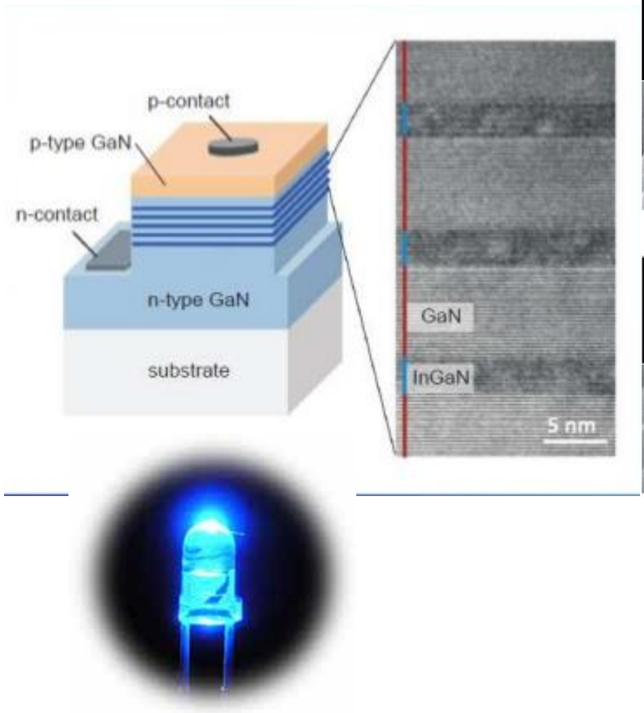
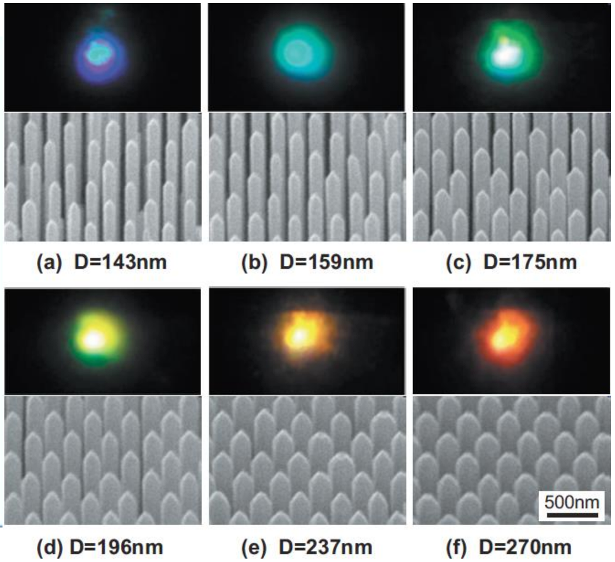
Semiconductor Nanostructures

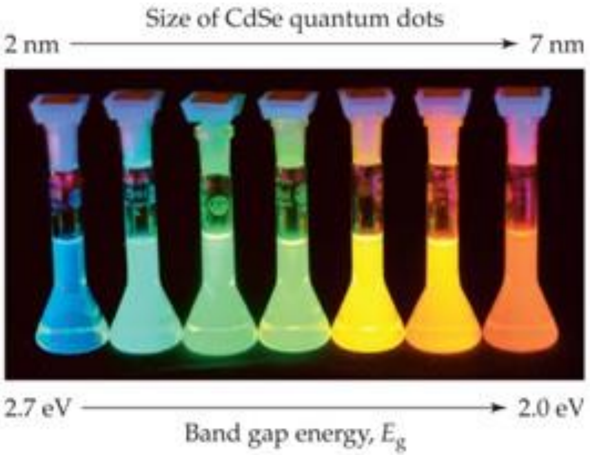
2D



1D



0D



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Outline

- What is a semiconductor?
- What changes when we reduce the size of a semiconductor?
- Semiconductor nanostructures and their applications in optoelectronics
- Characterisation of nanostructures

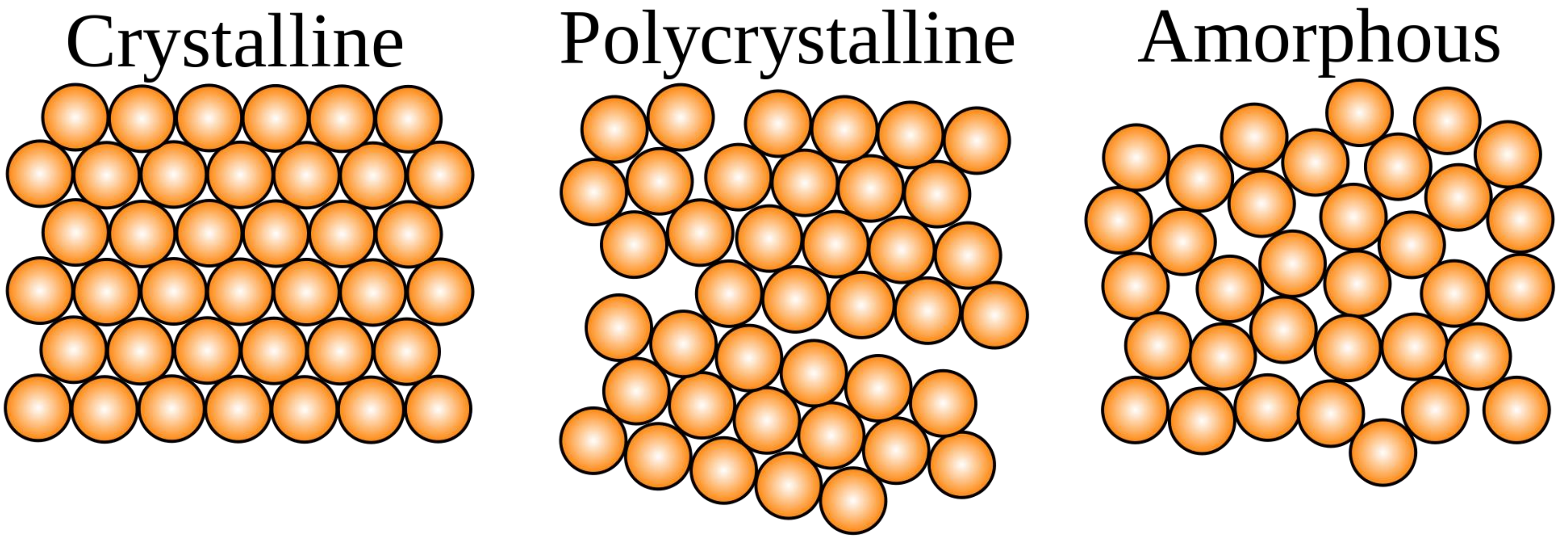
Bibliography

- Optical Properties of Solids, Mark Fox, Oxford University Press, 2001
- Light-Emitting Diodes, E. Fred Schubert, Cambridge University Press, 2007
- Semicondutor Physics and Devices, Donald A. Neamen, McGraw-Hill, 2003

What is a semiconductor?

- A semiconductor is a crystal that acts as insulator at low temperatures and as conductor at higher temperatures.
- The crystal can be single crystalline, polycrystalline or amorphous:

(In the following I will mainly discuss crystalline materials.)



https://www.toppr.com/guides/chemistry/the-solid-state/crystalline-and-amorphous-solids/

Semiconductor materials

Section from the periodic table

IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
							2 He 4.003
		5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.183
		13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.909	36 Kr 83.80
47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)

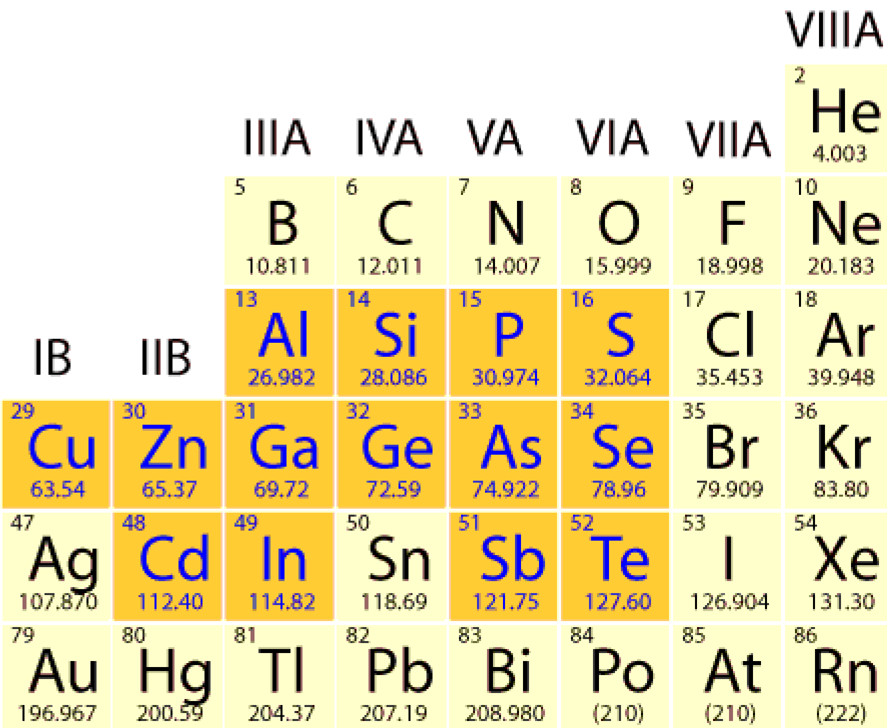
Si the most ubiquitous semiconductor

An ingot of silicon, consisting of a single large crystal of silicon. Such an ingot is sliced into individual wafers and then used to make a variety of semiconductor devices, including solar cells and computer chips.

- The symbol Si represents silicon with atomic number 14
- Atomic number = number of protons in nucleus = number of electrons in orbit
- The group number represents the number of valence electrons (i.e. electrons involved in chemical bonding)

Semiconductor materials

Section from the periodic table



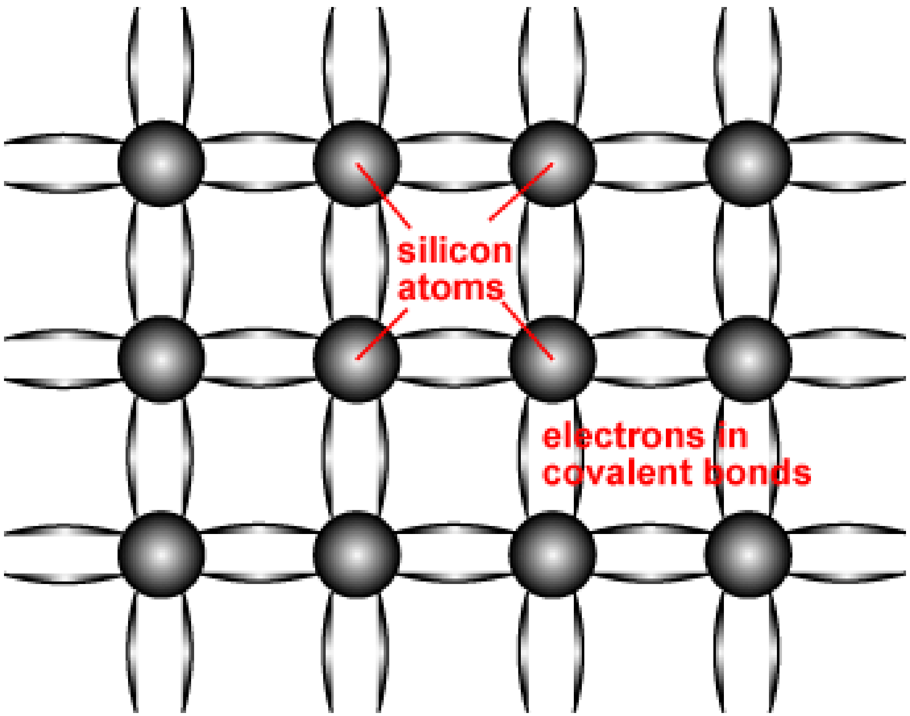
Semiconductors are grouped in "families":

Elemental	C, Si, Ge (group IV)
Compound	e.g. SiC (IV-IV) GaAs (III-V) GaN (III-V) ZnSe (II-VI)
Ternary	e.g. $CuInSe_2$

- On average all these typical semiconductor materials have 4 valence electrons per atom.
- By sharing their valence electrons with 4 neighbouring atoms their outer electron shell becomes completely filled.

Origin of bandgap: covalent bonds

- Atoms in group IV of the periodic table have four valence electrons and need four more electrons to complete the valence energy shell.



Schematic representation of covalent bonds in a silicon crystal lattice. Each line connecting the atoms represents an electron being shared between two atoms.

Since each Si atom has 4 Si-neighbours the valence shell is completely filled.

From the atom to the crystal

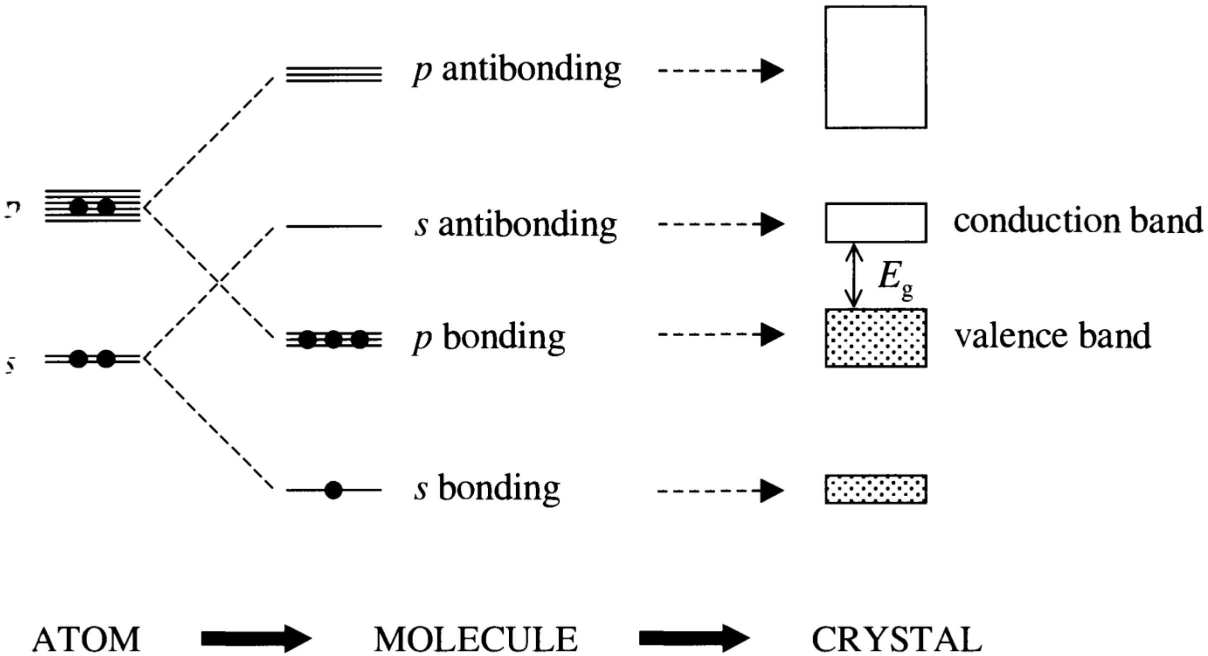


Fig. 3.3 Schematic diagram of the electron levels in a covalent crystal made from four-valent atoms such as germanium or binary compounds such as gallium arsenide. The *s* and *p* states of the atoms hybridize to form bonding and antibonding molecular orbitals, which then evolve into the conduction and valence bands of the semiconductor.

- According to **Pauli's exclusion principle** each state, characterised by a set of quantum numbers, can only be occupied by one electron.
- When atomic orbitals overlap they hybridize and form bonding and antibonding molecular orbits.
- In a crystal the overlap of many orbitals leads to energy regions with very high density of states forming "**bands**" separated by energy regions without any states (**bandgap**).
- For the chemical bonding and semiconducting properties only **valence and conduction bands** are interesting.

Band theory for solids

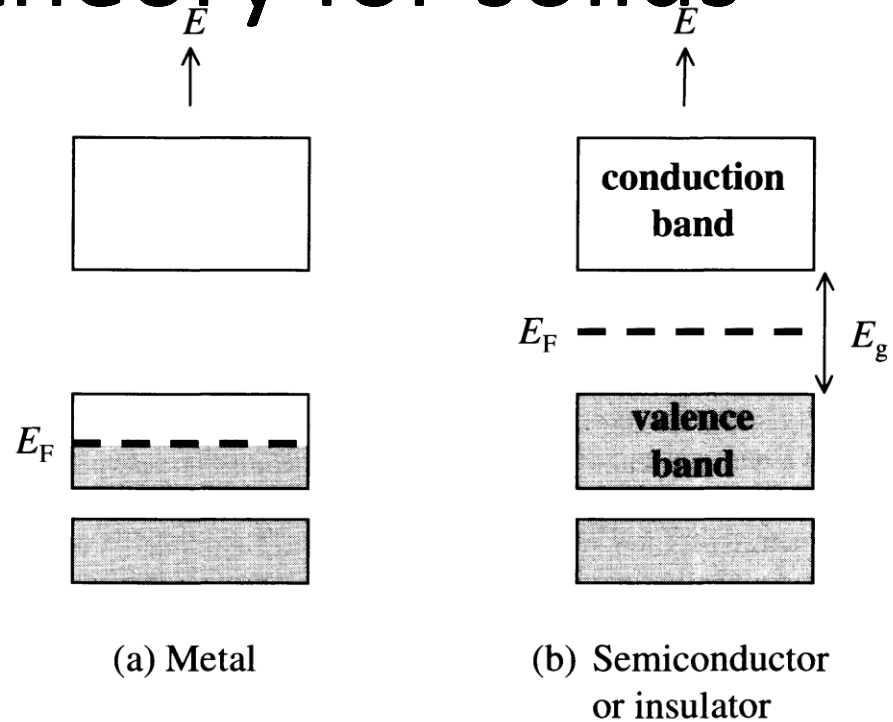


Fig. C.1 Energy level diagrams for (a) a monovalent or trivalent metal, and (b) a semiconductor or insulator. The bands are filled with electrons up to the Fermi level E_F. This is indicated by the shading.

- **Fermi energy/level E_F :** In the simplest definition, the energy below which all states are filled with electrons and above which all states are empty at T =0 K.
- In a metal the Fermi level lies within a band, electrons can move freely.
- In an insulator the valence band is fully filled and the conduction band is empty. Electrons are immobile.
- An intrinsic (perfect, without defects) semiconductor basically behaves like an insulator but has a smaller bandgap (no exact definition in terms of bandgap values).

Thermal excitation of charge carriers

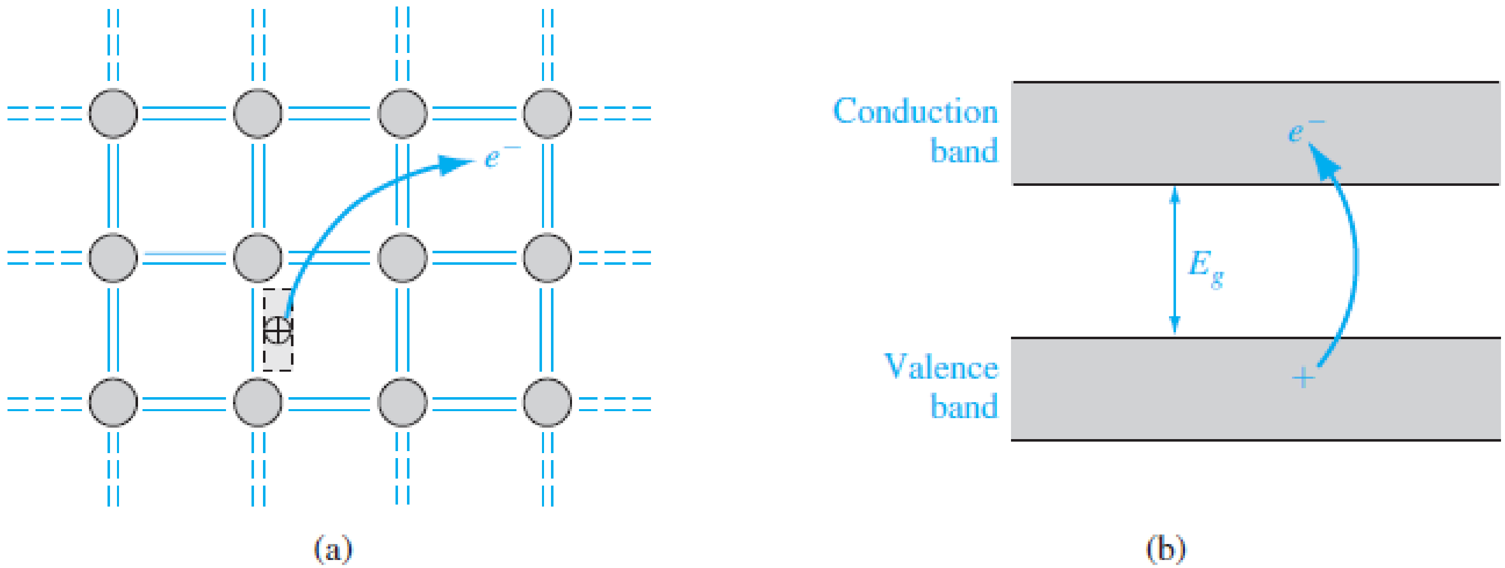


Figure 3.13 | (a) Two-dimensional representation of the breaking of a covalent bond. (b) Corresponding line representation of the energy band and the generation of a negative and positive charge with the breaking of a covalent bond.

- At T>0K, electrons may gain enough thermal energy (at least E_G) to break the covalent bond and jump into the conduction band. By doing so it leaves a positive empty state (a **hole**) in the valence band.
- Free electrons and holes are created in pairs (**e-h pairs**). Electrons in the conduction band and holes in the valence band are **free charge carriers** (free to move in the crystal).

Absorption

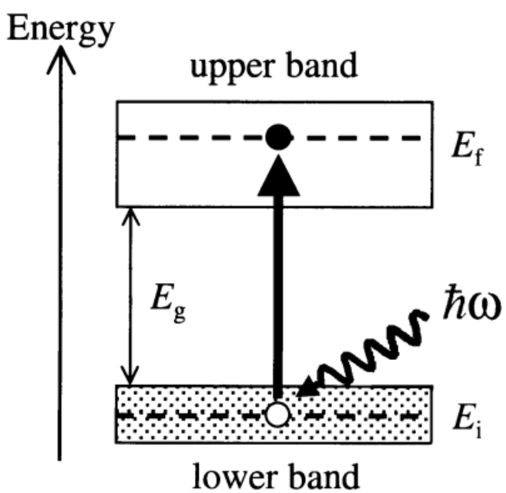


Fig. 3.1 Interband optical absorption between an initial state of energy E_i in an occupied lower band and a final state at energy E_f in an empty upper band. The energy difference between the two bands is E_g.

- A photon excites an electron from the VB to the CB (i.e. creating an **electron-hole pair**):
- $E_f = E_i + \hbar\omega$
- Since there is a continuous range of energy states the transitions will be possible in a continuous range of frequencies (in contrast to the absorption spectrum of atoms which consists of discrete lines).

What is the difference between Si and GaN?

What is the difference between Si and GaN?

Si

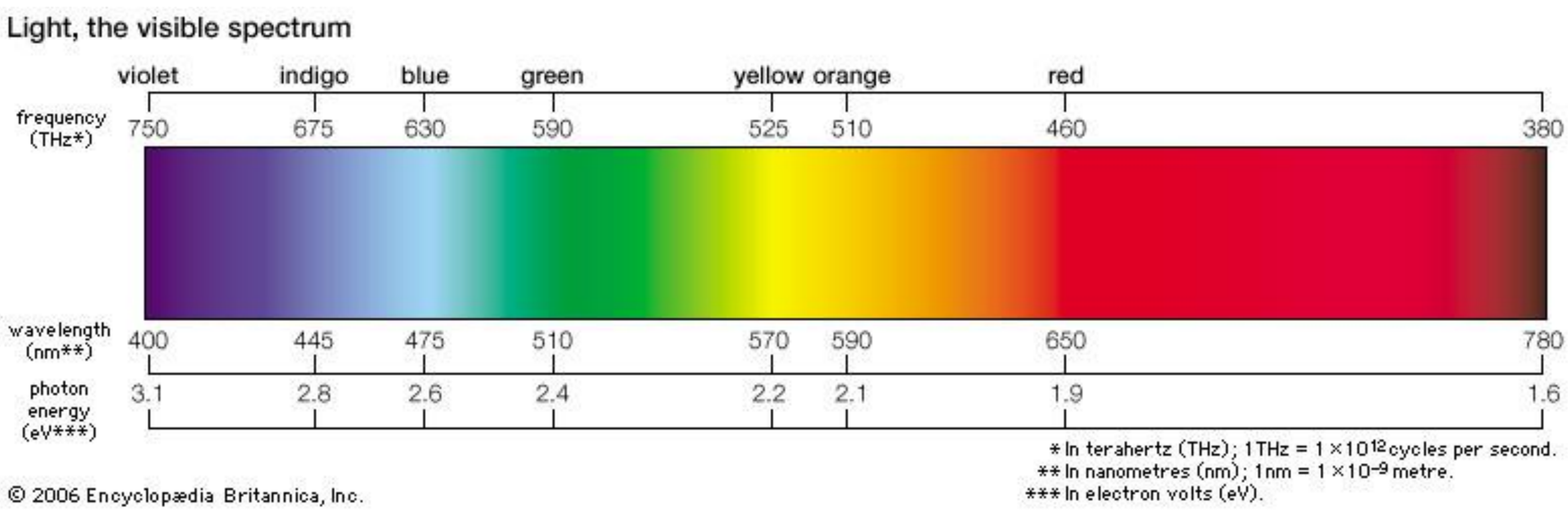
- Semiconductor with a narrow bandgap (1.1 eV)

→ Opaque for visible light

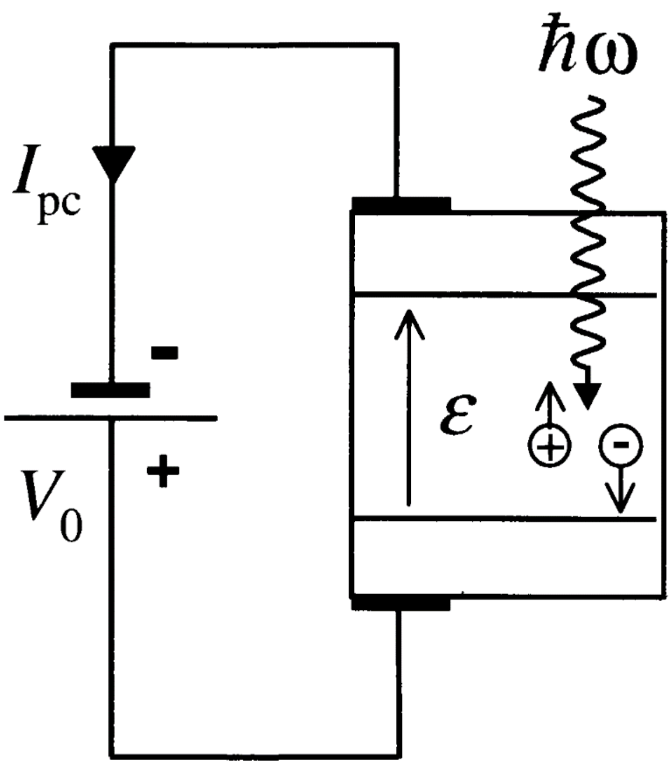
GaN

- Semiconductor with a wide bandgap (3.4 eV)

→ Transparent for visible light



Absorption: Photodetector



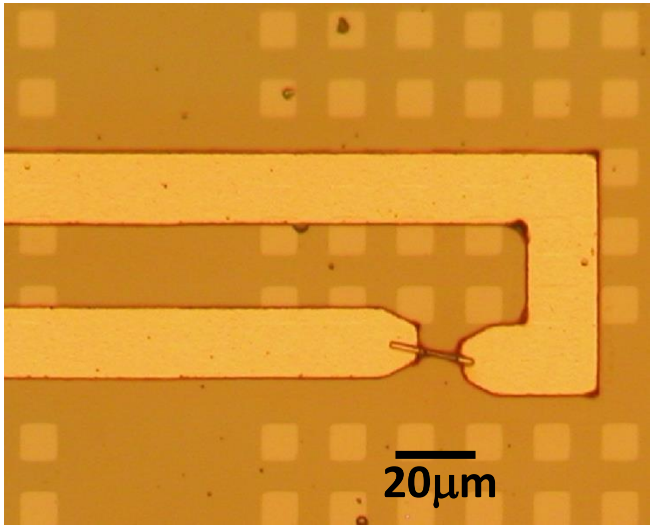
- Absorption of light (with $\hbar\omega \geq E_G$) by a semiconductor produces free electrons on the CB and holes in the VB
- Light can be detected by measuring the current in an external circuit or the change in resistance of the semiconductor.

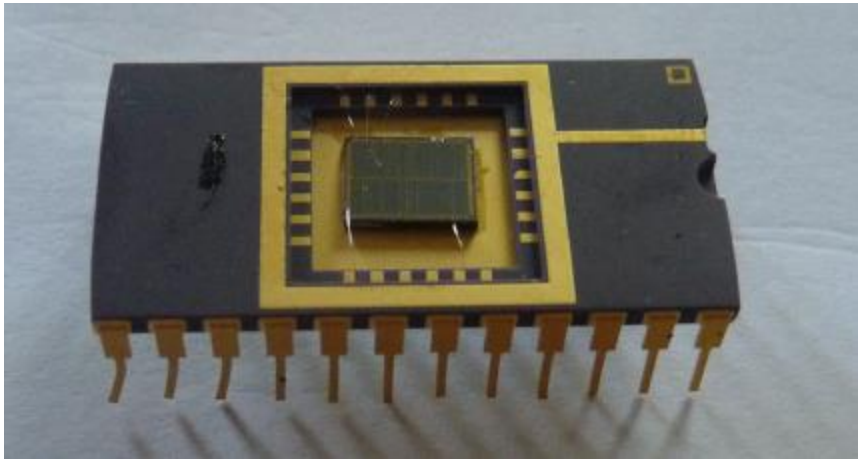
$\Rightarrow$ More sophisticated photodetectors are based on junctions (e.g. metal-semiconductor, pn-junctions etc.)

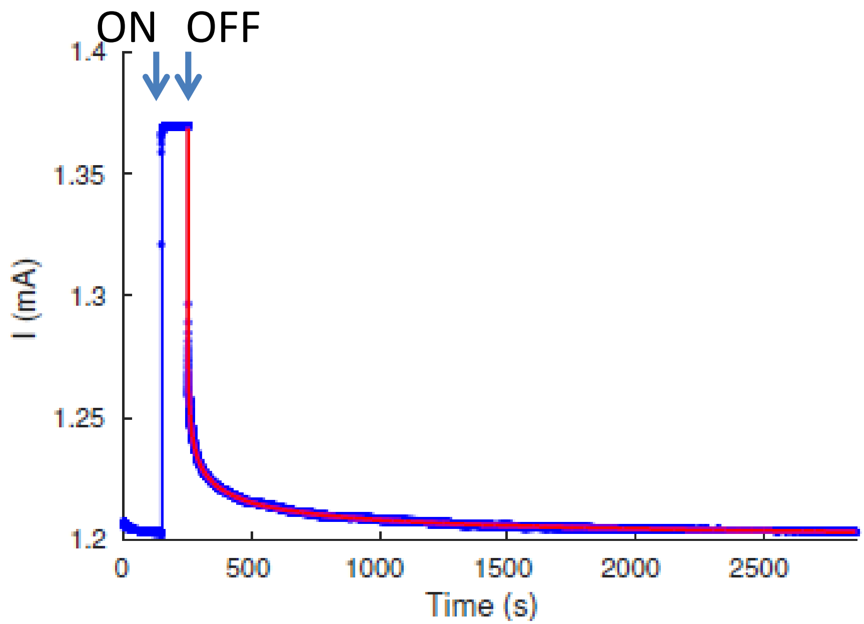
Absorption: Photodetector

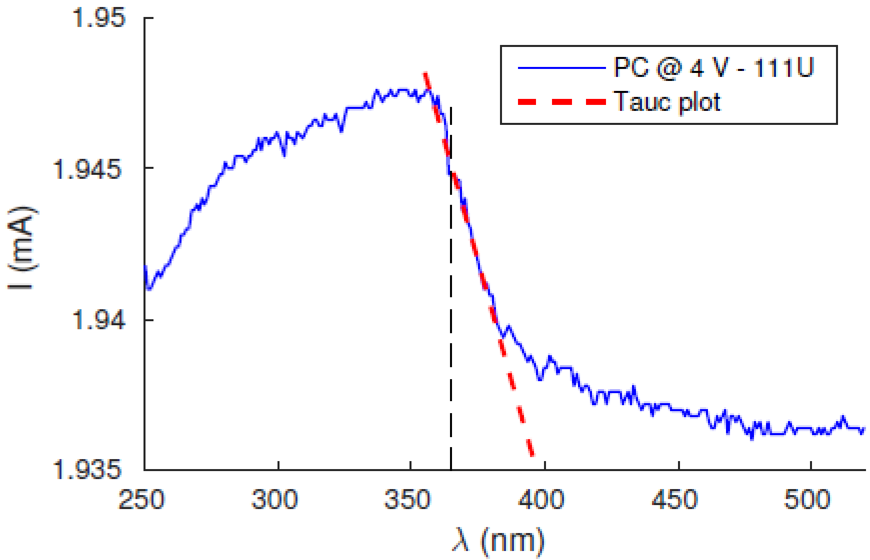
- GaN microwire photodetectors

D. Verheij, master thesis, IST, 2017







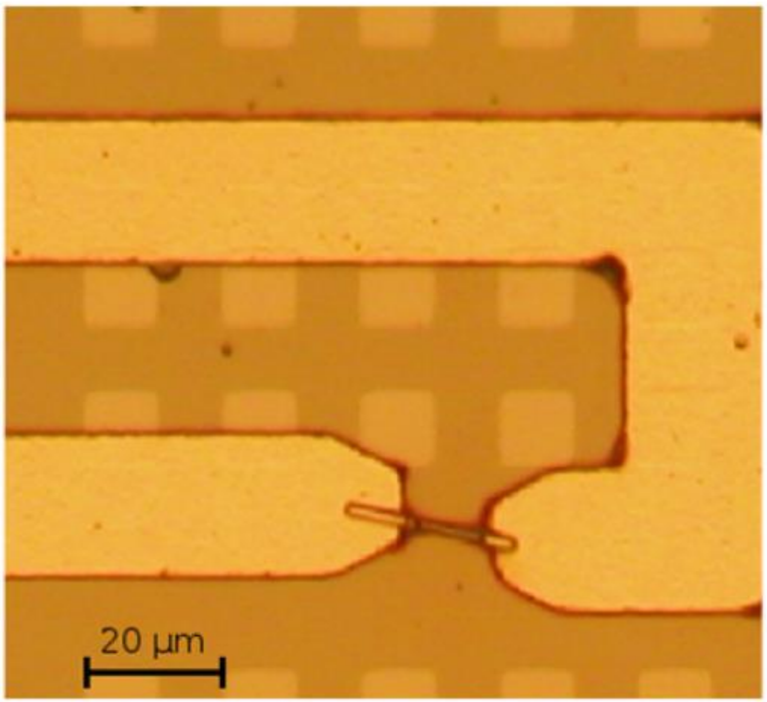


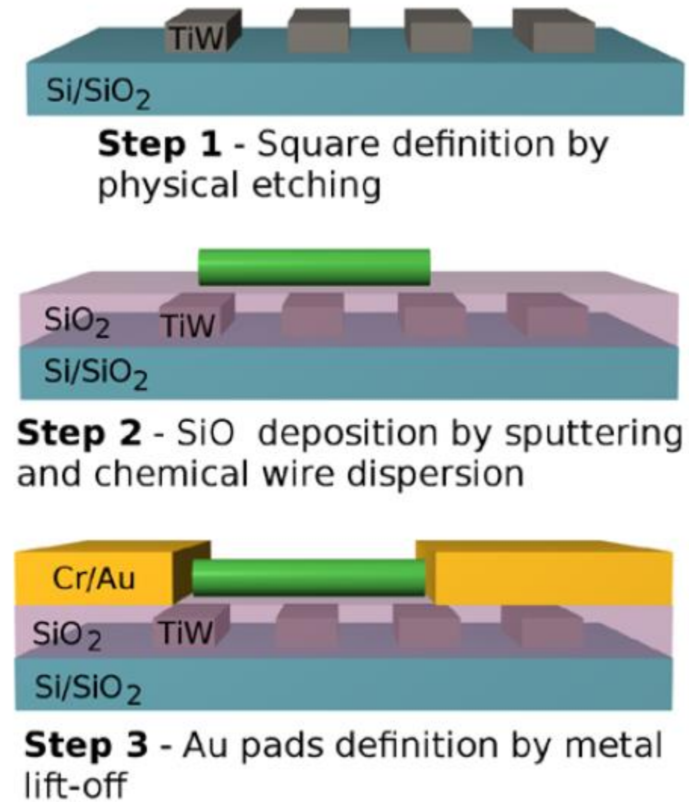
Absorption: Photodetector

- GaN microwire photodetectors

D. Verheij, master thesis, IST, 2017

The nano-fabrication challenge





Absorption: Photodetector Applications

Communications

- The radiation carries a signal which is read by a photodetector

$\rightarrow$ e.g. fiberoptic communications, remote controls

Remote sensing

- Radiation is the signal and gives information on an object or process.

$\rightarrow$ e.g. monitoring of UV radiation by sun, combustion, explosion etc.; automotive collision sensors (an IR laser signal is reflected and detected)

Thermal or optical excitation of charge carriers

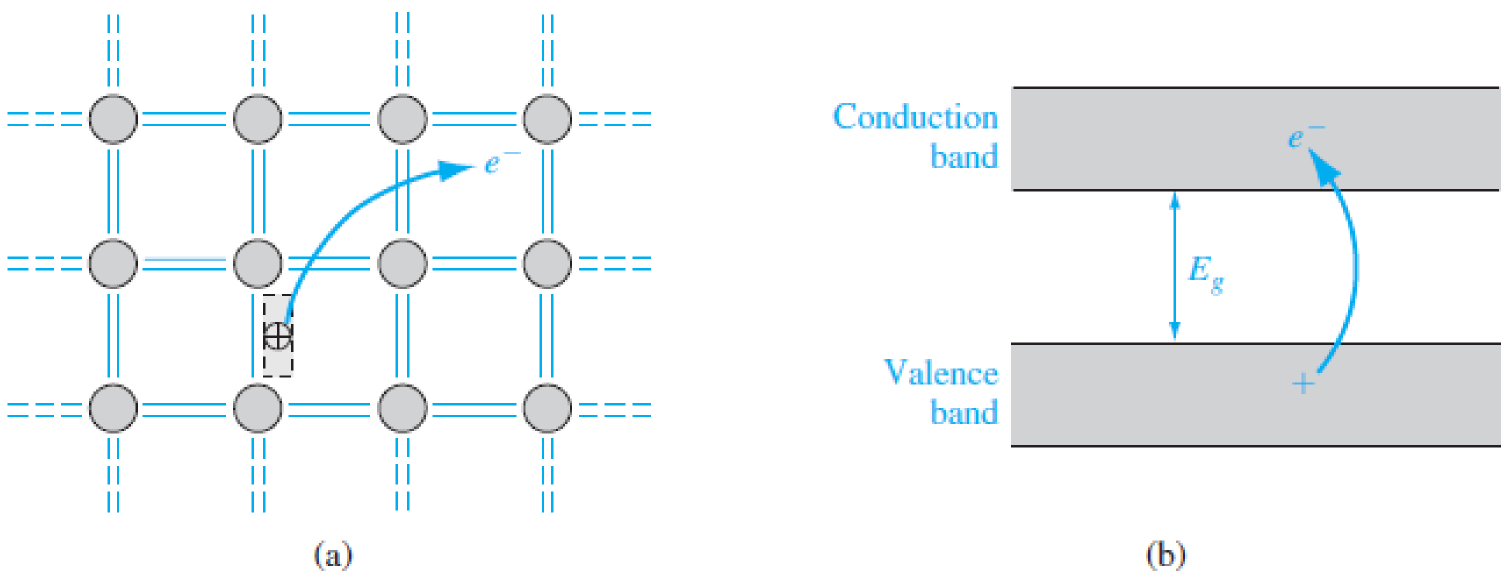


Figure 3.13 | (a) Two-dimensional representation of the breaking of a covalent bond. (b) Corresponding line representation of the energy band and the generation of a negative and positive charge with the breaking of a covalent bond.

Radiative and Non-radiative Recombination

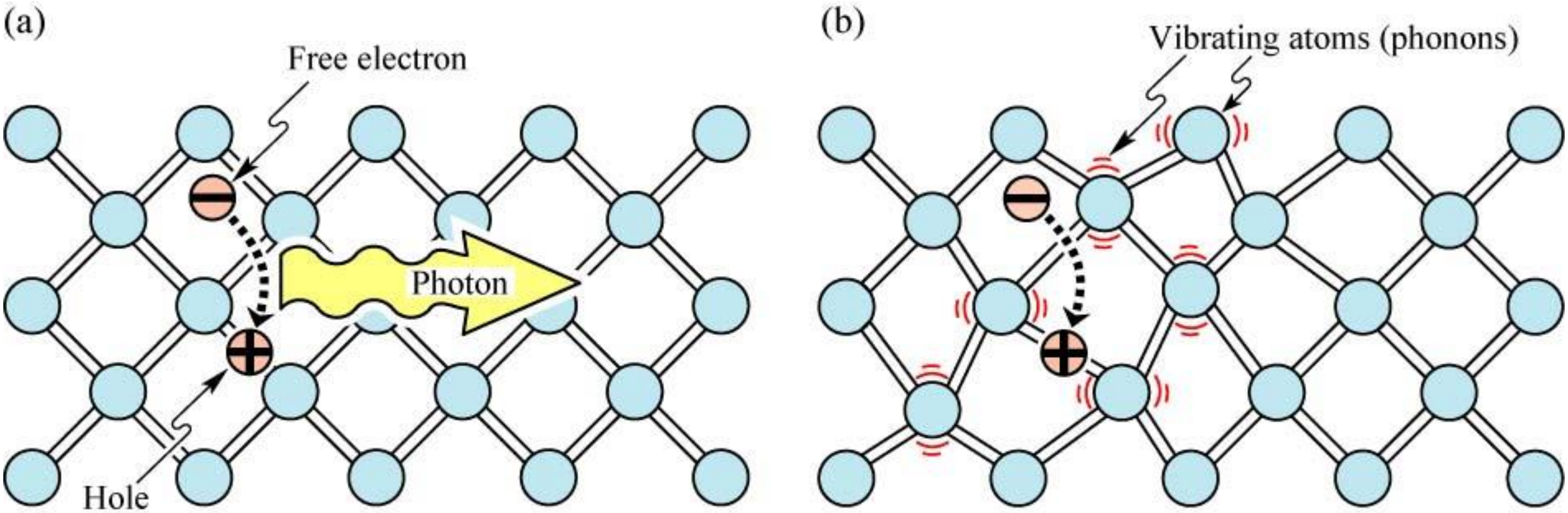


Fig. 2.5. (a) Radiative recombination of an electron-hole pair accompanied by the emission of a photon with energy $h\nu \approx E_g$. (b) In non-radiative recombination events, the energy released during the electron-hole recombination is converted to phonons (adopted from Shockley, 1950).

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Light-Emitting Diodes (Cambridge Univ. Press)
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- Creation of heat due to non-radiative recombination limits the efficiency of LEDs.
- This occurs in particular at crystal defects.

Radiative and Non-radiative Recombination

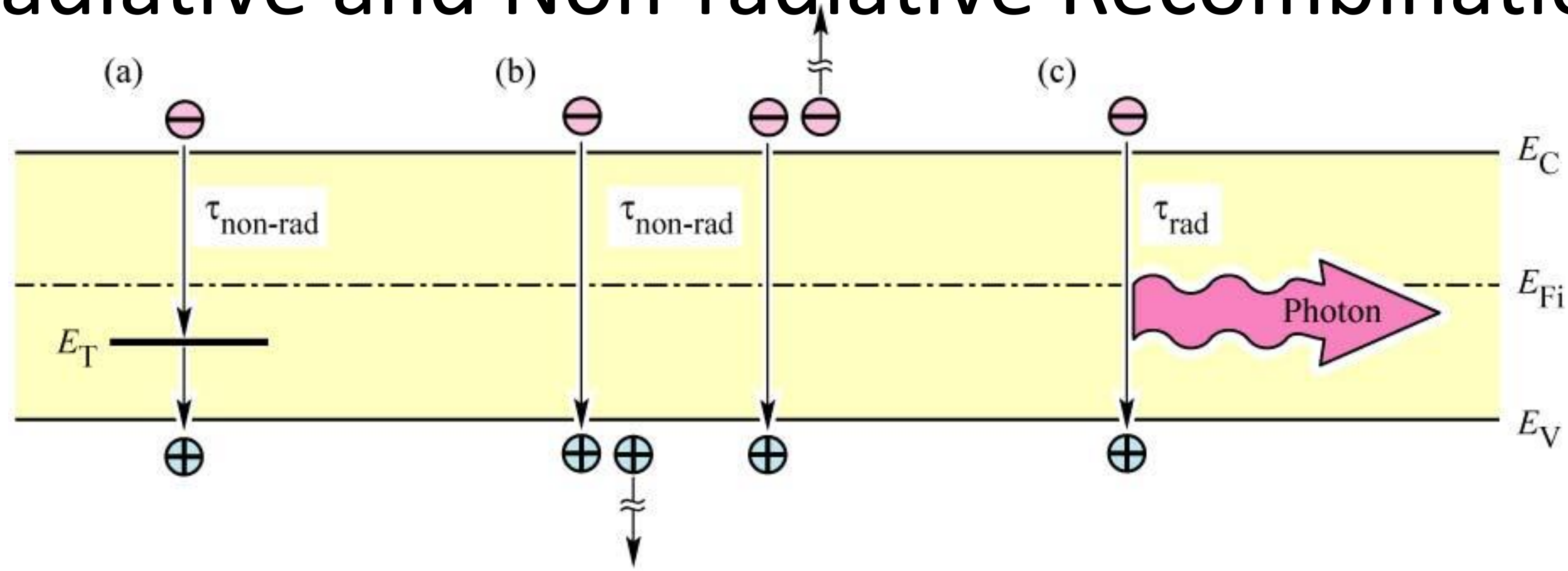

Fig. 2.6. Band diagram illustrating non-radiative recombination: (a) via a deep level, (b) via an Auger process and (c) radiative recombination.

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Competition between radiative and non-radiative processes:

- Radiative recombination (strong in direct bandgap semiconductors and desired process in LEDs and laser diodes)
- Non-radiative recombination via deep levels (called Shockley-Read-Hall recombination)
- Non-radiative Auger recombination (the energy is transferred to another change carrier)

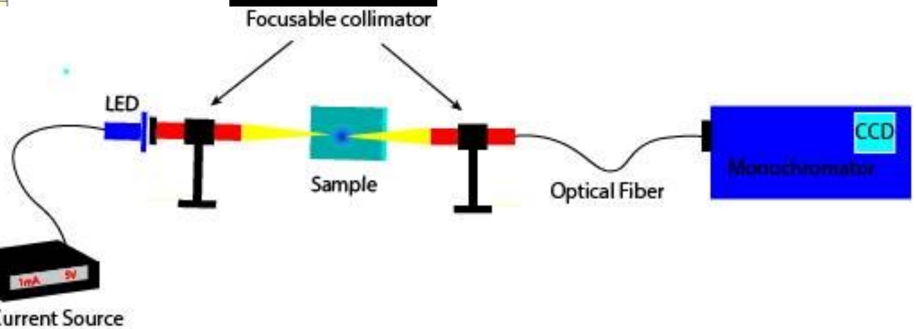
Photoluminescnce

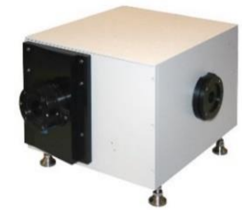
Focussing

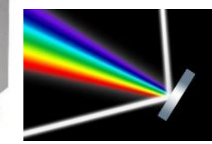
Excitation sources

Detection

- UV-VIS focusable collimator

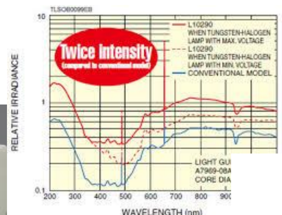






- Monochromator

Two gratings (1200 l/mm, 600 l/mm)



- Lamp UV-VIS

fiber light source outputs 200 to 1600 nm.

- LED’s UV-VIS

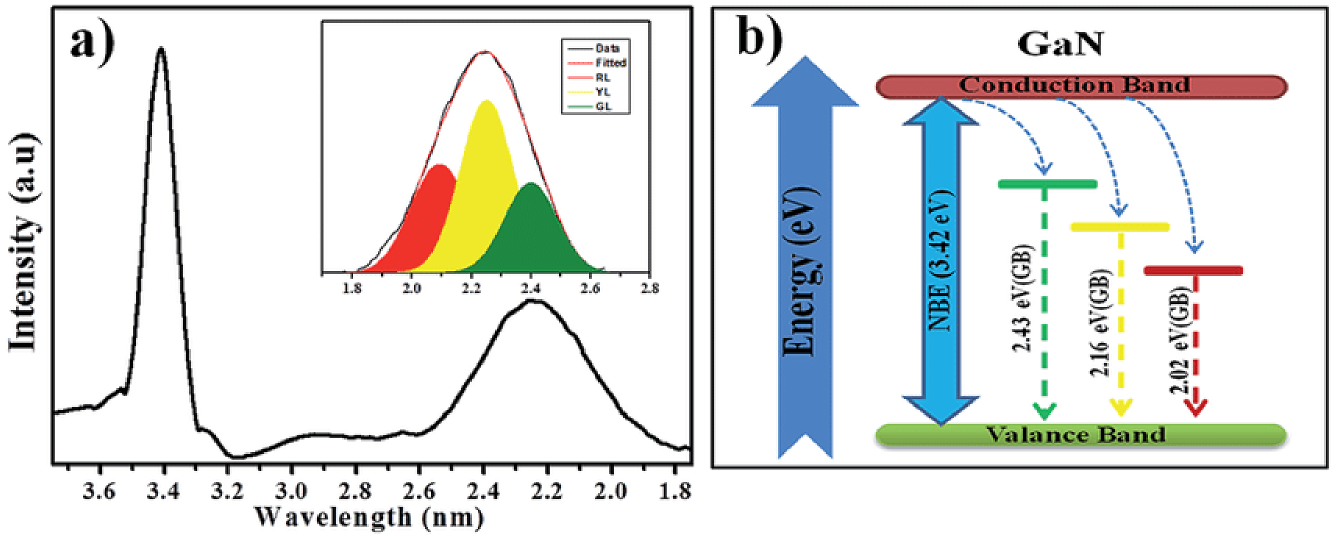
different wavelengths (240nm, 365nm, 405nm)

Adjusting the current source it is possible to tune the excitation density.

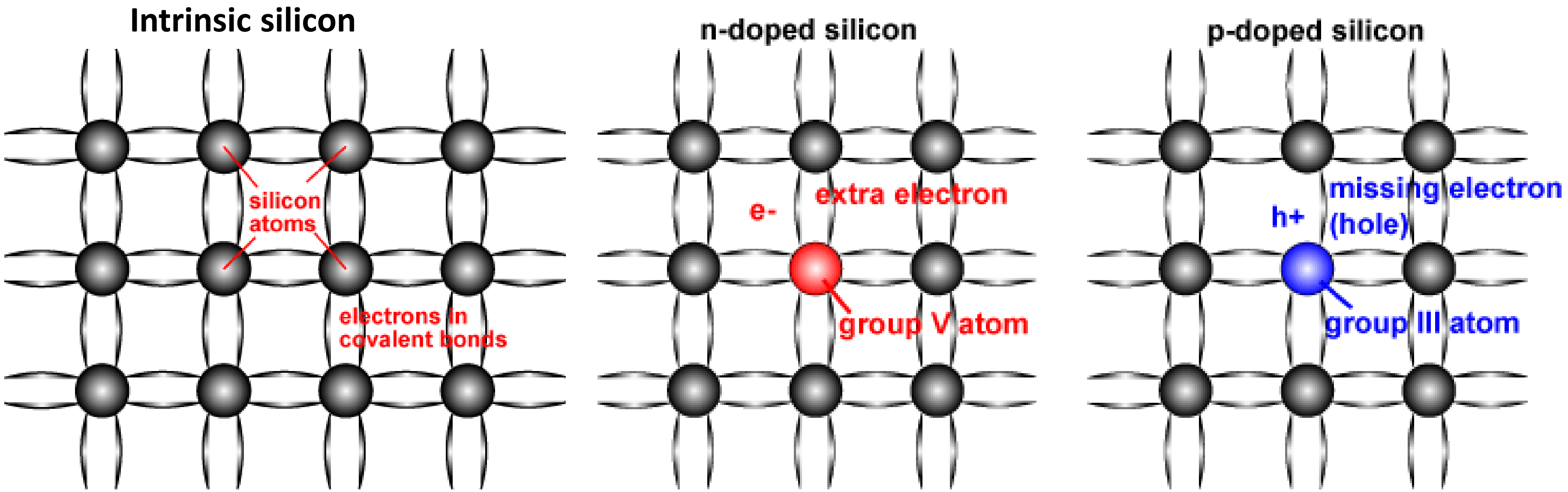
- CCD detector

Working in the UV-VIS.NIR (250nm-900nm)

Photoluminescence

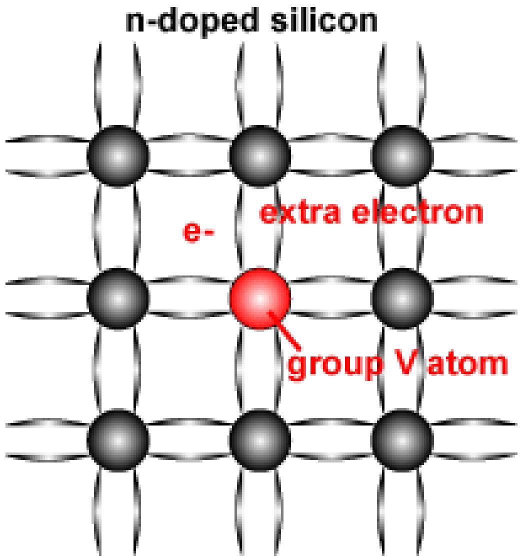


Doping



- **n-type doping:** replacing a Si atom by a group-V atom adds an extra electron to the conduction band (in Si usually thermal energy is sufficient at room temperature) which will be free to move (note the charge neutrality since the group-V atom is neutral). Electrons are **majority charge** carriers and holes are minority charge carriers.
- **p-type doping:** replacing a Si atom by a group-III atom causes a hole (one electron is missing for the bonding) in the valence band. Holes are **majority charge** carriers and electrons are minority charge carriers.

n-type doping: donor states



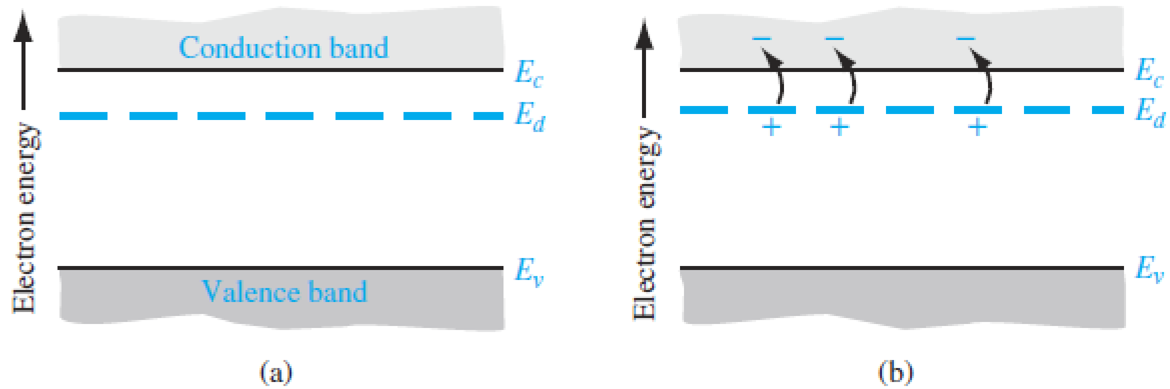
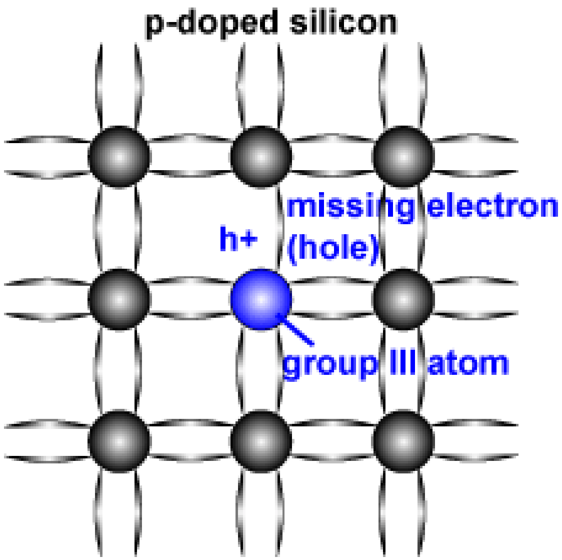


Figure 4.5 | The energy-band diagram showing (a) the discrete donor energy state and (b) the effect of a donor state being ionized.

- A donor impurity introduces **donor states** into the bandgap close to the conduction band.
- Depending on the exact position of the donor level and the temperature the "extra"-electron can be thermally excited to the conduction band.
- In Si the donor levels are close to the conduction band so that at room temperature the thermal energy kT is sufficient to ionize most of the donor states (in wide bandgap semiconductors this is not necessarily true).
- The **filled donor level is neutral**.
- The **empty donor level is positively charged** (ionised).

p-type doping: acceptor states



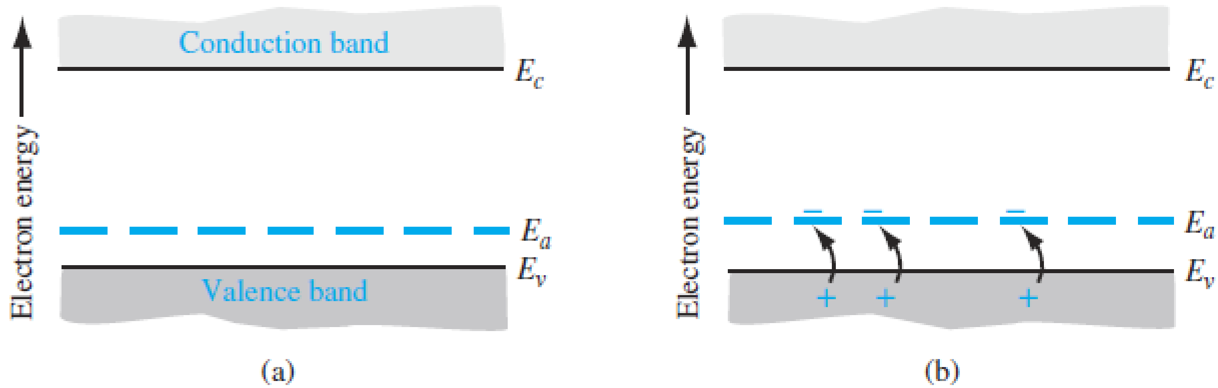
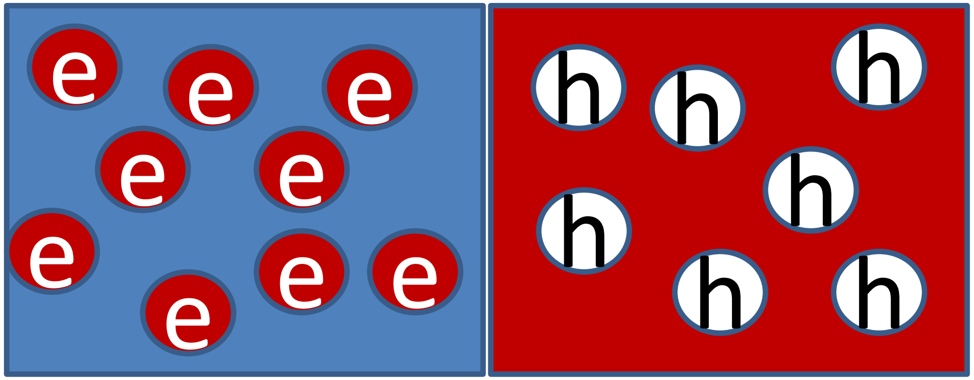


Figure 4.7 | The energy-band diagram showing (a) the discrete acceptor energy state and (b) the effect of an acceptor state being ionized.

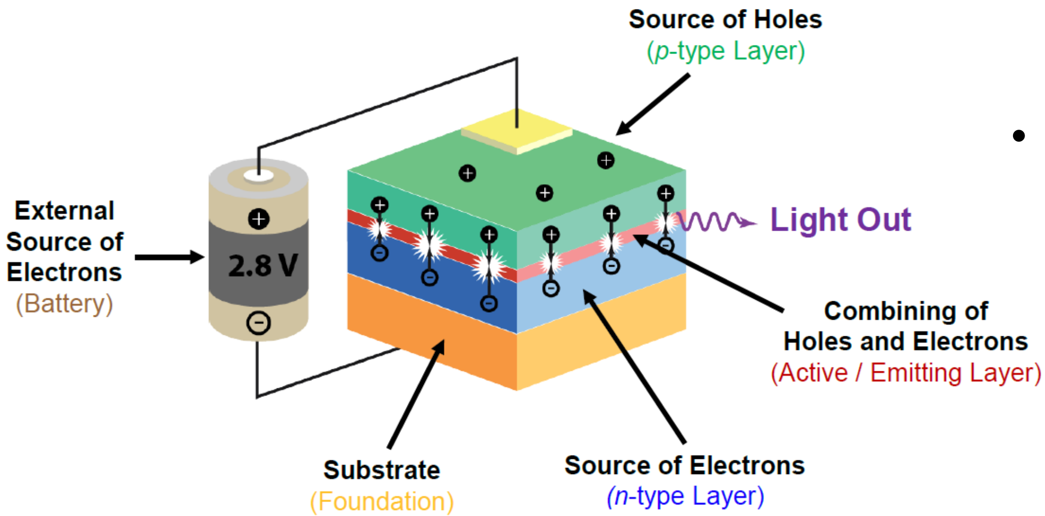
- An acceptor impurity introduces **acceptor states** into the bandgap close to the valence band.
- Depending on the exact position of the acceptor level and the temperature an electron from the valence band can be thermally excited to fill the acceptor level.
- In Si the acceptor levels are close to the valence band so that at room temperature the thermal energy kT is sufficient to ionize most of the acceptor states.
- The **unfilled acceptor level is neutral**.
- The **filled acceptor level is negatively charged** (ionised).

pn-Junction

- n-type semiconductor in contact with a p-type semiconductor

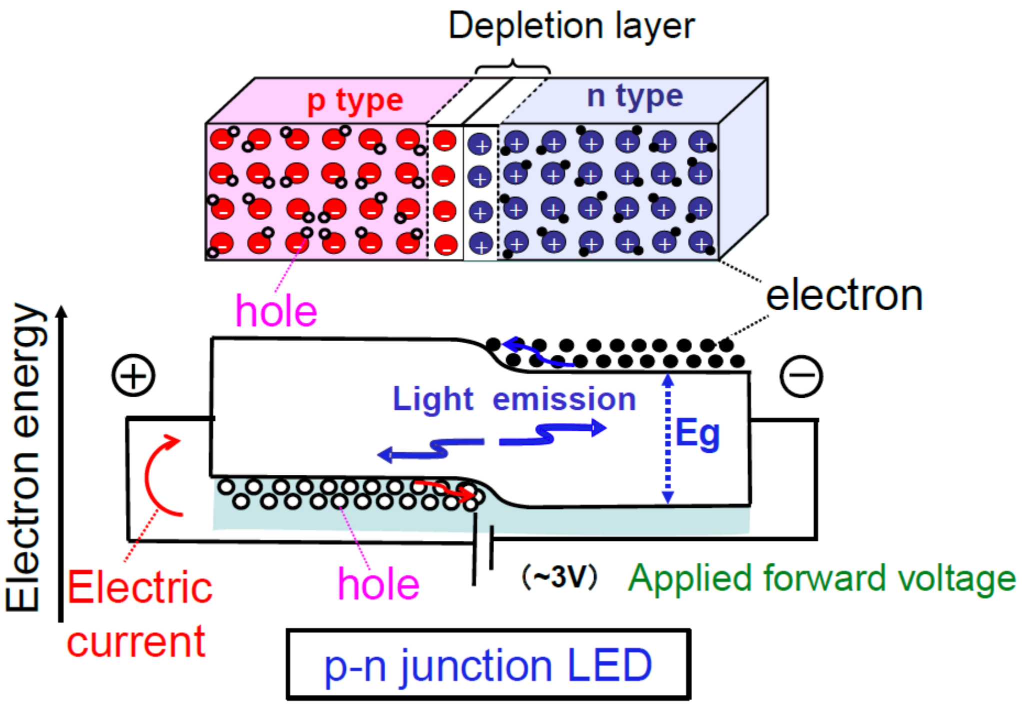


Light Emitting Diode



- Thin epitaxial layers are grown on a substrate forming a p-n junction

- When applying a forward bias, electrons can flow to the p-type layer and holes to the n-type layer.
- The e-h recombination leads to light emission where the wavelength (colour) depends on the bandgap energy of the semiconductor.



What is the forward voltage one needs to apply?

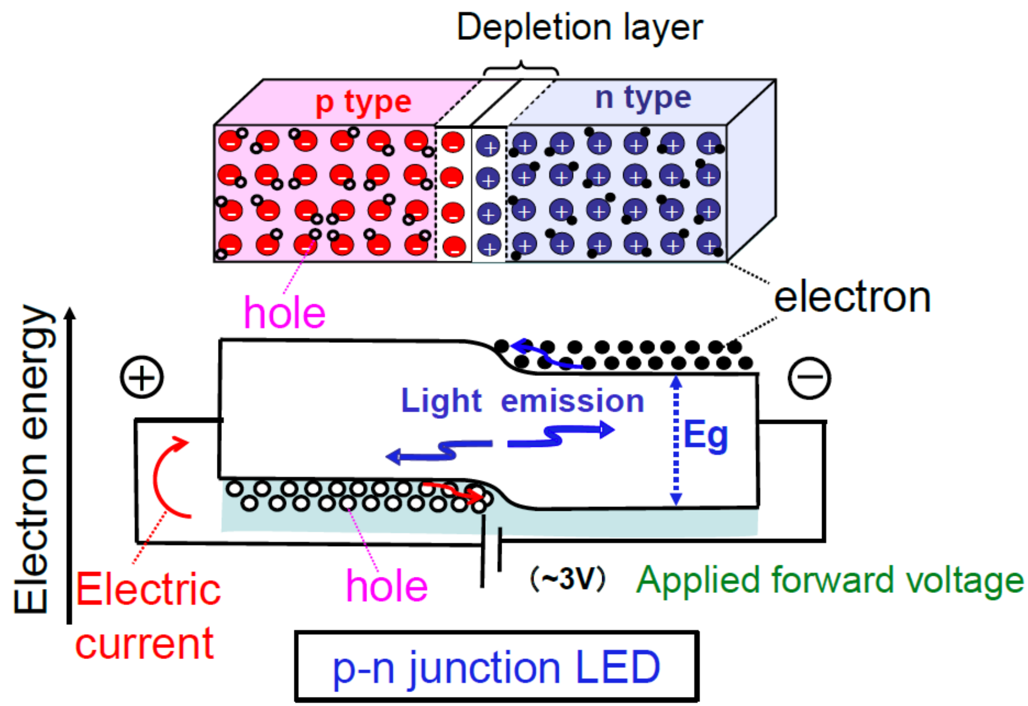
Light Emitting Diode

What is the forward voltage one needs to apply?

- Ideally each injected electron (with energy eV) leads to the emission of a photon (with energy hf).

- Considering the conservation of energy we expect:
$$hf = eV \leftrightarrow V \geq E_G/e$$

- Of course there are losses e.g. due to contact resistance. But on the other hand there is already some emission at lower voltage due to the thermal energy of charge carriers.



Internal Quantum Efficiency of an LED

- Total recombination rate is described by the ABC-model:

$$R = An + Bn^2 + Cn^3$$

n: Carrier concentration

A: Shockley-Read-Hall recombination due to deep levels

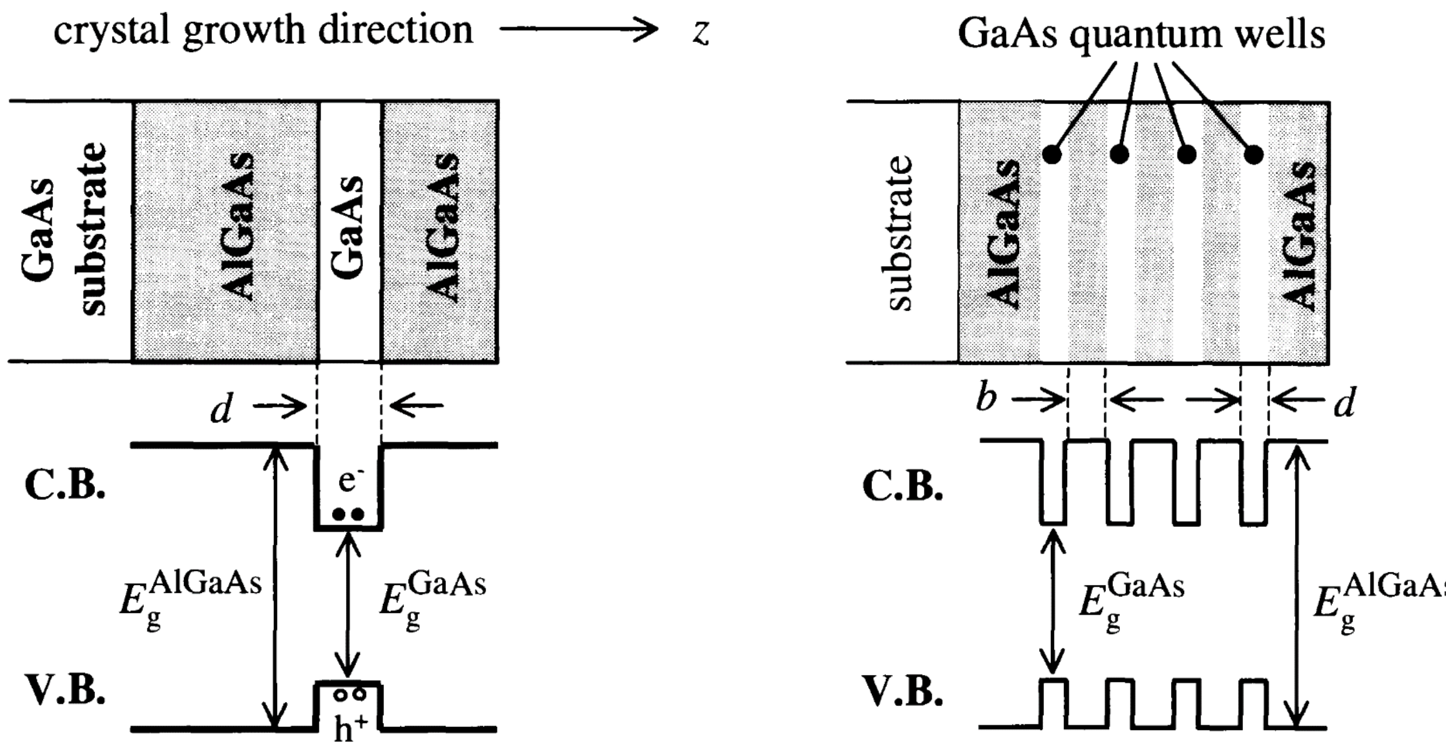
B: radiative recombination

C: Auger recombination

- Internal Quantum Efficiency:

$$IQE = \frac{radiative\ recombination\ rate}{total\ recombination\ rate} = \frac{Bn^2}{R}$$

Epitaxially grown QW



(a) Single quantum well

(b) MQW or superlattice

- Single QW: thin layer sandwiched between two thick layers with higher bandgap
- Multi QW: succession of several QWs separated by spacer layers with thickness b>d
- Superlattice: as MQW but with b~d

Double heterojunction/QW LED

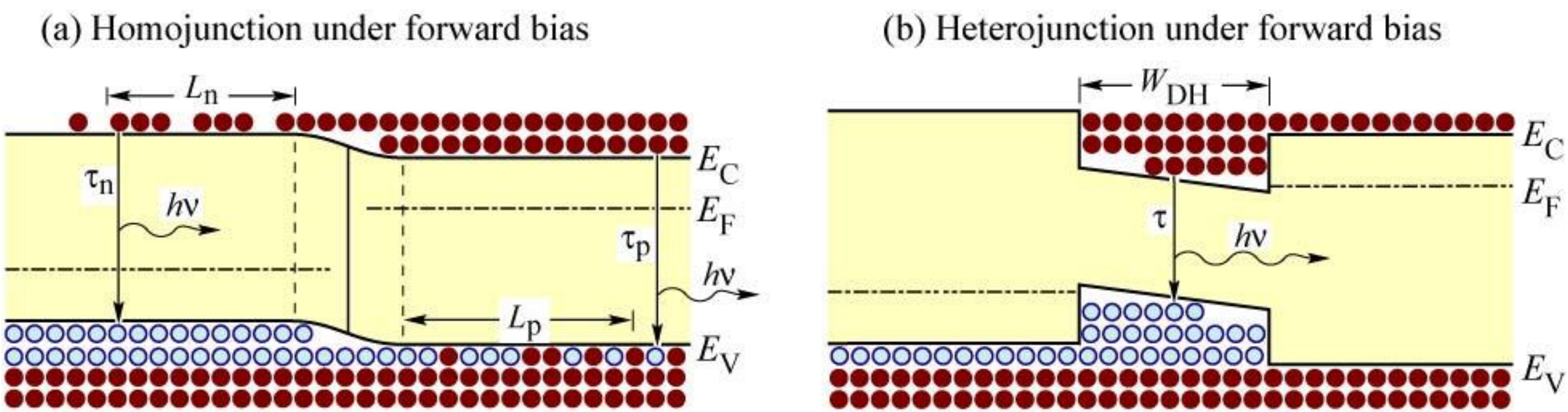


Fig. 7.2. Free carrier distribution in (a) a homojunction and (b) a heterojunction under forward bias conditions. In homojunctions, carriers are distributed over the diffusion length. In heterojunctions, carriers are confined to the well region.

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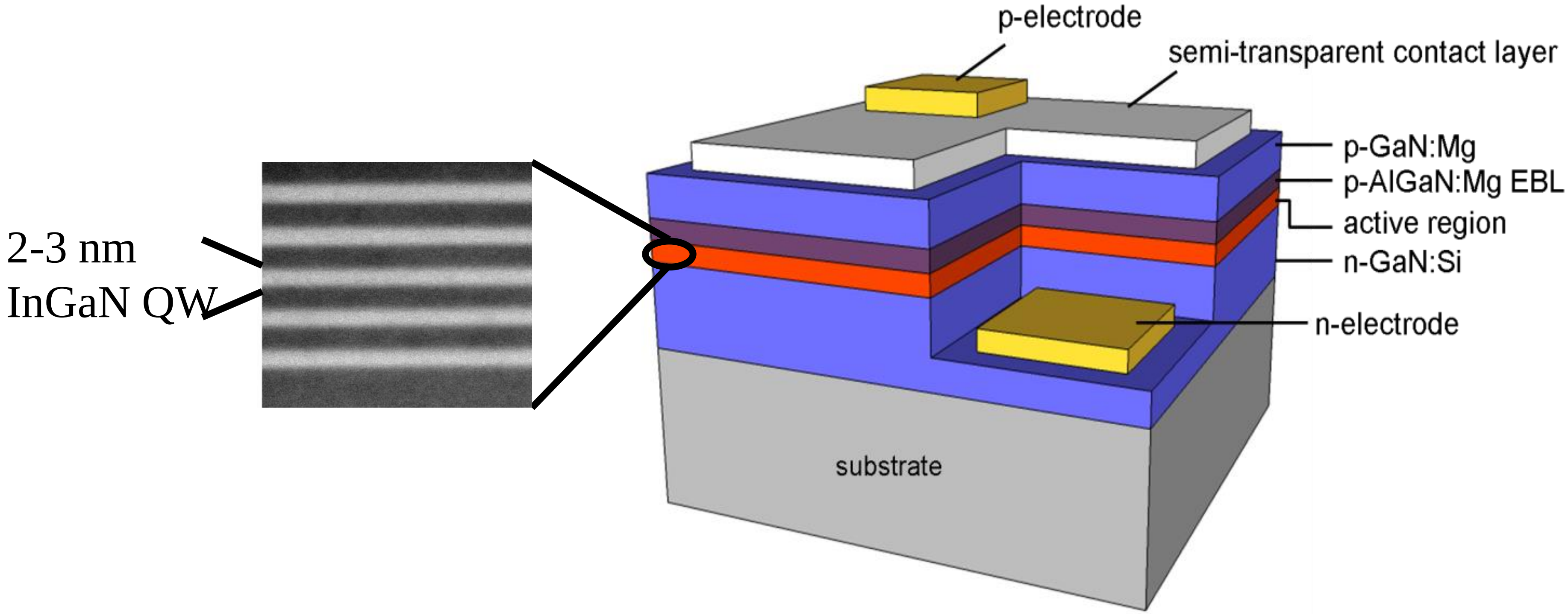
The confinement of carriers in the QW leads to higher efficiency due to:

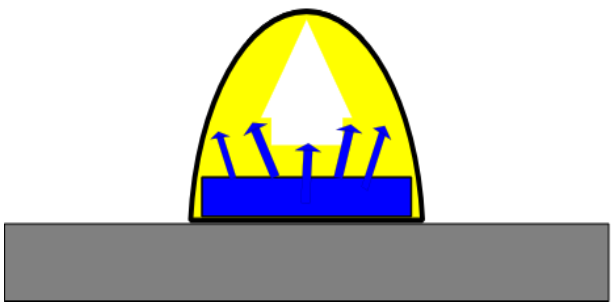
- Higher matrix element (higher electron-hole wave function overlap), this reduces the radiative lifetime and thus non-radiative transitions.
- Higher exciton binding energies,
- Higher carrier concentrations also lead to higher radiative carrier recombination (ABC-model: $R = An + Bn^2 + Cn^3$).

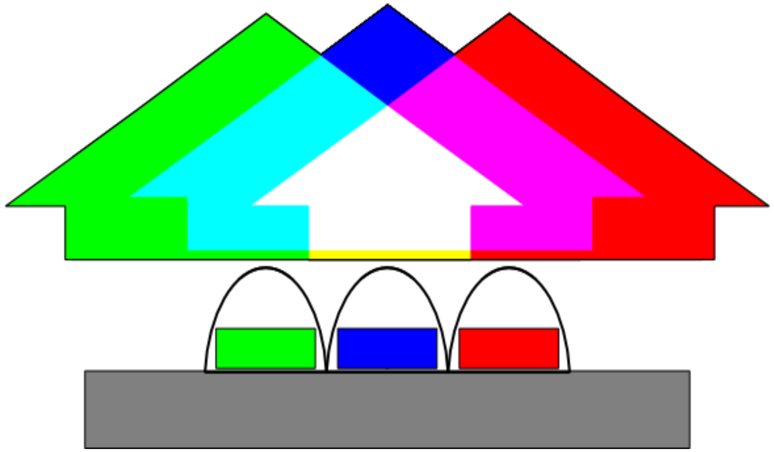
III-N Light Emitting Diodes



The emission wavelength depends on the InN content in the InGaN quantum wells (QW) and the thickness of the QWs

White Light Emitting Diodes



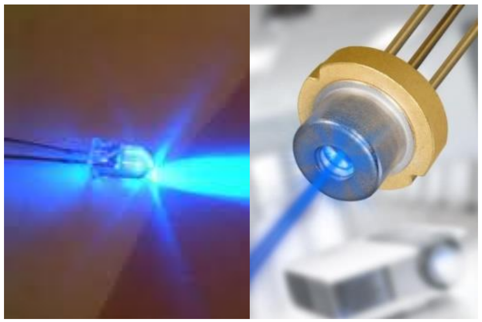


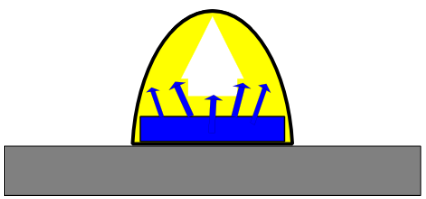
Current approach:
Blue LED + yellow emitting phosphor
→ Energy loss during absorption/emission

Envisaged approach:
Direct combination of three colour LEDs
→ Potentially more efficient
→ More versatile

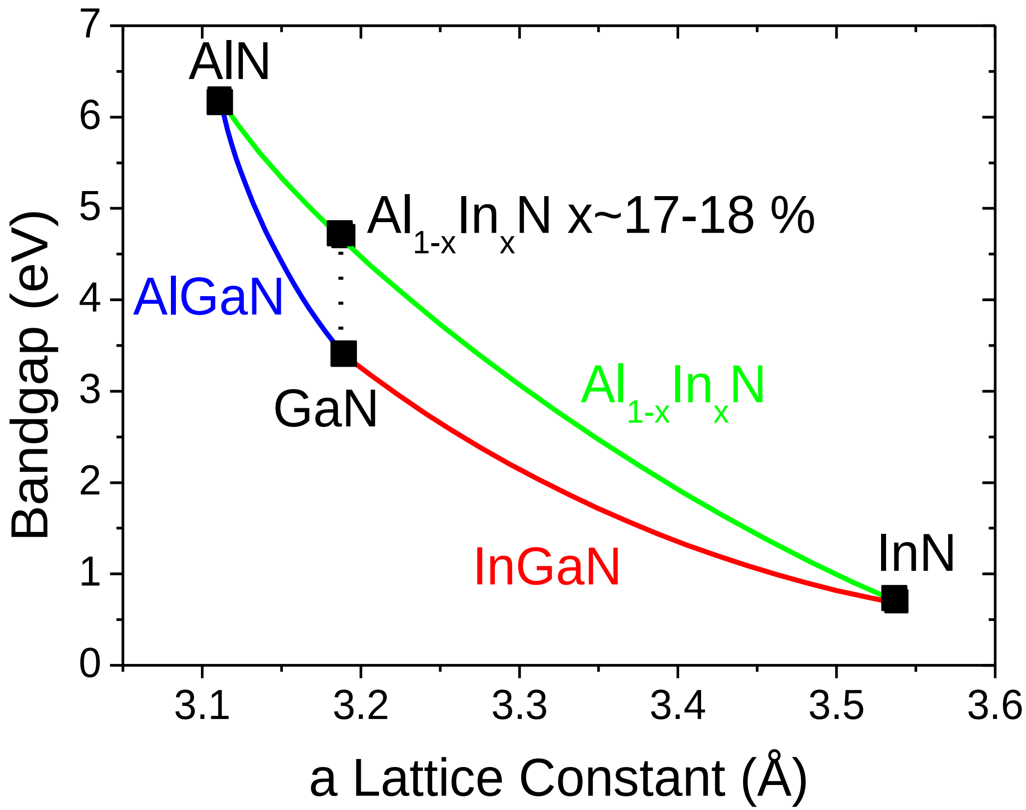
Group III Nitrides

InGaN:
LEDs, LASERS



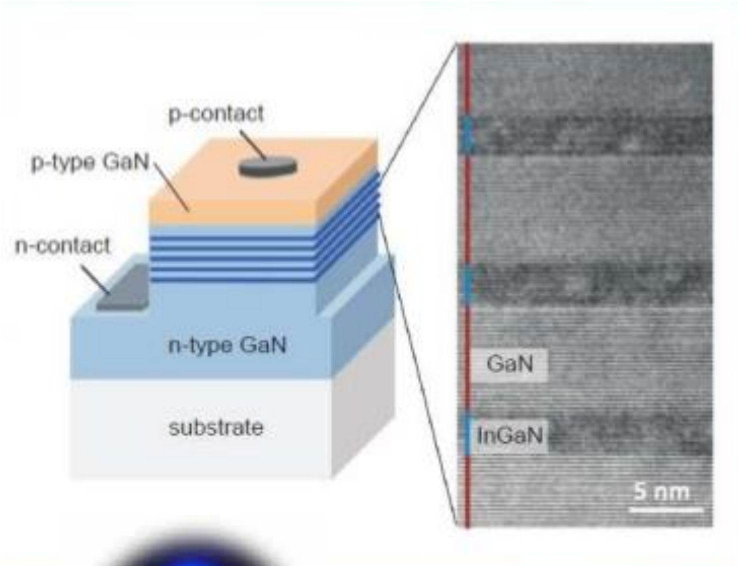


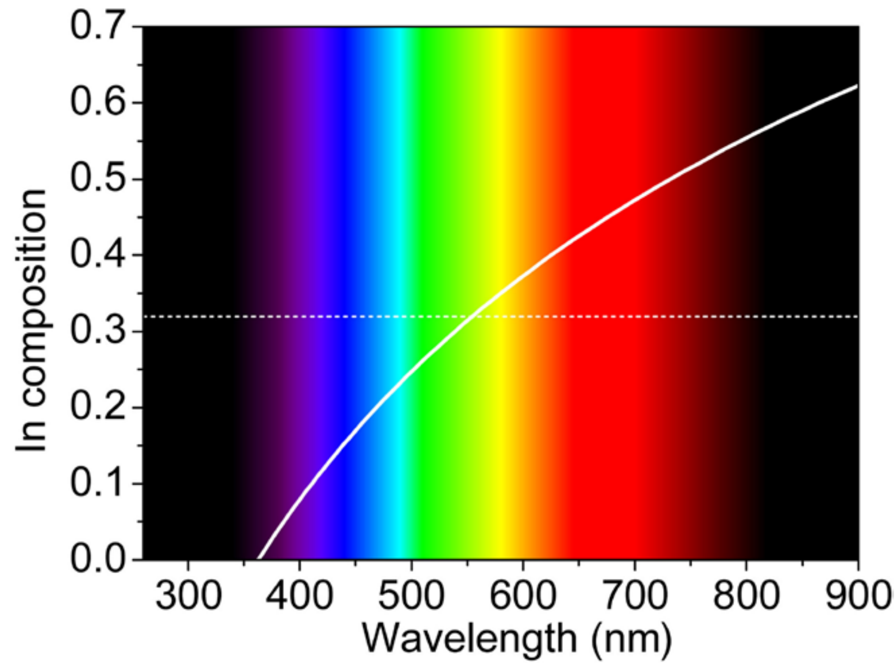
AlGaN/AlInN: UV emitters/detectors,
High power, high frequency electronics



Photodetectors and radiation sensors

III-N Light Emitting Diodes

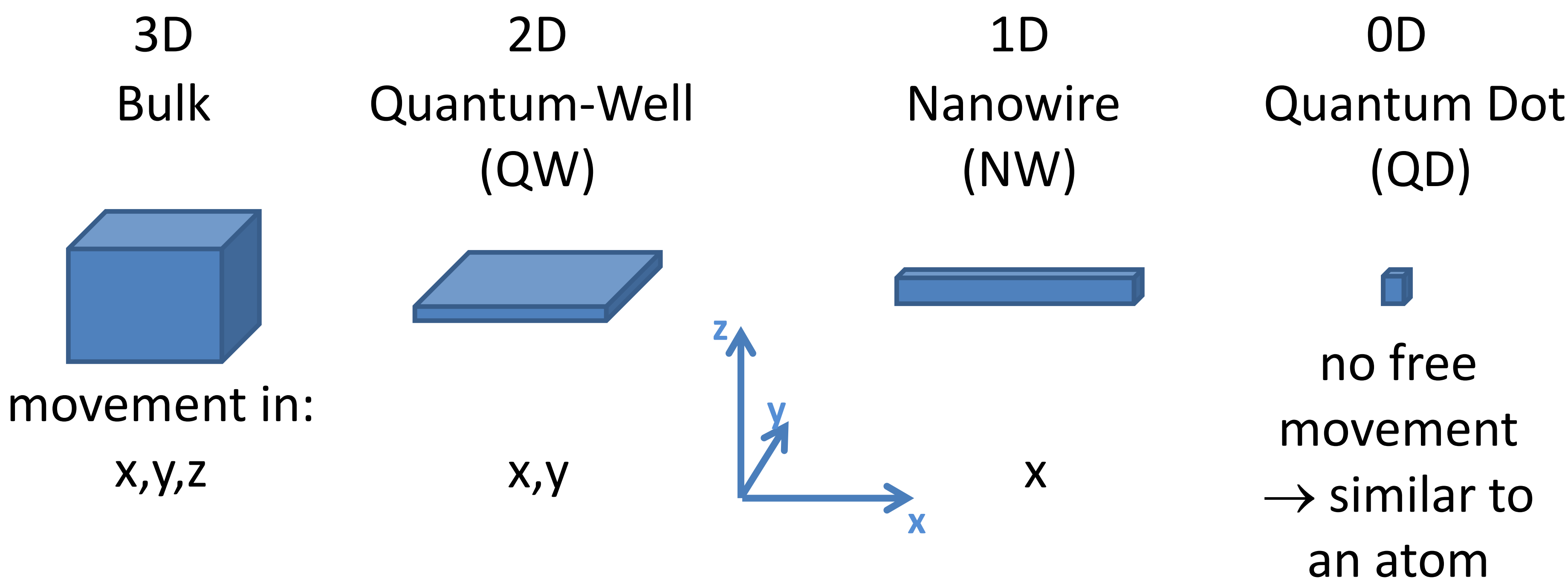




The emission wavelength depends on the InN content in the InGaN quantum wells (QW) and the thickness of the QWs

Quantum Confinement

- In a bulk semiconductor crystal electrons and holes are free to move in all three dimensions.
- In nanostructures electrons and holes are confined in one or more directions.

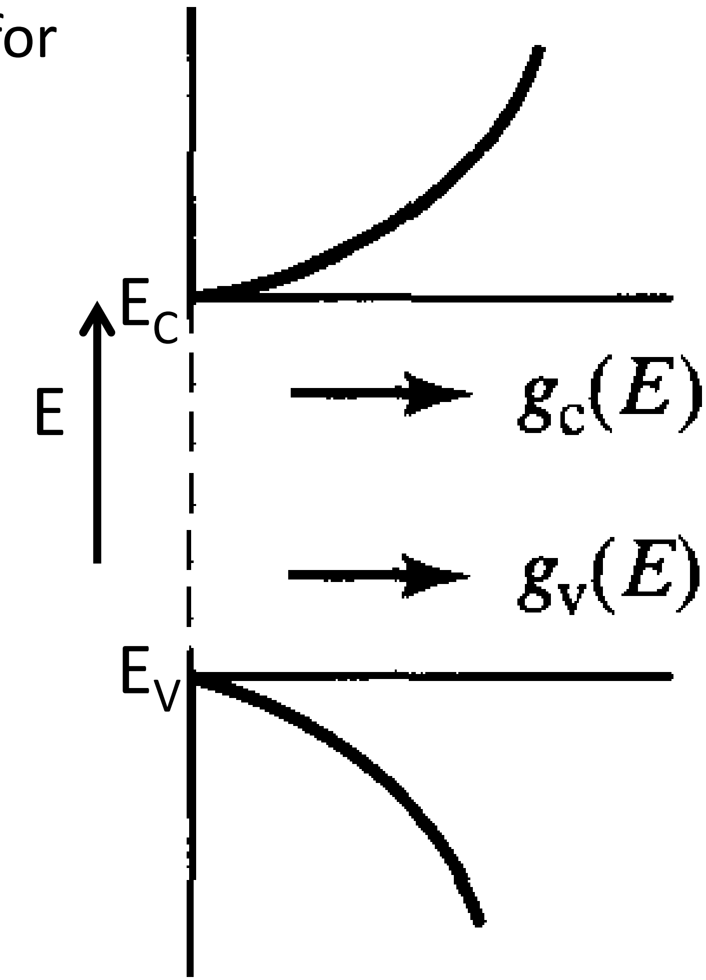


Density of states

- We saw that in Si every atom contributes with 4 (mostly filled) states to the valence band and 4 (mostly empty) states to the conduction band (i.e. a total of 4xN states, where N is the atomic density which has a magnitude in the order of the Avogadro constant $N_A=6\times10^{23}\ mol^{-1}$).
- The distribution of these states in energy is called the **Density of States (DOS)**.

Density of states of a bulk crystal

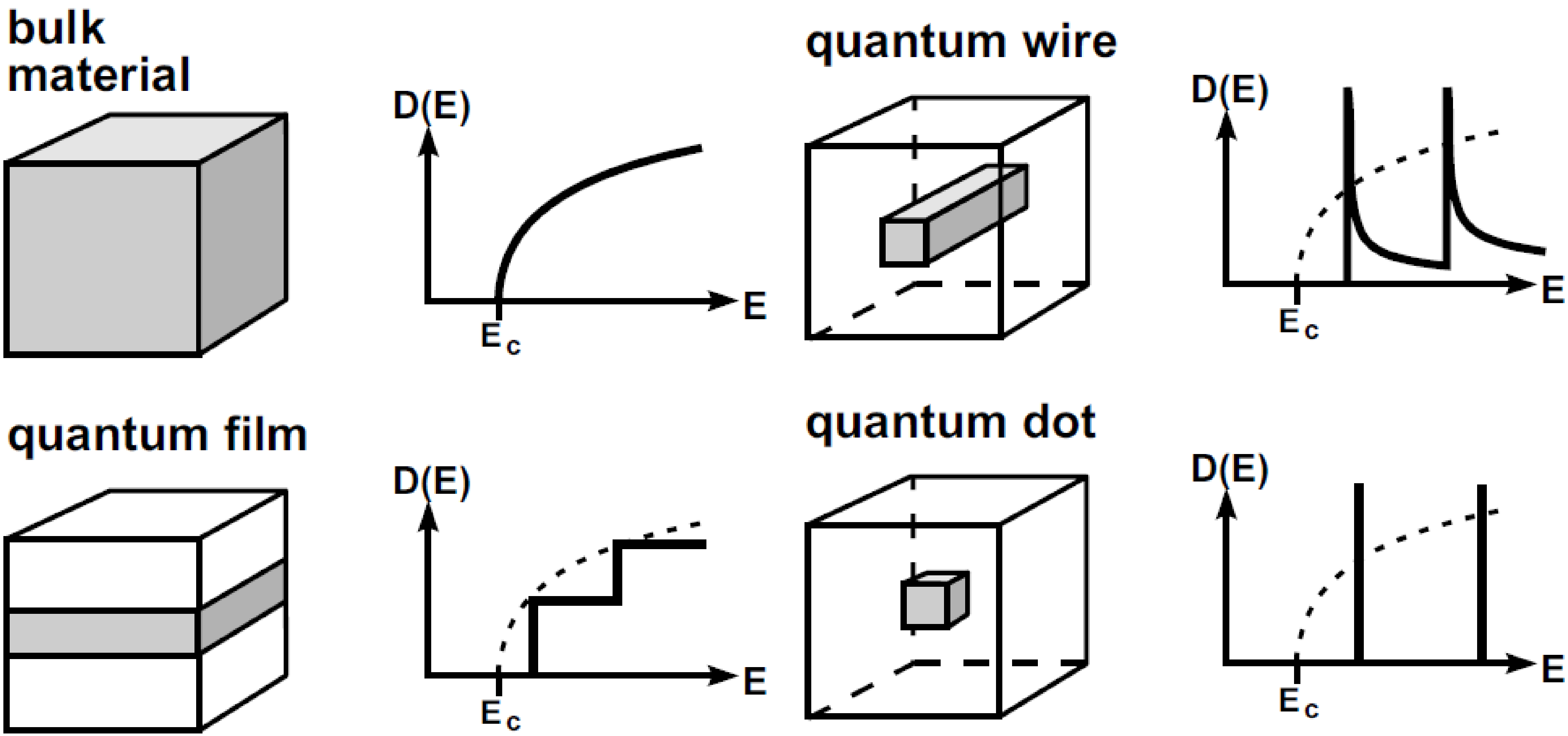
Expressions for the **DOS** can be calculated for the valence band, g_V, and the conduction band, g_C, using quantum mechanics:



$$g_C(E) = \frac{m_e{}^* \sqrt{2m_e{}^* \, (E - E_C)}}{\pi^2 \hbar^3} cm^{-3}eV^{-1}$$

$$g_V(E) = \frac{m_h{}^* \sqrt{2m_h{}^* \, (E_V - E)}}{\pi^2 \hbar^3} cm^{-3}eV^{-1}$$

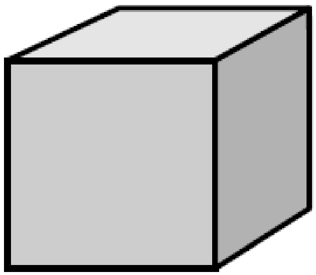
Nanostructures: Density of states

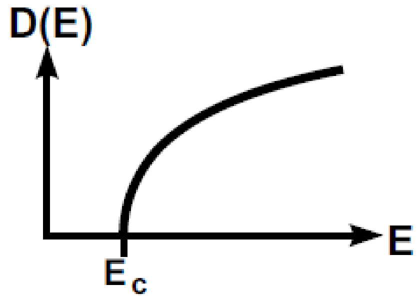


The quantization in a potential is ruled by the Schrödinger equation with appropriate boundary conditions.

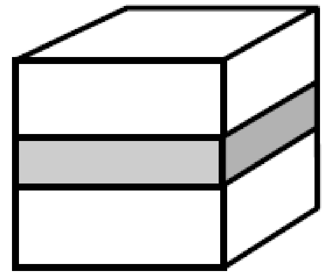
Experiment: Absorption bulk vs. QW

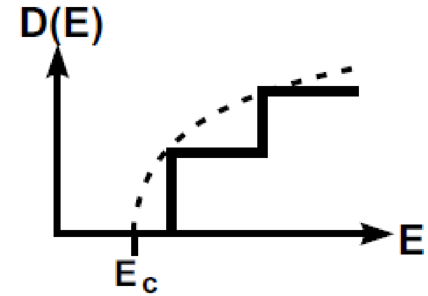
bulk material

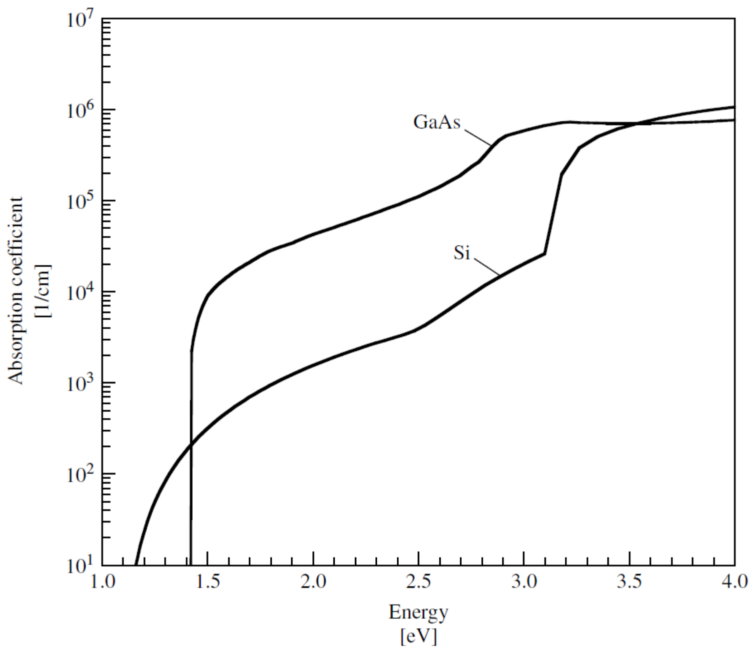


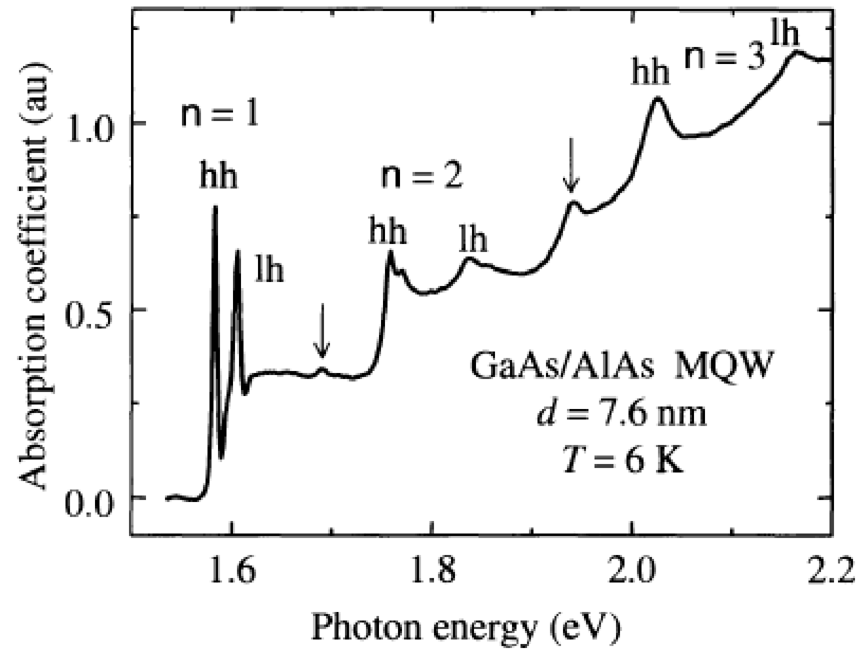


quantum film







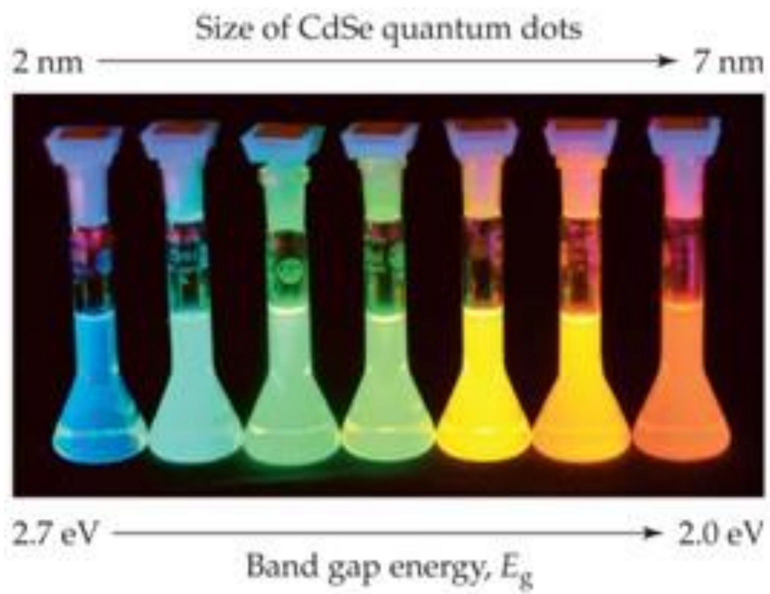


- Step-like absorption and increased bandgap in QW is clearly visible and agrees with the step-like density of states.

Quantum dots

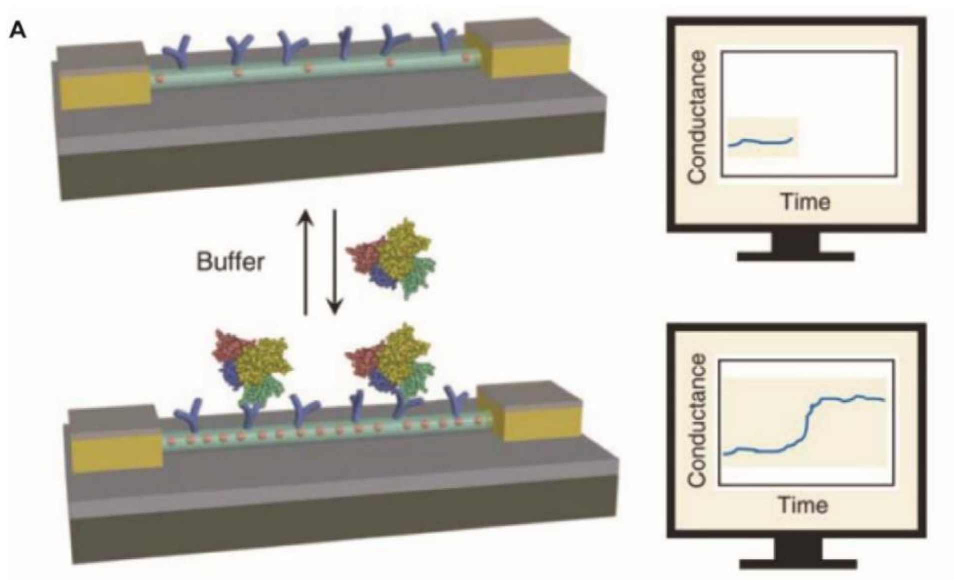
Further confinement e.g. in quantum dots will further increase optical efficiencies.

- The mixing of semiconductor quantum dots with glass is used in light filters, church windows (even in medieval times);
- LCD screens as bright, efficient and pure colour light sources;
- solar cells for multi-wavelength absorption of the entire solar spectrum;
- For medical and biological applications for fluorescence imaging.



Nanosensors

Further applications of semiconductor nanostructures may not be based on quantum effects but on the large surface-to-volume ratio: nanowires UV sensors, chemical sensors, biological sensors.



Adsorption of biomolecules or chemical molecules change the conductance of a nanowire or 2D sheet.

Summary

- Quantum confinement in 1,2 or 3 dimensions changes the absorption and emission properties of semiconductors (change of transition probabilities and density of states).
- Absorption edge and emission increase in energy when the dimension of the nanostructure is in the order of the de Broglie wavelength of the particle.

$\rightarrow$ Allows tuning of optical properties

- Confinement in QW LEDs increases electron-hole overlap, increases the exciton binding energy, increases the carrier density

$\rightarrow$ Increased efficiency compared to simple pn-junctions

Summary

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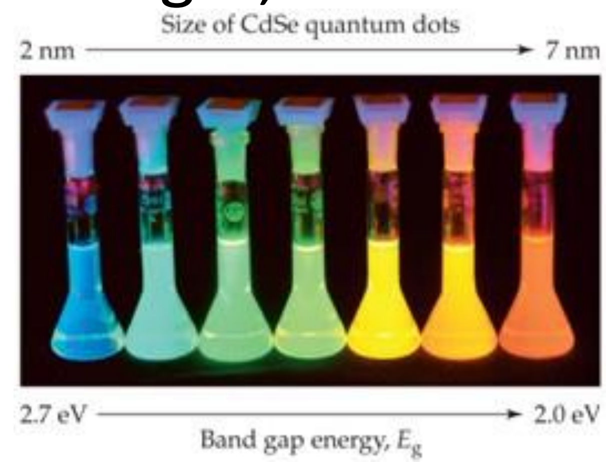

- Further applications of semiconductor nanostructures may not be based on quantum effects but on the large surface-to-volume ratio: nanowires UV sensors, chemical and bio sensors