

Electronic states of crystalline materials

Dr. Erika Balog

Department of Biophysics and Radiation Biology



Solids

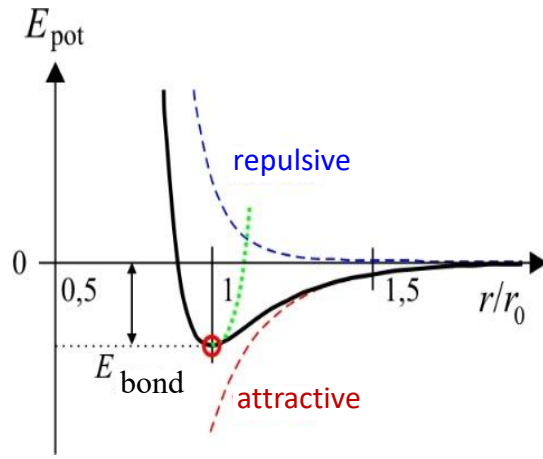
A. Crystalline materials

- Periodic long-range order
- Lattice - elementary cell (in nature 14 different, “Bravais-lattices”)
- According to the nature of interactions (bonds) of the structural elements:
 - covalent bond: atomic lattice (Si)
 - ionic bond: ionic lattice (NaCl)
 - metallic bond: metal lattice (positive ions)
 - secondary bonds: molecular lattice (molecules eg. lysozyme)

B. Amorphous materials

glass-like, viscous “fluids”

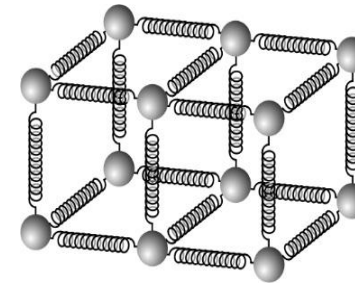
Bravais-lattices			
$\beta \neq 90^\circ$ $a \neq c$	$\beta \neq 90^\circ$ $a \neq c$		
$a \neq b \neq c$	$a \neq b \neq c$	$a \neq b \neq c$	$a \neq b \neq c$
$a \neq c$		$a \neq c$	
$\alpha \neq 90^\circ$			
$\gamma = 120^\circ$			



- the minimum can be approximated by a parabola.

$$E_{pot} = k (r - r_0)^2$$

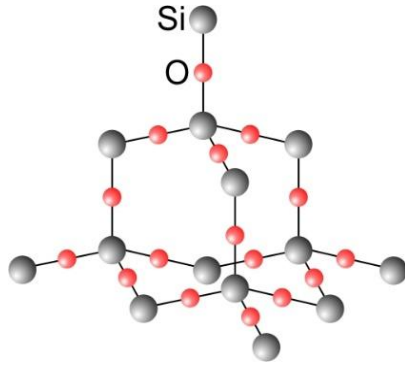
$$F = -k r$$



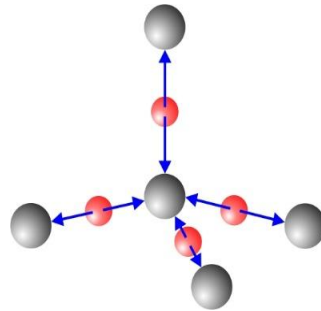
- crystal: a spatial lattice made up of mass points connected by springs.
- the atoms perform oscillatory motion around their equilibrium positions.
- if the temperature increases, the amplitude of vibration increases.
- however, due to the asymmetric potential well, the motion is not symmetric: on average, the atoms spend more time at greater distances from their equilibrium positions.

Thermal expansion

Piezoelectric effect



quartz (SiO₂) crystal



- dipole: the center of +/- charges does not coincide.

$$p = q \cdot l$$

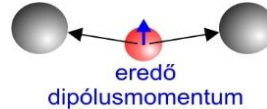
p – dipole moment

q – charge

l – distance between the center of +/- charges

- the sum of dipole moments (because of the tetrahedral crystal symmetry) is 0.

if pressure is applied on the crystal:



voltage can be measured between the two point of the crystal

the dipole moment of bended
Si – O – Si bonds is not 0

Direct piezoelectric effect

Piezoelectric effect

Direct piezoelectric effect:

applying pressure on the crystal (deform)



voltage can be measured between two points of the crystal

ultrasound detection

Invers piezoelectric effect:

applying voltage on the crystal



the crystal is deformed

applying periodic voltage on the crystal



the crystal is deformed periodically = vibrates

choosing the proper frequency of the voltage

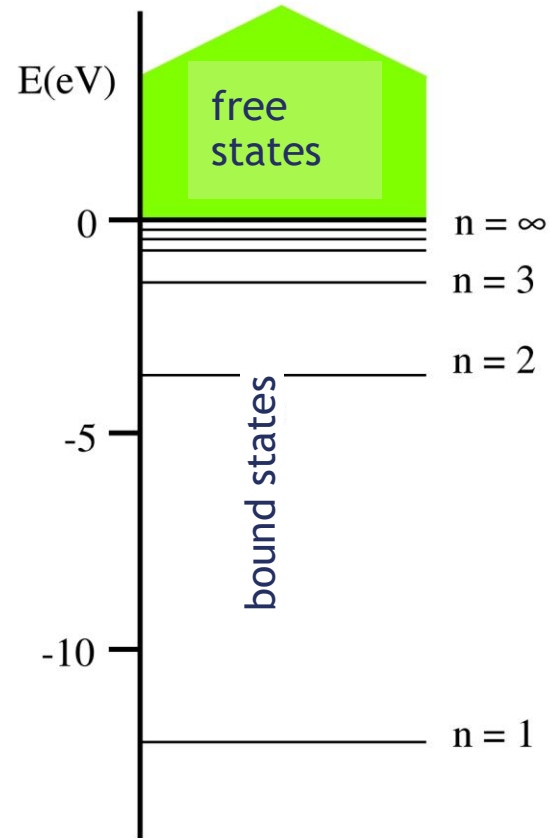


ultrasound generarion

Energy levels in crystals

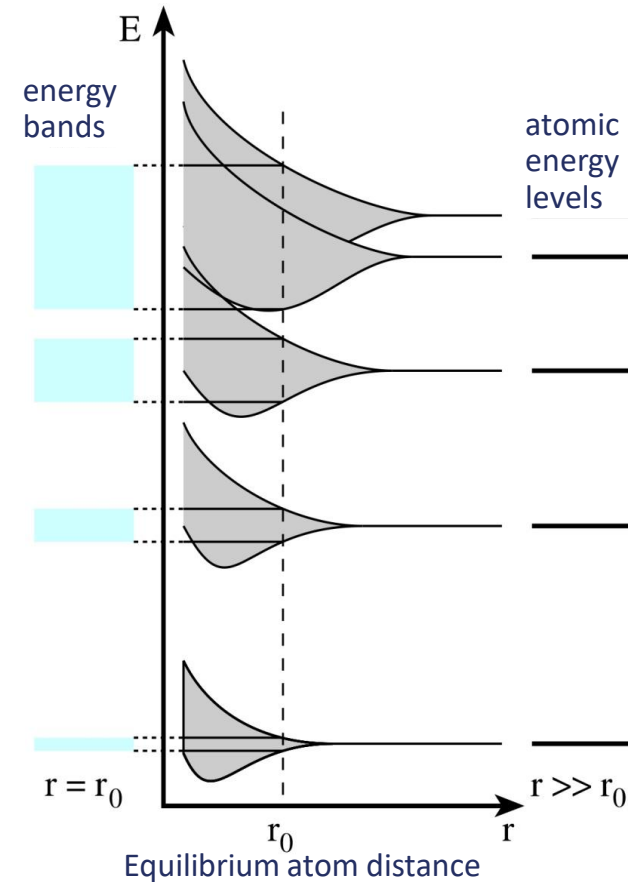
Isolated hydrogen atom

- No interaction with other atoms
- Discrete (quantized) energy levels
- Pauli's principle: there can not be two electrons bound to the same atom with all 4 quantum numbers being identical



Crystal

- Atoms interact
- consequence of Pauli's principle: in order to avoid identical quantum states, the discrete atomic energy levels of interacting atoms split, forming energy bands
- Nearby levels merge into energy bands



Solids with different bands structure

@T=300 K, $k_B T \sim 0.023$ eV

Completely saturated

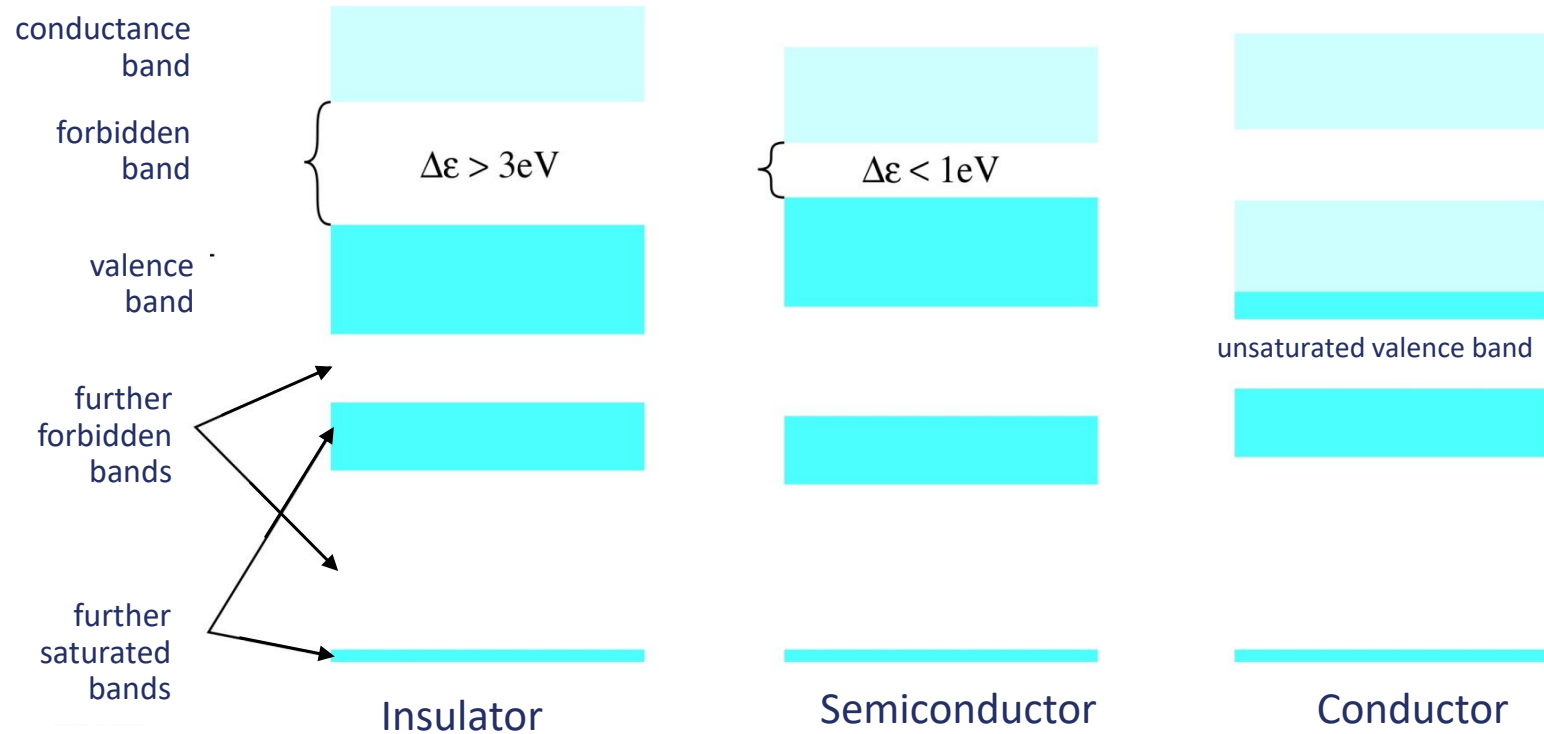
Unsaturated

$$\Delta\varepsilon \gg kT$$

$$\Delta\varepsilon > kT$$

$$\frac{n_{conduct}}{n_{valence}} = e^{-\frac{\Delta\varepsilon}{k_B T}}$$

$$\text{Conductance: } \sigma \sim \frac{1}{T}$$



- No electrical conduction
- Energy of visible photons insufficient to transfer electrons across band gap; hence, optically transparent (e.g., diamond)

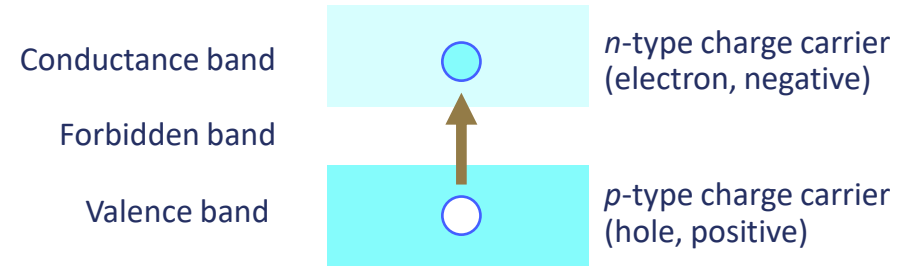
- Band gap may be crossed by thermal activation
- Electron-hole pair forms
- Visible photons are absorbed: not transparent

- No forbidden band: good electrical conductor
- Not transparent

Semiconductors

A. Pure semiconductors

- Two types of charge carriers (n , p):



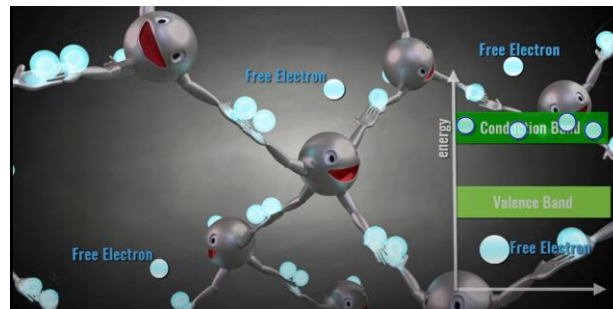
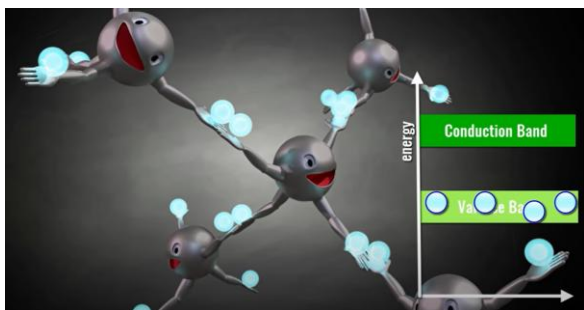
- Electrical conductance is temperature-dependent:

$$\sigma = konst \cdot e^{-\frac{\Delta\varepsilon}{2k_B T}}$$

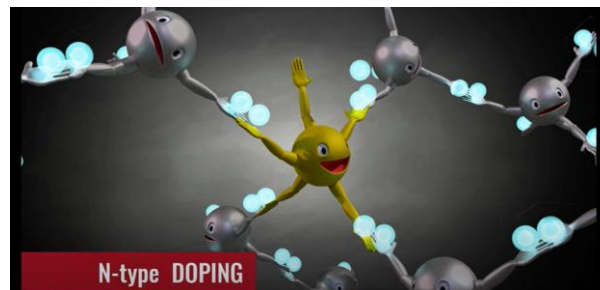
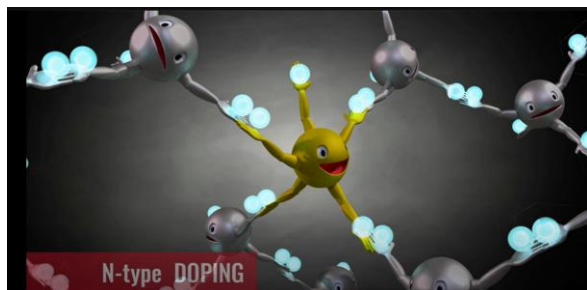
- Width of forbidden band ($\Delta\varepsilon$) < 3 eV
- Crossing of forbidden band may be evoked by the absorption of visible light (1.5-3 eV): $hf_{vis} > \Delta\varepsilon$
- Forbidden band may be crossed by thermal activation
- Optically not transparent



Si



Si



Si - P

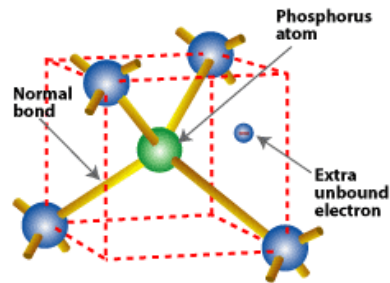
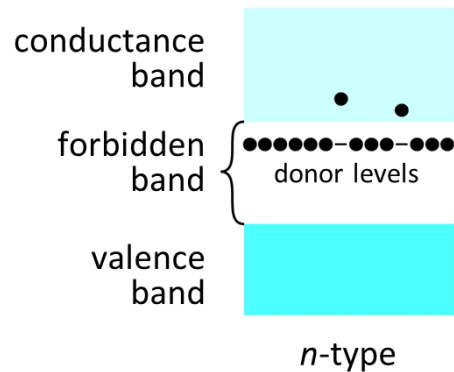
Semiconductors

B. Doped semiconductors

Dopant: - small number of foreign atoms in between the host atoms of the lattice:
- provides a new electron state that narrows the forbidden band

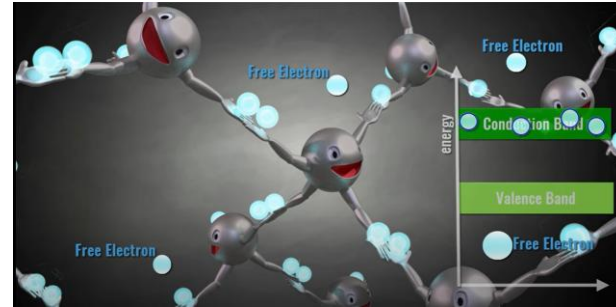
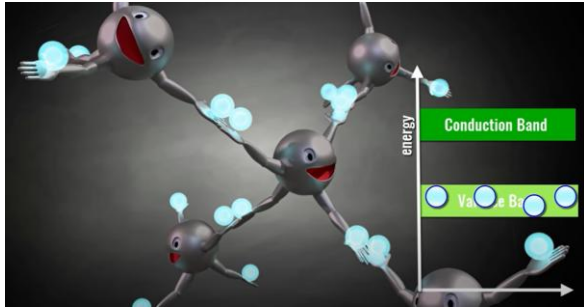
$$\frac{N_{host}}{N_{dopant}} \approx 10^6$$

n-type semiconductor (*e*-donor): 5-valence dopant (P, As, Bi) in a 4-valence host (Si, Ge)

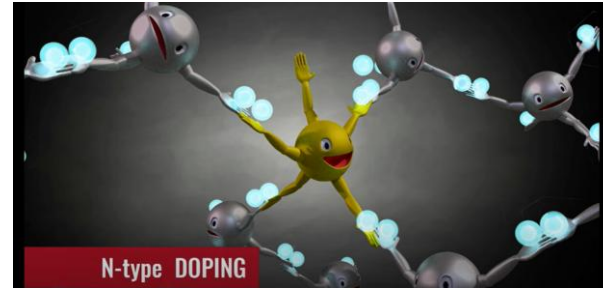
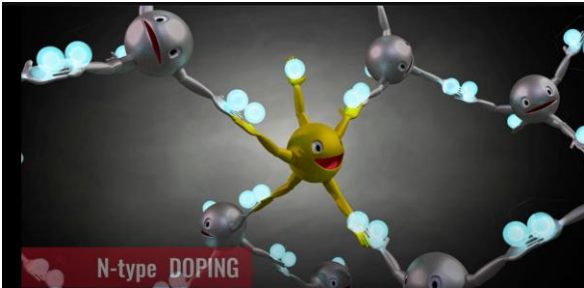




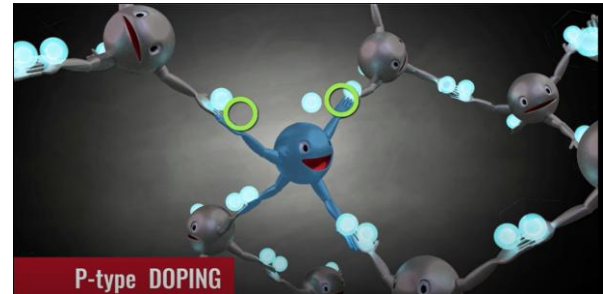
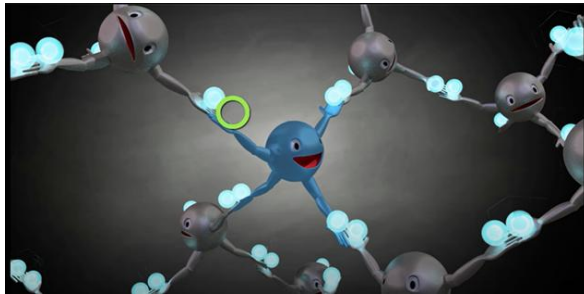
Si



Si



Si - P



Si - B

Semiconductors

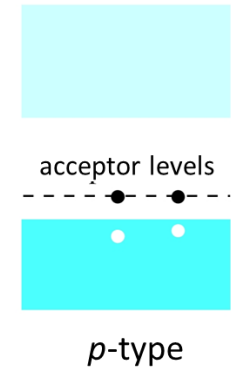
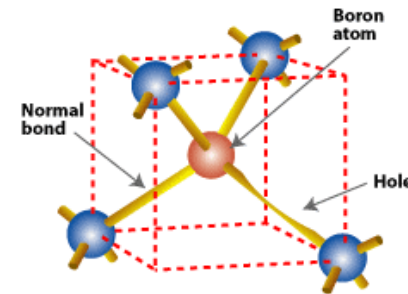
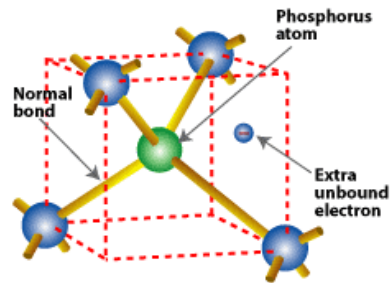
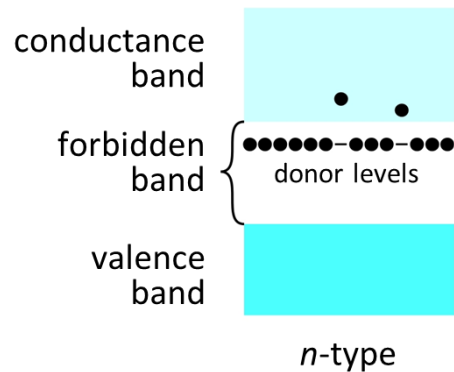
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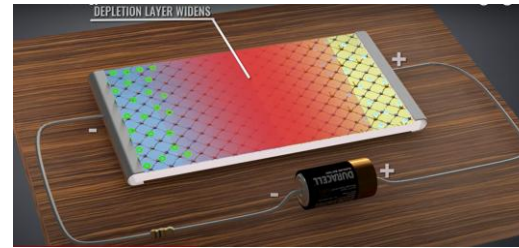
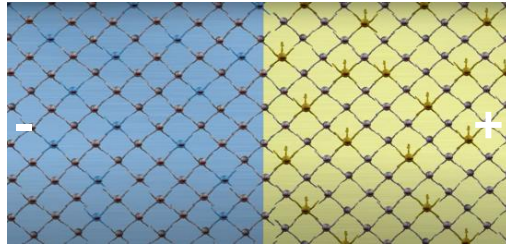
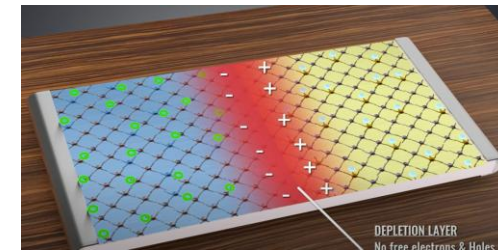
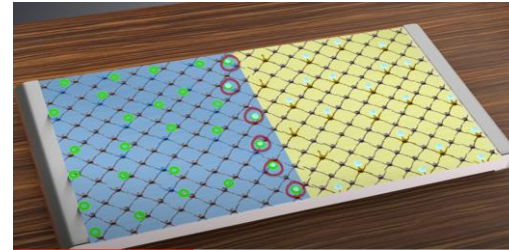
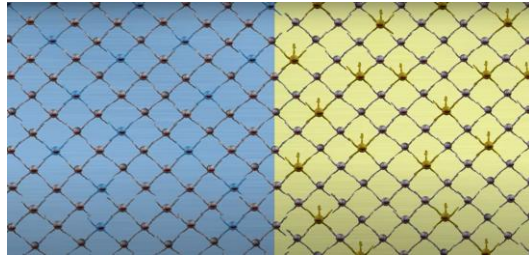
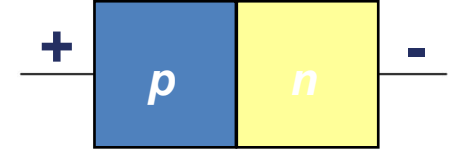
n-type semiconductor (e^- -donor): 5-valence dopant (P, As, Bi) in a 4-valence host (Si, Ge)

p-type semiconductor (e^- -acceptor): 3-valence dopant (Al, Ga, In, B) in a 4-valence host (Si, Ge)



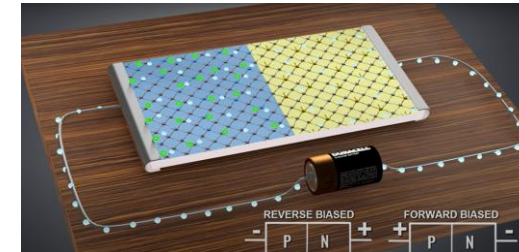
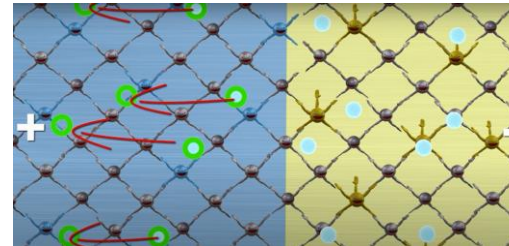
Diode

- microelectronic devices constructed by adjoining doped, *p*- and *n*-type semiconductors



- reverse biasing

- asymmetric conductance

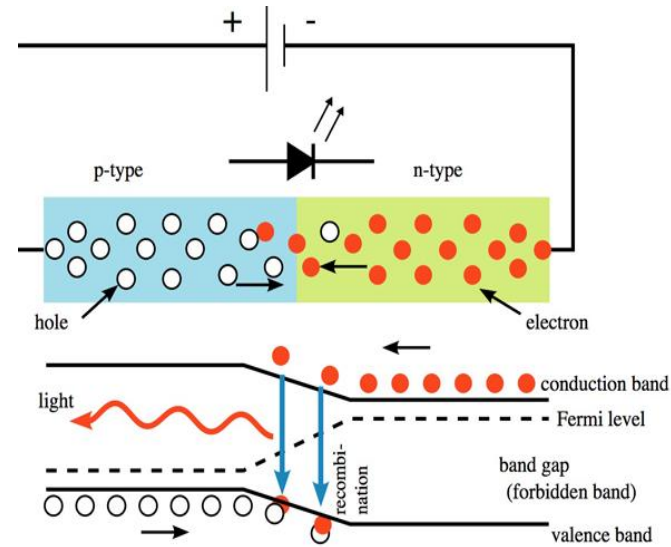
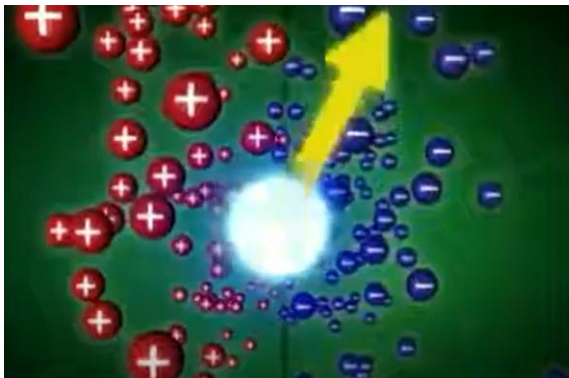
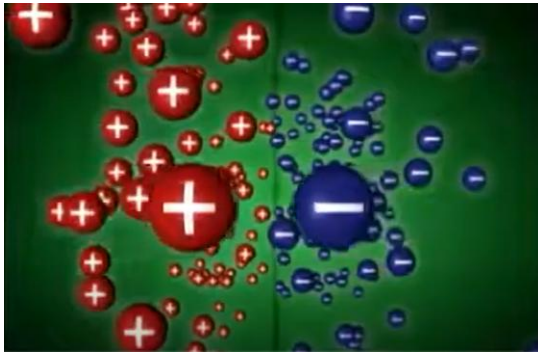
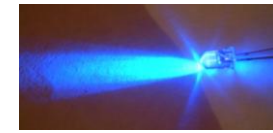


- forward biasing

Usage:

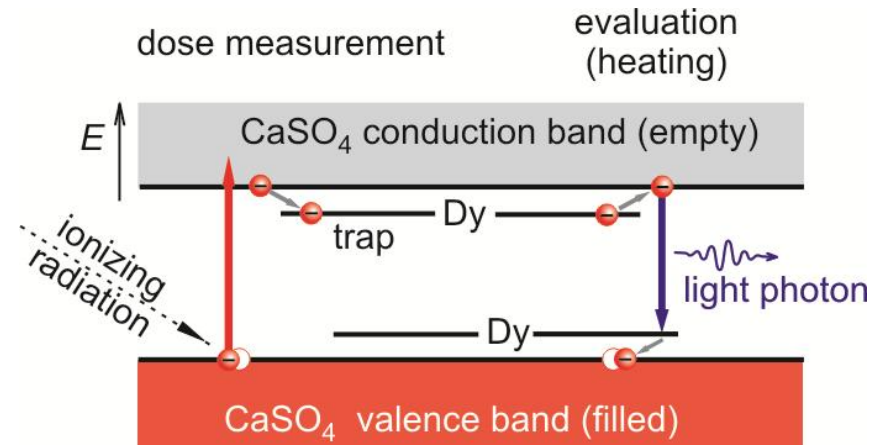
- electrical voltage → light emission, LED
- illumination → voltage → CCD pixel

Light Emitting Diode (LED)



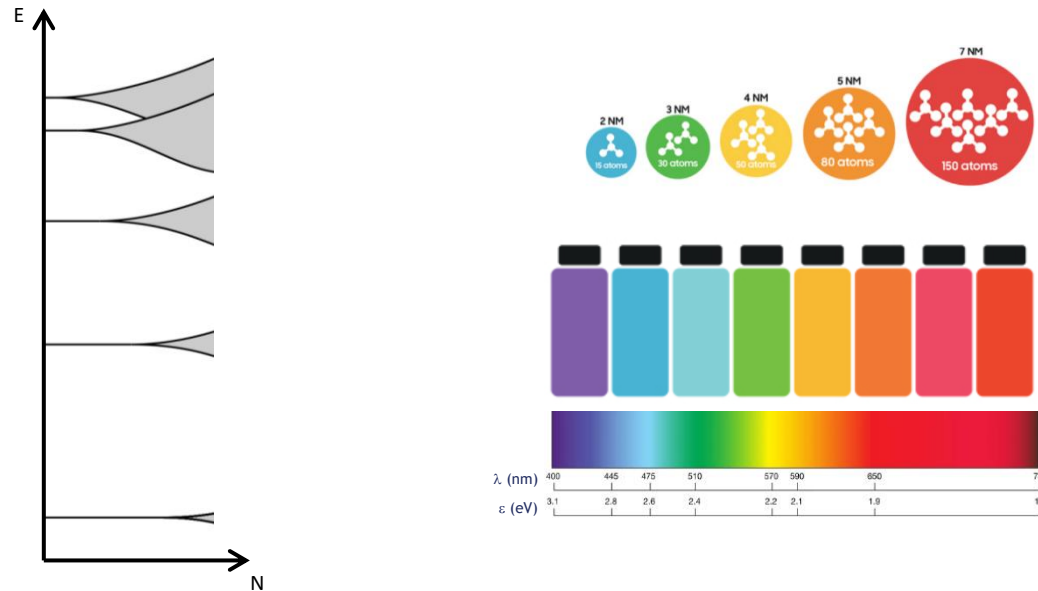
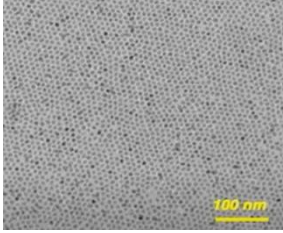
Isamu Akasaki, Shuji Nakamura, Hiroshi Amano, Nobel-prize 2014

Thermoluminescent dosimeter



Quantum dots:

- very small (nm size) semiconductors, made of 100-1000 of atoms.
- their size determines their properties: the energy of the emitted light depends on the size of the quantum dot.
- the width of the forbidden band determines the energy (colour) of the fluorescent light.
- the energy is inversely proportional to the size of the quantum dot.



Usage:

- imaging in cells (they are the same size as proteins),
- lasers, microscopes
- medical imaging, TV-QLED



Mounji G. Bawendi, Louis E. Brus, Alexei I. Ekimov
Nobel-prize in chemistry 2023