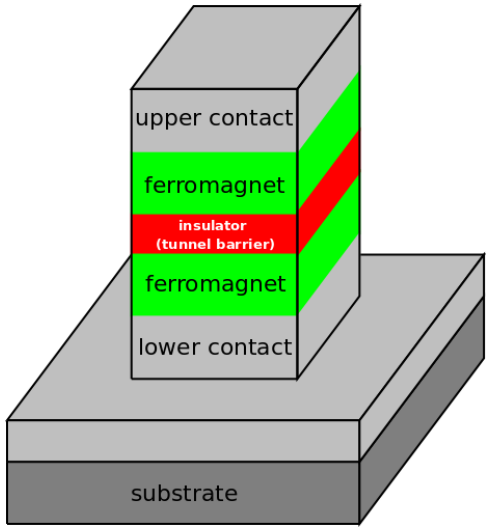
Fe/MgO interface in MTJ

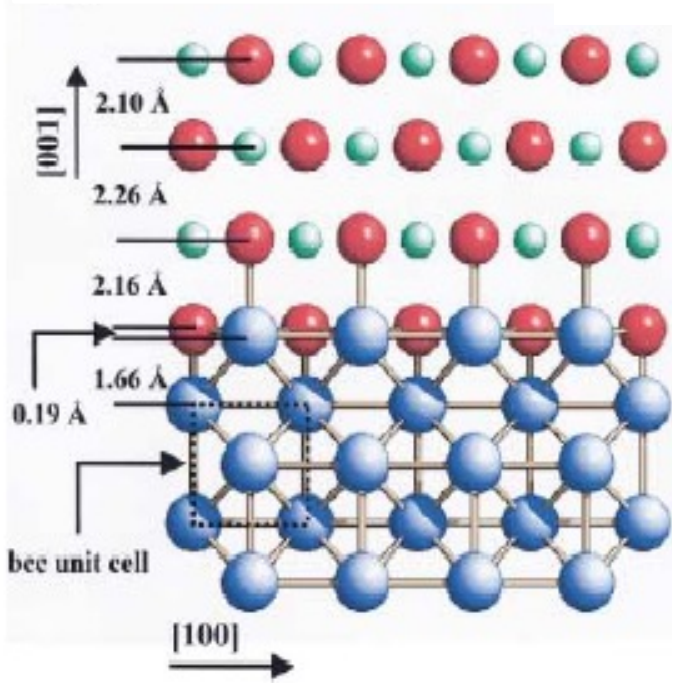


1) Control of the
oxidation at the interface

2) Control of the
magnetization of the
different layers

3) Control of the layer purity
Sources of impurities:
evaporators, evaporating
materials, UHV residual gas
(in 10^{-6} mbar every second
each surface atomic site is
touched by an atom of the
residual gas), etc.

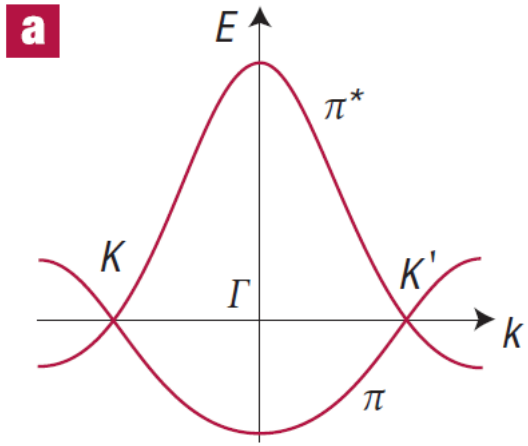
O
Mg
Fe

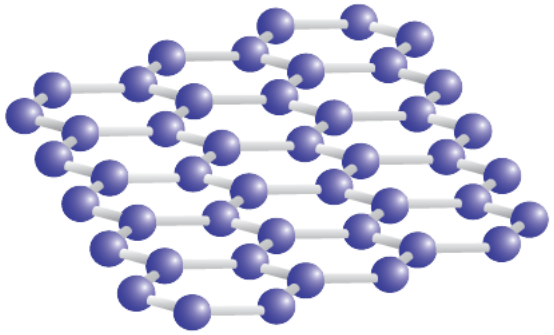


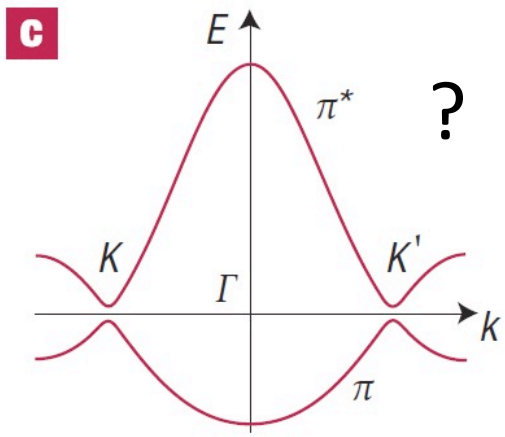
Graphene band structure

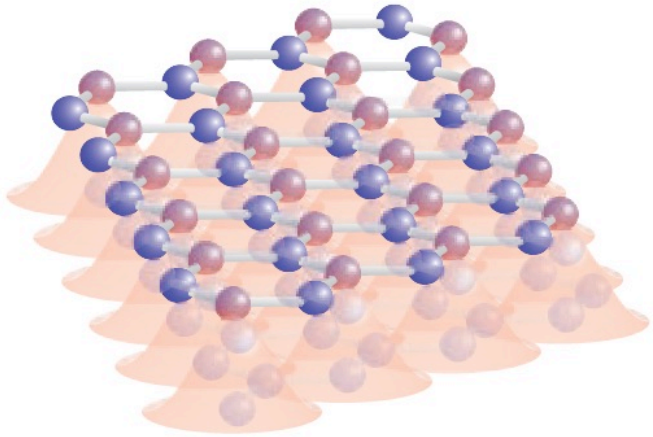
Free-standing

Surface supported





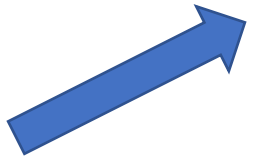


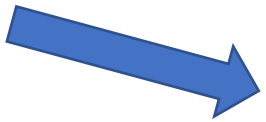


How do we measure the graphene band structure?

K. Novoselov , *Nat. Mater.* **6**, 720 (2007)

Spectroscopy





Valence DOS → UPS

Band structure → ARUPS (ARPES)

Chemical composition → XPS, Auger

Magnetism → XMCD

Bond orientation → XLD

Structure modification → EXAFS

…

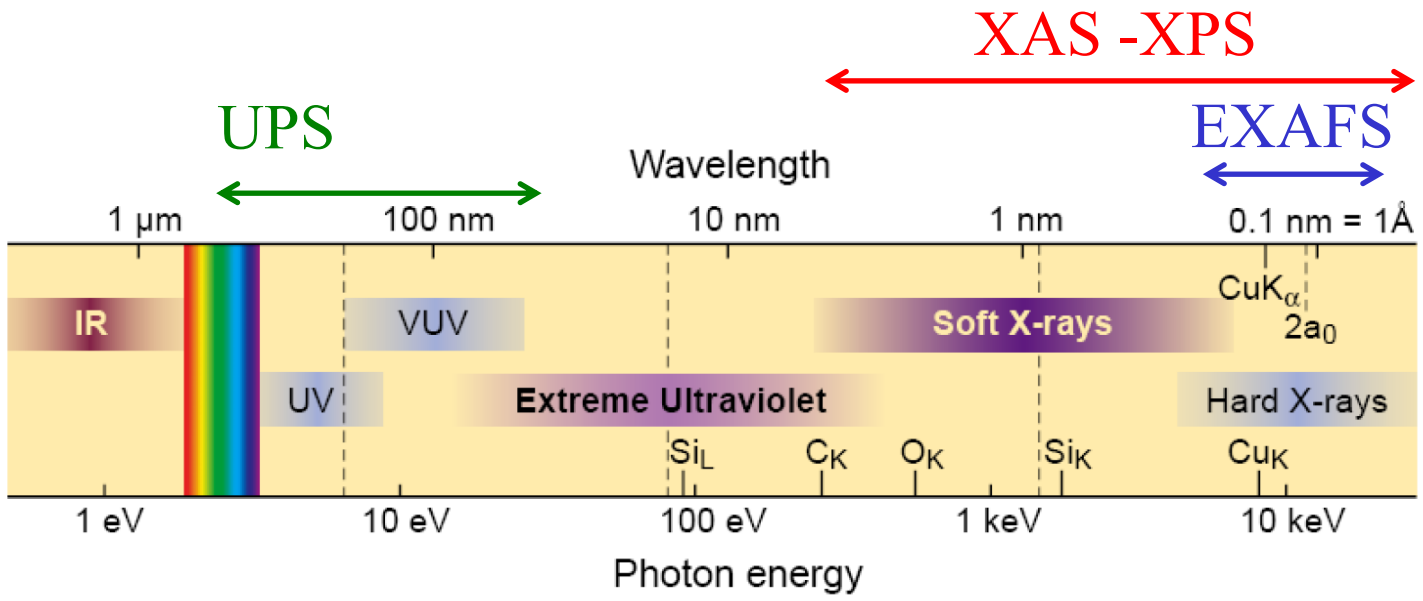
…

Spectroscopy techniques

Technique	Probe	Measure
Auger	electron	electron
XPS, UPS, ARPES	photon	electron
XAS, EXAFS	photon	photon / electron

The choice of the technique depends on the information we want to acquire

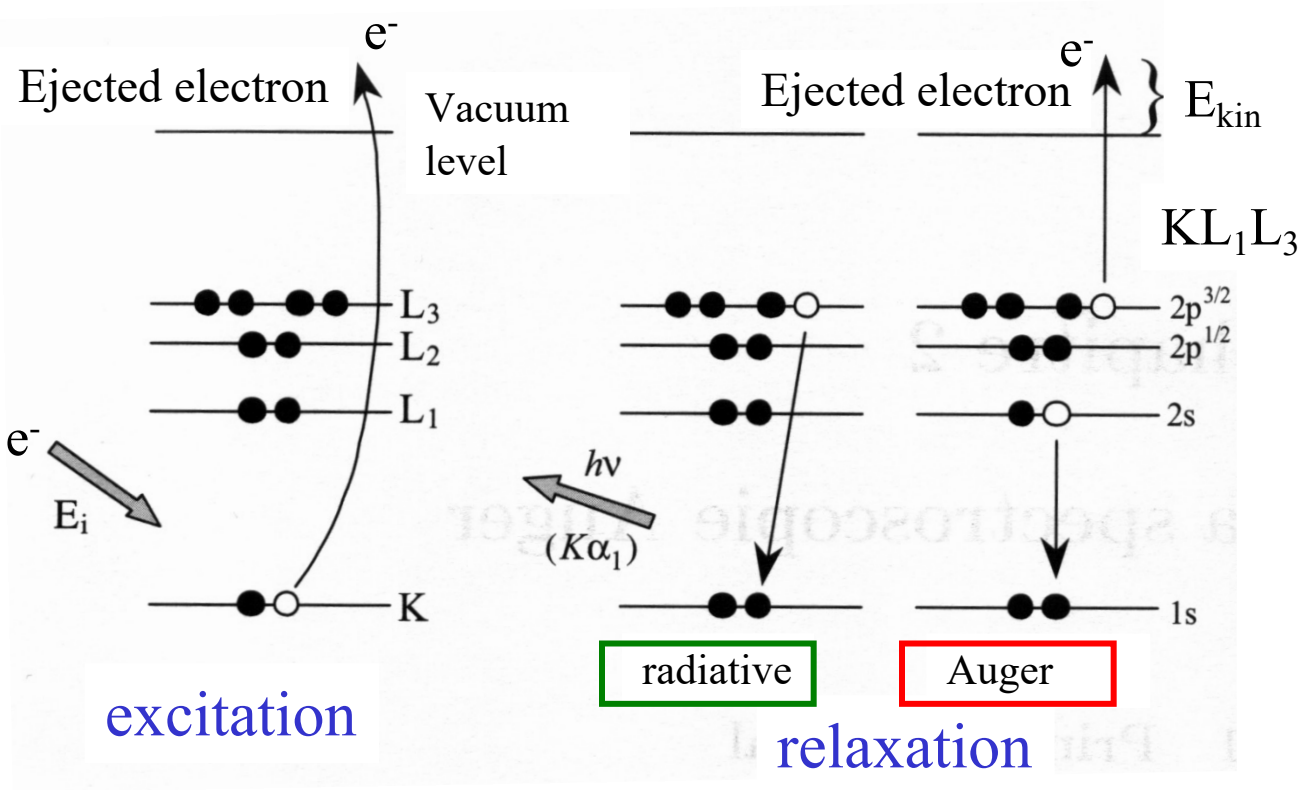
Electromagnetic spectrum



$E = h\nu = hc/\lambda$; $c = 3\ 10^{8}$ m/s; $h = 6.6\ 10^{-34}$ Js

The Auger process

Auger spectroscopy is based upon an electron in - electron out process.



E_{bind} : binding energy of the electronic level
typically referred to E_F and not to E_{vac} →
one needs to consider also the work function Φ (3-5 eV)

$$E_{kin} = E_{bind}(K) - E_{bind}(L_1) - E_{bind}(L_3) - \Phi$$

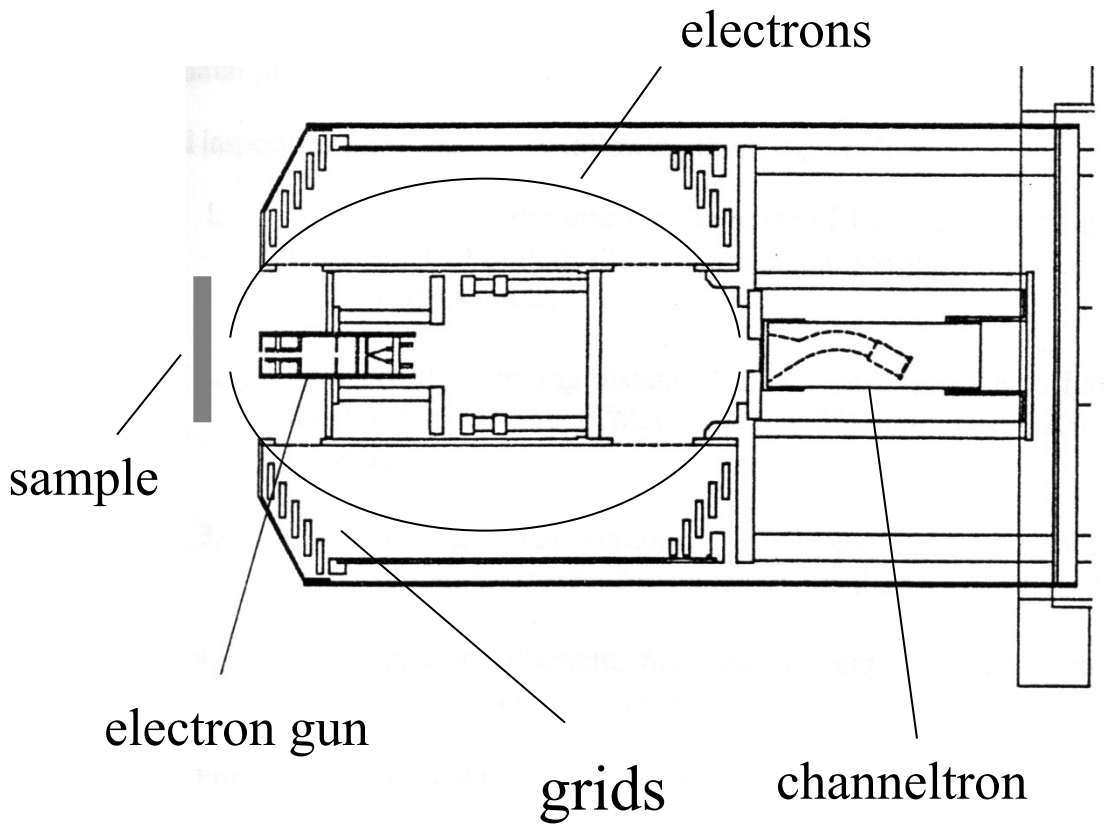
$E_{bind}(L_i)$ and $E_{bind}(K)$ depend on the elements →
E_{kin} does not depend on $E_{incident}$

↓

chemical sensitivity

simple description neglecting screening and final state effects

Auger experimental setup



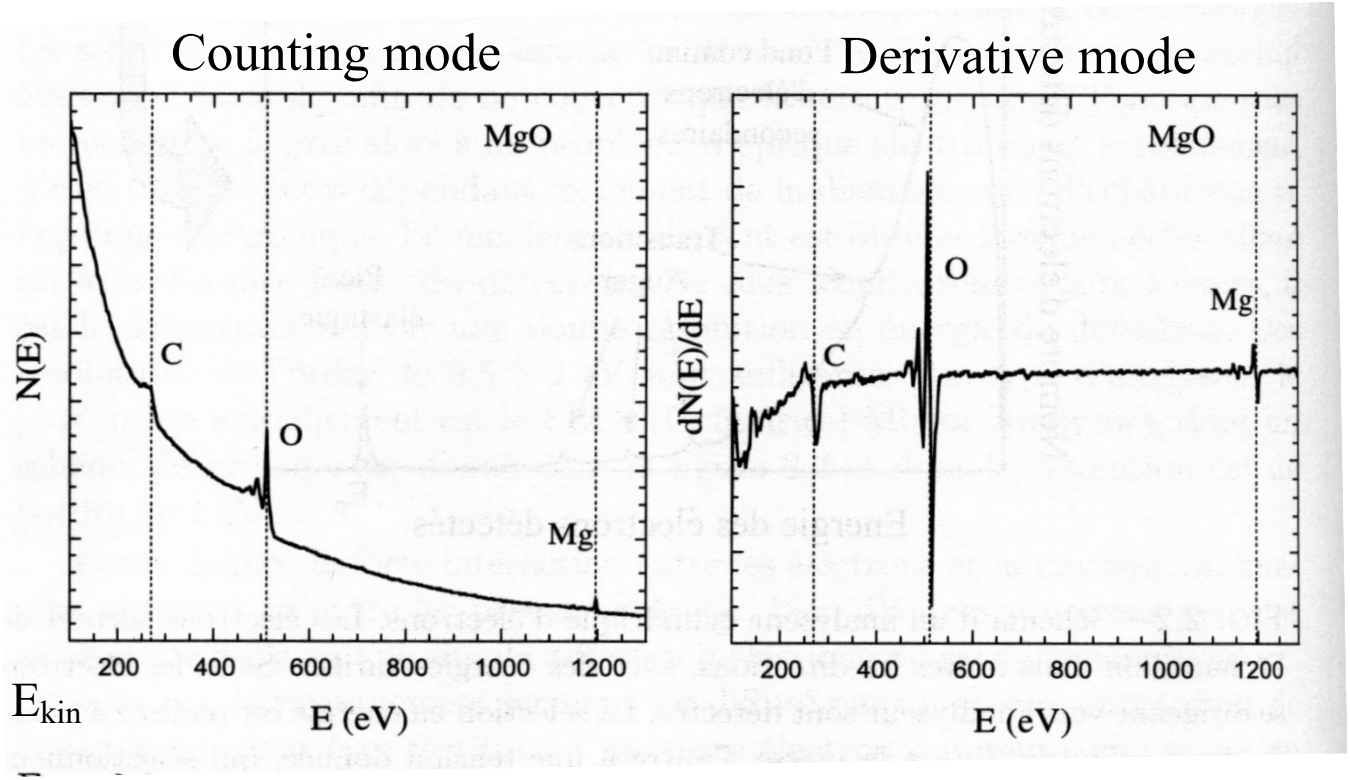
Electron energy: in 1- 10 keV
out 0.01 – 2 keV

detection limit ~ 0.5% of a monolayer

Auger spectrum: number of emitted electrons as a function of their kinetics energy

Auger spectrum

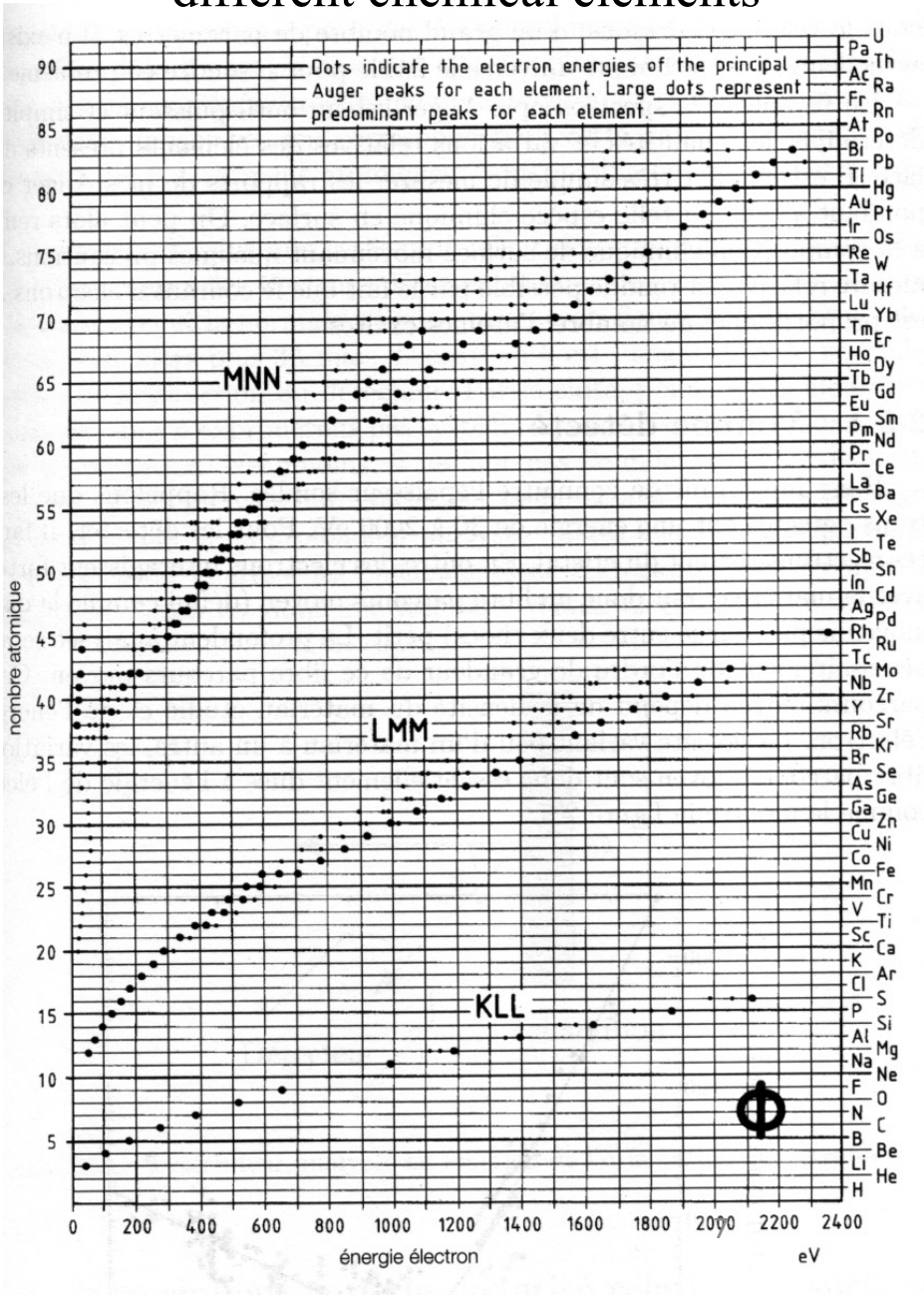
Example: MgO



The monotonic background is due to multi-scattered electrons

The energy transitions are characteristic of the element → chemical sensitivity

main Auger transitions for the different chemical elements

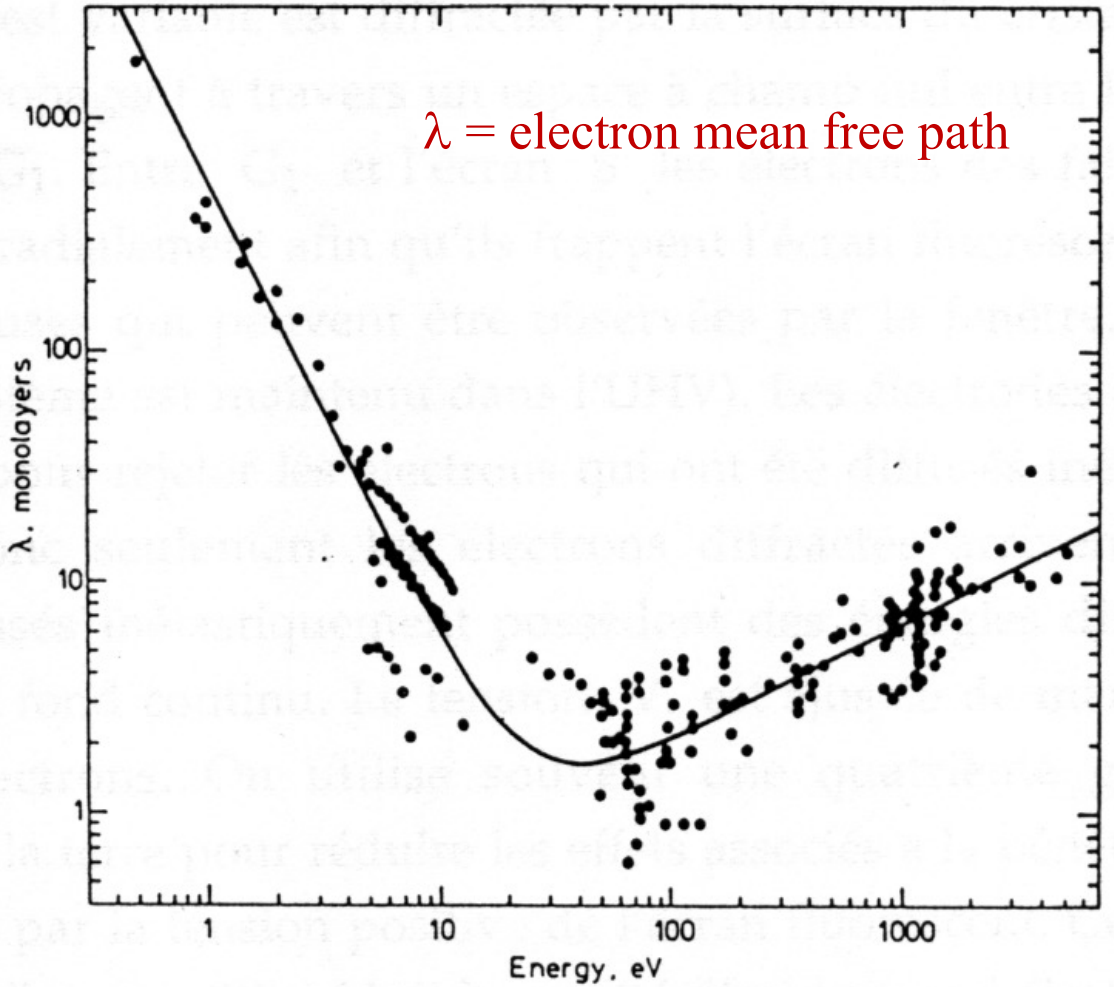


Surface sensitivity

Auger electrons (detected at surface) coming from depth z:
$I(z) = I(0) \exp(-z/\lambda)$

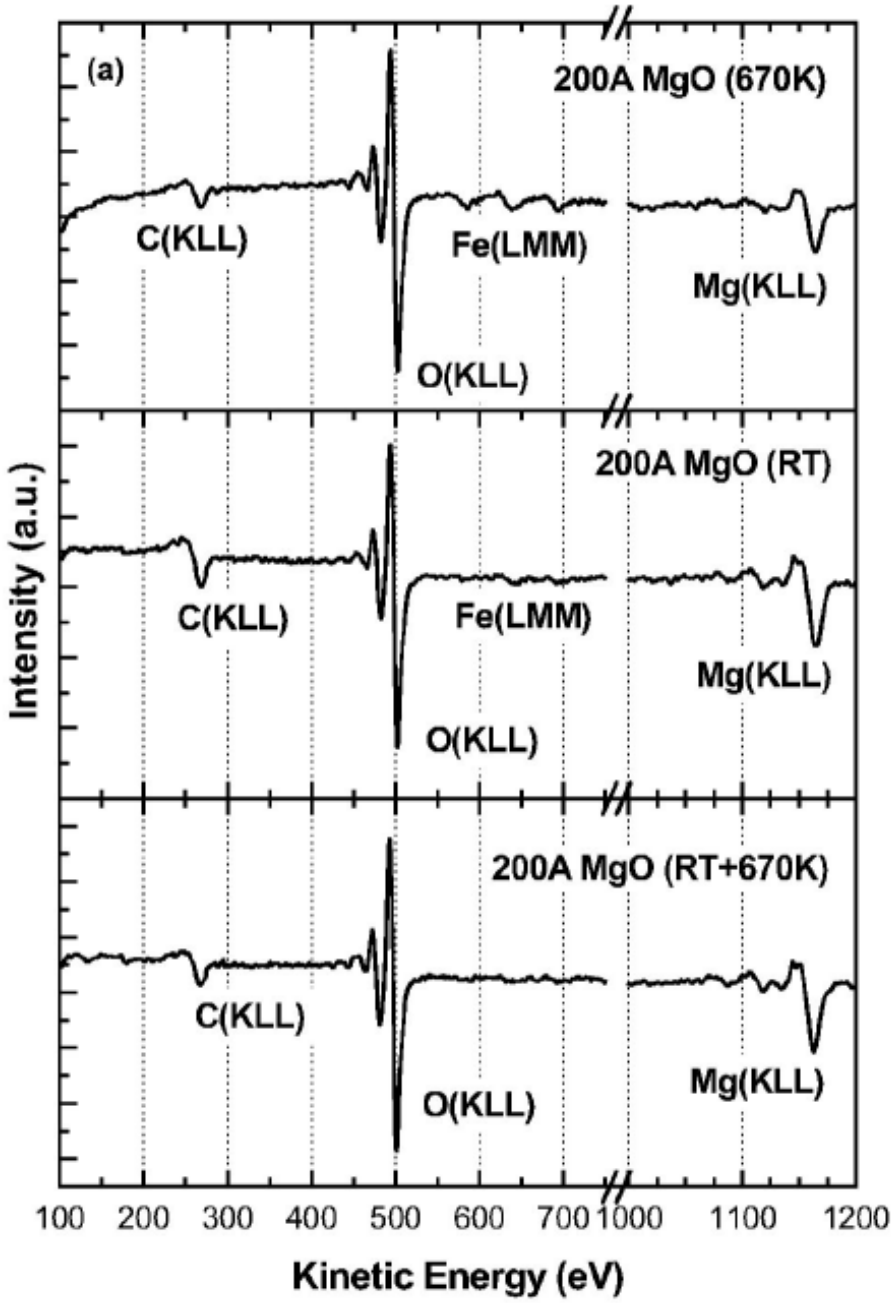
Total Auger electron current measured at surface:
$I = \int_0^z I(z)\, dz = I(0)\, \lambda\, (1-\exp(-z/\lambda))$

surface sensitivity is given by the limited mean free path of the outcoming electrons



Depth sensitivity: 95% of the signal coming from a film with infinite thickness D. How much is D?
$I(D) = I(0)\, \lambda\, (1-\exp(-D/\lambda)) = 0.95\, I(0)\, \lambda$
$\rightarrow D = -\lambda \ln(0.05) \sim 3\, \lambda$

Example: MgO/Fe(001)



Intense Fe absorption peaks:
MgO does not wet completely the Fe bottom electrode (columnar growth with pits)

Weak Fe absorption peaks:
rough MgO layer

No Fe signal:
annealing of the room T grown sample gives rise to a continuous, pore free, layer.

J. Appl. Phys. **97**, 036104 (2005)

Photoelectron spectroscopy / Photoemission

Exciting particle: photon

Emitted particle: electron

The energy of a photon is given by the Einstein relation:

$$E = h\ \nu$$

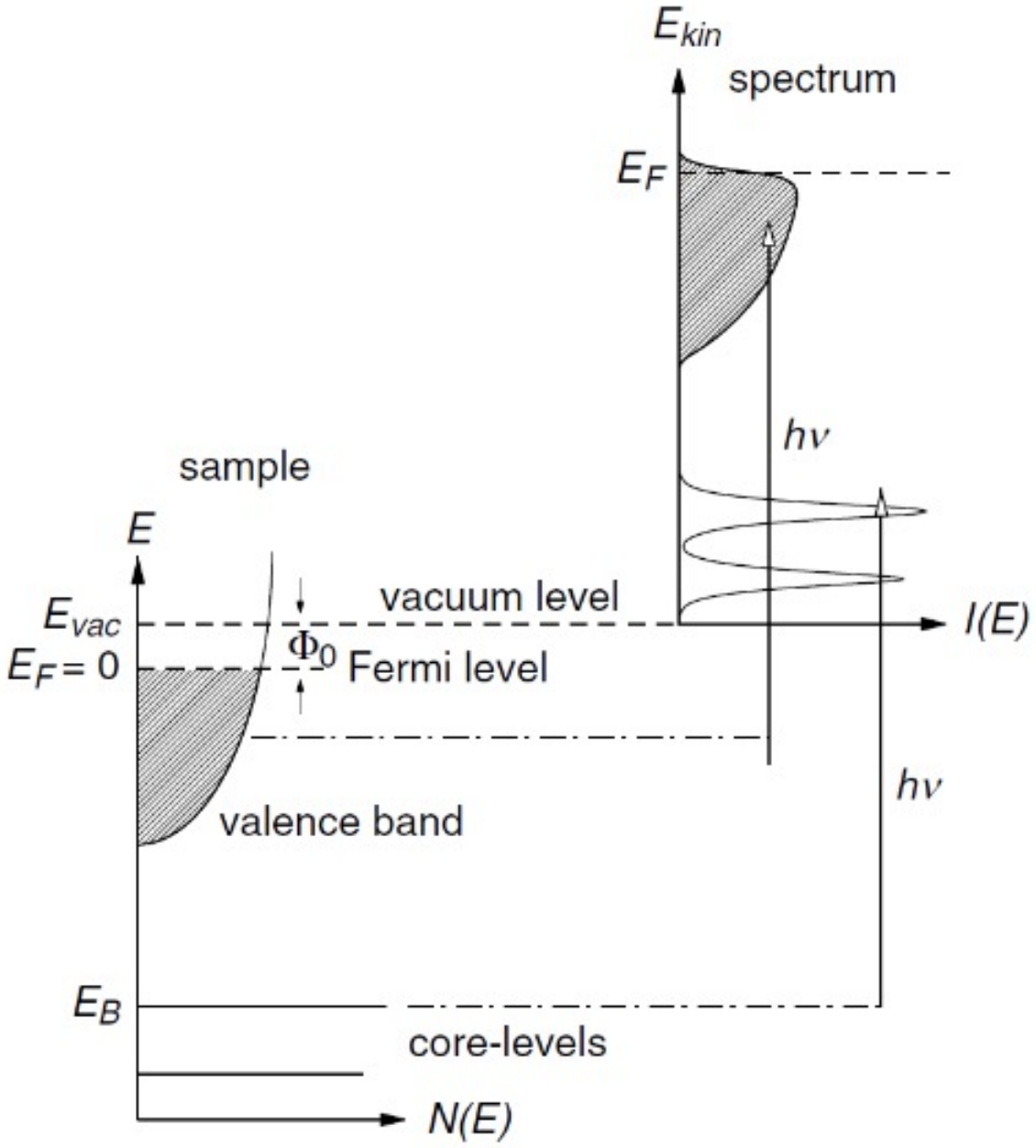
e^-

h - Planck constant (6.62×10^{-34} J s)

ν – frequency (Hz) of the radiation

$$E_{kin} = h\nu - E_{bind} - \Phi$$

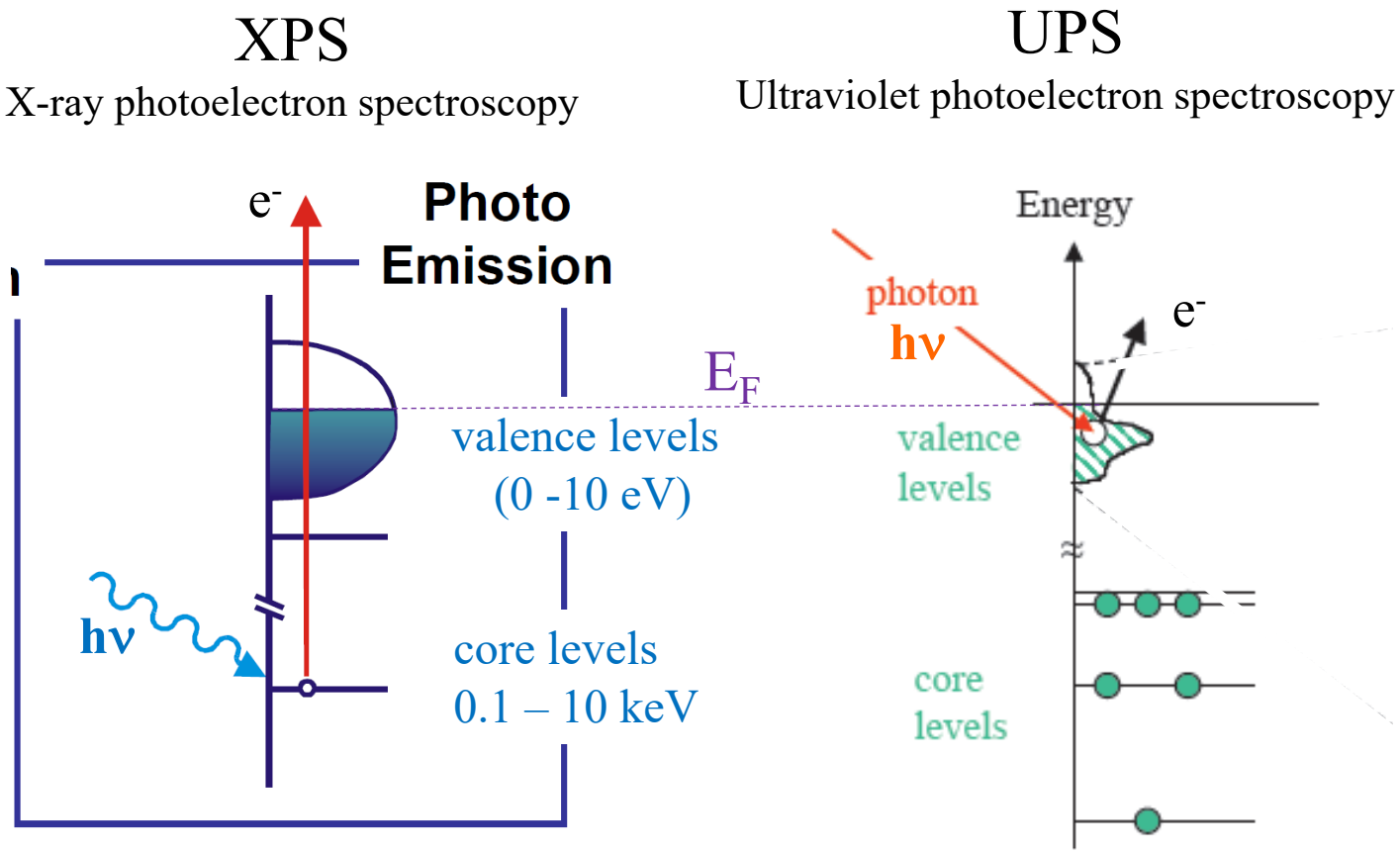
E_{kin} is the kinetic energy of the emitted electron
→ it depends on the level that has been excited



XPS *vs.* UPS: core *vs.* valence state excitation

X ray photons (0.2 –10 keV) → to investigate core levels
UV photons (10 - 100 eV) → to investigate valence levels

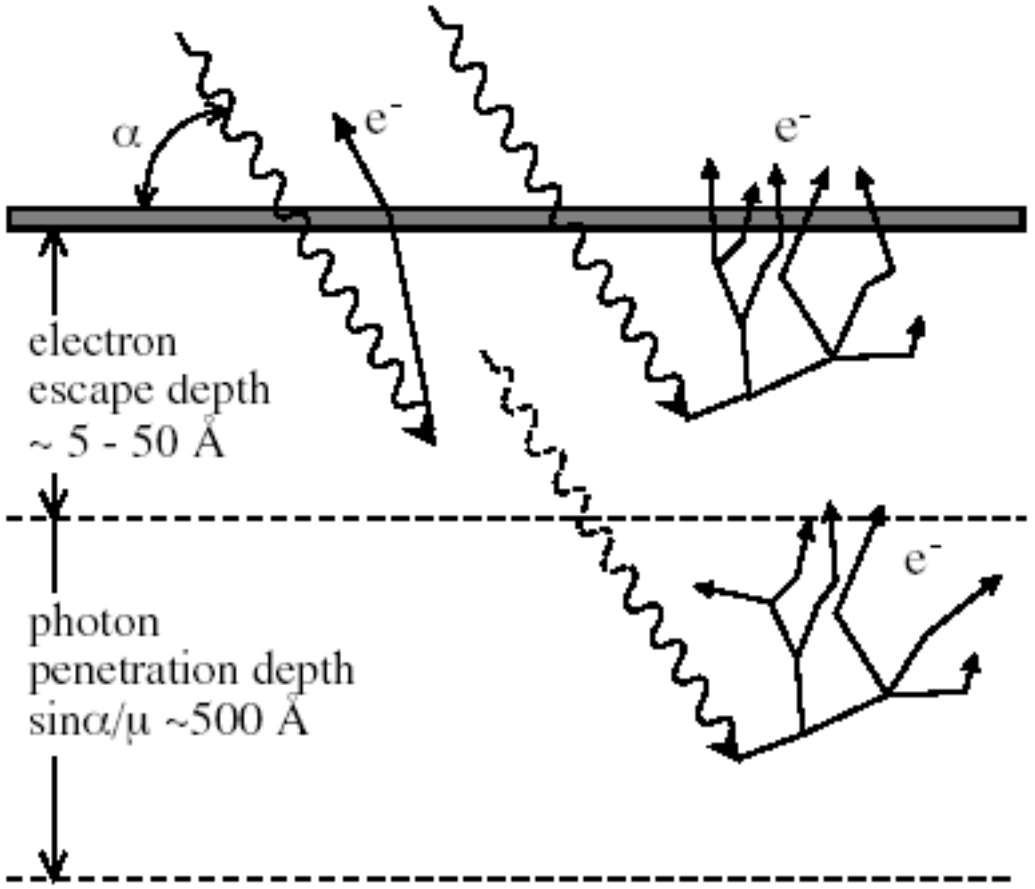
although energy distinction between core and valence is not strict
(depends on element)



Surface sensitivity

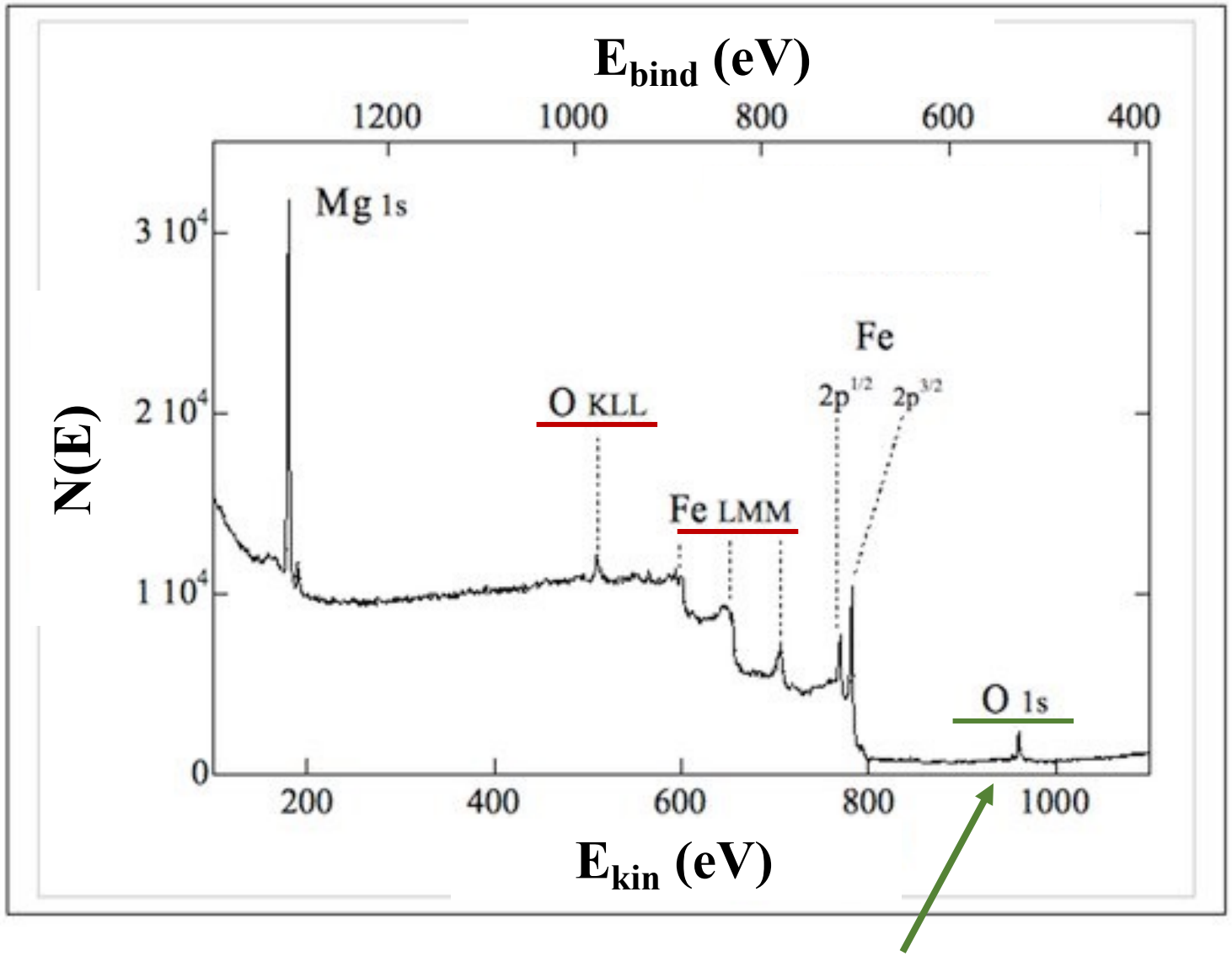
Photon penetration depth > 1-10 μm

-> surface sensitivity is given by the reduced mean free path of the outcoming electrons



Example XPS spectrum: MgO/Fe

$h\nu = 1486$ eV

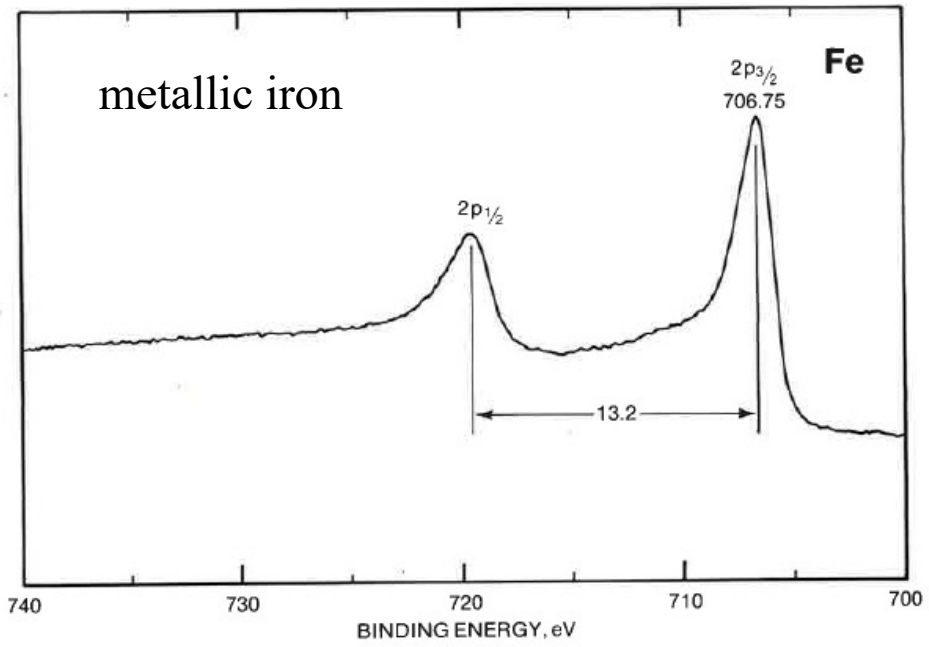


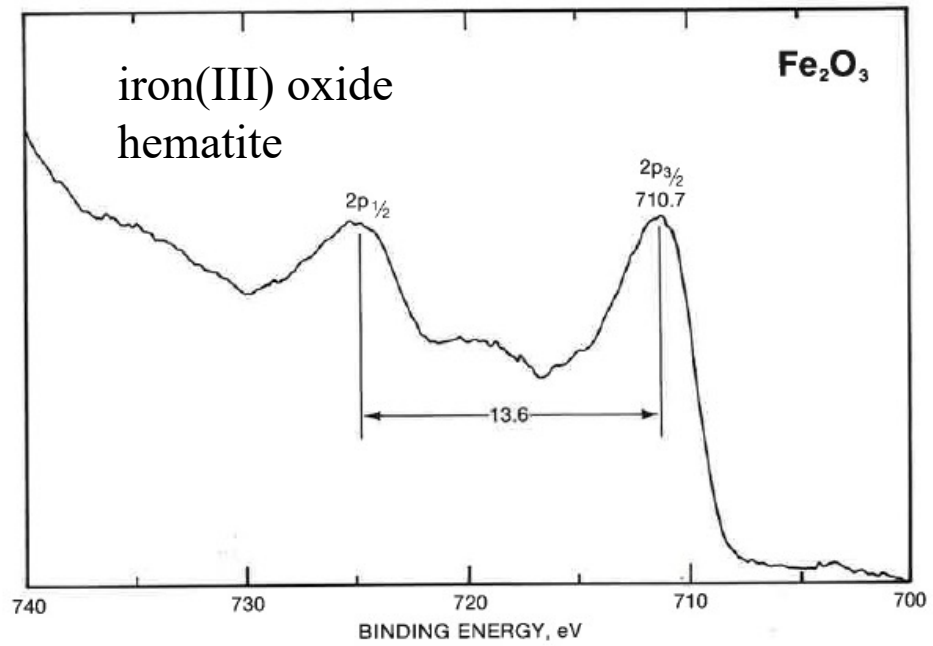
Auger electrons are also visible.
They can be recognized since their energy position does not depend on the energy of the photons

Ex.: deduce the energy of O 1s (K edge) : $E_{bind} = h\nu - E_{kin}$ $(-\Phi) = 1486 - 946 = 540$ eV

XPS spectrum: Fe 2p (L_2, L_3); chemical shift

atomic:
[Ar] $3d^6\ 4s^2$





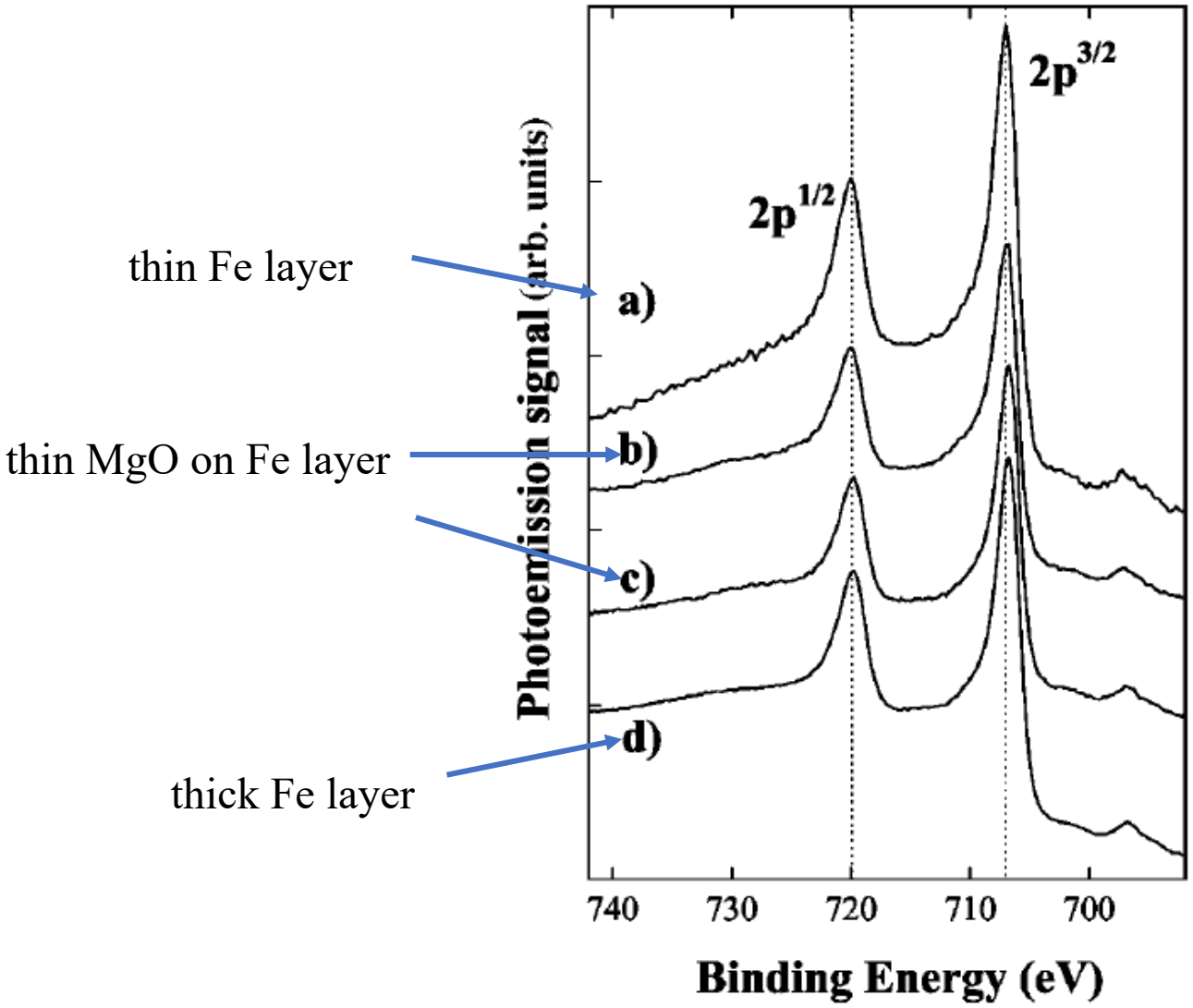
2p levels are split by the spin-orbit coupling
j = l+s, l-s
l=1
s=1/2
j= 3/2, 1/2
based on degeneracy (2j+1), intensity ratio:
$2p_{1/2} : 2p_{3/2} = 1:2$
The anti-parallel alignment is more favorable, has a lower energy and therefore appears at higher binding energy

+3 oxidation state:
Fe "loses" the two 4s electrons and one 3d electron

chemical shift correlated with overall charge on atom:
reduced charge → reduced coulomb screening
→ increased binding energy
(mainly an initial state effect)

peak energy → oxidation state

XPS spectrum: MgO/Fe, Fe 2p



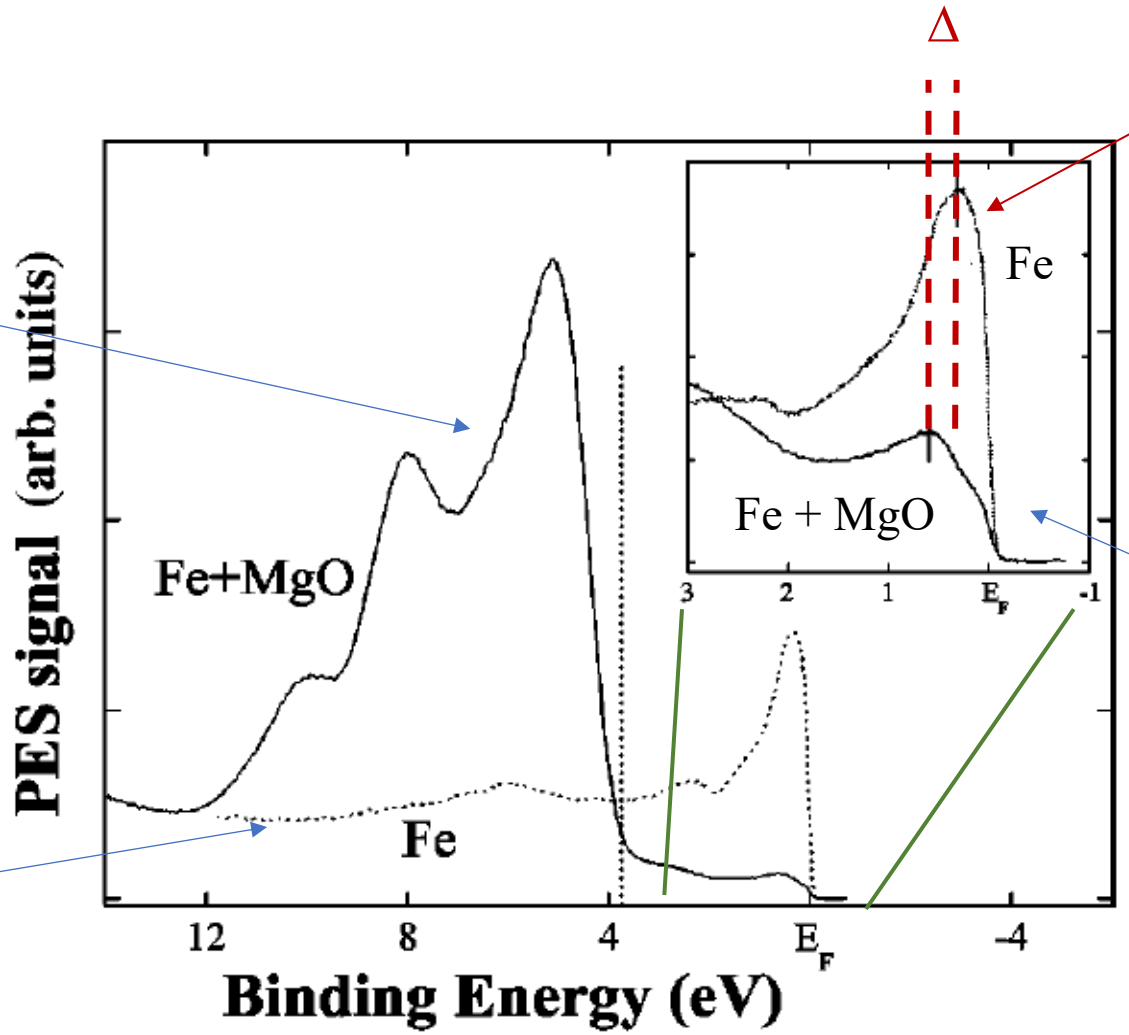
no modification of the Fe 2p spectrum upon MgO growth (no shift, only the intensity changes)
→ adding the MgO does not oxidize the Fe surface

Sicot *et al*. Phys. Rev. B **68**, 184406 (2003)

Example UPS spectrum: MgO/Fe

- MgO is an insulator with a gap of 8 eV
- Fe electronic structure: [Ar] $3d^6\ 4s^2$

$h\nu = 40.8$ eV



Modification of the Fe DOS

Spectral intensity dominated by the MgO contribution

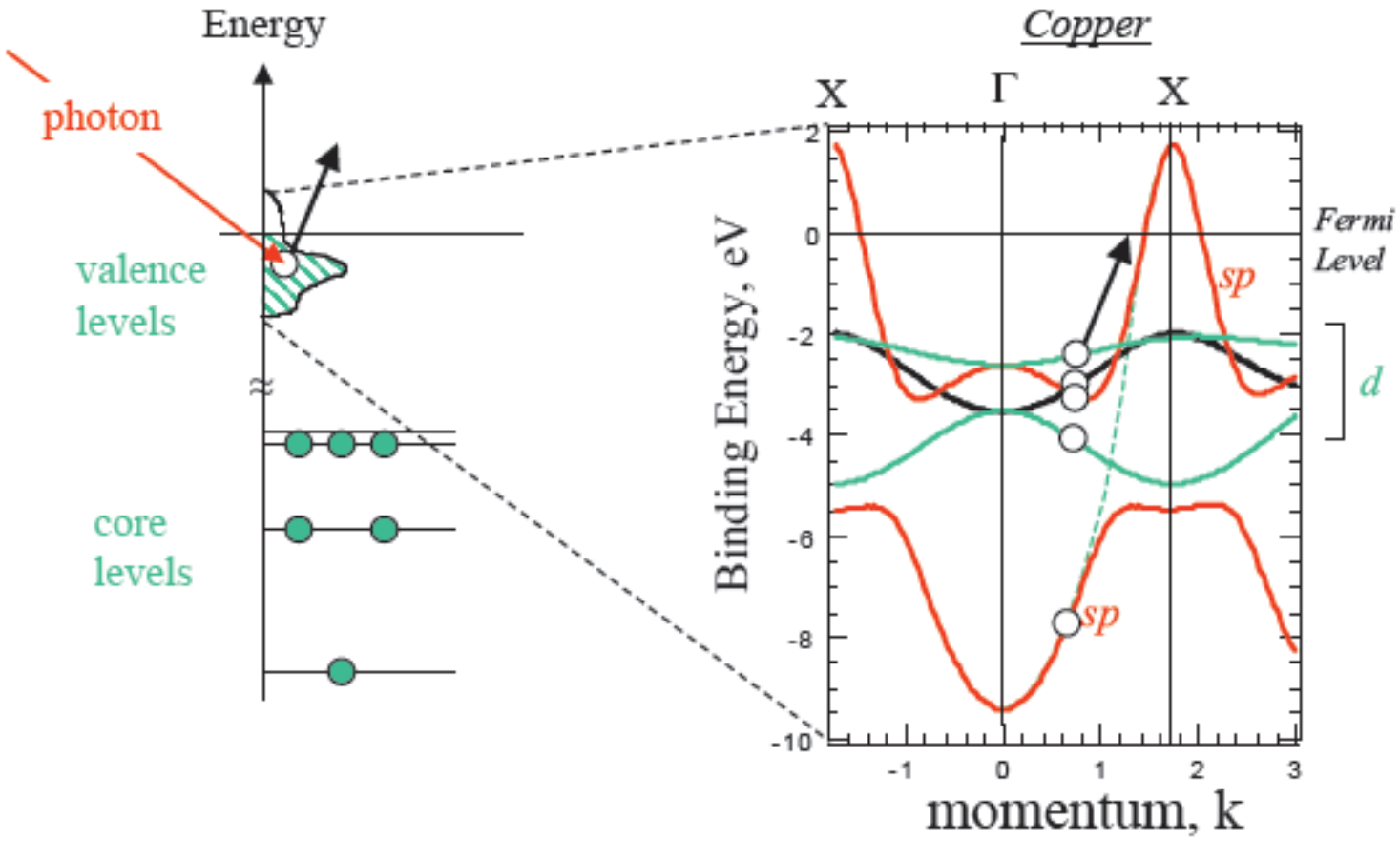
Spectral intensity dominated by the Fe contribution (no MgO state in the energy gap)

Spectrum of Fe before MgO growth

Sicot *et al*. Phys. Rev. B **68**, 184406 (2003)

UPS *vs* ARUPS (or ARPES)

UV photons (10 - 100 eV) → to investigate valence levels
ARUPS: Angle Resolved UPS
ARPES: Angle Resolved PhotoElectron Spectroscopy



UPS is k-integrated

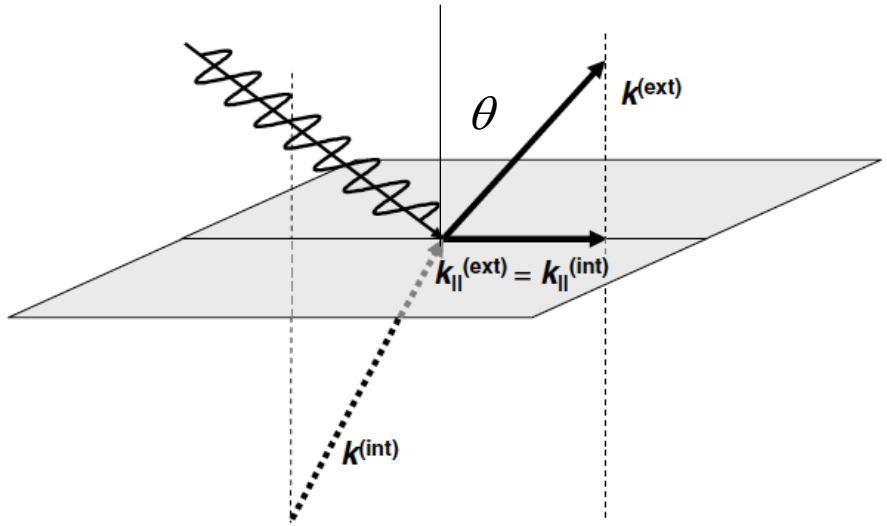
ARPES can measure the wave vector k and the energy at the same time (band structure)

STM gives only access to the DOS as a function of energy, but no information on k (with exceptions, as for example the standing wave of 2D gas at metal surfaces)

ARUPS (or ARPES)

Three-step model (valid also for XPS and UPS):

1) The electron is excited from an initial to a final state within the crystal;
2) The electron travels through the solid towards the surface without scattering;
3) The electron crosses the surface and is emitted into the vacuum with a certain kinetic energy E_{kin}.



photon momentum negligible: $p_e = \hbar k = (2mE_{kin})^{1/2}$ -> ~ 5 10^{-25} for 1 eV electron

$p_{hv} = E/c$ -> ~ 5 10^{-28} for 1 eV photon

momentum conservation: due to symmetry translation breaking at the surface (only 2D), only the momentum component parallel to the surface is conserved, modulo a reciprocal surface vector:

$$\hbar \boldsymbol{k}_{/\!/,i} = \hbar \boldsymbol{k}_{/\!/,f} + \boldsymbol{G}$$

$$\hbar k_{/\!/,f} = \sqrt{2mE_{kin}}\sin\theta$$

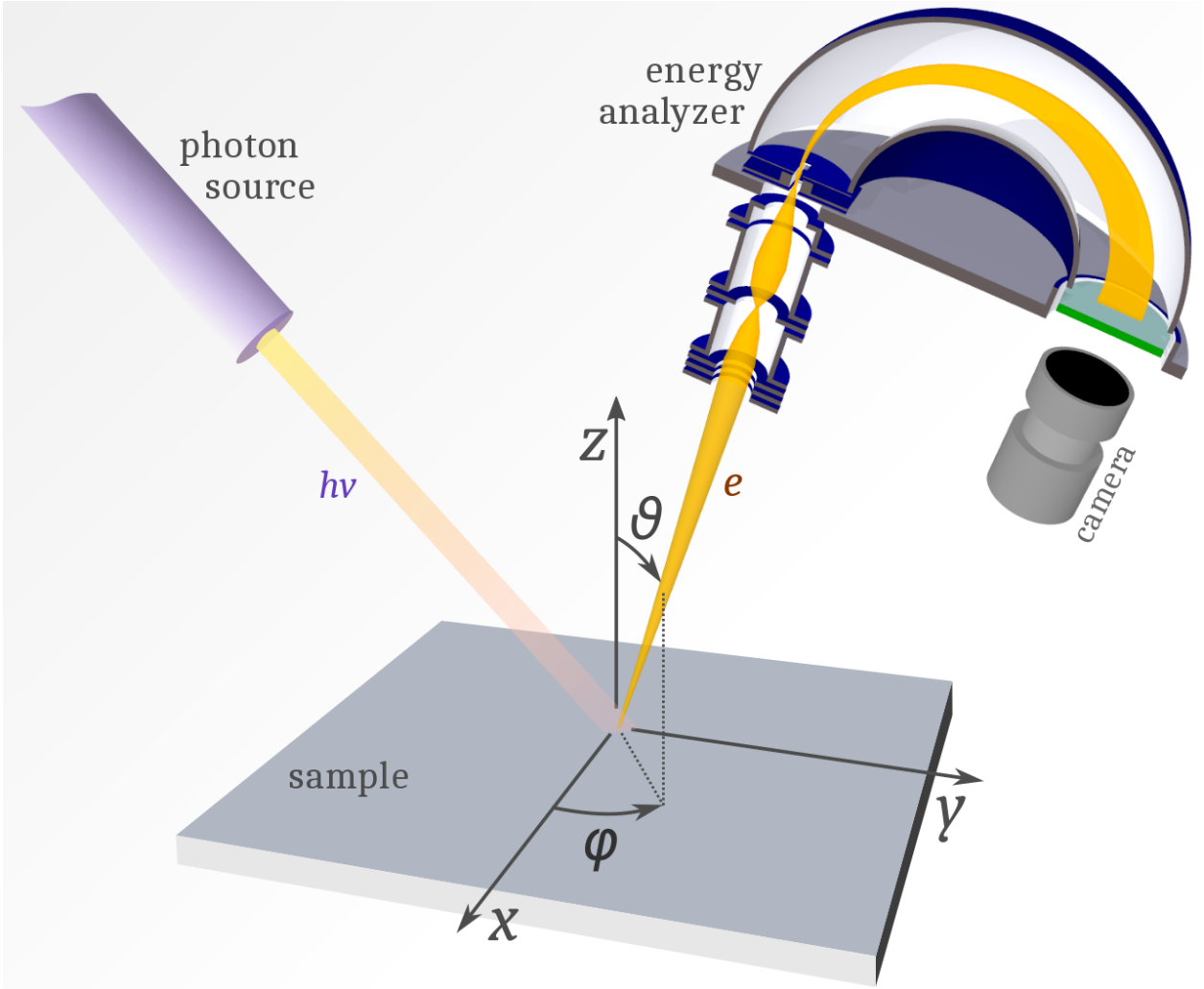
Energy conservation: $E_{kin} = h\nu - E_{bind} - \Phi$

$$\hbar k_{/\!/,i} = \sqrt{2m(h\nu - E_{bind} - \Phi)}\sin\theta$$

→ Measurement of E *vs* k
Band structure

The $k_{||}$-vector of surface states is fully determined by the $k_{||}$-vector of the photoemitted electron. The perpendicular component of the k-vector of bulk states remains unknown, but can be established by special techniques (approx: free electron final state; exact: triangulation, Bragg plane method,...9s

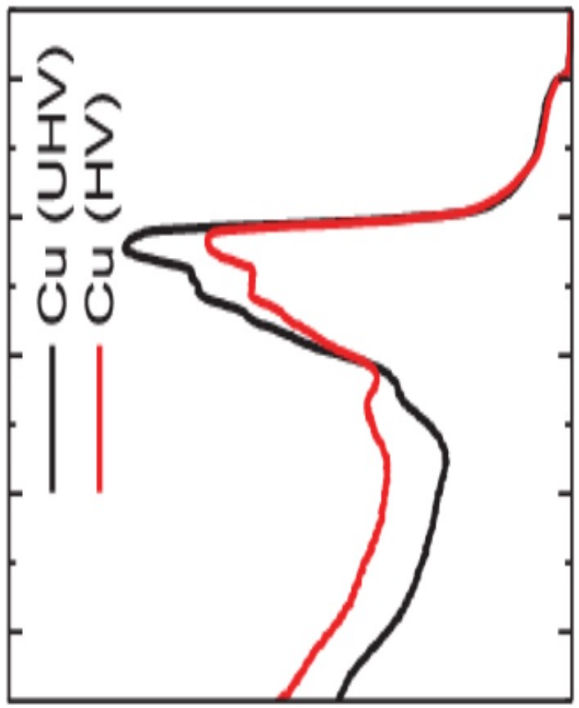
ARUPS (or ARPES)



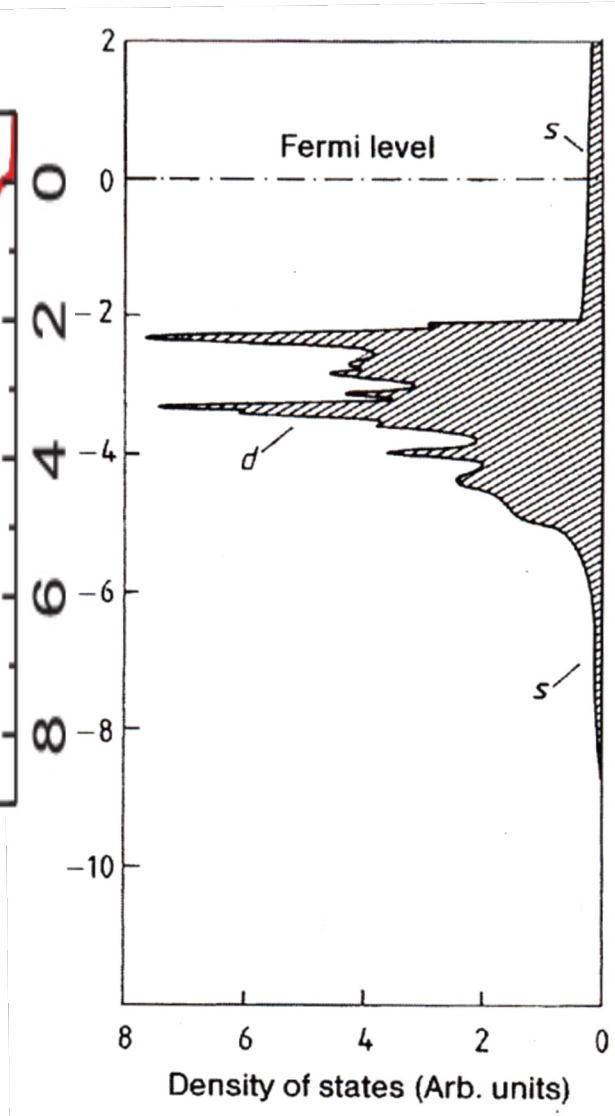
Picture from https://fr.wikipedia.org/wiki/Spectroscopie_photo%C3%A9lectronique_r%C3%A9solue_en_angle

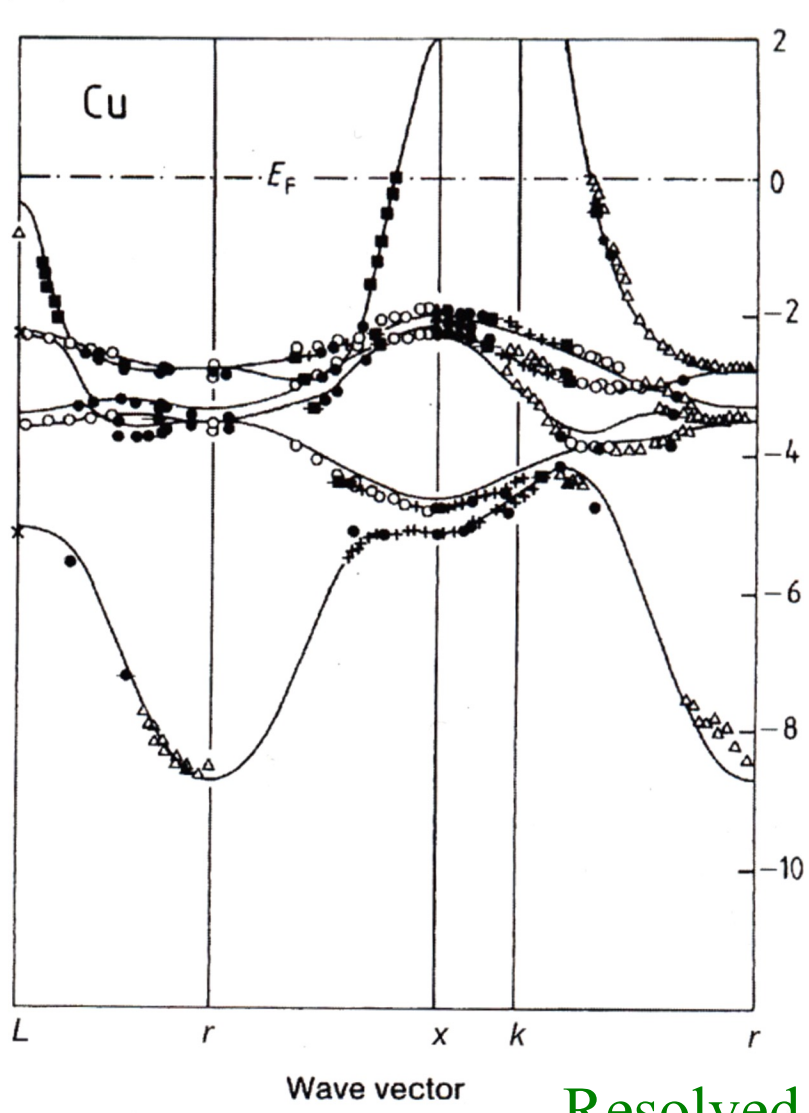
UPS

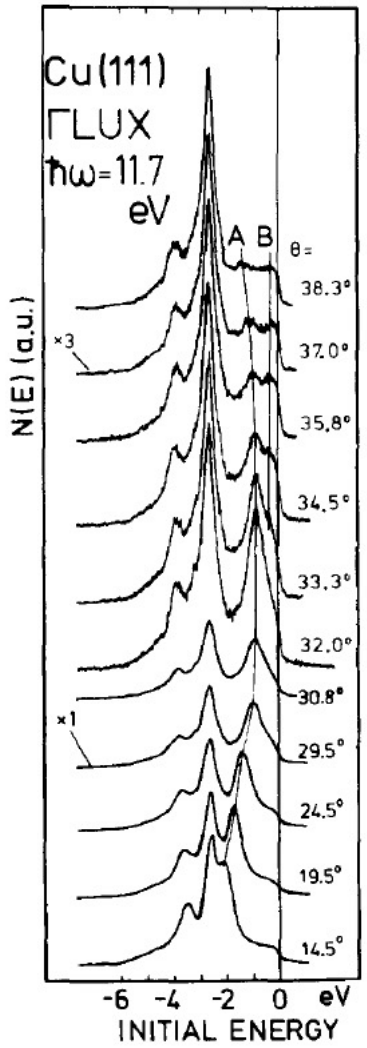
ARUPS



Intensity (counts)



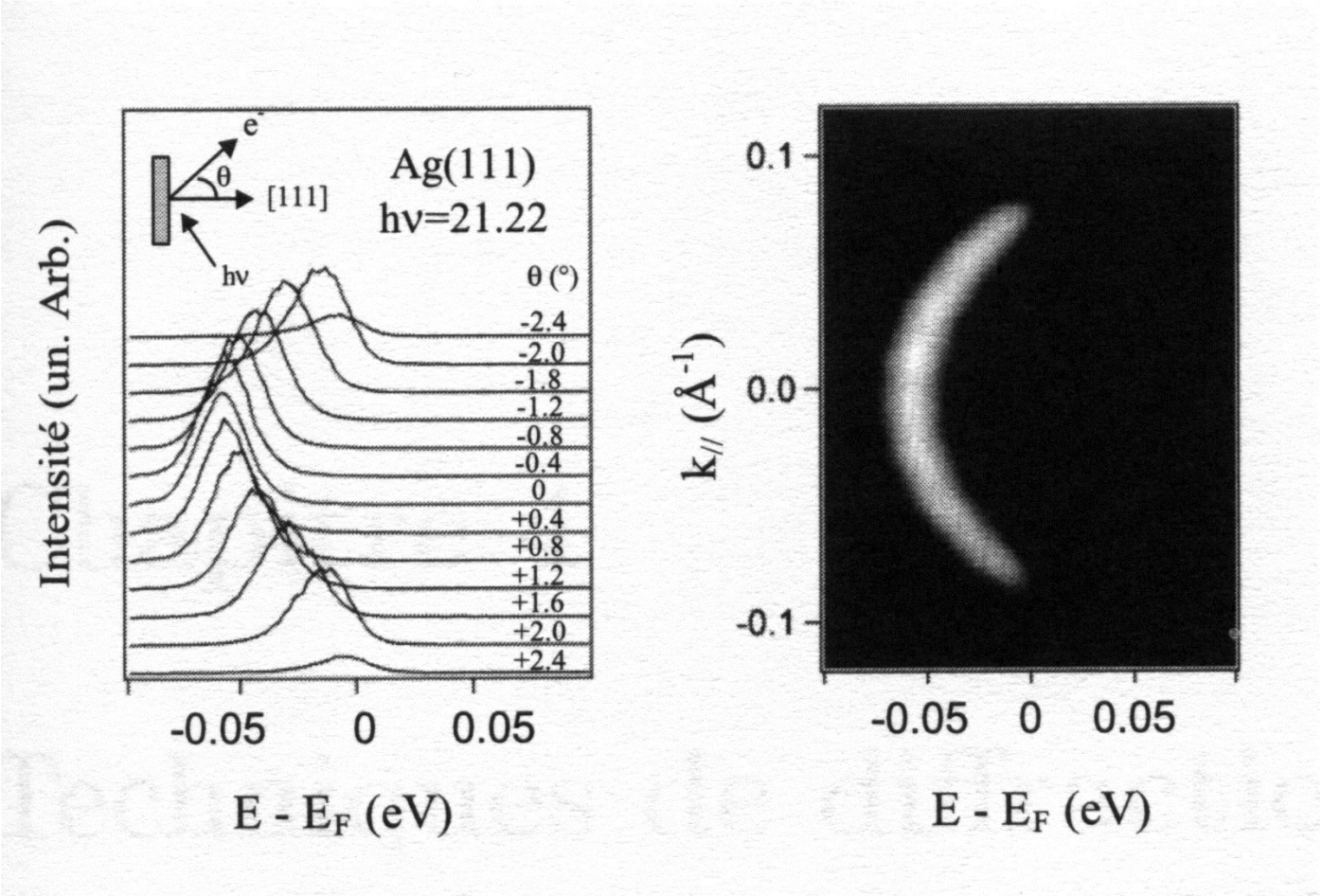




Integrated in k-space

Resolved in k-space:
band structure

Example: 2D system, Ag(111) Surface State

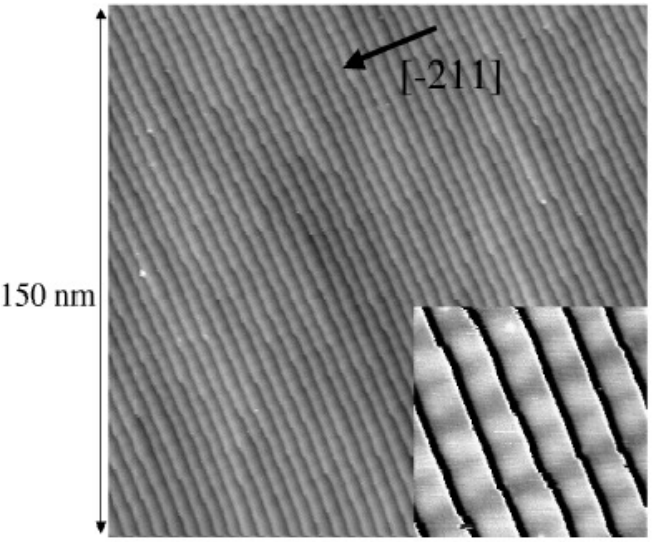


Surface states behave likes a 2D gas of free electrons

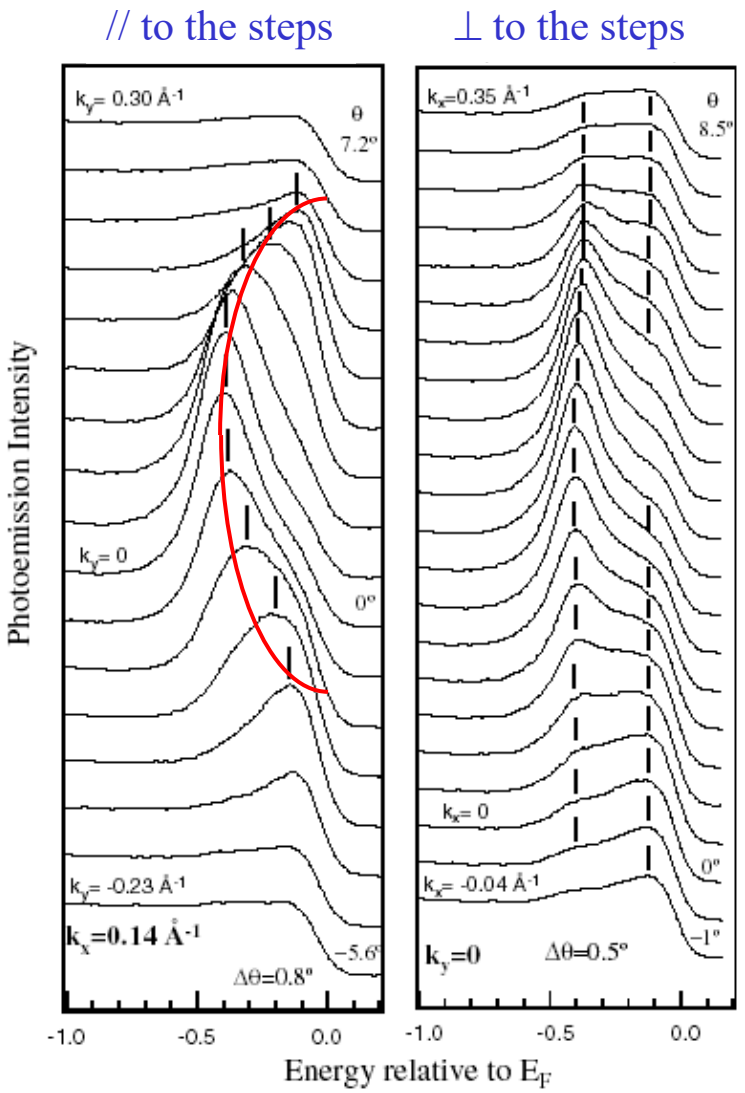
$$E_s = E_F - E_0 + 1/2m^* (\hbar k)^2$$

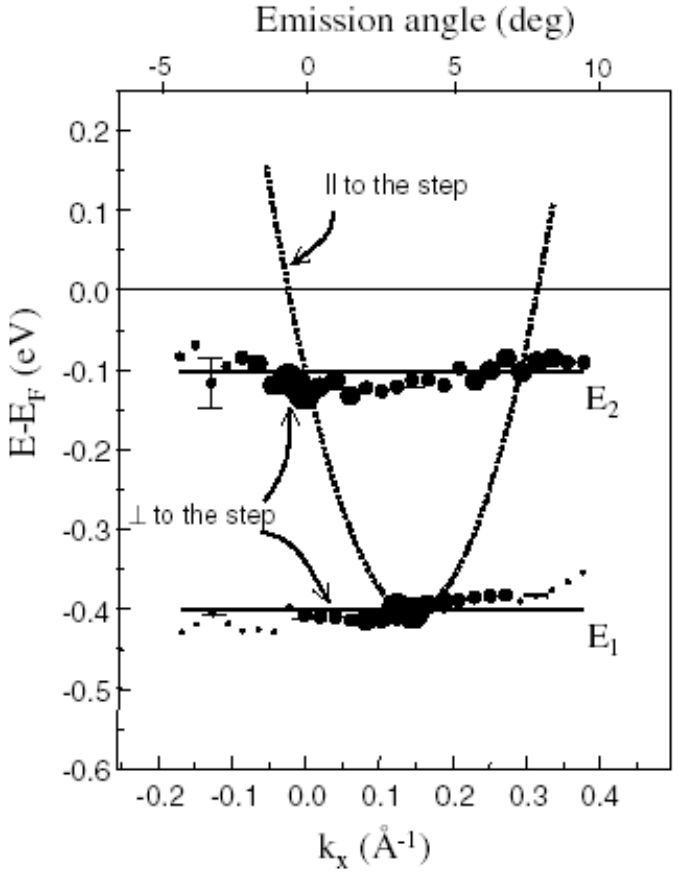
m* -> effective mass of the surface state electron

Example: confined surface states on Au(788)



L = terrace size = 3.8 nm





$\Psi_{\underline{k}}(\underline{r}) \approx \exp(ik_{//}y)\sin(k_{\perp}x)$

$k_{\perp} = n\pi/L$

$E_n = E_F - E_0 + n^2/2m^*(\hbar\pi/L)^2$

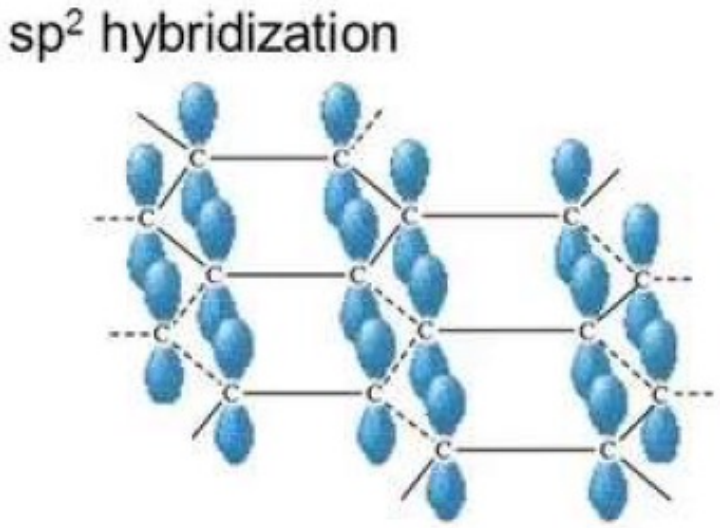
A. Mugarza et al., Phys. Rev. Lett. **87**, 107601 (2001)

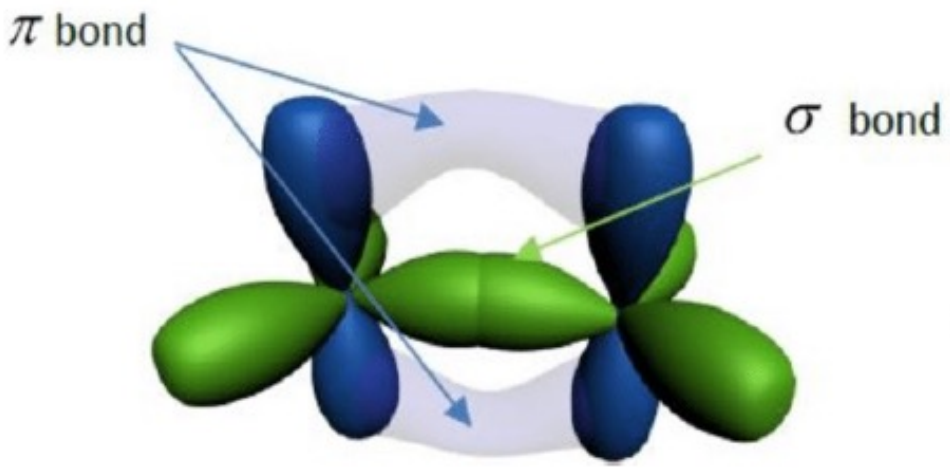
One dimensional quantum well of width L perpendicular to the steps

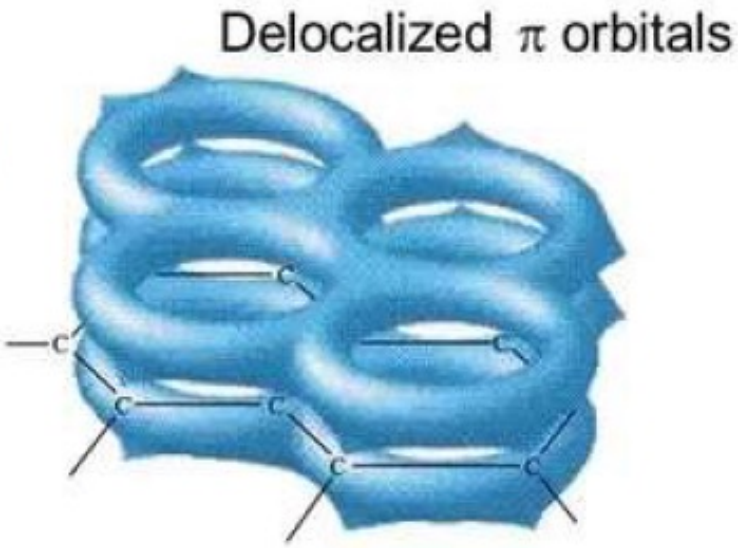
Graphene π bands

sp^2 hybridization to form σ bonds in the graphene plane

p_z orbital stick out perpendicular to the surface and form π orbitals

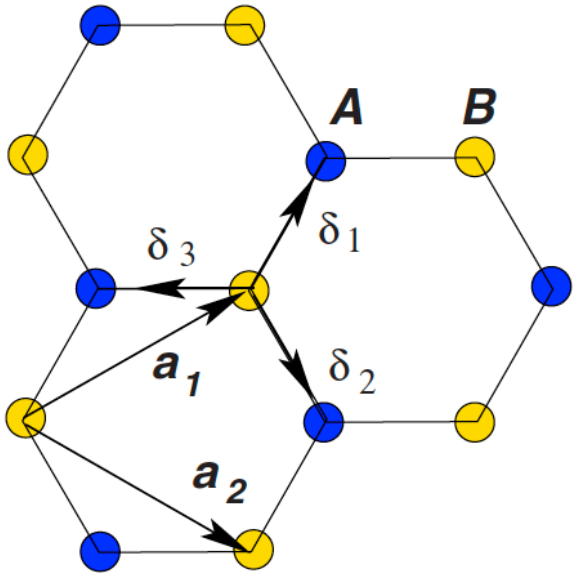


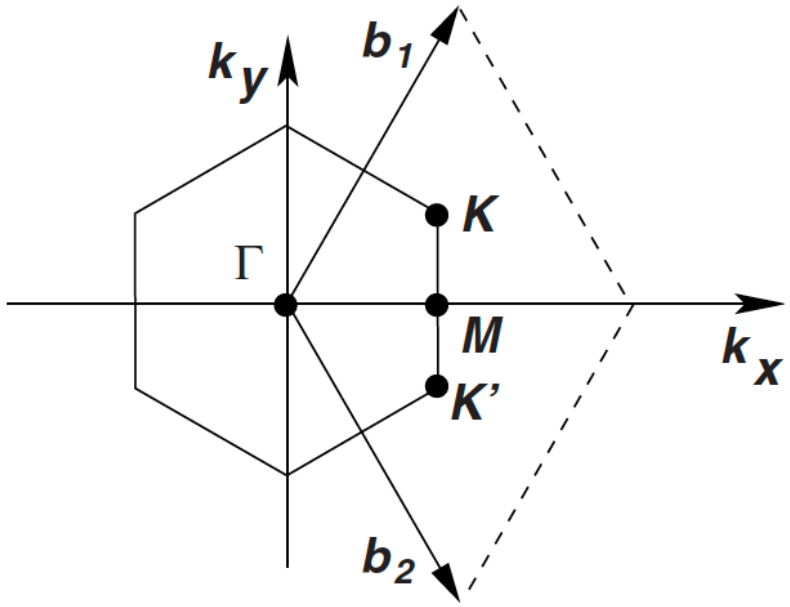




Graphene

Tight-binding description of the π bands (originating from p_z)

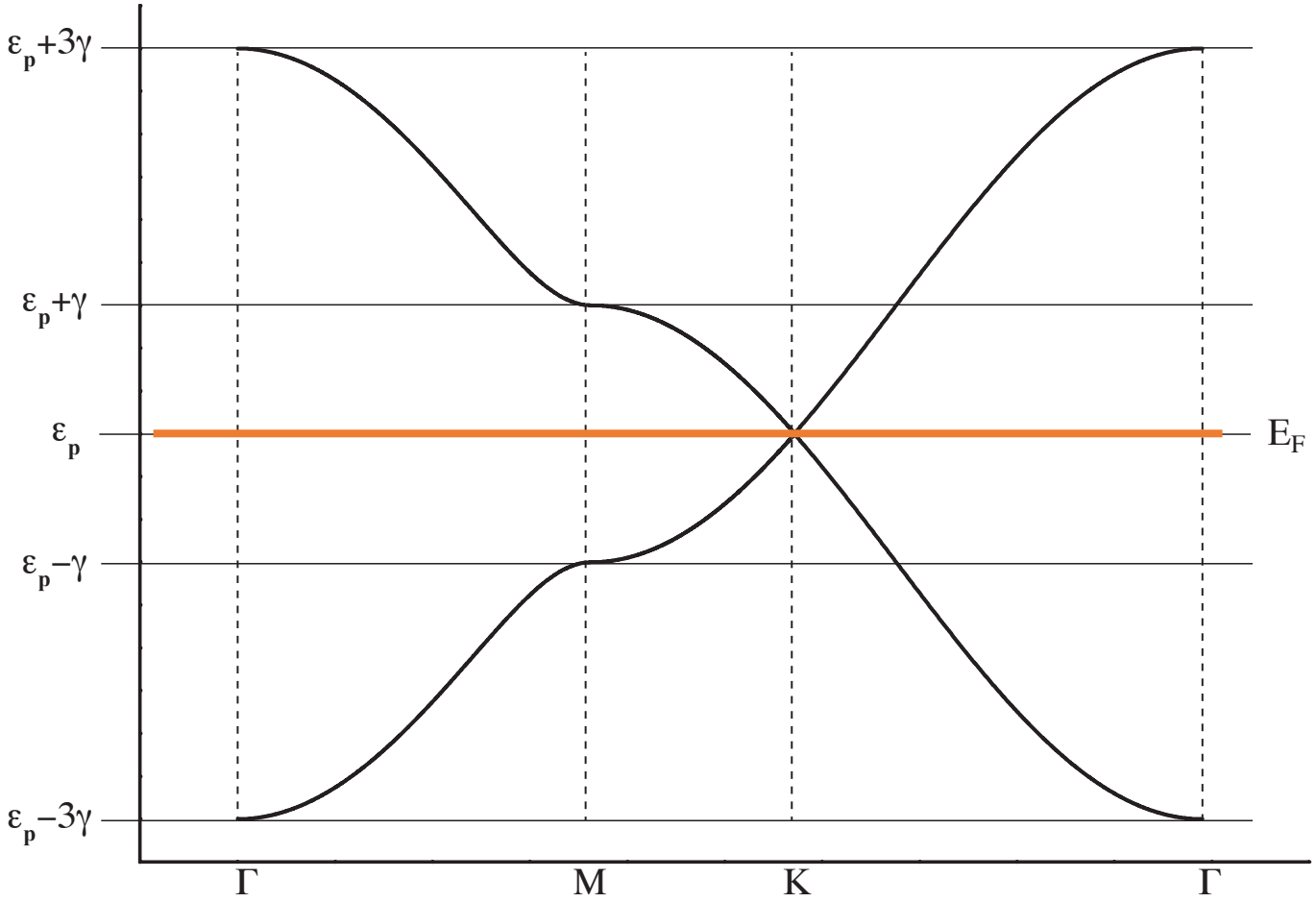




- triangular Bravais lattice with a base formed of two atoms (A and B)
- A and B sublattices
- for each atom, the 3 nearest neighbors belong to the other sublattice
- non-zero hopping parameter only for nn
- starting from Bloch wavefunctions localized on A and B, we build the wavefunctions describing the π bands
- find the expression for their energy vs k in the FBZ

Graphene

$$E(\vec{k}) = \varepsilon_p \pm \gamma\sqrt{1 + 4\cos^2\frac{k_x a}{2} + 4\cos\frac{k_x a}{2}\cos\frac{k_y a\sqrt{3}}{2}}$$



What about filling?

- N unit cells → N values of k in FBZ → 2N states counting the spin
- there are two bands

→ overall 4N states

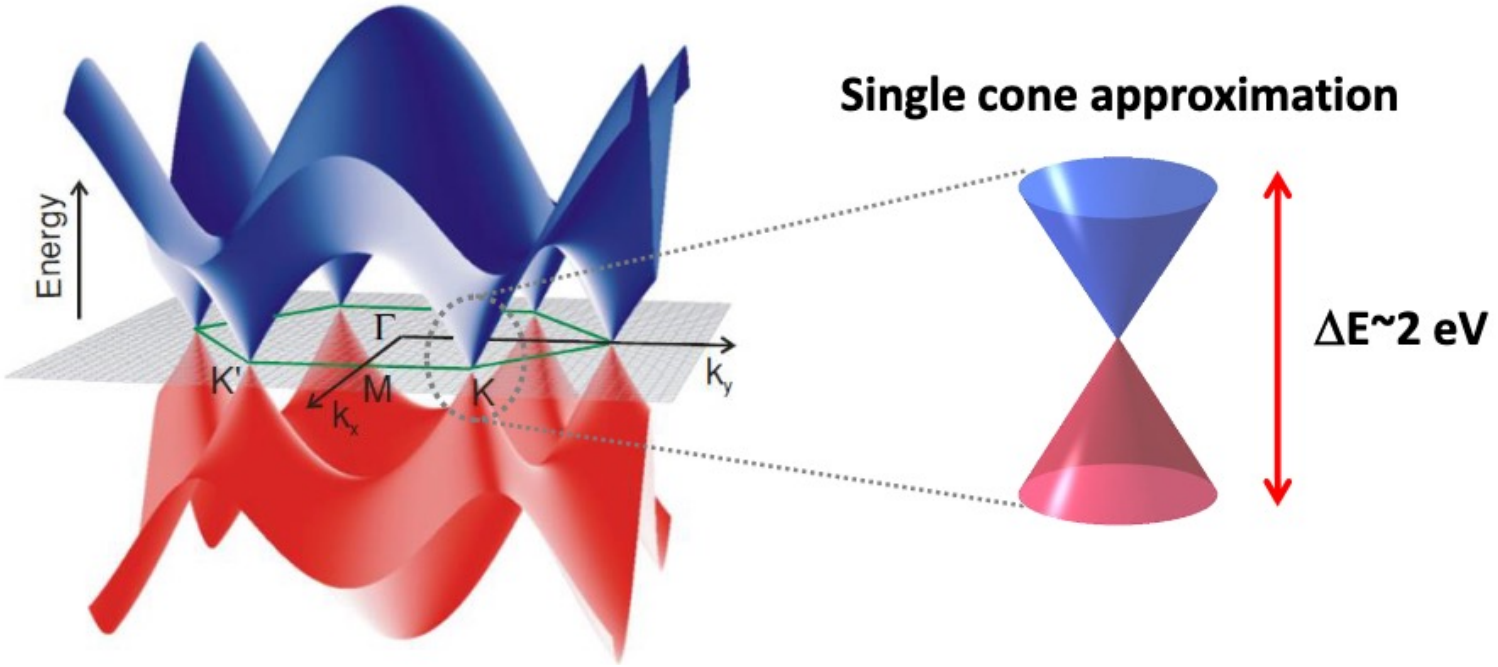
- each C atom contributes one p_z (→ π) orbital with one electron
- two C atoms per unit cell

→ 2N electrons

→ E_F is in the middle of the two bands

graphene is a semimetal (or zero-gap semiconductor)

Graphene



Around K and K' points, the energy dispersion is linear, very different from the usual quadratic dependency.

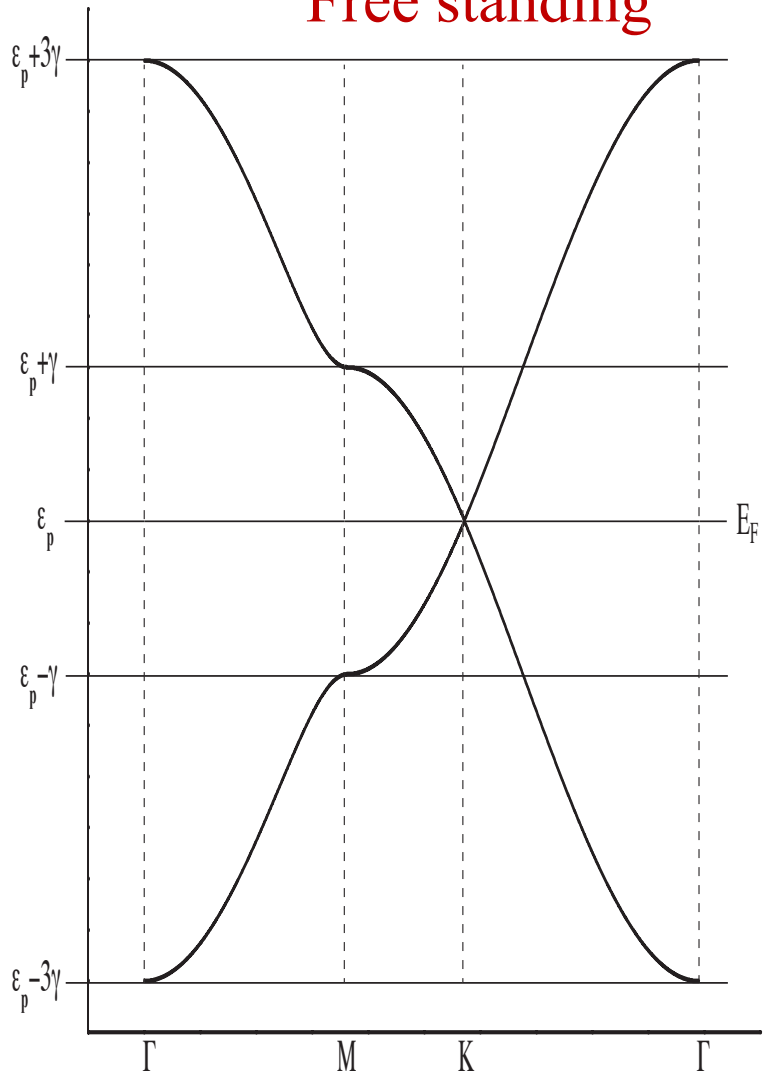
It can be shown that (wavevector k centered on K or K'):

$$E = \pm \hbar v_F k$$

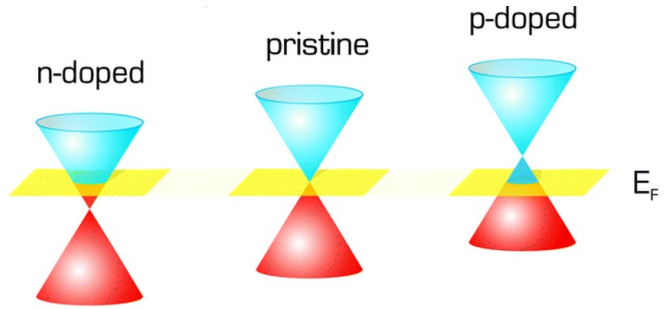
$$v_F = \frac{3|\gamma|a}{2\hbar}$$

for ideal, free-standing graphene E_F coincides with the Dirac points

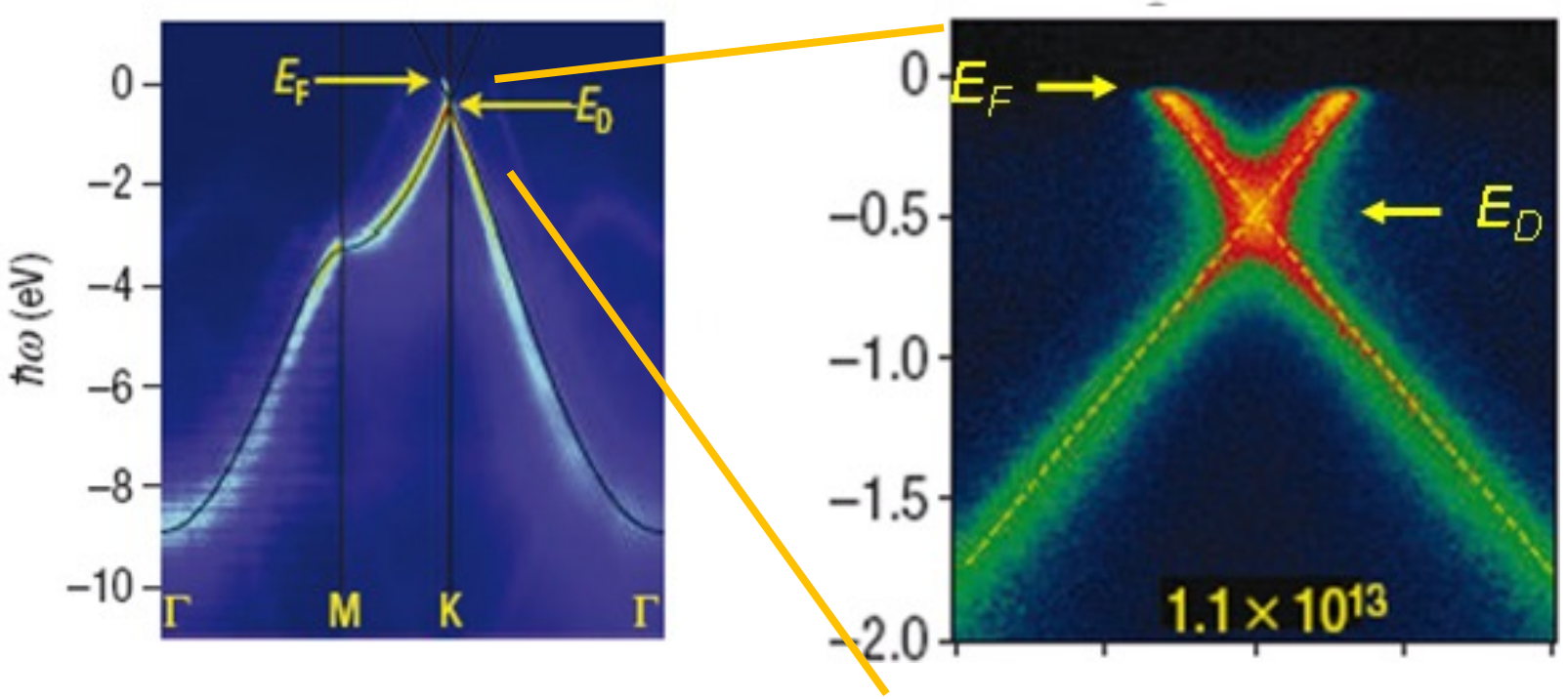
Free standing



Epitaxial graphene



Graphene on SiC



The Dirac point (E_D) is at Fermi level in free standing graphene

On SiC E_D = -0.5 eV (below Fermi level) due to graphene-substrate hybridization

Nature Materials **6,** 183–191 (2007)

Gap opening ?

graphene: semimetal or zero-gap semiconductor

technological advantages for graphene to be a semiconductor instead of a semimetal, specifically in electronic applications (transistor)

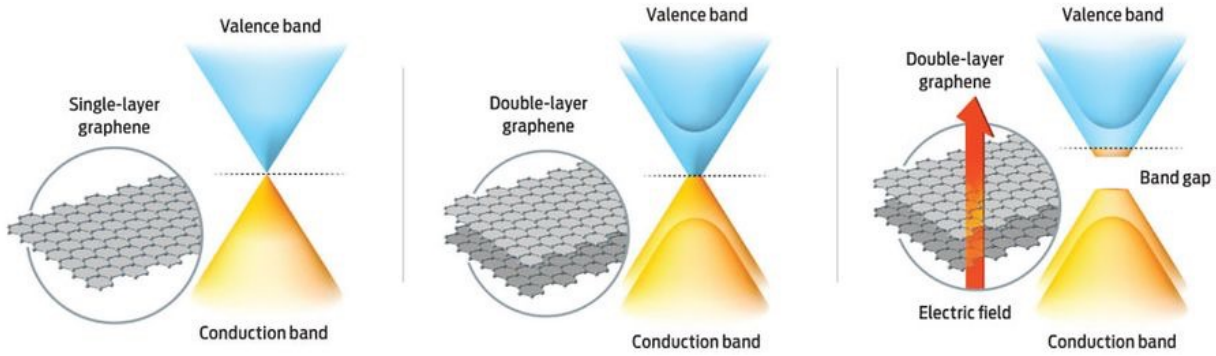
possible paths:

- geometrically confine graphene into nanoribbons or quantum dots
- grow graphene on substrates that induce lattice potentials that open a gap

- bilayer graphene + field effect
- twisted bilayer graphene
- bilayer graphene + strain

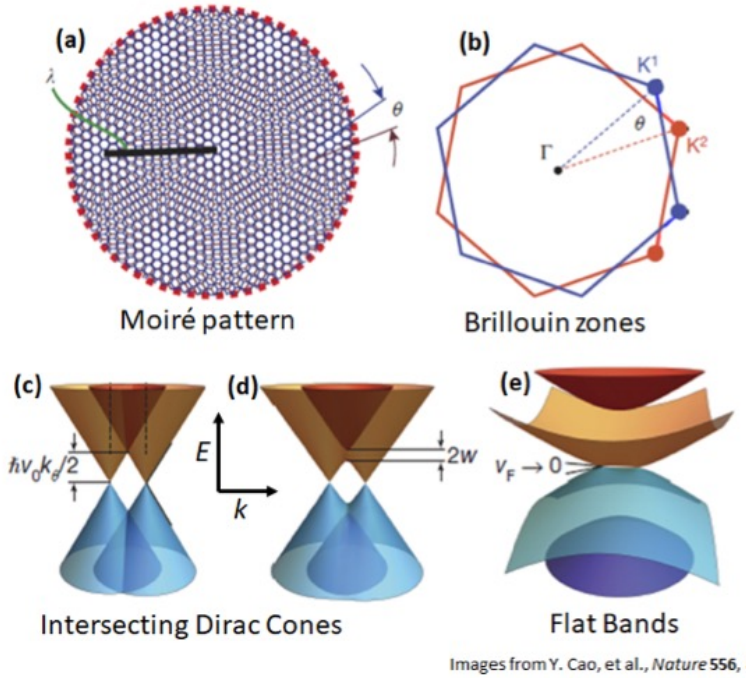
- other 2D materials (h-BN, MoS_2, ...)

Widely tunable bandgap in bilayer graphene



doi.org/10.1038/nature08105

Twisted Bilayer Graphene: Moiré-induced Electronic Structure



Images from Y. Cao, et al., *Nature* 556, 80 (2019)