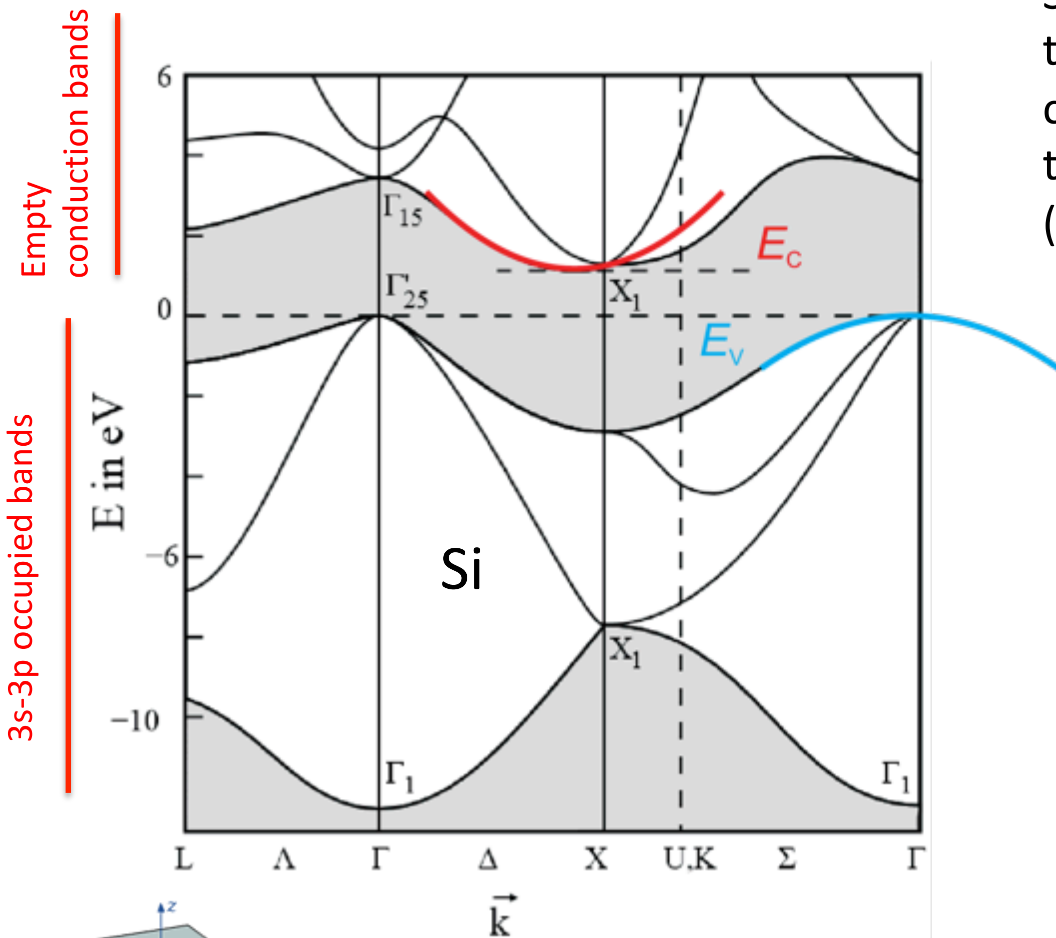
Solid State Physics
December the 3rd, 2020

- Silicon, photon momentum, direct gap, photovoltaics
- Defects can be good ! (Exercise 21)
- Surface states (Exercise 20)
- Graphene and hexagonal Boron-Nitride (an history of on-site energies) (Exercise 16)

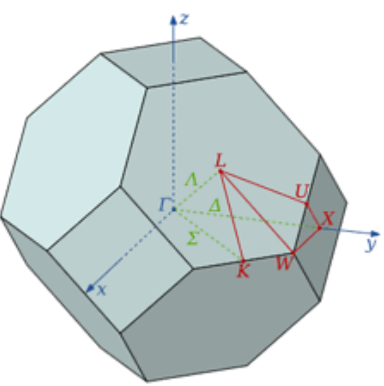
Direct and indirect gap in silicon



Silicon is an indirect gap semiconductor: the top of the valence bands (at zone center Γ) is not at the same k-vector than the bottom of the conduction bands (along ΓX close to X).

Indirect (smallest) gap : 1.17 eV
Direct gap at Γ = 3.4 eV

In this plot, the zero of energy has been set arbitrarily to the top of the valence bands. The occupied bands originating from the 1s and 2s atomic levels are much much lower in energy and are not shown.



Brillouin zone

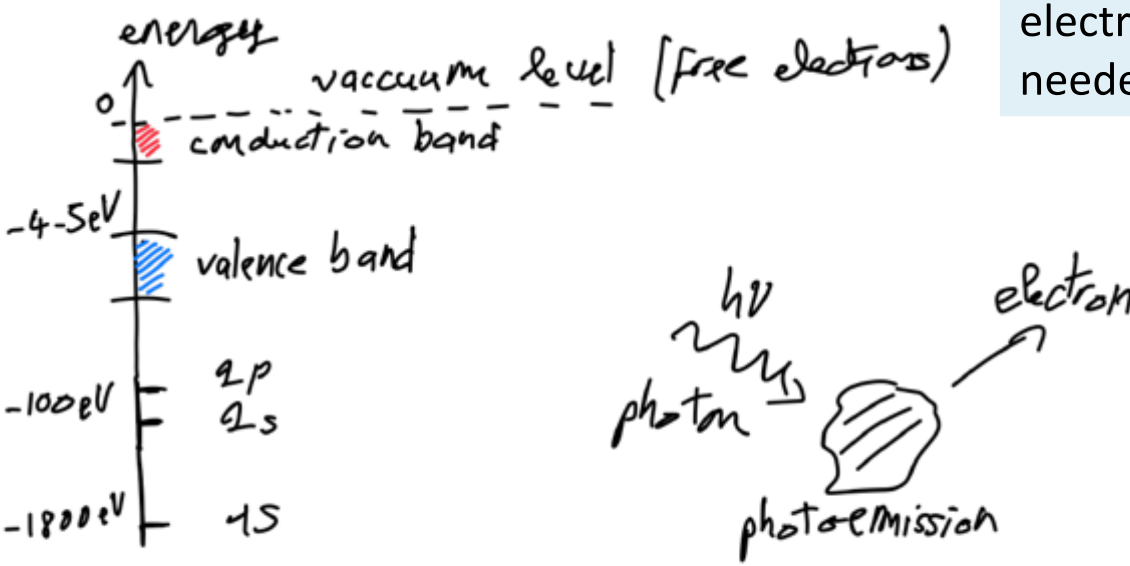
Difference of k-vector between top of valence bands and bottom of conduction bands : typically

$$\pi/a \simeq 1\mathring{A}^{-1} \quad \text{with} \quad a = 2 - 4\mathring{A}$$

Brillouin zone boundary

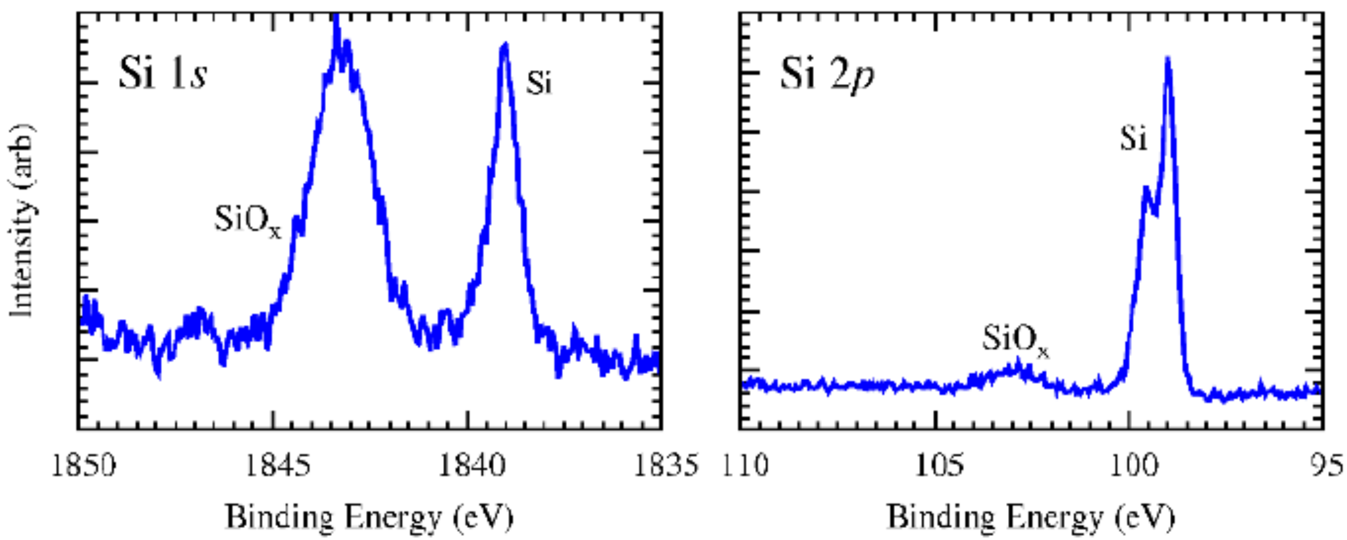
Spectroscopy of core states by photoemission

Photoemission : measure energy of electrons by the energy of the photons needed to eject electrons from the solid !

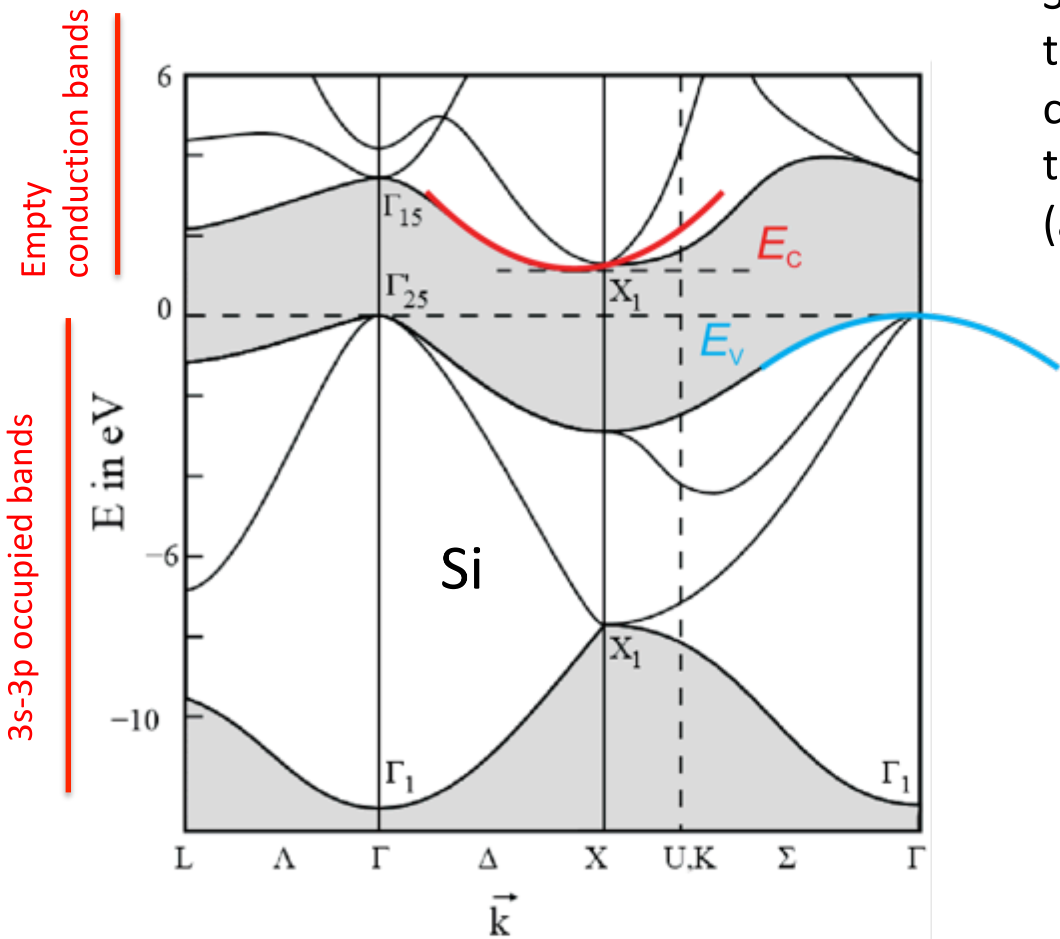


Core levels bands have very small band width since the core atomic orbitals are very localized => hopping energy is very small

Core-levels photoemission on silicon and SiO2



Direct and indirect gap in silicon



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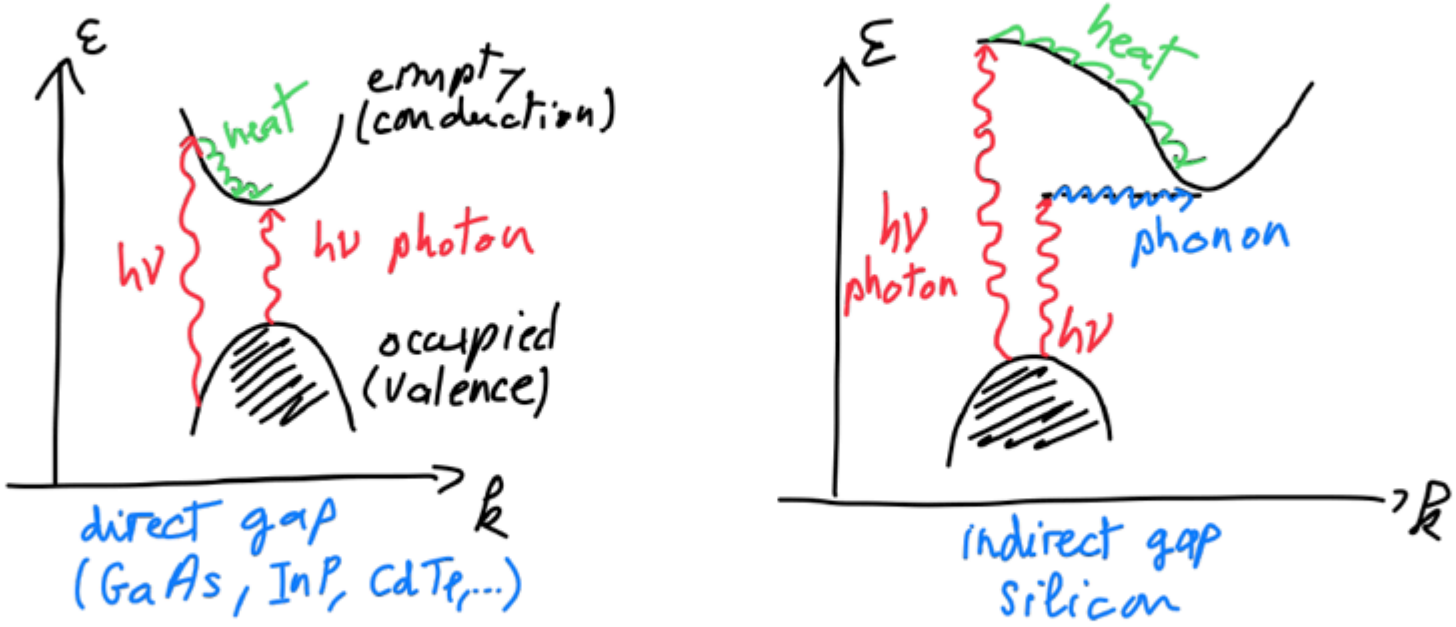
Photons wavevector are much much smaller

$$E = h\nu = 1.17eV \implies \lambda = \frac{c}{\nu} = 1060 \text{ nms} \implies k = \frac{2\pi}{\lambda} = 6 \times 10^{-4} \ \mathring{A}^{-1}$$

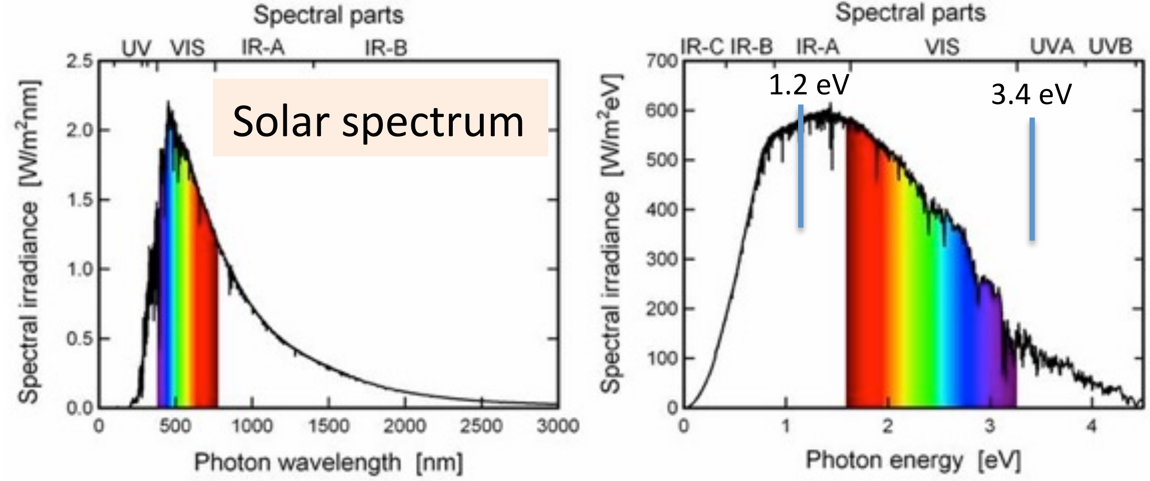
$$E = h\nu = 3.4eV \implies \lambda = \frac{c}{\nu} = 365 \text{ nms} \implies k = \frac{2\pi}{\lambda} = 1.7 \times 10^{-3} \ \mathring{A}^{-1}$$



Optical absorption : need to enforce conservation of energy but also of momentum !!
Photons have a lot of energy but <u>no momentum =></u> Photon absorption induce <u>vertical transitions</u> (do not change the k-vector of electrons)

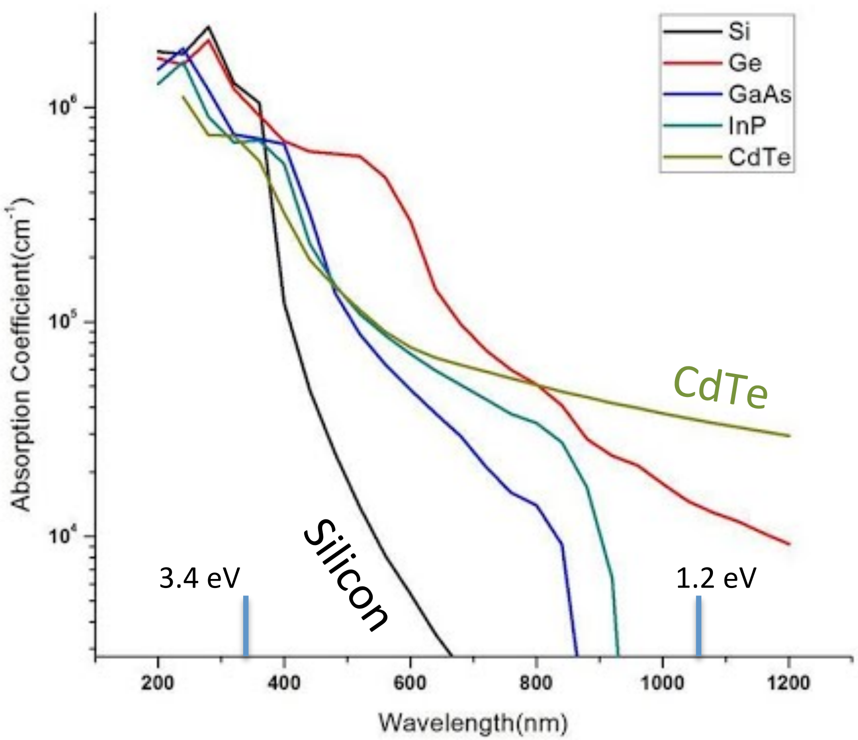
To absorb or emit photons at the energy of an indirect gap, one needs the help of a phonon that have small energy (a few dozens of meVs) but same momentum (π/a) as electrons : this is a complicated process with limited probability !

Electrons excited above the minimum energy gap relax to the bottom of the conduction bands by emitting phonons (heat) => electronic energy lost to heat.



The Si indirect gap (1.17 eV) is nicely located close to the maximum of sun emission but the direct gap (3.4 eV) is too large for absorbing sun light => Si absorption is limited since phonons must be involved (complicated processes)

Evolution of the absorption coefficient in function of the incident light wavelength for Si, Ge, GaAs, InP and CdTe, at room temperature



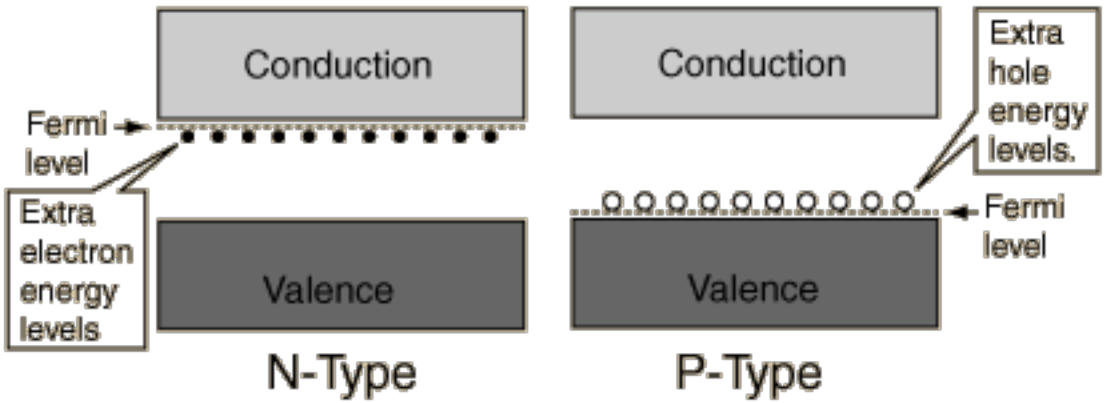
Ideally, we want a 1.3-1.4 direct gap semiconductor !!

Nevertheless, Silicon is cheap, abundant, not toxic, etc. and a long history of industrial processing.

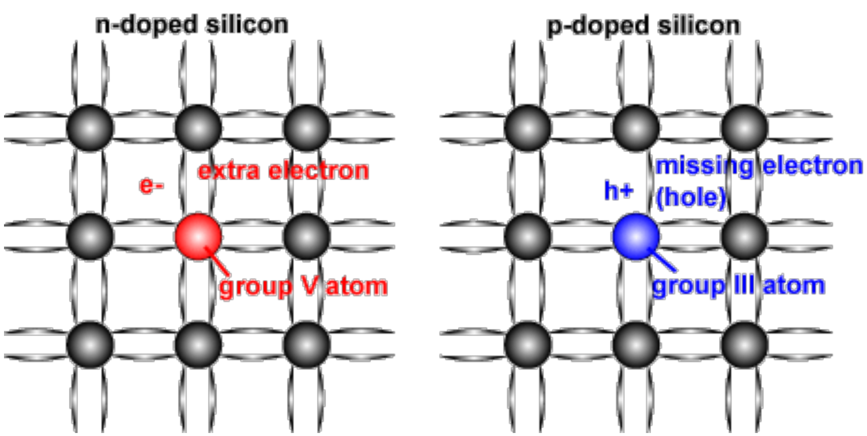
The increase of efficiency obtained with other direct band gap materials (III-V, II-VI, etc.) may not be worth the cost of the materials, changing the industrial routines, etc.

Defect states and doping

Defects in materials are not always a problem : sometimes defects are needed !!
In semiconductors and insulators, defects create additional energy levels in the gap that can be extremely useful for doping and/or generating new photon adsorption/emission lines.



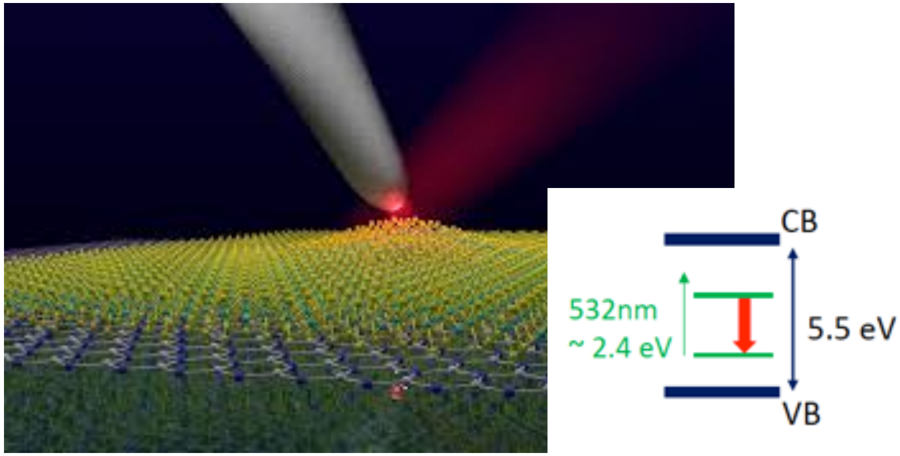
If defect levels are within room temperature of band edges, an added electron or hole on these levels can « jump » into the valence or conduction bands of the semiconductor to create a small current.



Defect states and colour centers in gems

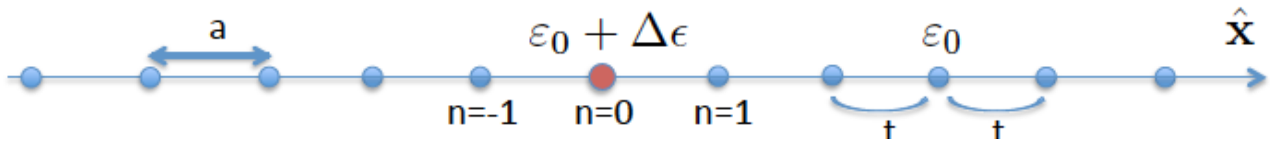
The color of diamonds and gemstones are related to defects that create novel absorption lines. Green color : radiations have knocked atoms out of their equilibrium positions; Violet : hydrogen impurities; etc.

Defect states and « one-by-one » photon emission at room temperature



Localized defects in 2D semiconductors or insulators (h-BN, dichalcogenides, etc.) create two levels in the gap (one occupied, the other empty) that can absorb or emit light at specific wavelength. Exists also in 3D insulators (e.g. the NV$^-$ center in diamond)

Exercise 21 : Localized defect states : a 1D tight-binding model



In the absence of defect, the chain band structure is : $\varepsilon(k) = \varepsilon_0 + 2t\cos(ka)$

In the presence of defect, wavefunctions are perturbed and are not perfect Bloch states close to the impurity but can still be written as a linear combination of atomic orbitals :

$$\psi(x) = \sum_m c_m \phi^{at}(x - ma) \quad \text{with} \quad \hat{H}|\psi\rangle = \varepsilon|\psi\rangle$$

Project the eigenvalue equation $\hat{H}|\psi\rangle = \varepsilon|\psi\rangle$ on the $\langle\phi^{at}(x - na)|$

$$\sum_m c_m \langle\phi^{at}(x - na)|\hat{H}|\phi^{at}(x - ma)\rangle = \varepsilon \sum_m c_m \langle\phi^{at}(x - na)|\phi^{at}(x - ma)\rangle$$

$$\left[\begin{array}{ll} (n > 0) & c_n\varepsilon_0 + t(c_{n-1} + c_{n+1}) = \varepsilon c_n \\ (n = 0) & c_0(\varepsilon_0 + \Delta\varepsilon) + t(c_{-1} + c_{+1}) = \varepsilon c_0 \end{array}\right.$$

Assume localized defect state (exponential decay away from the impurity) :

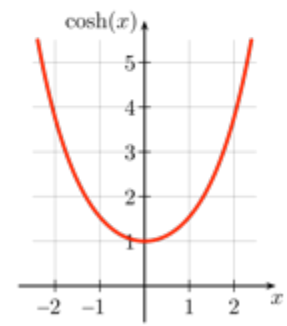
$$\psi_d(x) = A \sum_n e^{-\gamma |n| a} \phi^{at}(x - na) \quad \Rightarrow \quad c_n = A e^{-\gamma |n| a}$$

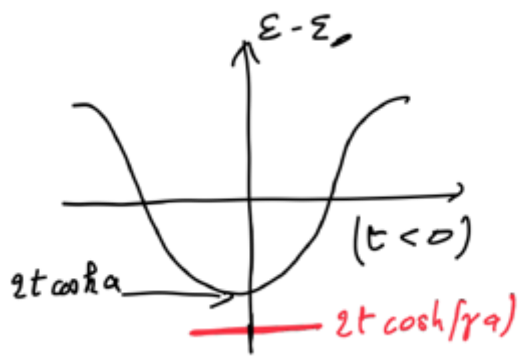
Plug this expression for c_n in the 2 previous equations :

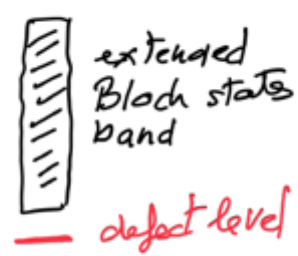
$$(n > 0) \qquad (\varepsilon_0 - \varepsilon) + t(e^{-\gamma a} + e^{+\gamma a}) = 0$$

$$(n = 0) \qquad (\varepsilon_0 + \Delta\varepsilon - \varepsilon) + t(e^{-\gamma a} + e^{-\gamma a}) = 0$$

$$\varepsilon = \varepsilon_0 + 2t \cosh(\gamma a) \quad \text{with} \quad \cosh(\gamma a) > 1$$



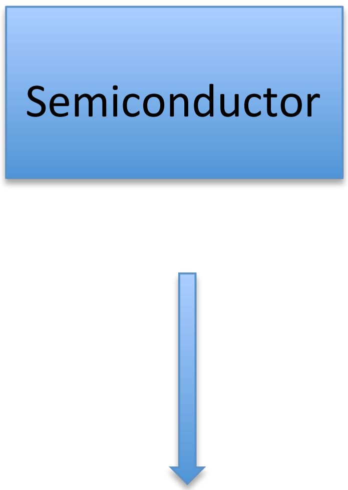


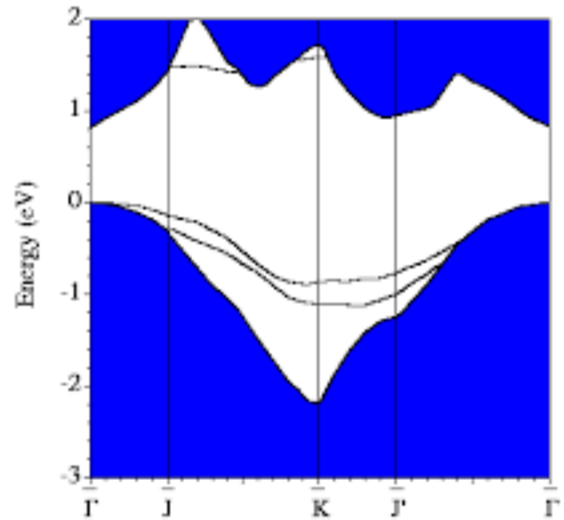


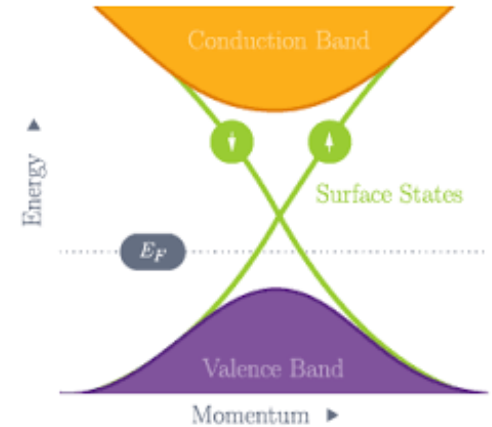
Surface states : 2D electronic states in the gap of insulators can develop at the surface !

Surface states in the gap !

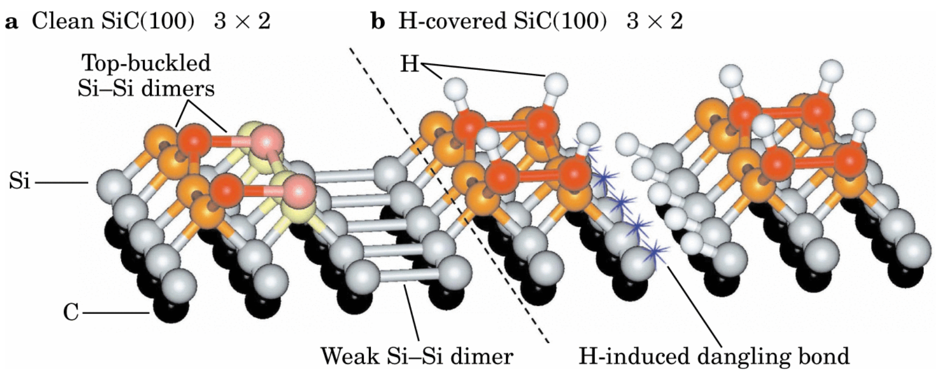
Surface







Topological Insulator



There are electronic states localized at the surface with energies different from Bloch states in the bulk

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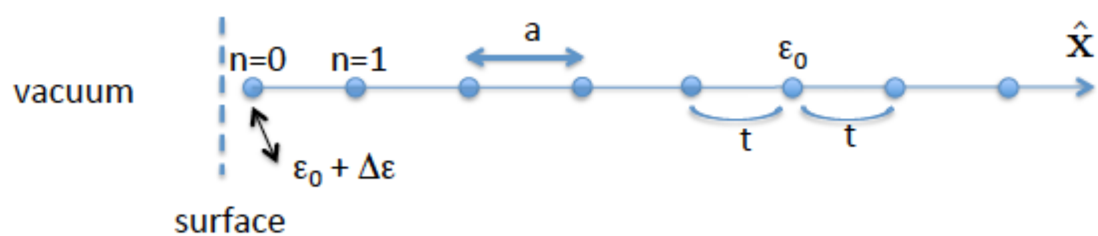
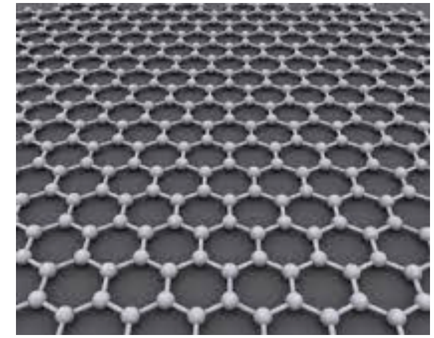
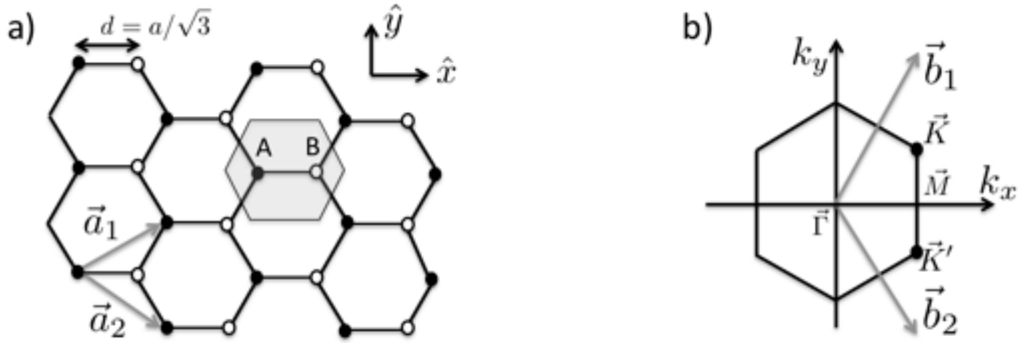
Exercise 20 : localized surface states



The ionicity gap : graphene versus hexagonal boron-nitride (h-BN)

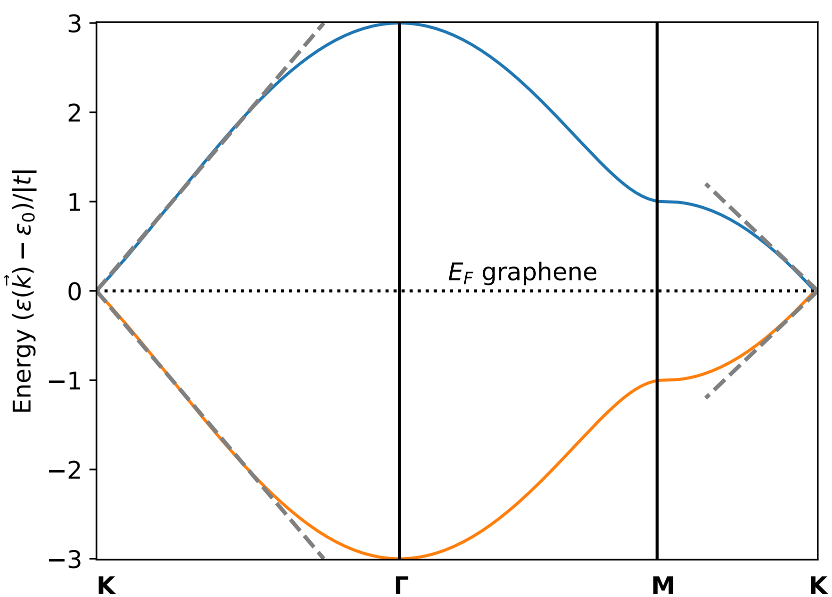




$$\vec{a}_1 = a\left(\frac{\sqrt{3}}{2}\hat{x} + \frac{1}{2}\hat{y}\right) \qquad \vec{a}_2 = a\left(\frac{\sqrt{3}}{2}\hat{x} - \frac{1}{2}\hat{y}\right)$$

$$\vec{b}_1 = \frac{4\pi}{a\sqrt{3}}\left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right) \qquad \vec{b}_2 = \frac{4\pi}{a\sqrt{3}}\left(\frac{1}{2}, -\frac{\sqrt{3}}{2}\right)$$

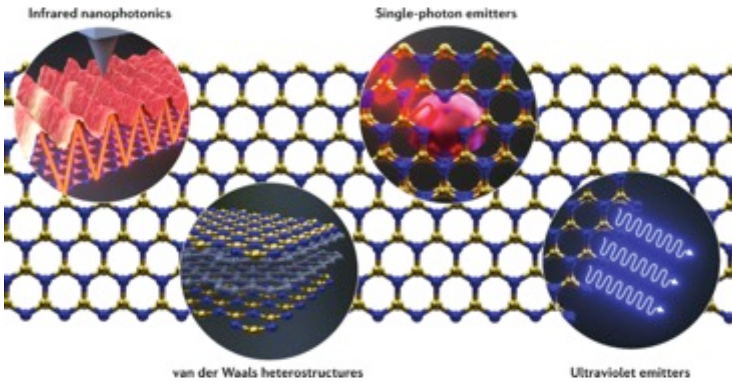
Graphene : hexagonal 2D network with 2 carbon atoms/cell : the A and B atoms are both carbon atoms with same onsite energy.

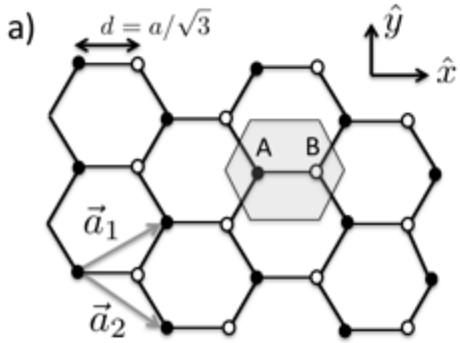


Graphene is a semi-metal : there is not gap between occupied and empty bands but the two bands touch in very few states => very few electrons can jump into conduction bands at room T !!

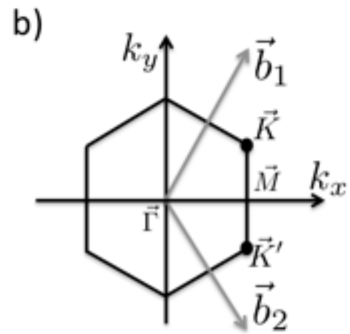
Exercise 23

The ionicity gap : hexagonal boron-nitride (h-BN)





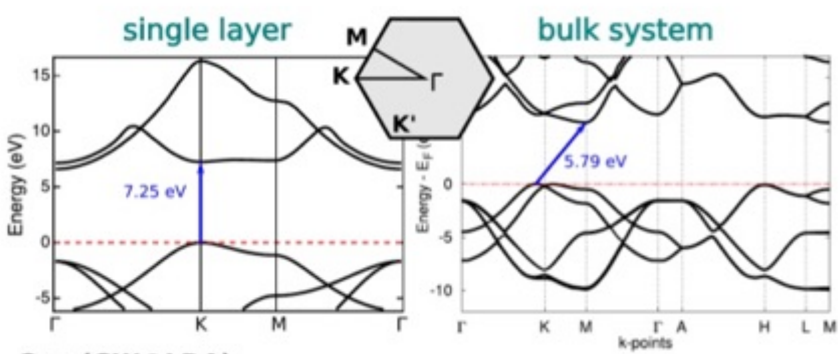
$$\vec{a}_1 = a\left(\frac{\sqrt{3}}{2}\hat{x} + \frac{1}{2}\hat{y}\right) \qquad \vec{a}_2 = a\left(\frac{\sqrt{3}}{2}\hat{x} - \frac{1}{2}\hat{y}\right)$$



$$\vec{b}_1 = \frac{4\pi}{a\sqrt{3}}\left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right) \qquad \vec{b}_2 = \frac{4\pi}{a\sqrt{3}}\left(\frac{1}{2}, -\frac{\sqrt{3}}{2}\right)$$

h-BN : hexagonal 2D network with 2 carbon atoms/cell : the A and B atoms are boron and nitrogen atoms with different onsite energy.

h-BN band structure

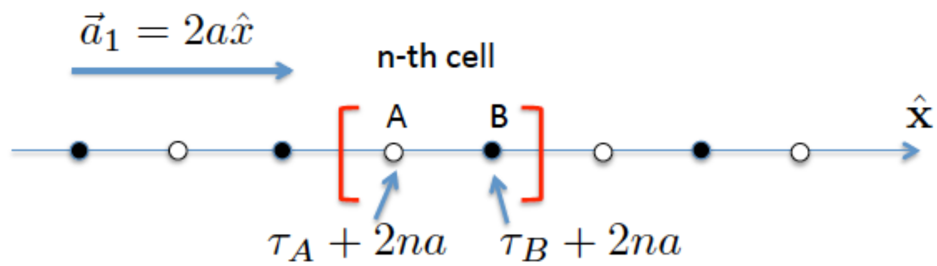


Gap (GW@LDA):
Single layer= 7.25 eV direct @ K
Bulk= 5.79 eV indirect ~K→M

h-BN is a large band gap insulator (larger than diamond !)

Exercise 16

Exercise 16 : Tight-binding model for a 1D ionic crystal



Following our lectures notes, since their are two atomic orbitals per unit cell (one of type A and the other of type B), Bloch states are linear combination of a basis Bloch state made out of atomic orbitals of type A and another made out of atomic orbitals of type B

$$\psi_k^A(r) = \frac{1}{\sqrt{N_C}} \sum_n^{N_C} e^{ik(\tau_A + 2na)} \phi_A^{at}(r - \tau_A - 2na)$$

$$\psi_k^B(r) = \frac{1}{\sqrt{N_C}} \sum_n^{N_C} e^{ik(\tau_B + 2na)} \phi_B^{at}(r - \tau_B - 2na)$$

$$(I) \qquad \alpha(\varepsilon_A^0 - \varepsilon_k) + \beta H_{AB} = 0$$

$$(II) \qquad \alpha H_{BA} + \beta(\varepsilon_B^0 - \varepsilon_k) = 0$$

$$(\varepsilon_k - \varepsilon_A^0)(\varepsilon_k - \varepsilon_B^0) = 4t^2 \cos^2(ka)$$

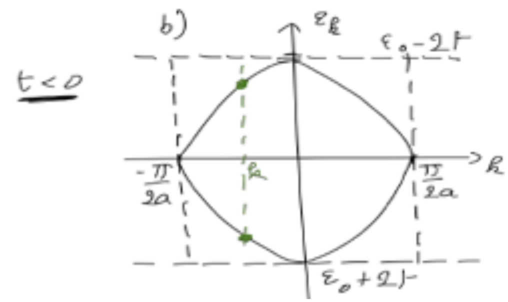
Exercise 16 : Tight-binding model for a 1D ionic crystal

$$(\varepsilon_k - \varepsilon_A^0)(\varepsilon_k - \varepsilon_B^0) = 4t^2\cos^2(ka)$$

Case 1) When A and B atoms are of the same species with same onsite energies:

$\varepsilon_A^0 = \varepsilon_B^0 = \varepsilon^0$ then there is no gap between the upper and lower bands :

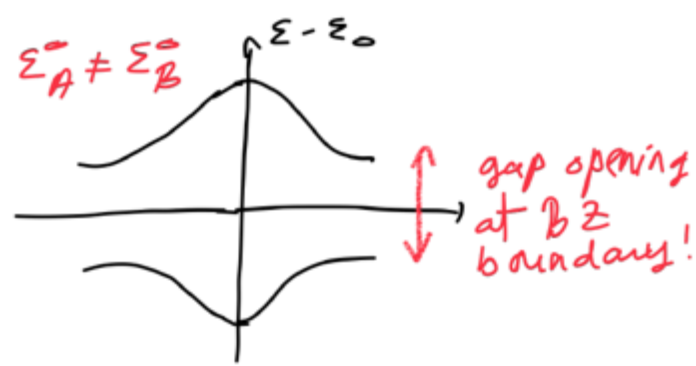
$$\varepsilon_k = \varepsilon^0 \pm 2t\cos(ka)$$



Case 2) When A and B atoms are of different species with different onsite energies:

$\varepsilon_A^0 \neq \varepsilon_B^0$ then a gap opens between the upper and lower bands !!

This gap is called the ionicity gap because it occurs in ionic systems with different types of atoms. Depending on the difference of onsite energies, the gap can be large or small …



End of SSP lectures

Exam … Wednesday 16/12/2020   14h-16h
TD A103-TD A105

All the best for the following !!!!!!!