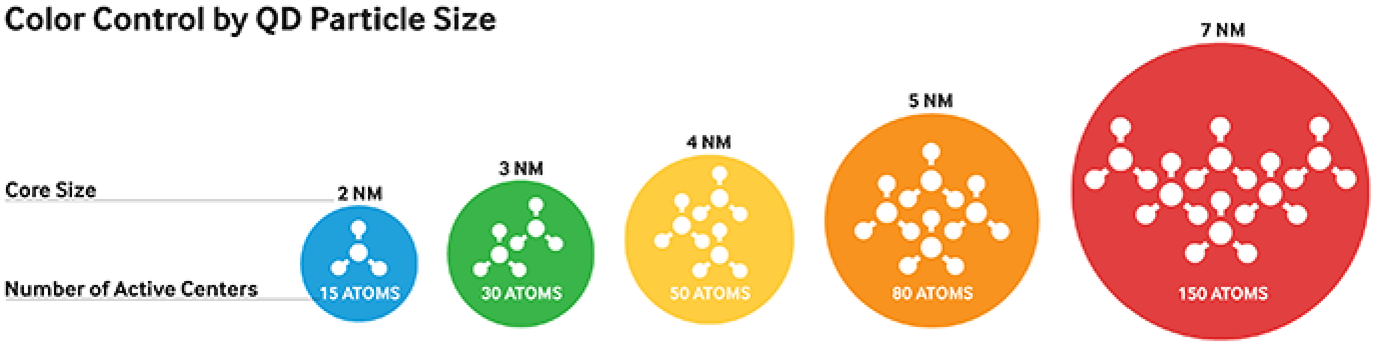


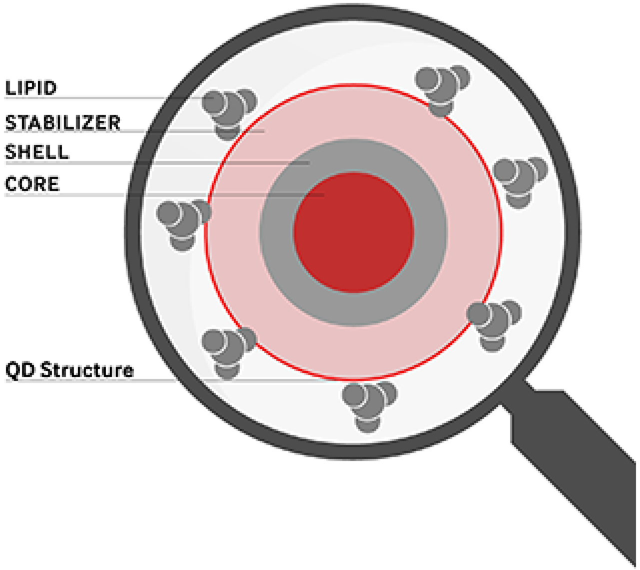


Initial imperfections on the substrate

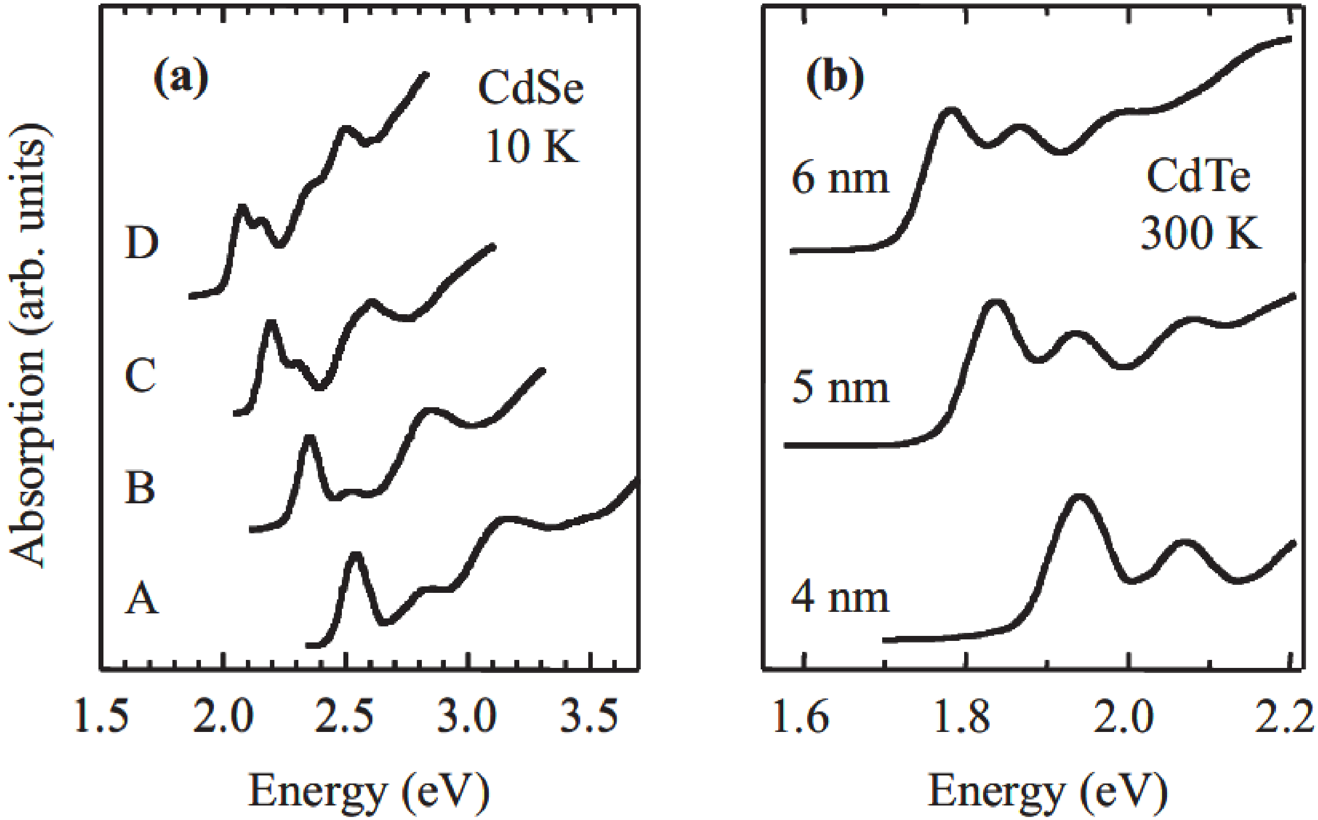
Shadow effect leads to tilted column growth.

Colloidal quantum dots





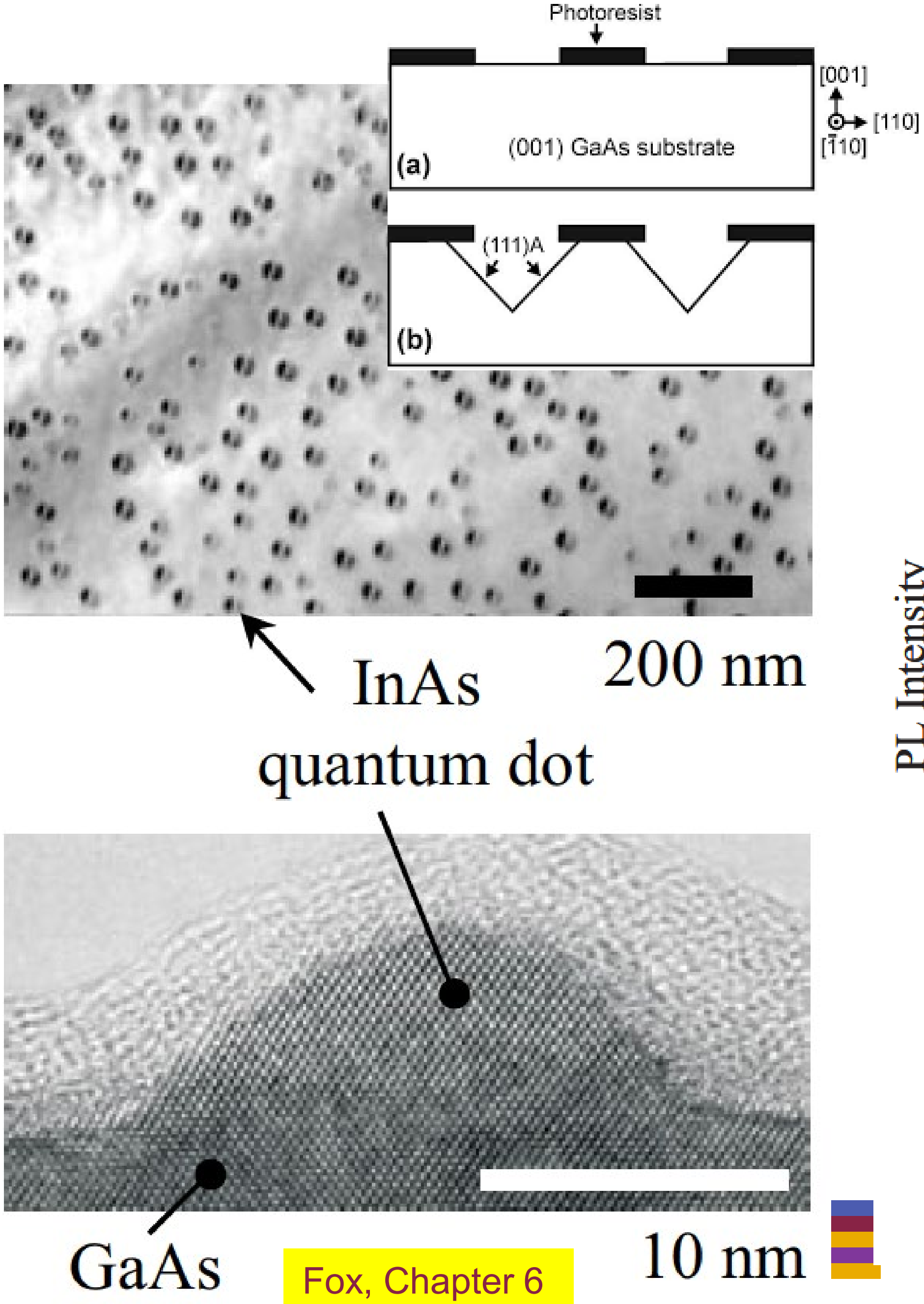
Colloidal quantum dots



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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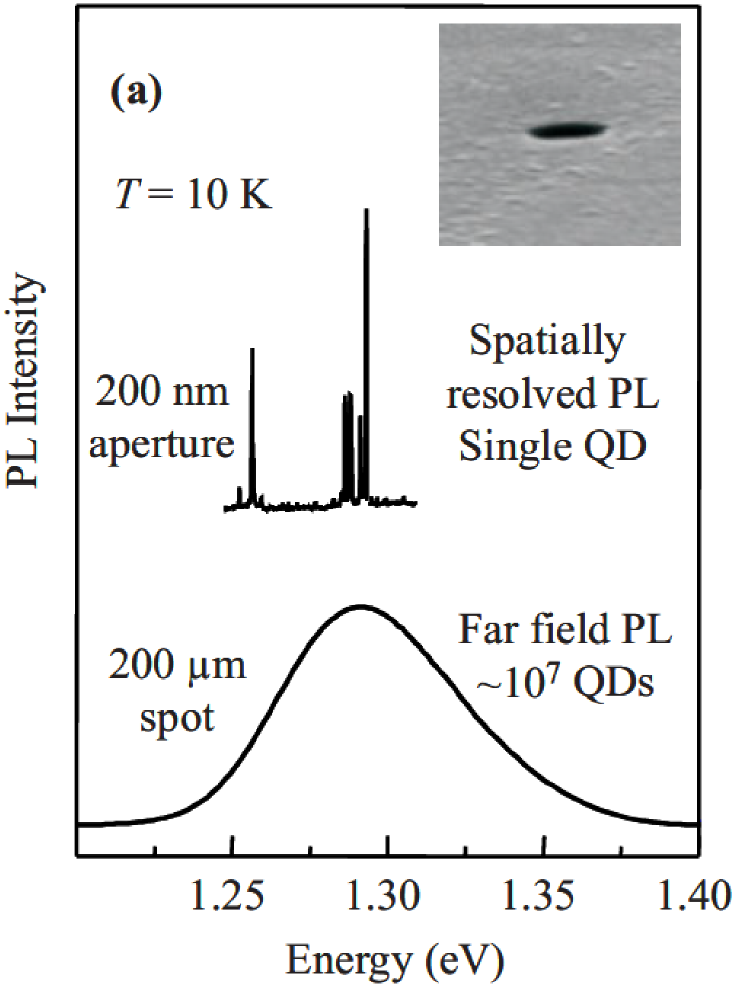
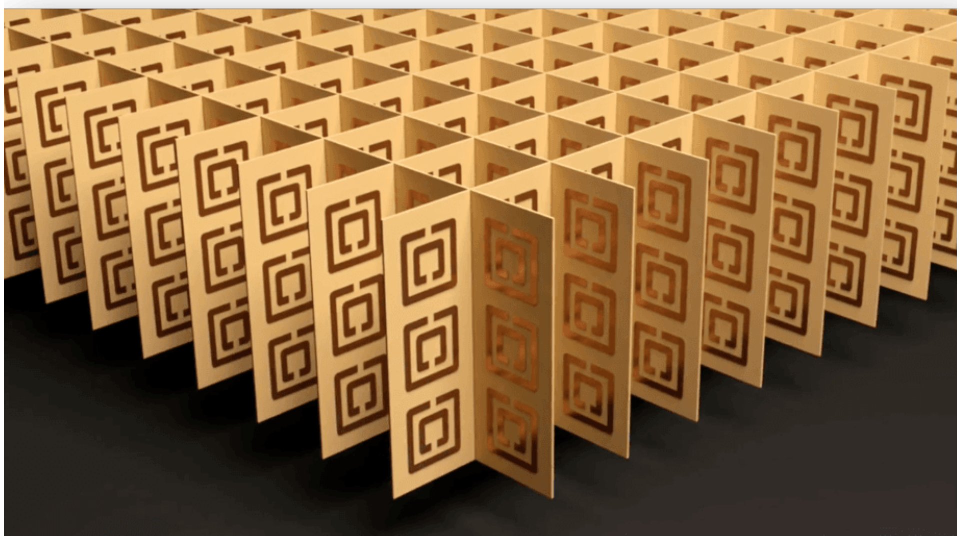
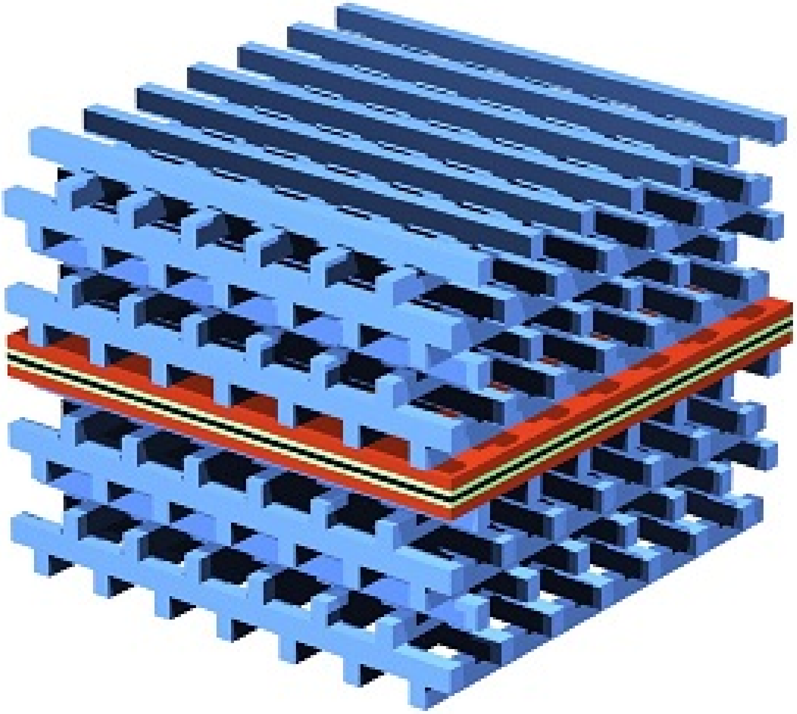
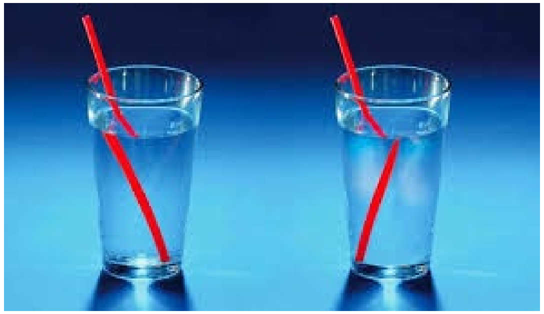


Metamaterials







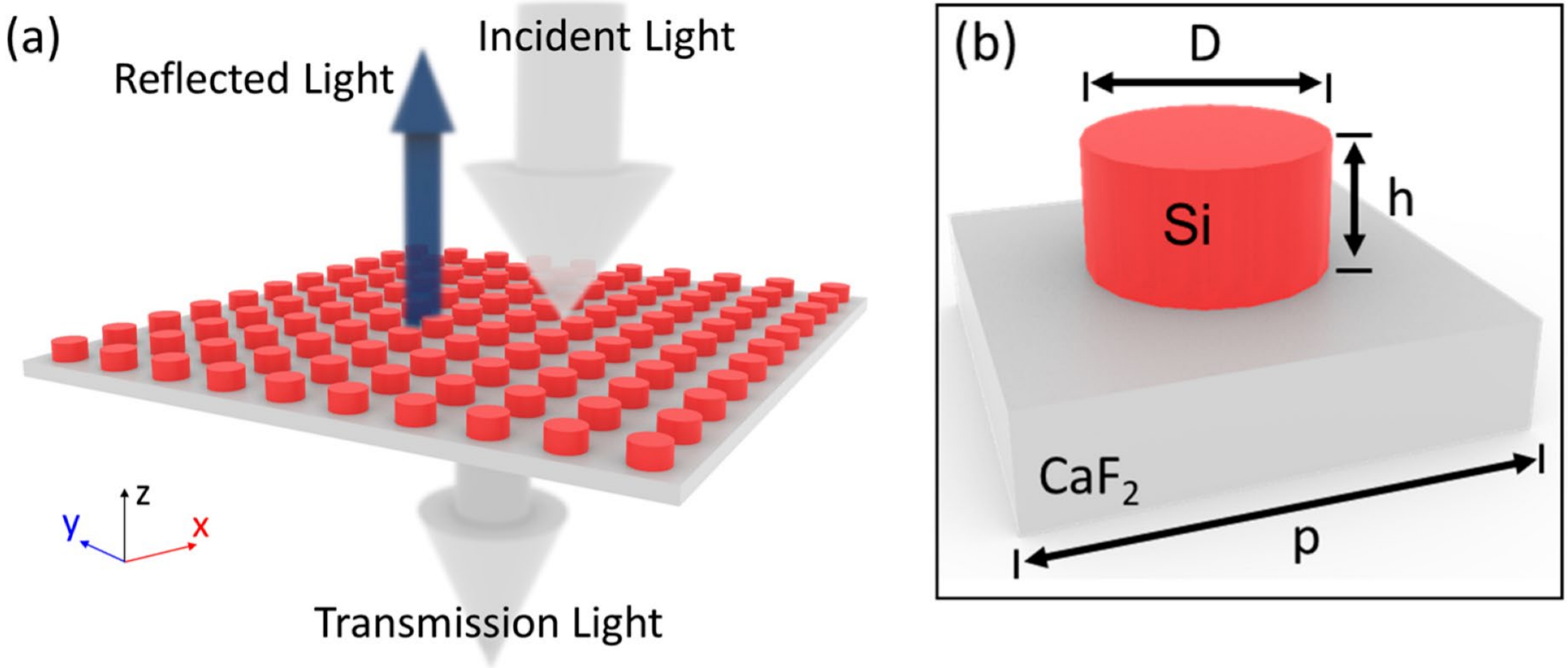
Faraday: $\vec{k} \times \vec{E}_0 = \omega \mu \mu_0 \vec{H}_0$

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

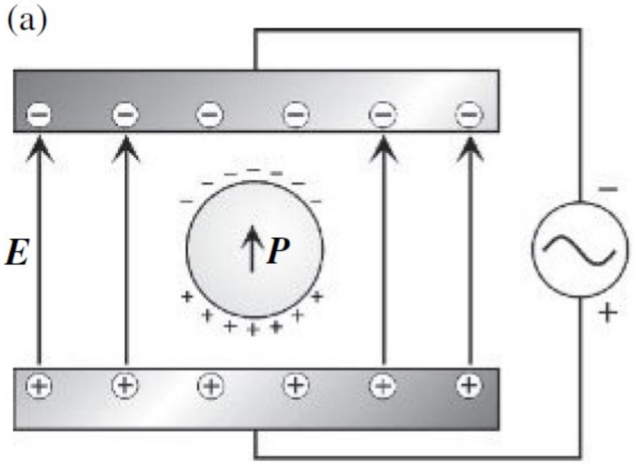


Metasurfaces can be designed to have reflection, absorption, and emission properties not possible in homogeneous materials. Especially useful for sensors and antennas.

Modeling Metamaterials and Metasurfaces

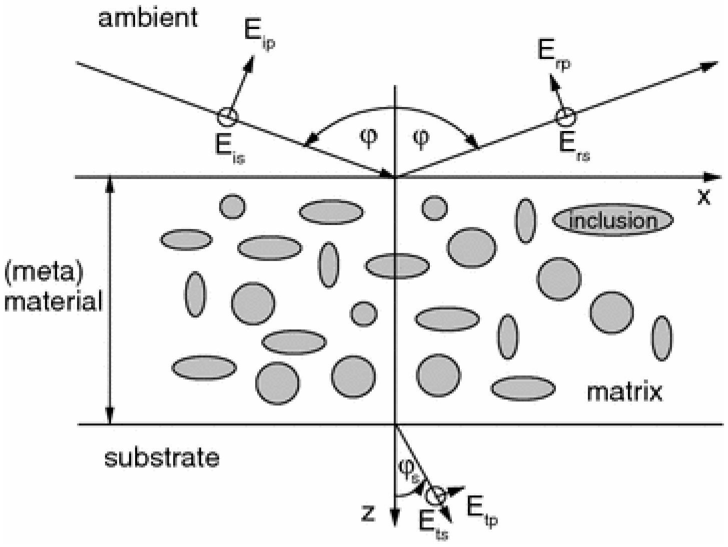
Bruggeman effective medium approximation (BEMA)

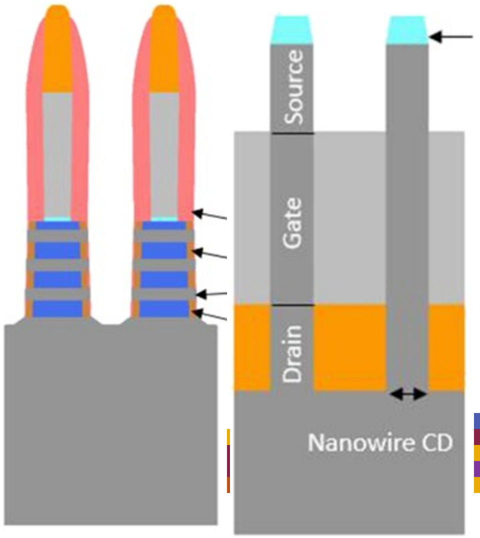
$$\sum_{i=1}^{n} f_i \frac{\varepsilon_i - \varepsilon}{\varepsilon_i + 2\varepsilon} = 0$$

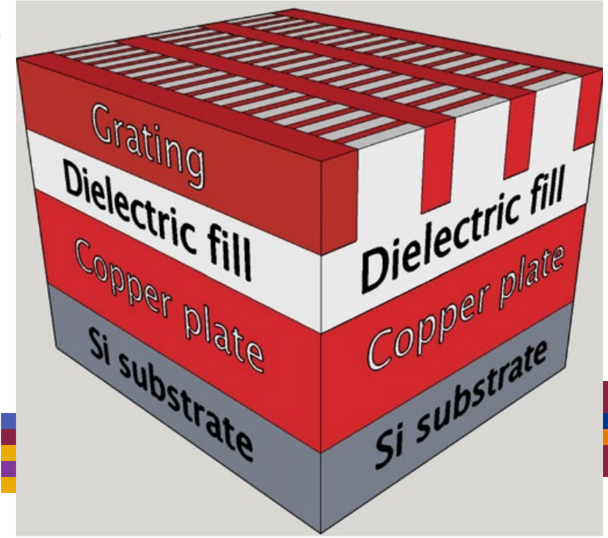


Rigorous coupled wave approximation:

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

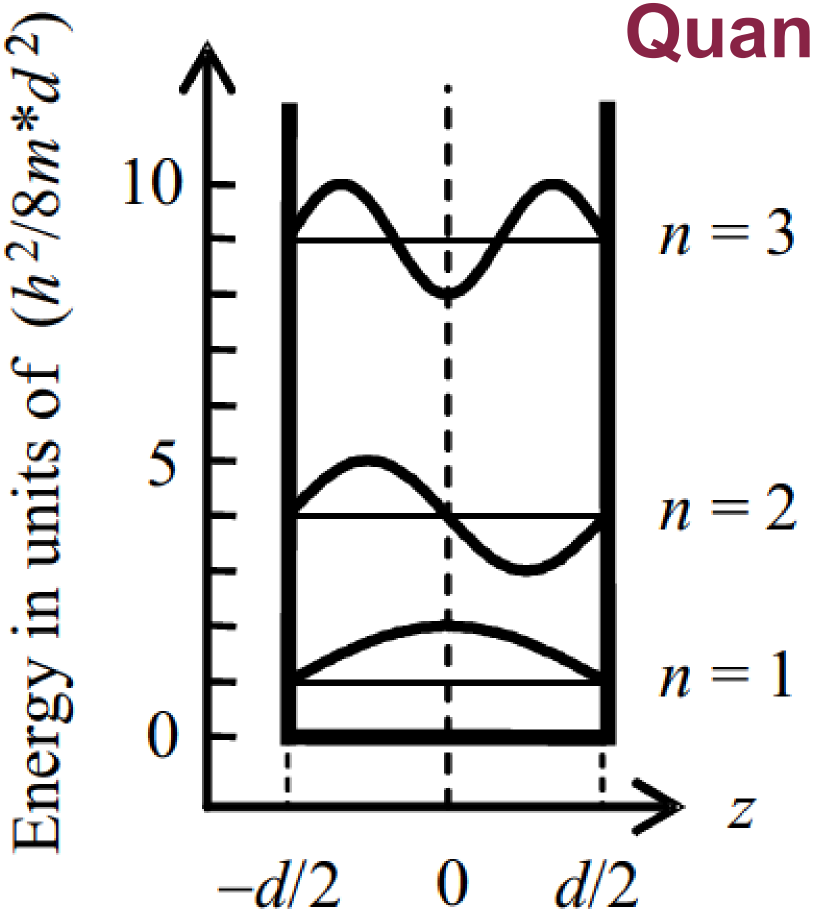






Schmidt, JAP **114**083519 (2013)
Diebold, APL Mater. **6**, 058201 (2018)

Quantum well with infinite barriers

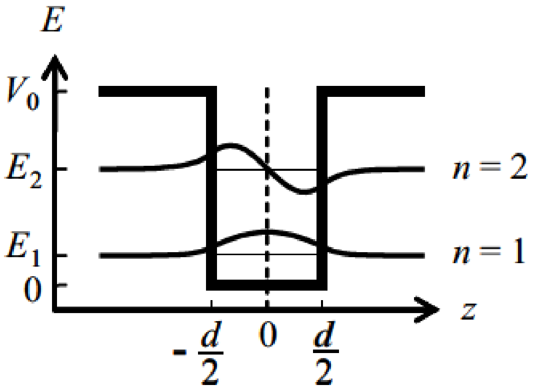


$$\Psi(x,y,z) = \psi(x,y)\varphi(z)$$

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

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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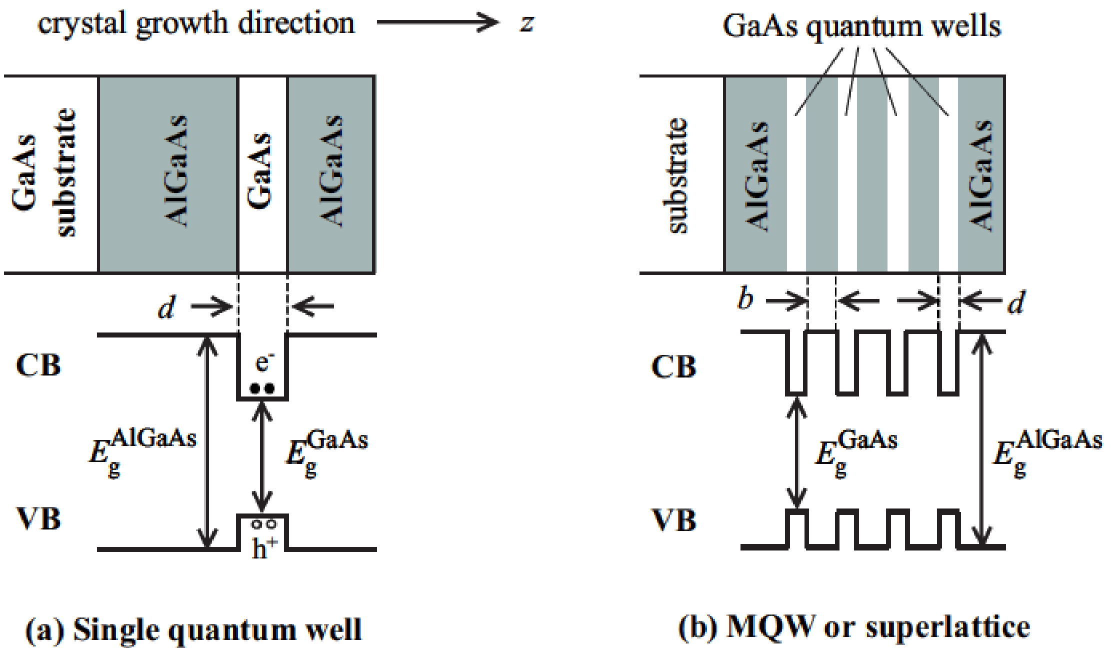
Quantum wells and superlattices (or MQW)



(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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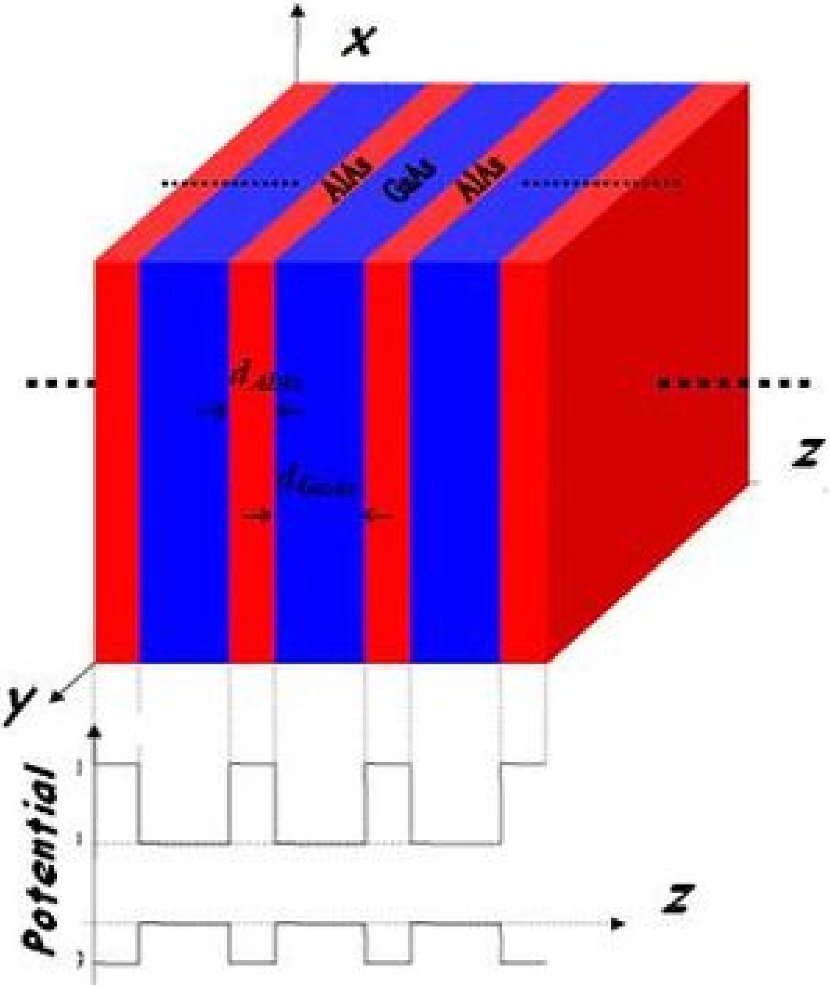
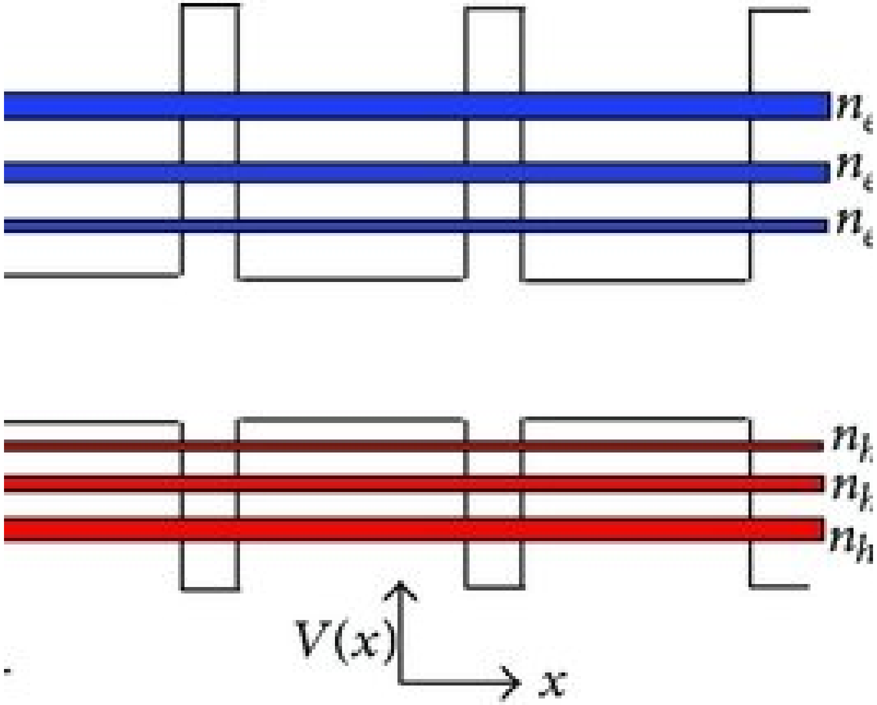
Superlattice minibands



CB

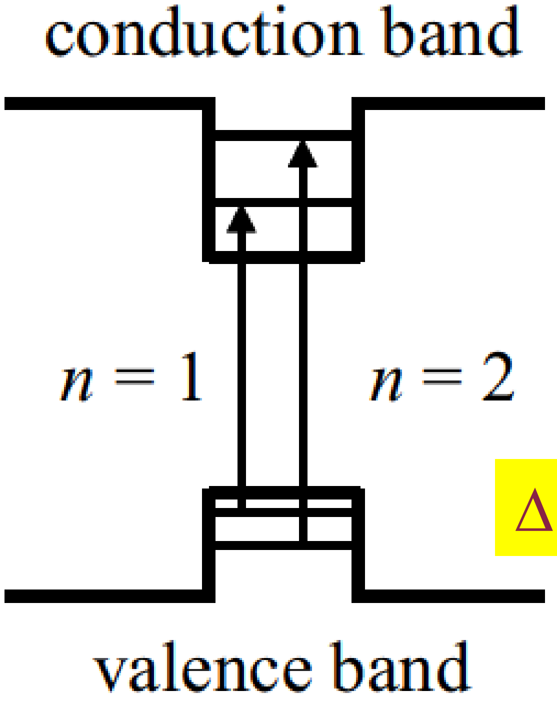


VB

Enhanced absorption/emission in quantum structures

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

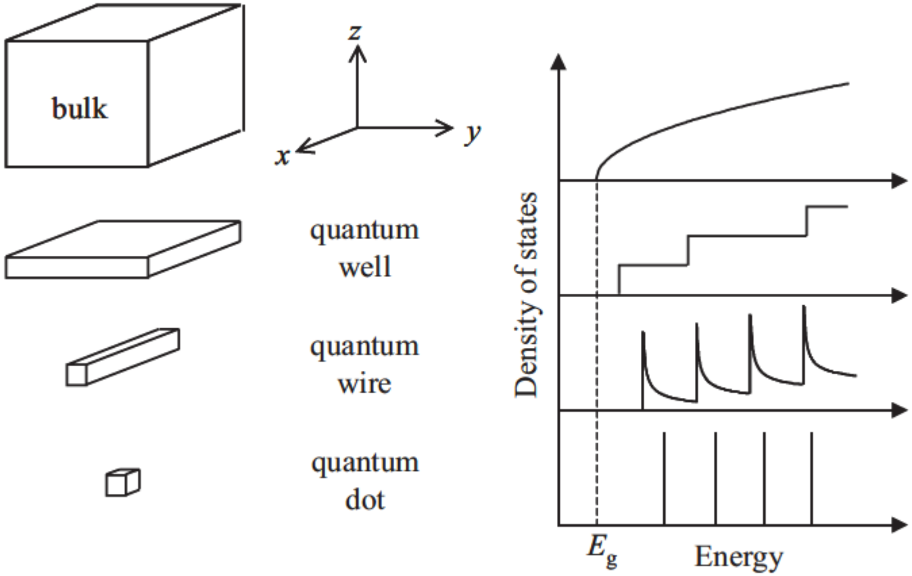
Confinement enhances overlap matrix element



(l=0)

Δn=0

(l=1)



Modified density of states

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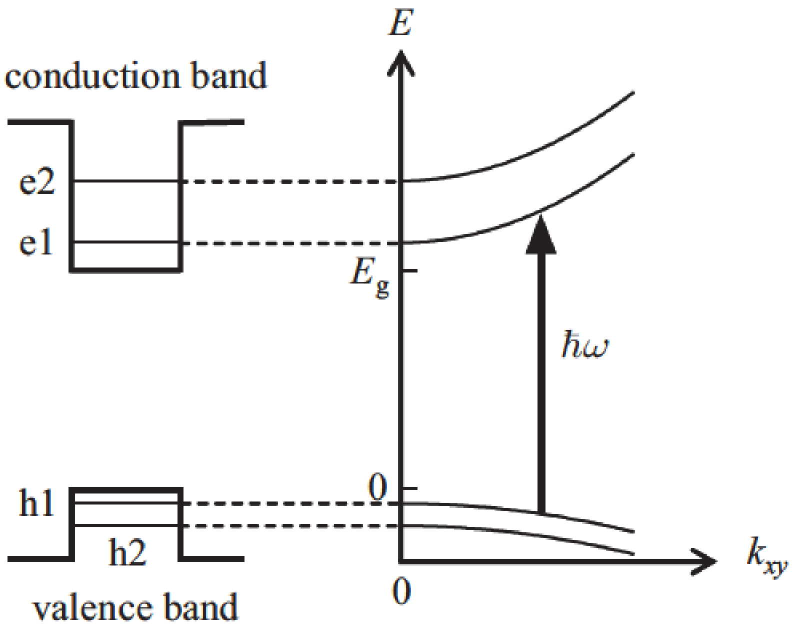
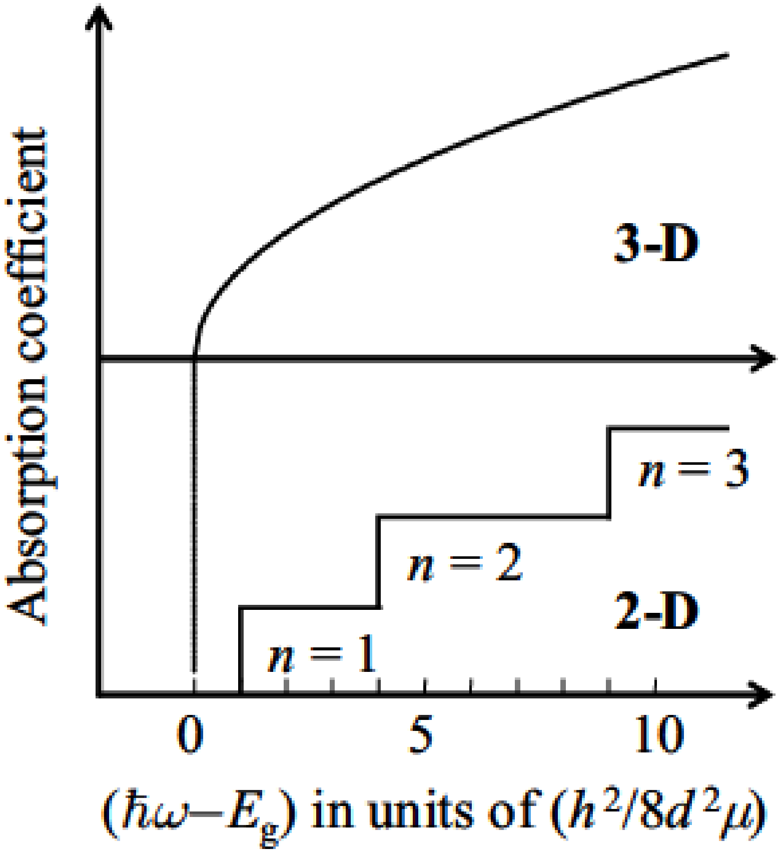
Quantum well absorption



Electron and hole subbands



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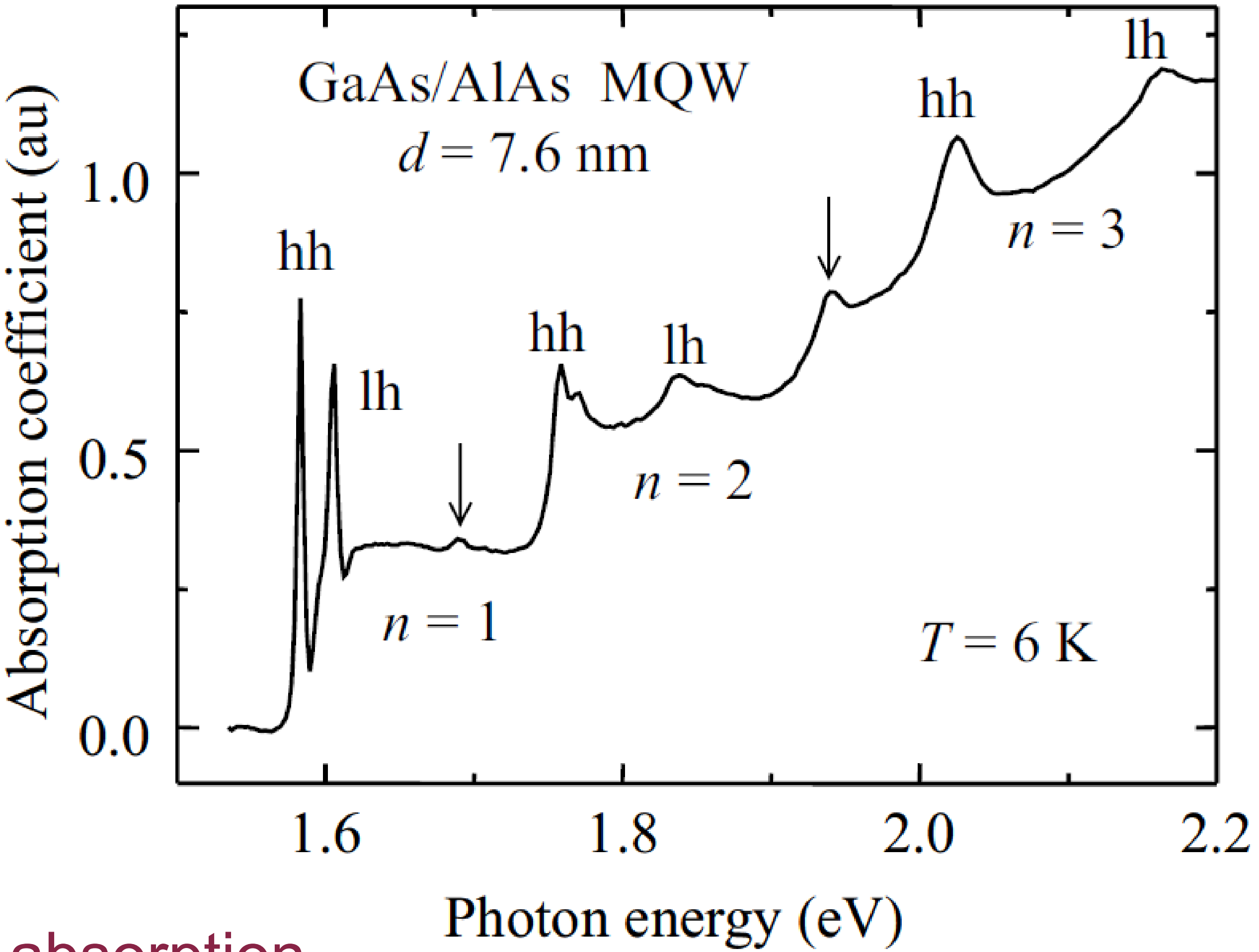
Quantum well absorption in GaAs/AlAs MQW



Steps: 2-D absorption

Peaks: Discrete excitons (arrows show forbidden transitions)

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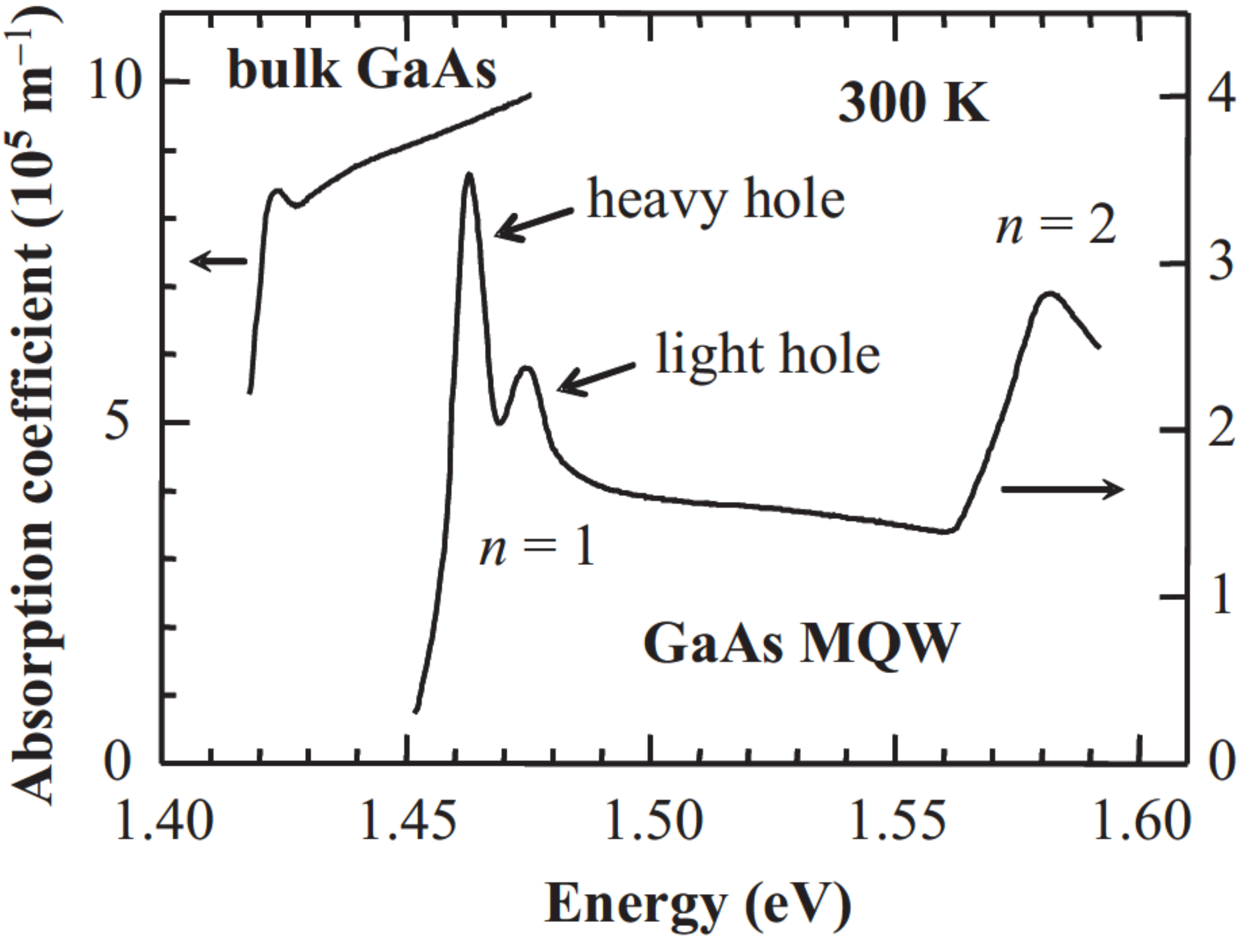
Excitonic effects are enhanced in quantum wells



Bulk GaAs:
R_X=4.2 meV

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

hh/lh splitting:
Confinement or strain ???

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

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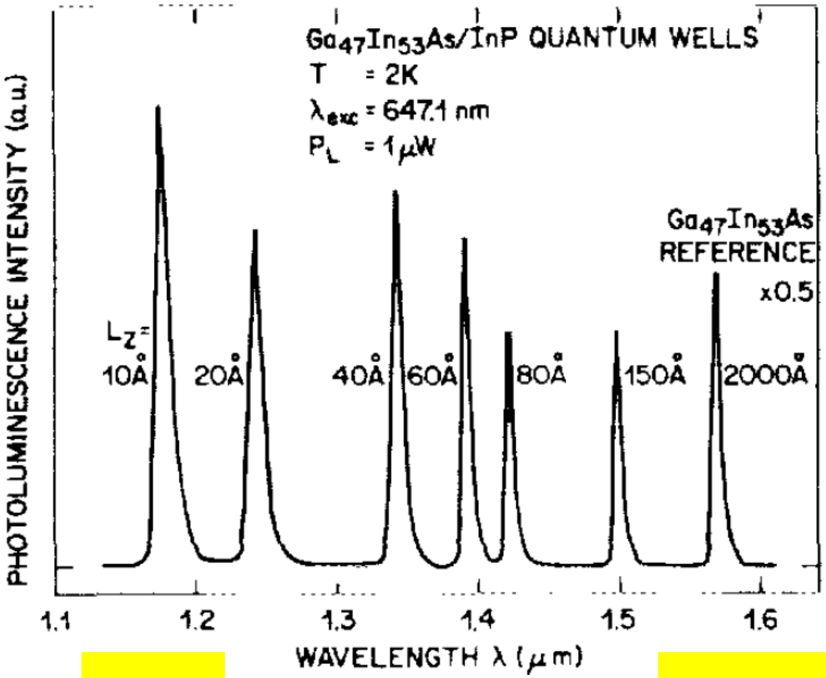
Confinement shifts in quantum wells

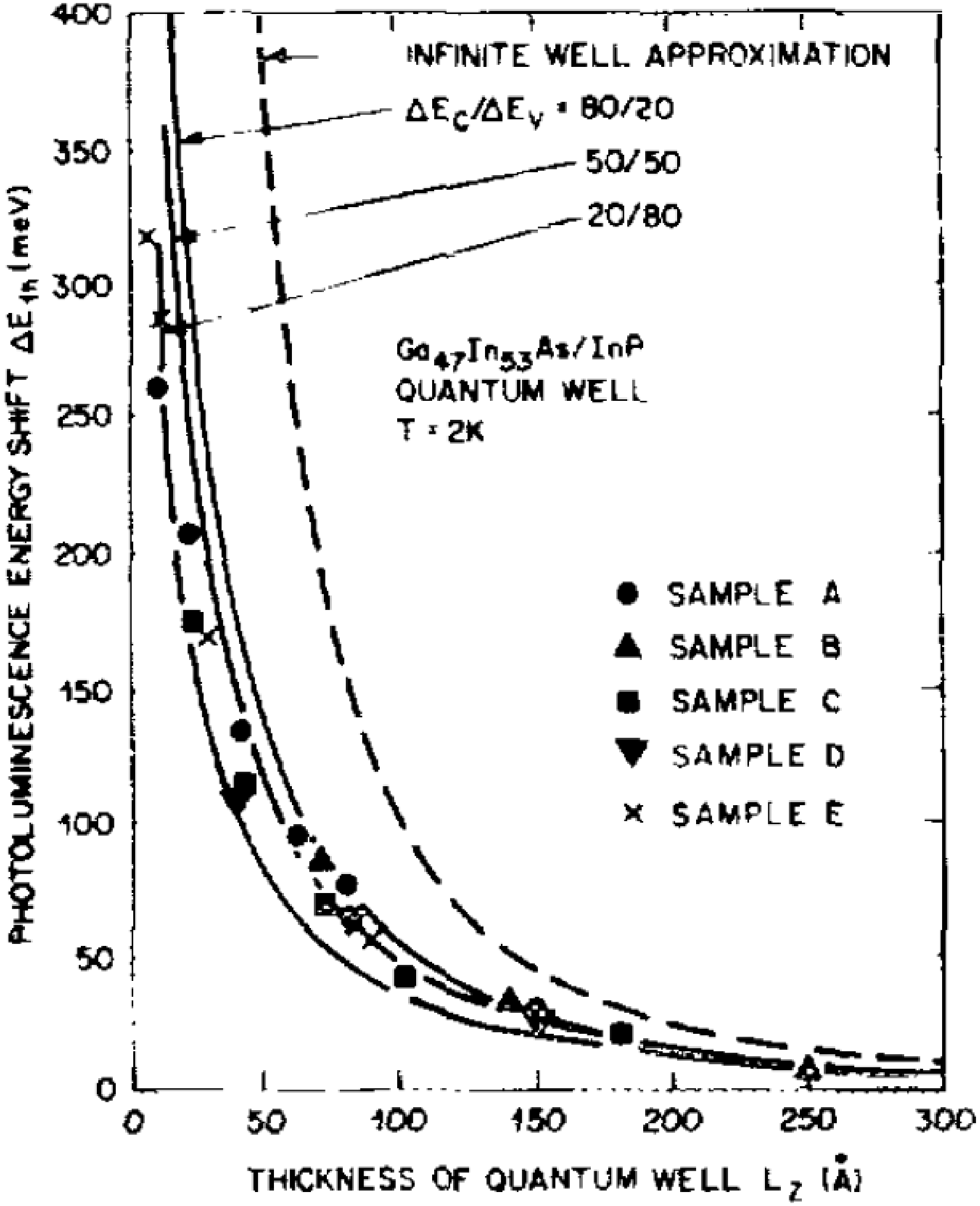
$$\hbar\omega = E_g + E_{hh1} + E_{e1}$$



thin

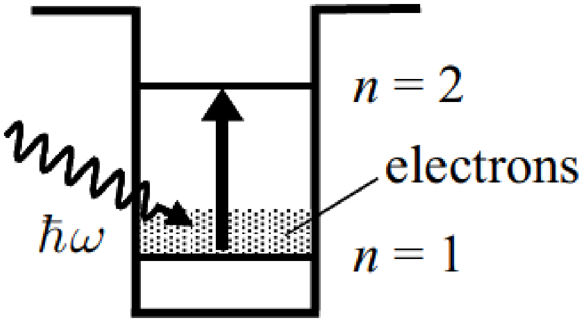
thick

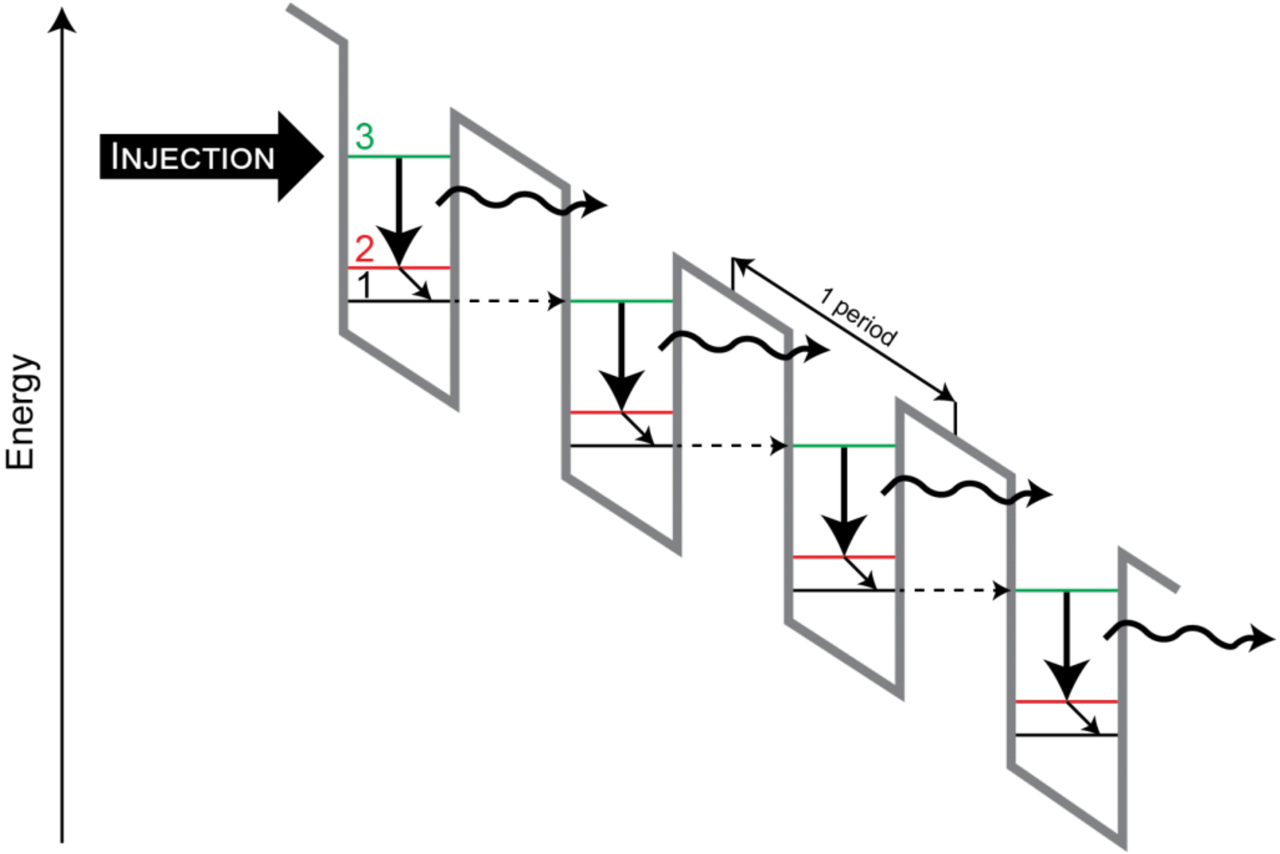
$$\Delta E = \frac{\hbar^2}{2m}\left(\frac{n\pi}{d}\right)^2$$



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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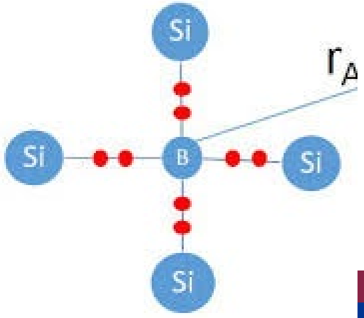
Defects

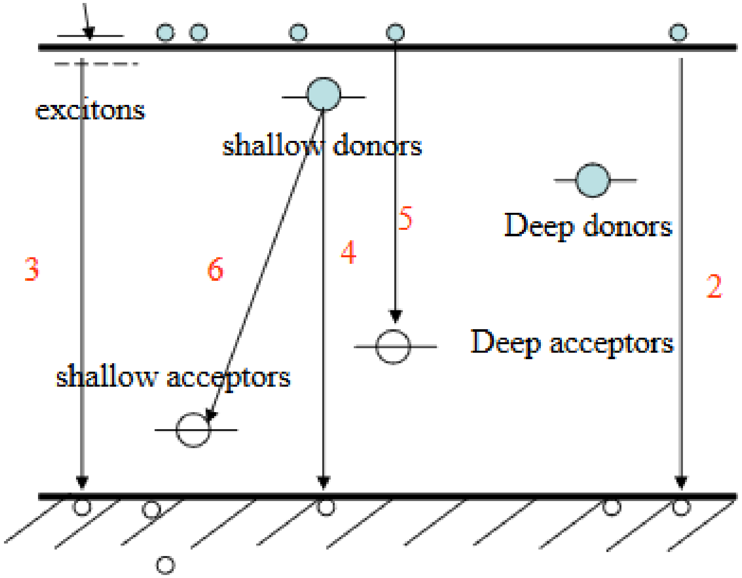
Vacancy	V_A	missing atom
Interstitial	I_A	extra atom between lattice sites
Substitutional	C_A	defect atom replaces host atom
Antisite		atoms are switched
Frenkel defect pair	V_A-I_A	atom moved to interstitial site

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

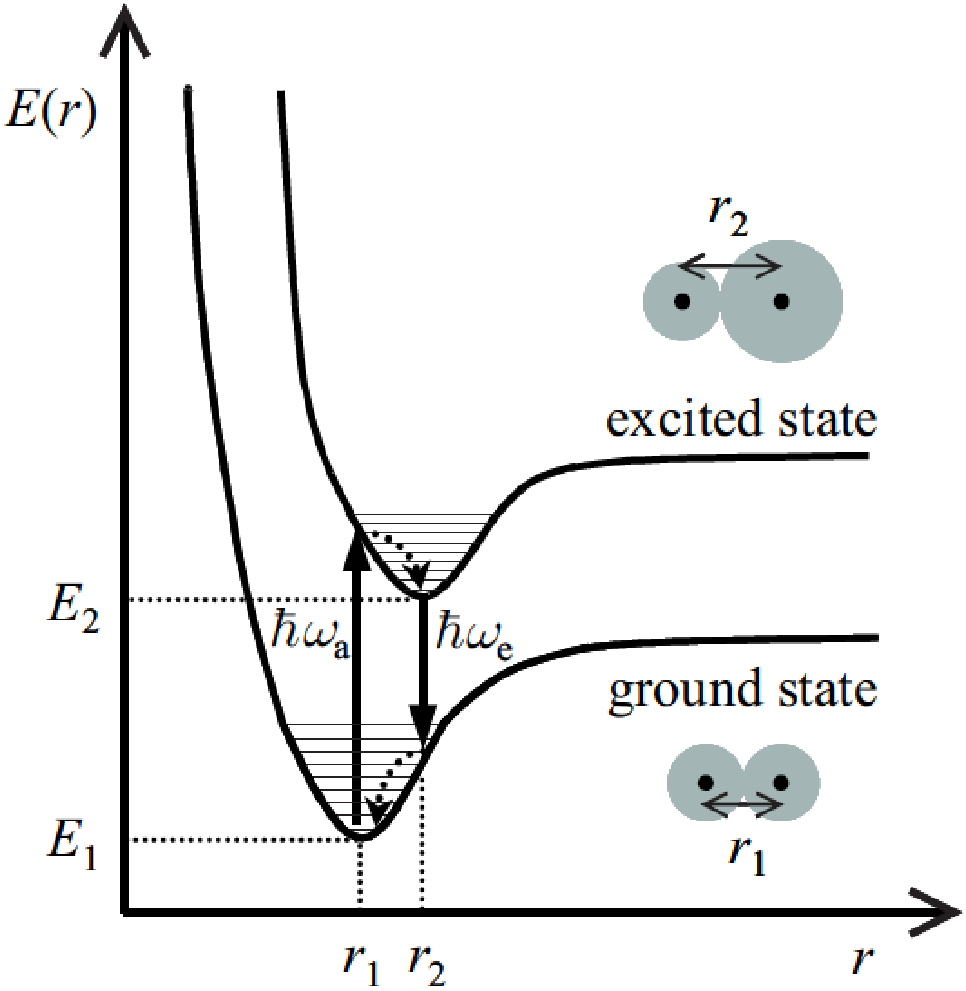
Shallow and **deep** defects.

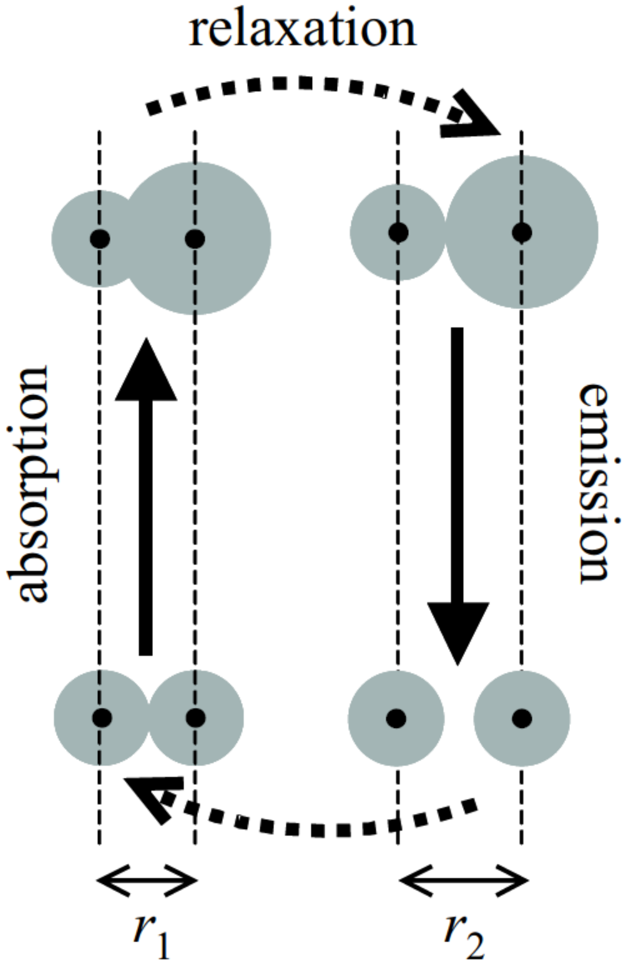




Yu & Cardona

Defects: Frank-Condon principle





Born-Oppenheimer approximation

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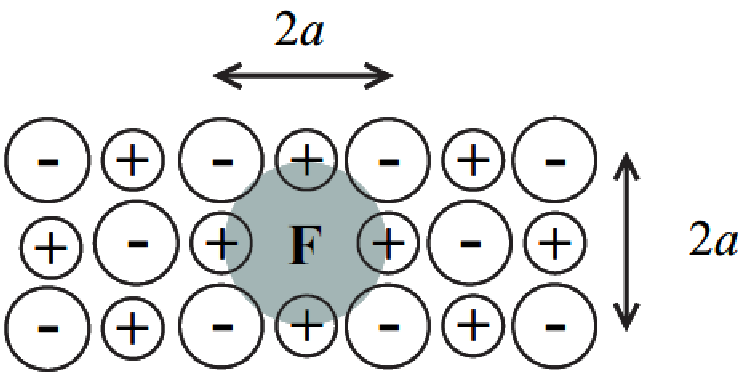
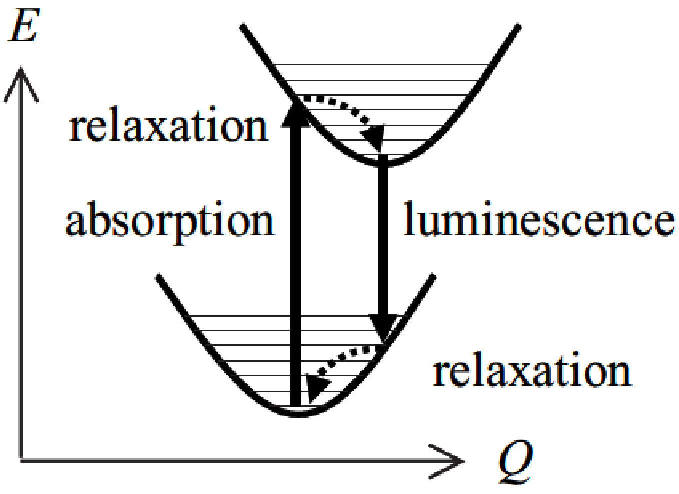
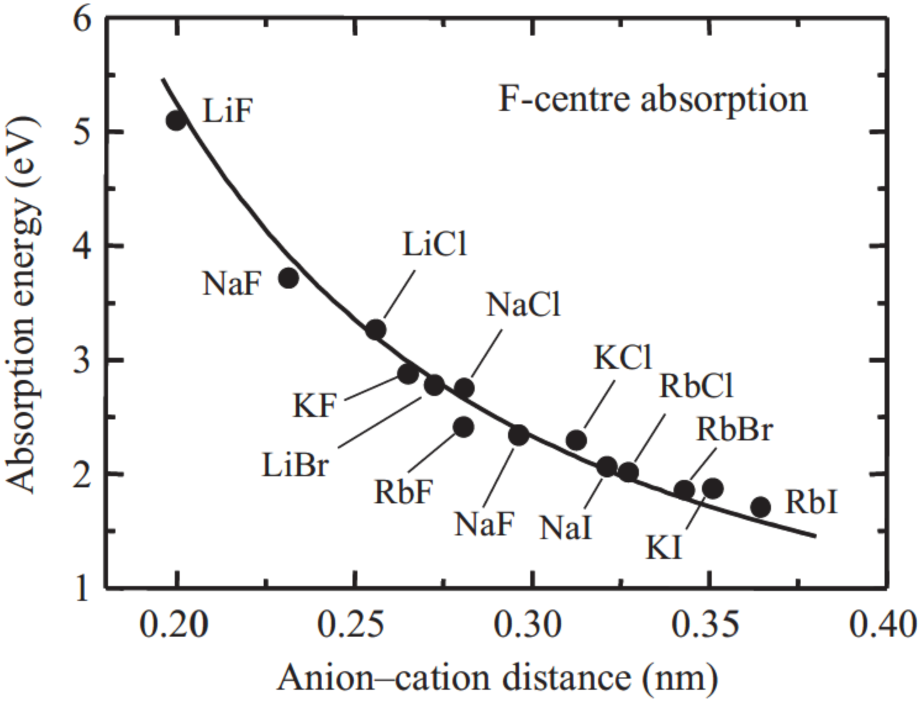
Defects: Color centers (F-centers)





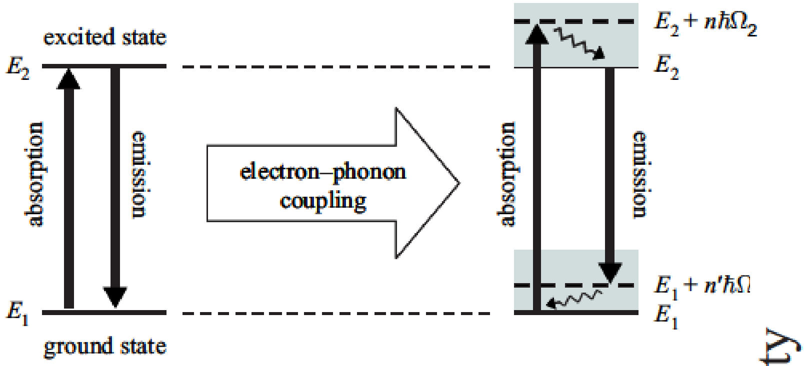


Alkali halide: large-gap insulator
Vacancy: positively charged hole

F-center: electron trapped at anion vacancy.

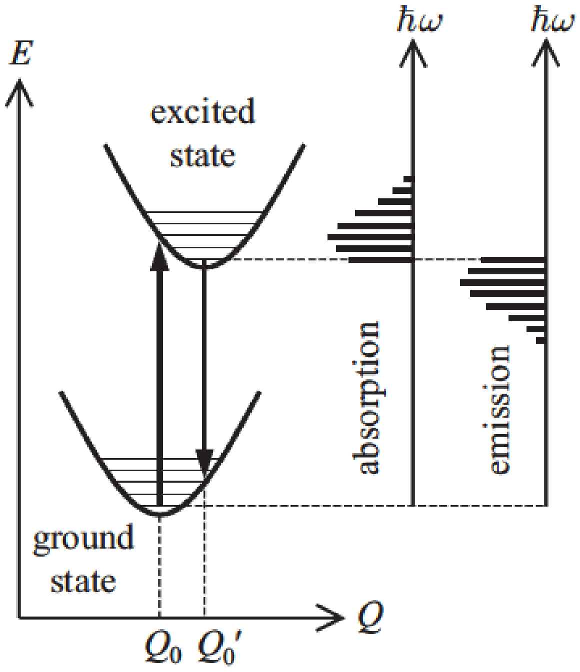
Fox, Chapter 9

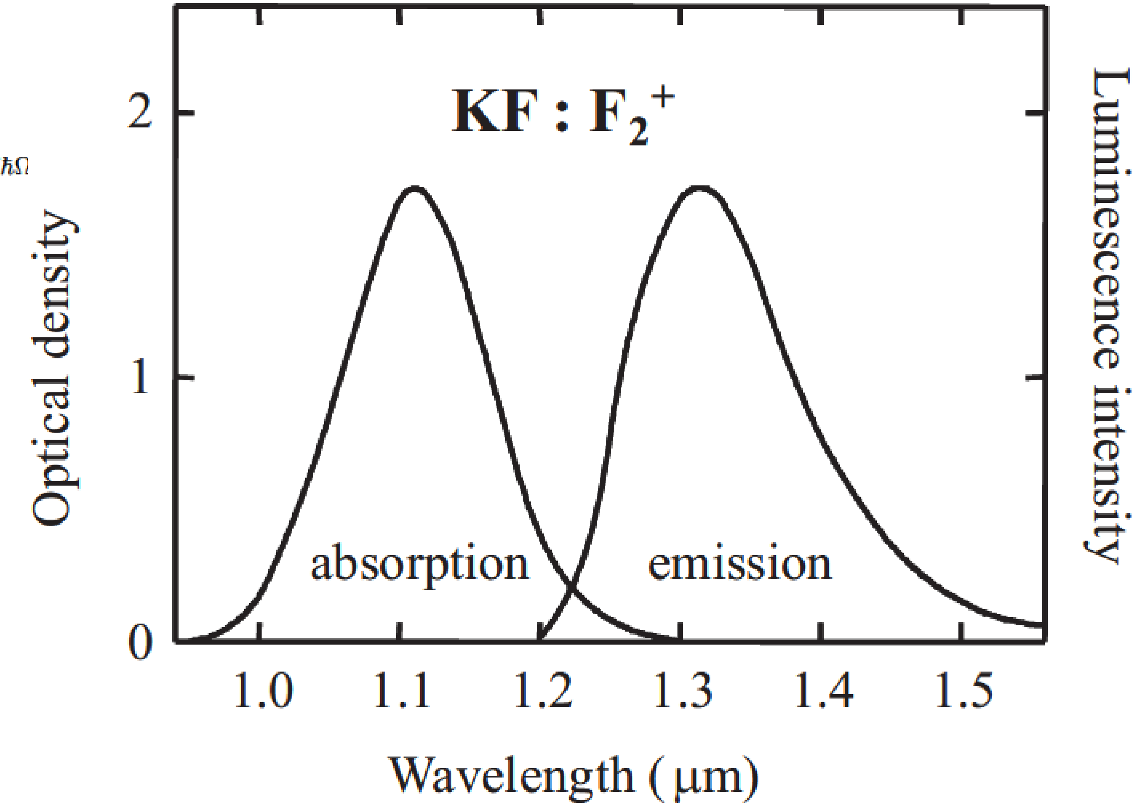
Defects: Shift between absorption and emission



(a) Isolated atom

(b) Atom doped into a vibronic solid





Two vacancies, one electron
Color-center lasers

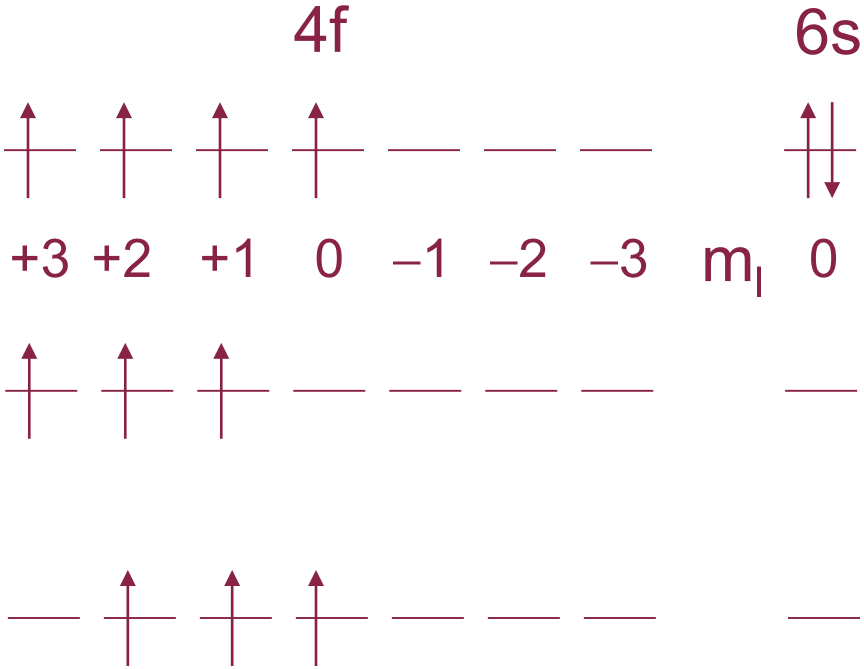
Fox, Chapter 8,9

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: $^4I_4$

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

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

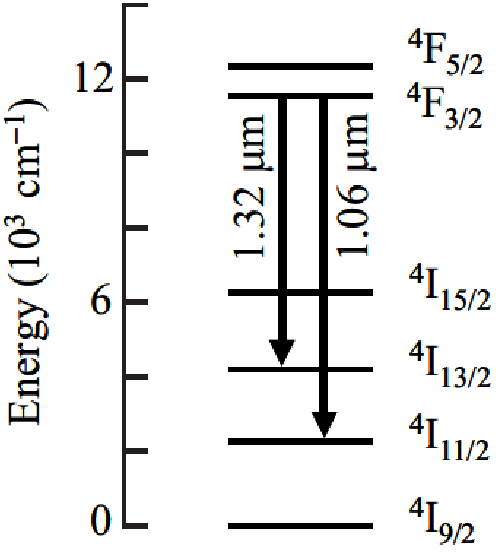
Nd^{3+}: $4f^3\ 6s^0$ S=3/2, L=6, J=9/2

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

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

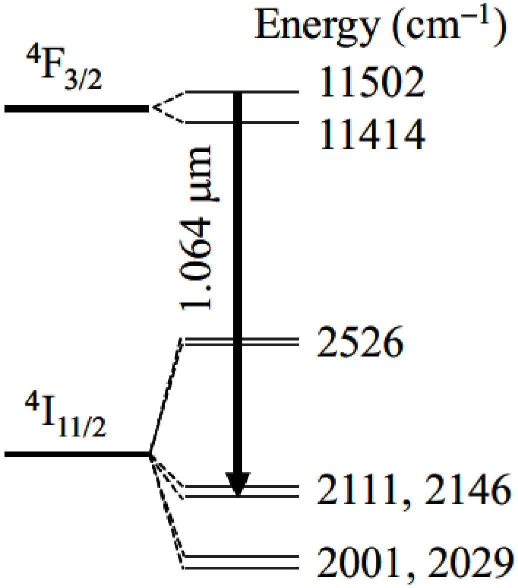
Fox, Chapter 9

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



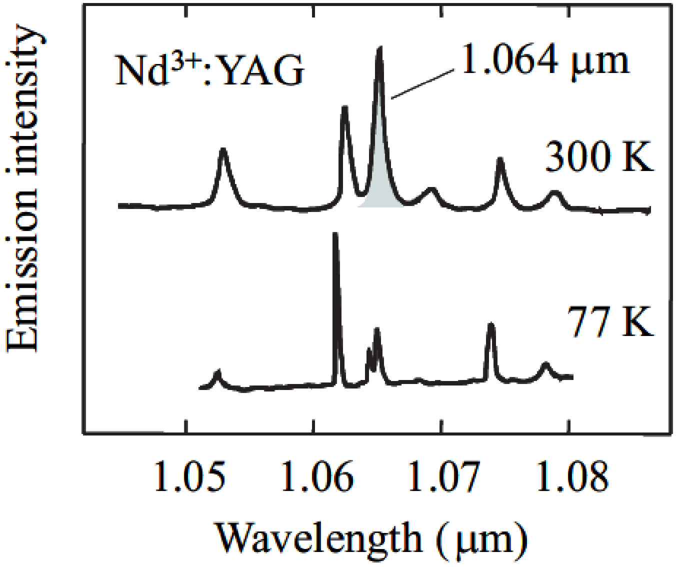
Atomic configuration

ΔJ=4 or 5 forbidden



Weak crystal-field splitting

Transition weakly allowed with crystal-field splitting



YAG: $Y_3Al_5O_{12}$

Nd:YAG lasers

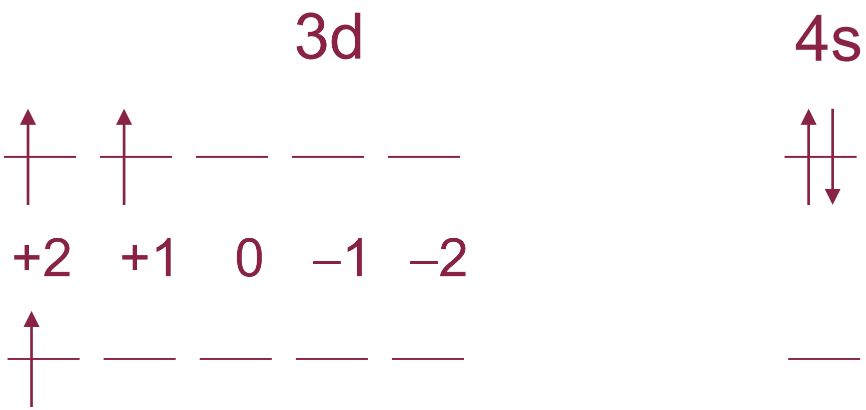
YAG: 1064 nm

$YLiF_4$: 1053 nm

Broad (120 GHz)

Fox, Chapter 9

Defects: Transition metal ions (Ti:sapphire)

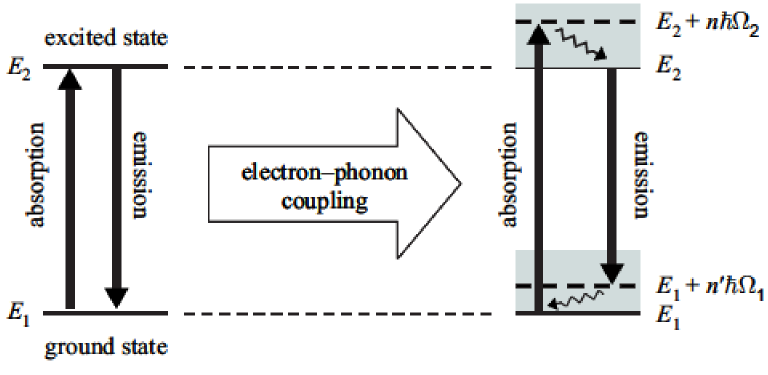


atom: $^3F_2$

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



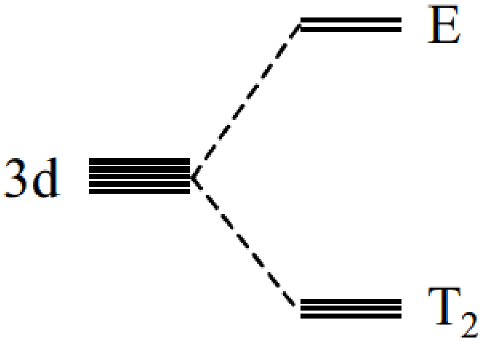
(a) Isolated atom

(b) Atom doped into a vibronic solid

Strong vibronic coupling

Broad lines (gain spectrum)

Good for ultrafast lasers

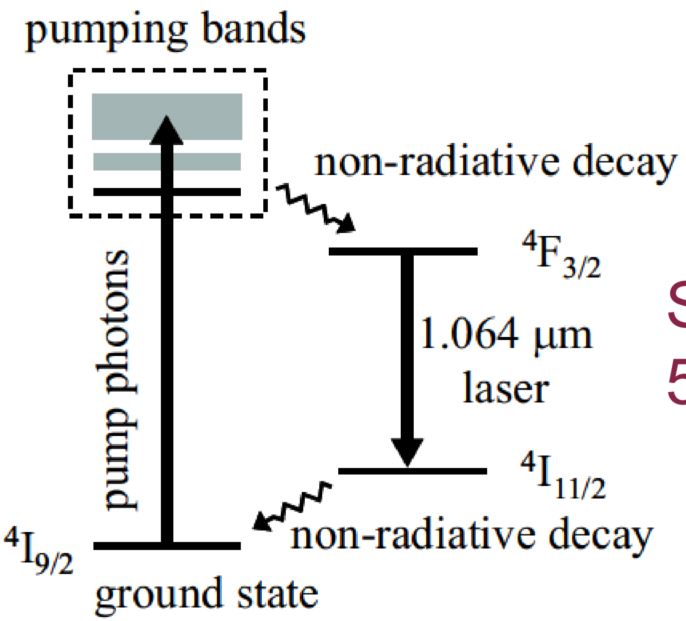


Strong crystal-field splitting

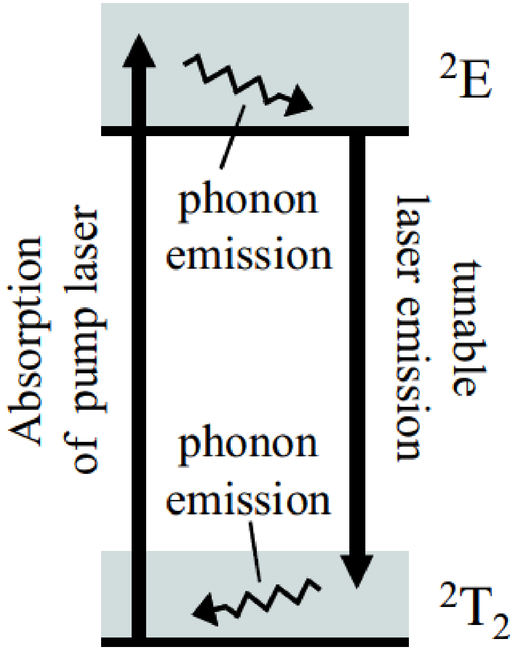
Depends on crystal environment

Fox, Chapter 9

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



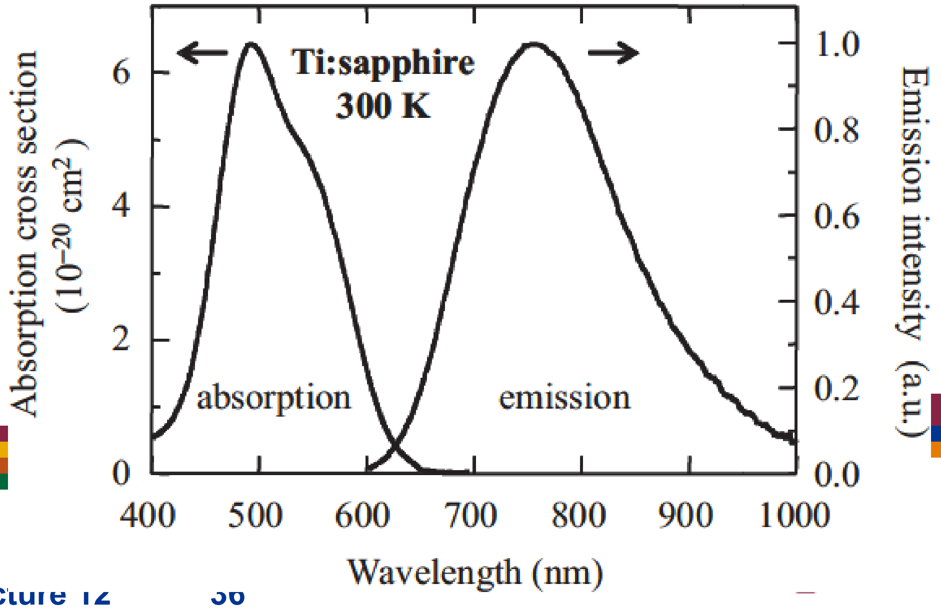
SHG
532 nm



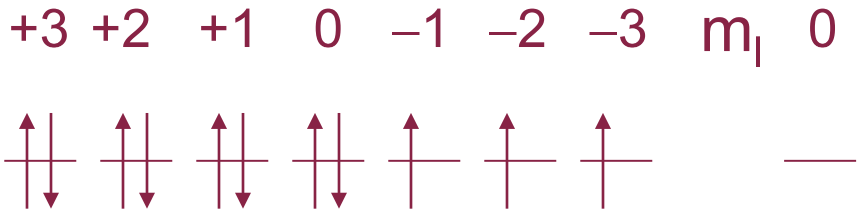
Pumping with

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

Fox, Chapter 9

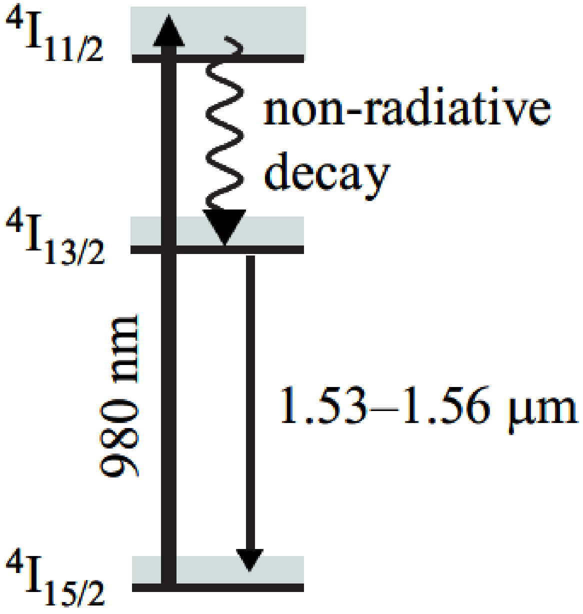


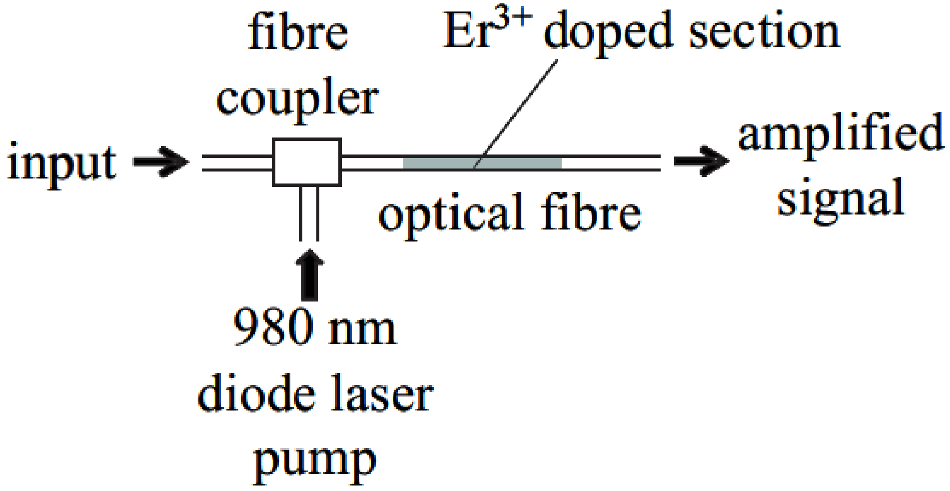
Erbium fiber laser



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

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



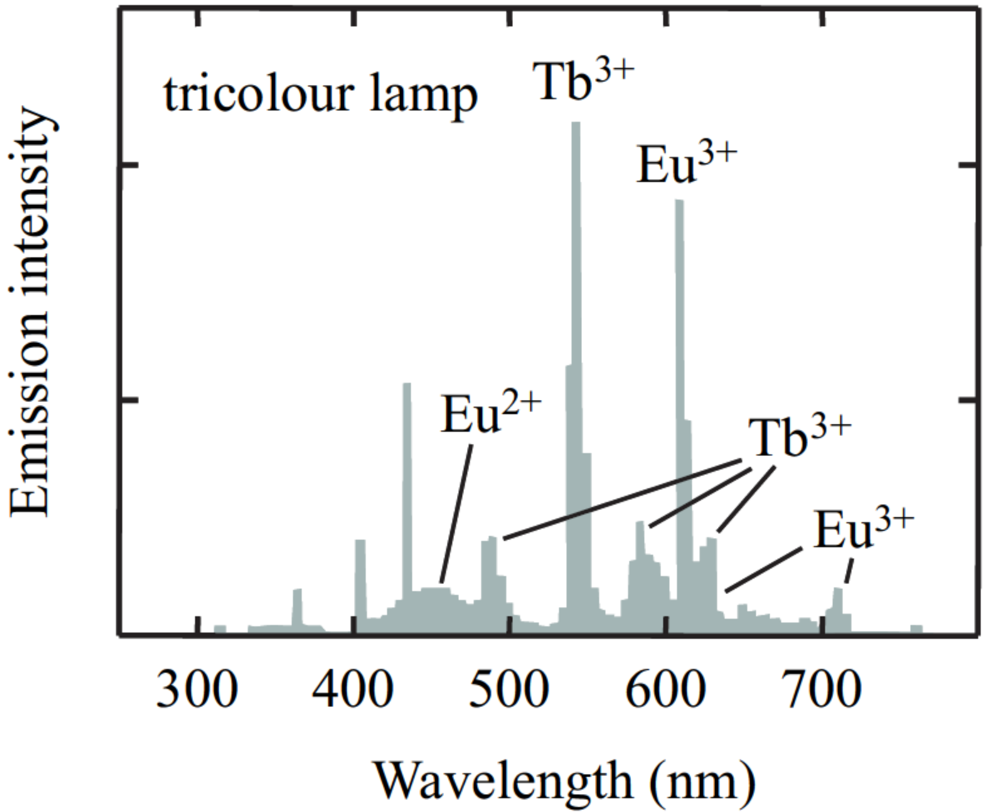


Pumped with 980 nm diode laser.
Important for telecommunications.

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)

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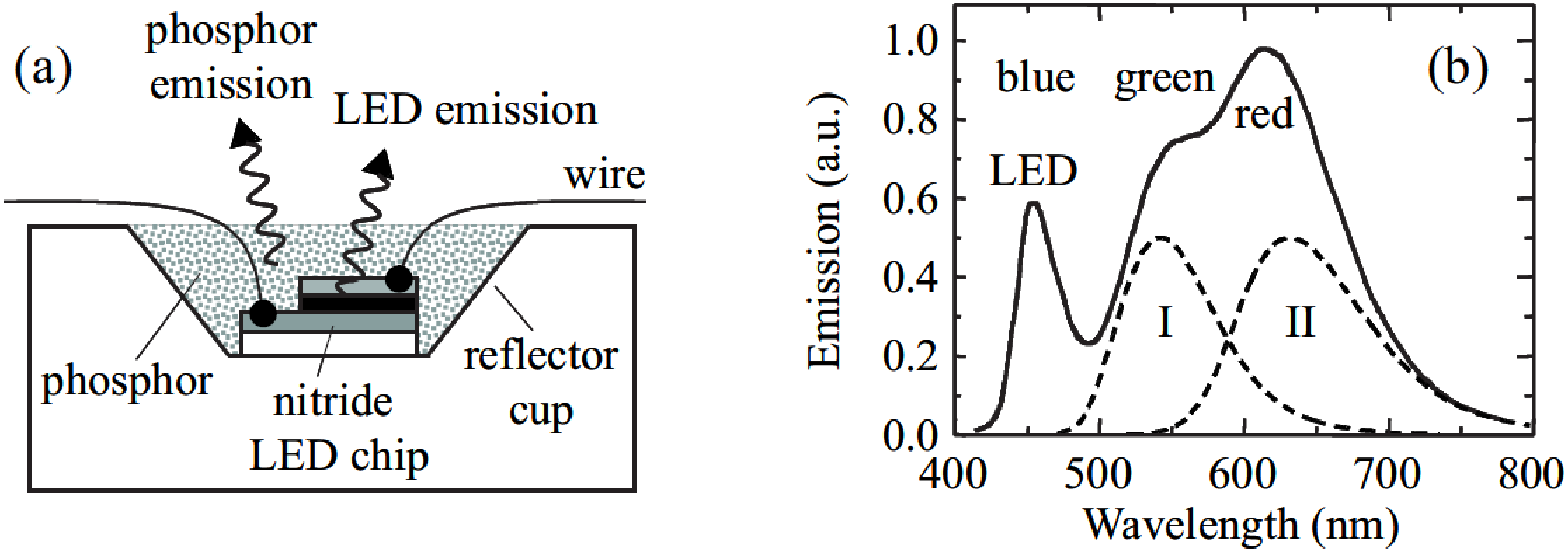
White light emitting diodes (white LEDs)



Blue InGaN LED with green and red phosphors

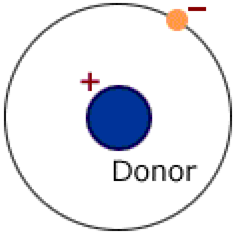
I: $SrSi_2O_2N_2:Eu^{2+}$

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

Color temperature: 3200 K

Fox, Chapter 9

Shallow (hydrogenic) defect: Si donor in GaAs



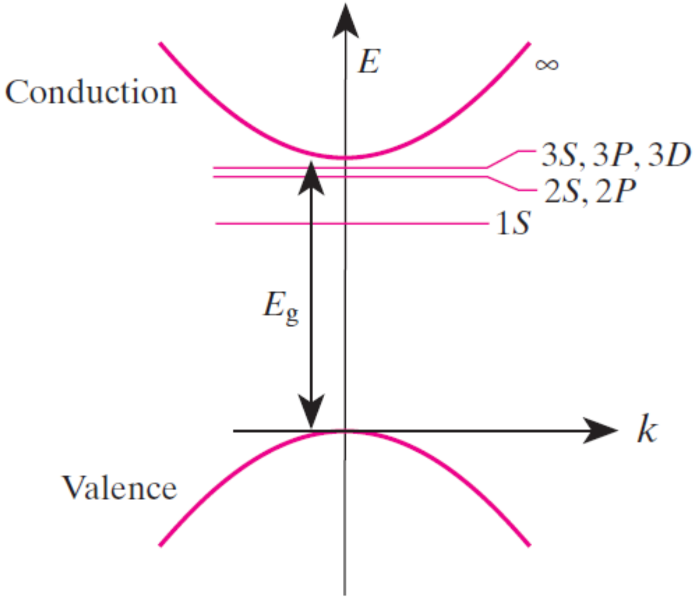
Extra valence electron
P nucleus positively charged (but screened in crystal)
Hydrogen-like energy spectrum (screened, heavy)

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

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

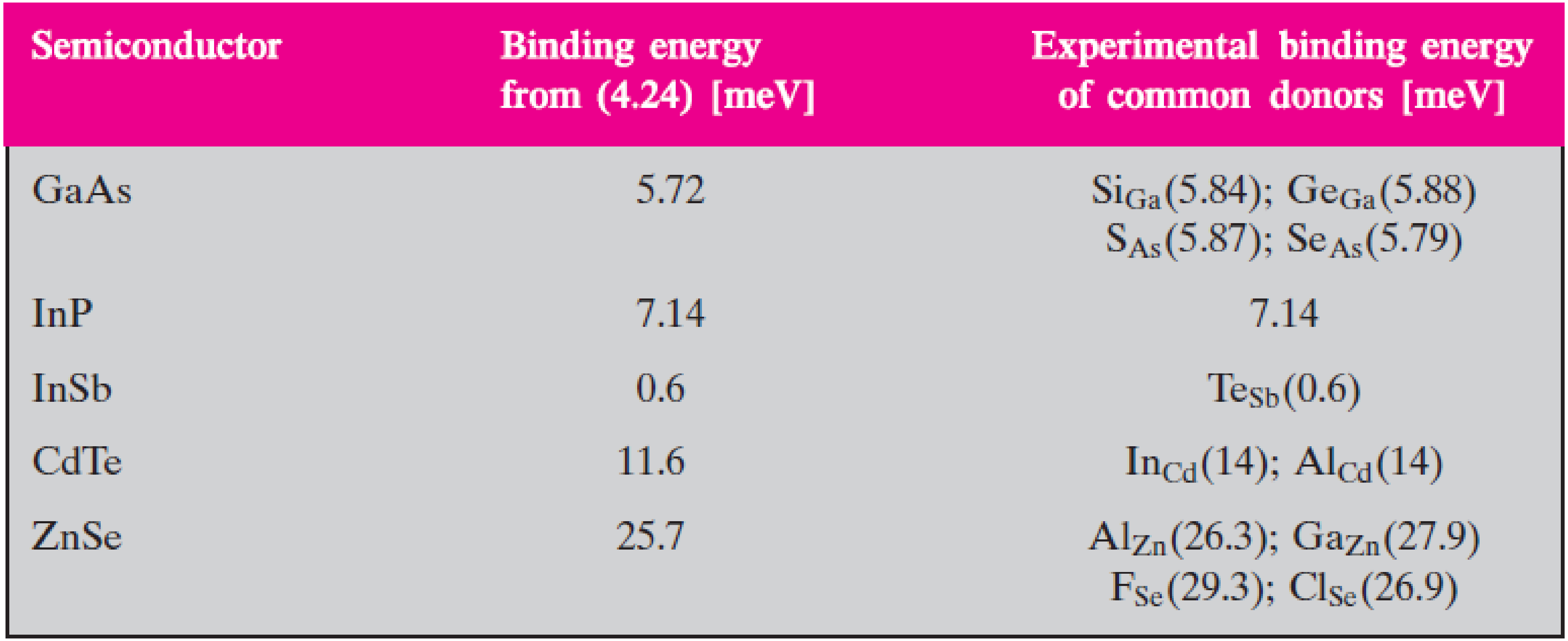
Binding energy: $\boxed{R = \frac{m^*}{m_0}\frac{1}{\varepsilon_s^2}\frac{e^4 m_0}{2\hbar^2(4\pi\varepsilon_0)^2}}$

Bohr radius.
Similar to exciton problem.



Yu & Cardona

Shallow (hydrogenic) defect: Si donor in GaAs

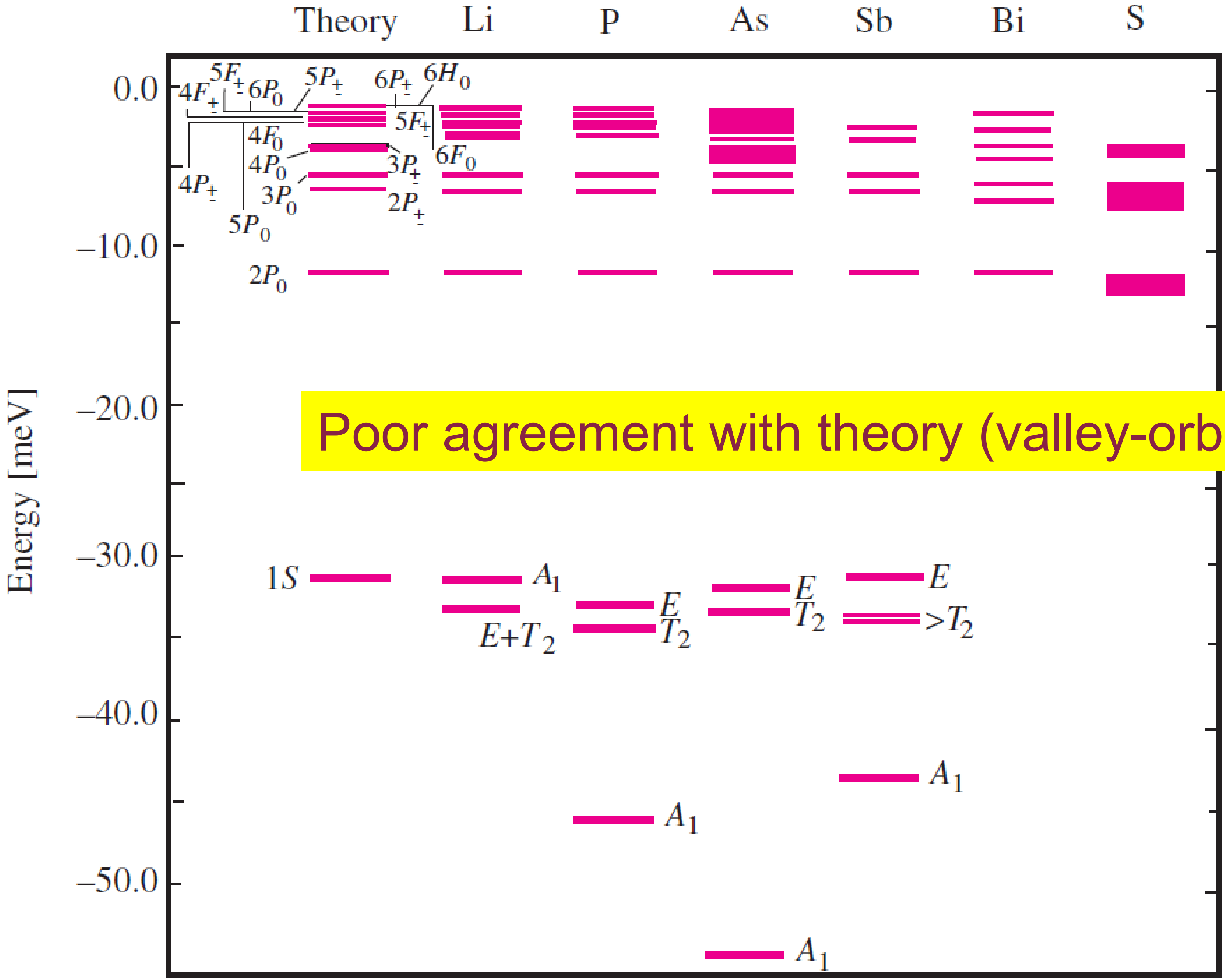


Semiconductor	Binding energy from (4.24) [meV]	Experimental binding energy of common donors [meV]
GaAs	5.72	Si_{Ga}(5.84); Ge_{Ga}(5.88) S_{As}(5.87); Se_{As}(5.79)
InP	7.14	7.14
InSb	0.6	Te_{Sb}(0.6)
CdTe	11.6	In_{Cd}(14); Al_{Cd}(14)
ZnSe	25.7	Al_{Zn}(26.3); Ga_{Zn}(27.9) F_{Se}(29.3); Cl_{Se}(26.9)

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

Yu & Cardona

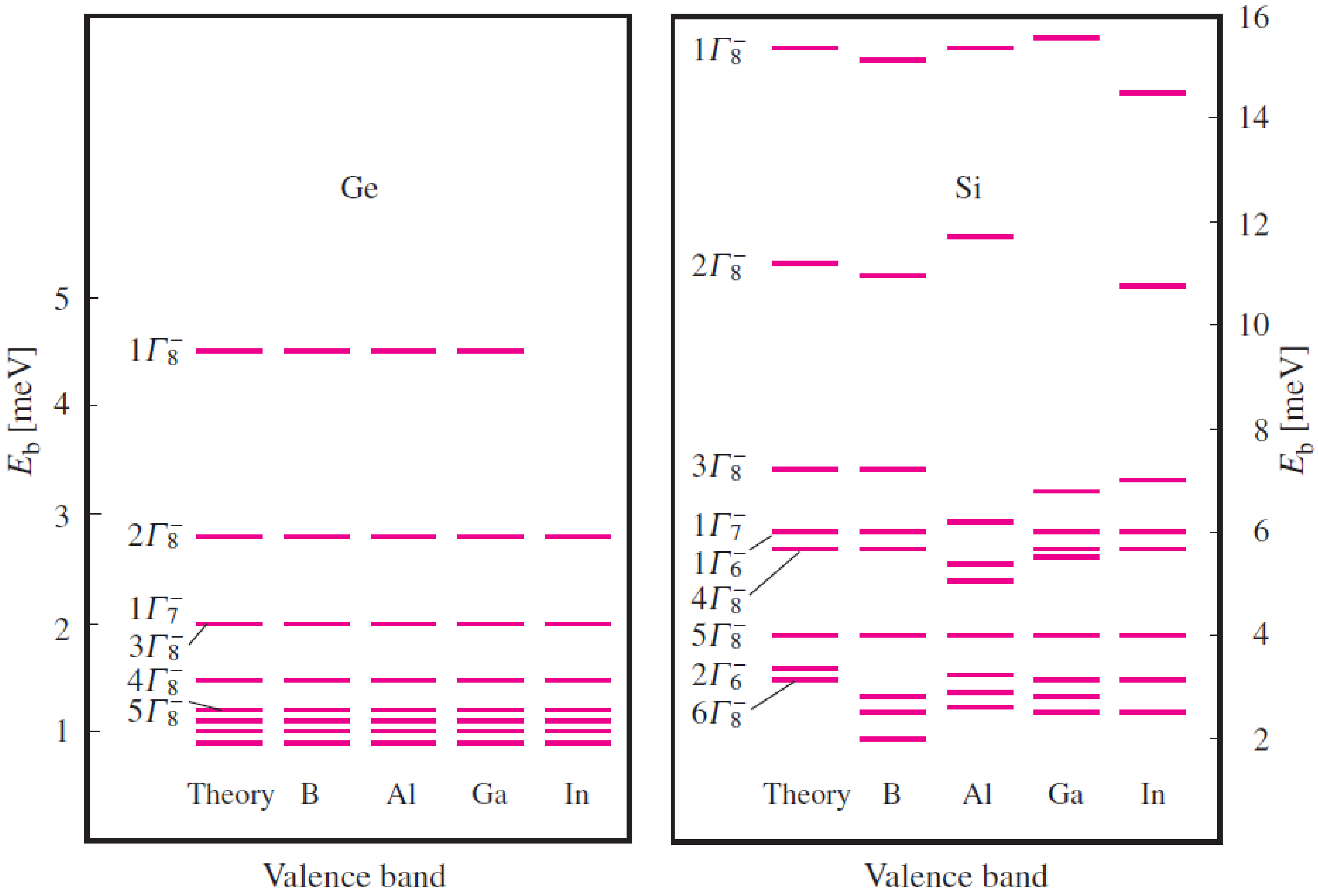
Shallow (hydrogenic) defect: Donors in Si and Ge



Poor agreement with theory (valley-orbit coupling)

Yu & Cardona

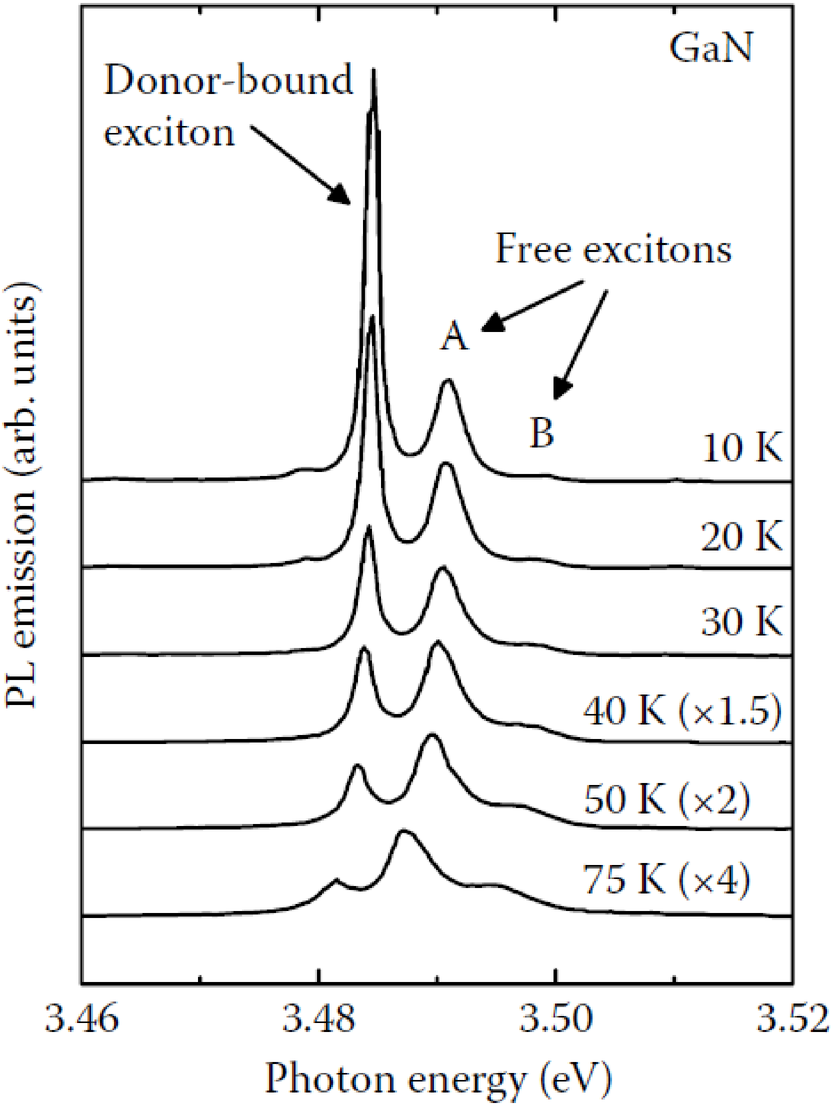
Shallow (hydrogenic) defect: Acceptors in Si and Ge

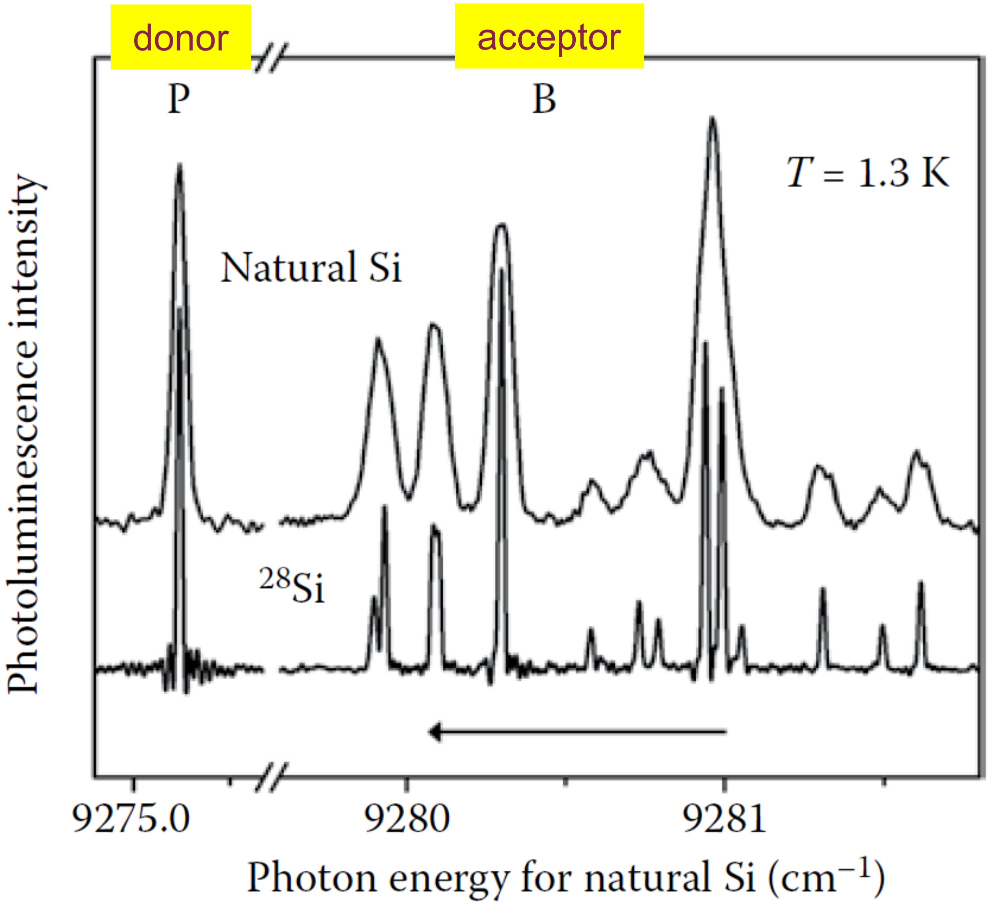


Need to include valence band warping (Luttinger theory) and other corrections.

Yu & Cardona

Free and bound excitons (photoluminescence)



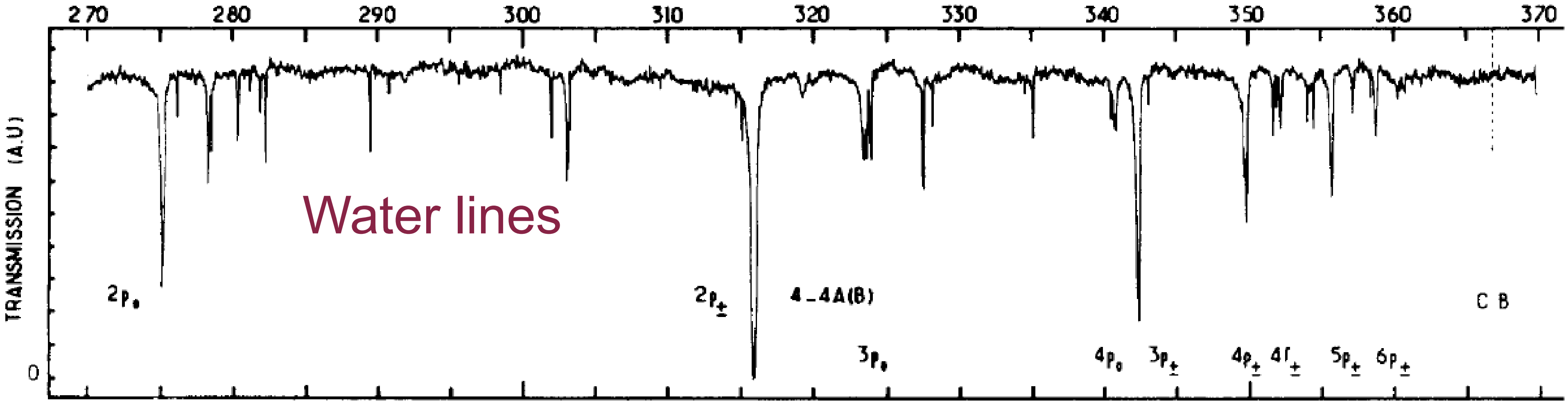


Band to defect recombination shifted from free exciton energy.

McClusky & Haller, Dopants and Defects

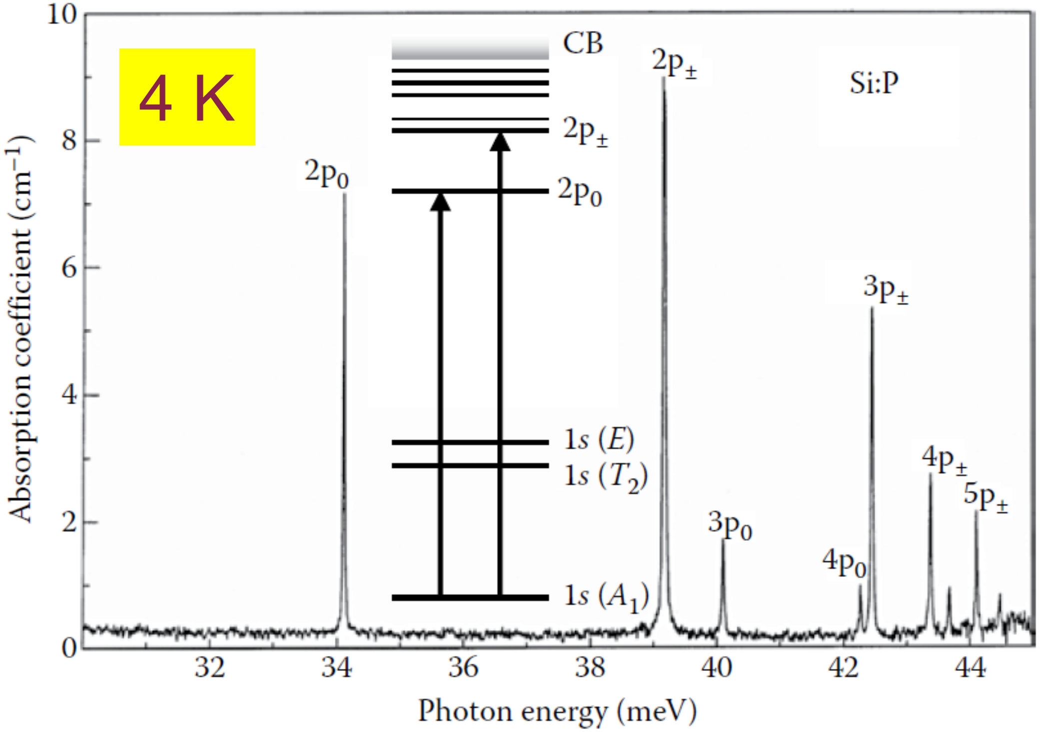
Infrared defect spectroscopy: P donor in Si

Energy (cm^{-1})



Water lines

4 K

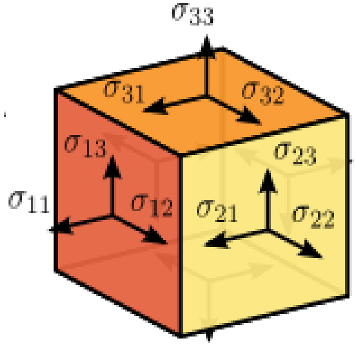


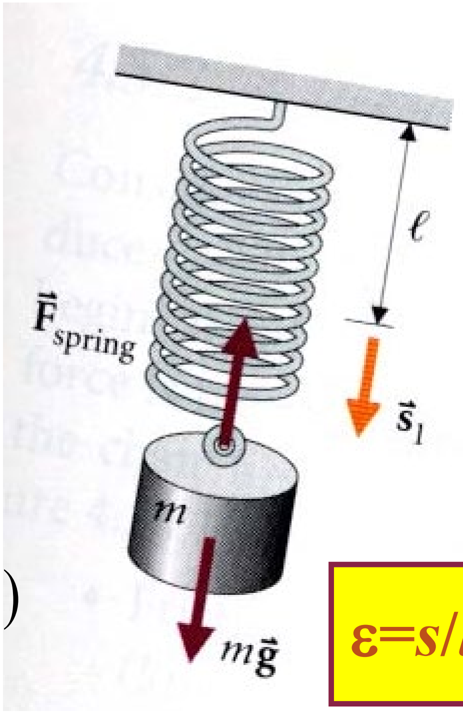
McClusky & Haller, Dopants and Defects
A.K. Ramdas, PRB **23**, 2082 (1981)
Pajot, Solid State Commun. **31**, 759 (1979)

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 **S**, stiffness tensor **c** (6x6 2nd rank tensors)

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

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

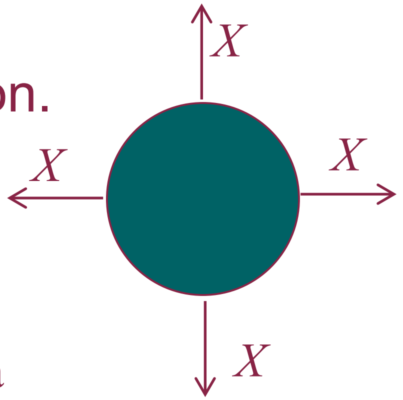
Spring: Strain is ε=*s*/*l*, Relative change in length.

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

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

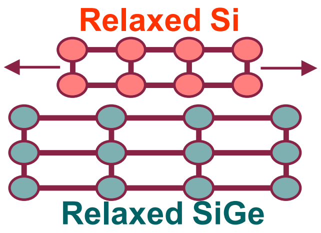
compressive vertical strain

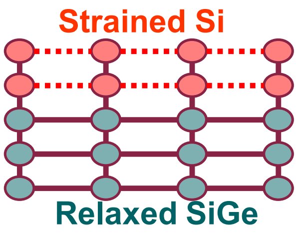
- Hydrostatic strain component: tensile (>0), softens phonons, gap decreases

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

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

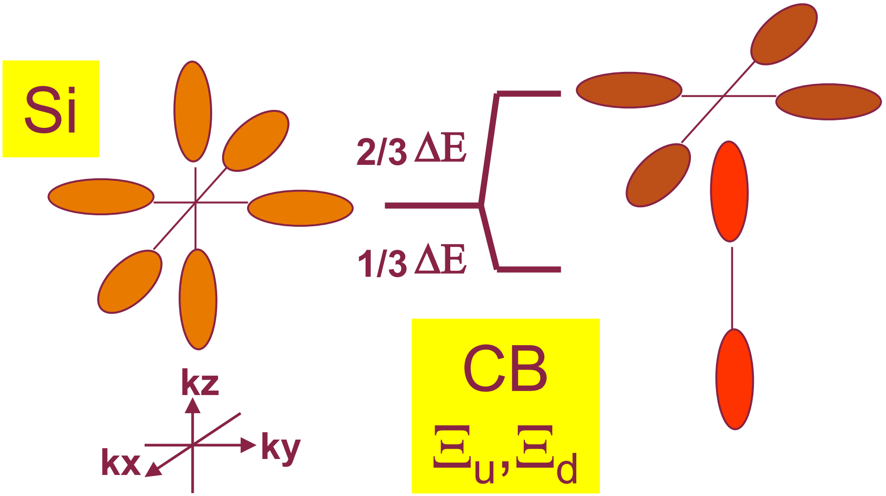
$$\varepsilon_{\text{S}} = \left(\varepsilon_{||} - \varepsilon_{\perp}\right)/3$$

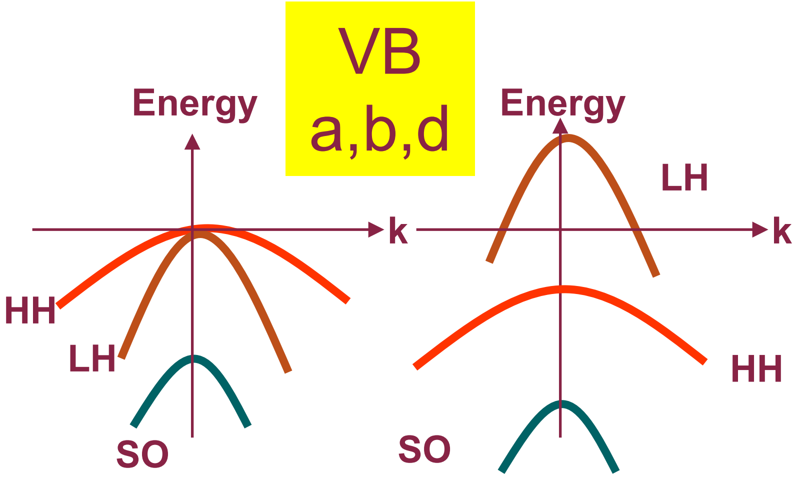




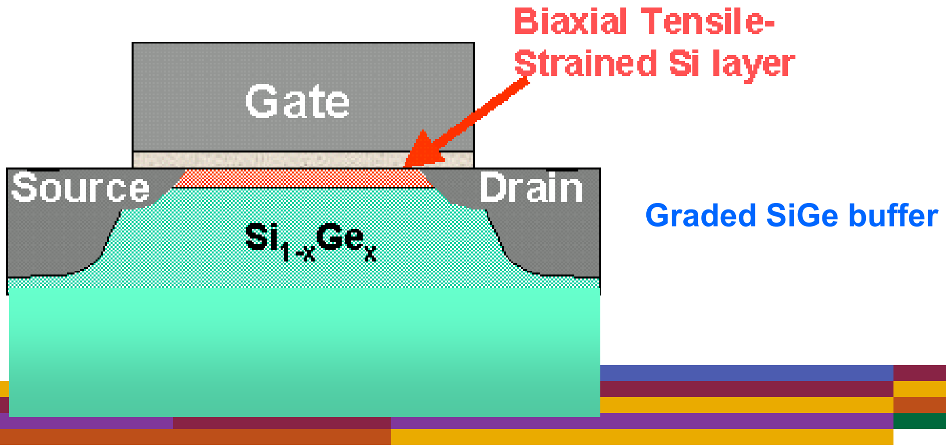
S. Zollner, *Properties of Silicon-Germanium-Carbon Alloys: Growth, Properties, Applications*

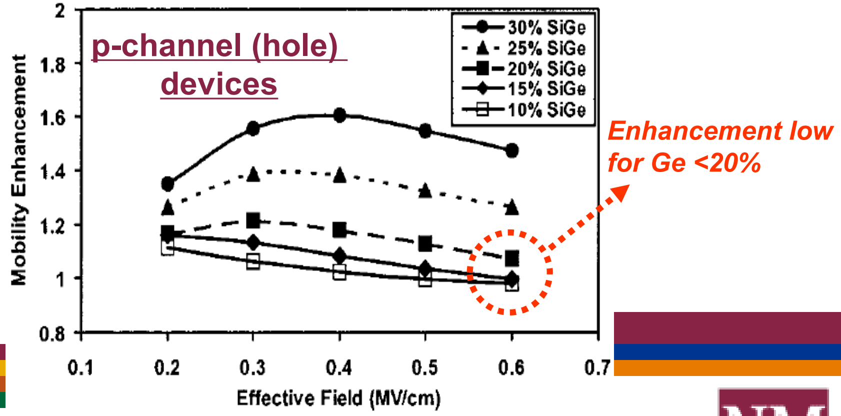
Thin Strained Silicon Layers for CMOS



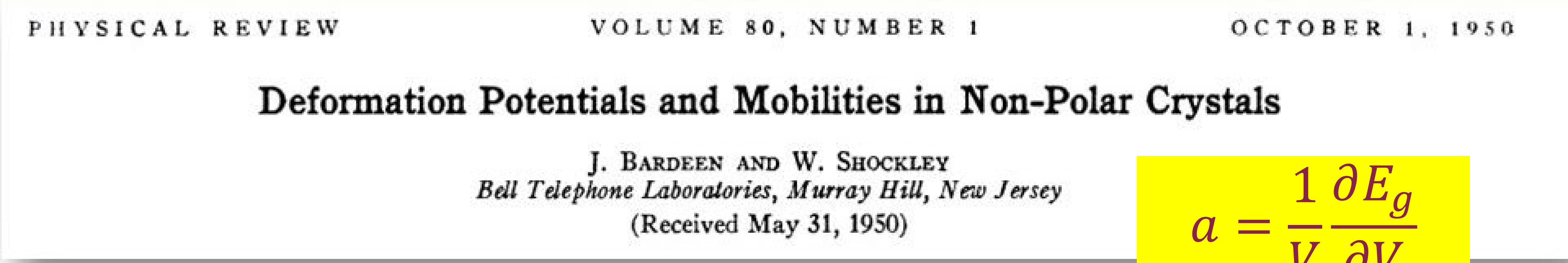


- Biaxial tension lowers band gaps, reduces effective masses, and splits bands/valleys (reduced intervalley and inter-valence band scattering).
- Silicon under biaxial tension has higher electron and hole mobilities and therefore offers better transport properties than bulk silicon.





Deformation potentials



PHYSICAL REVIEW VOLUME 80, NUMBER 1 OCTOBER 1, 1950

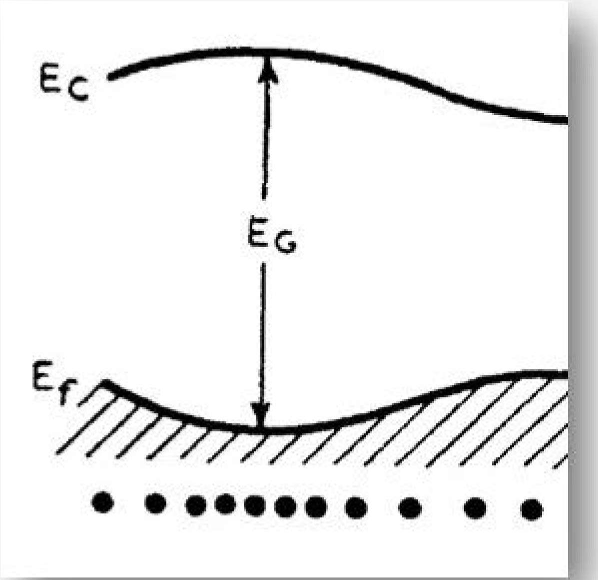
Deformation Potentials and Mobilities in Non-Polar Crystals

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**