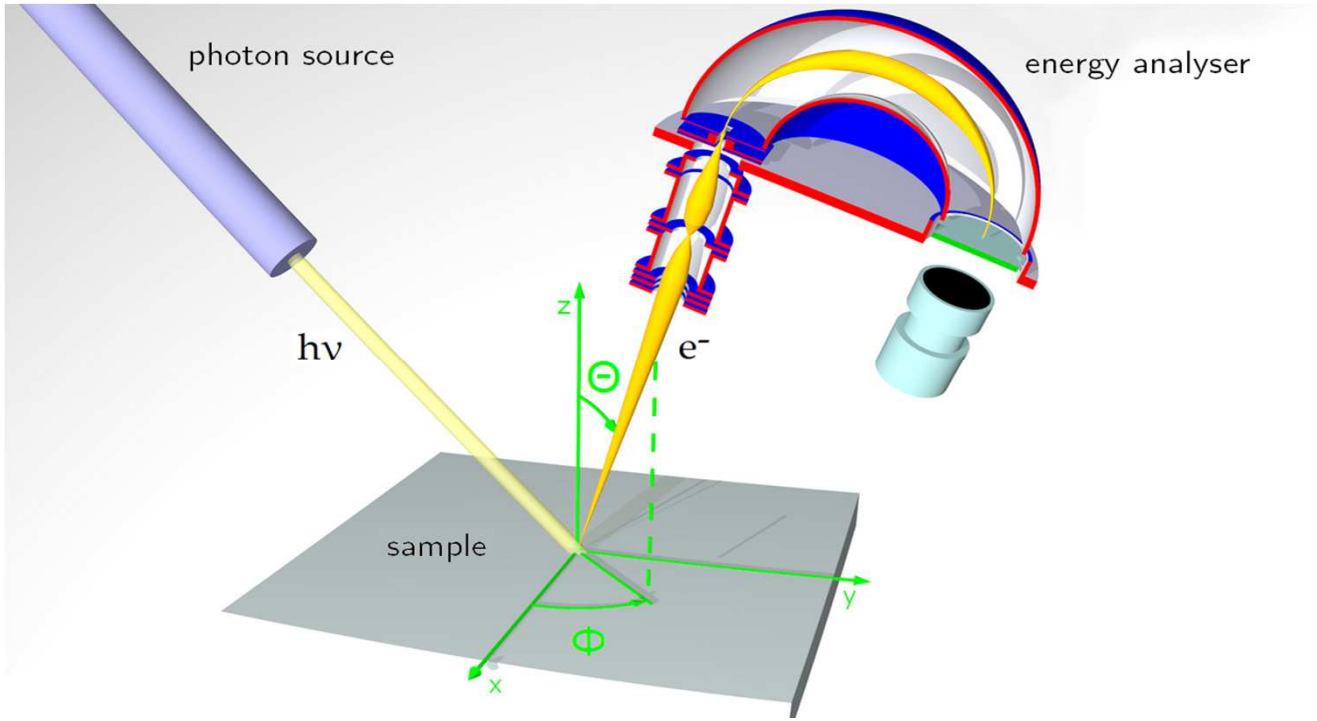
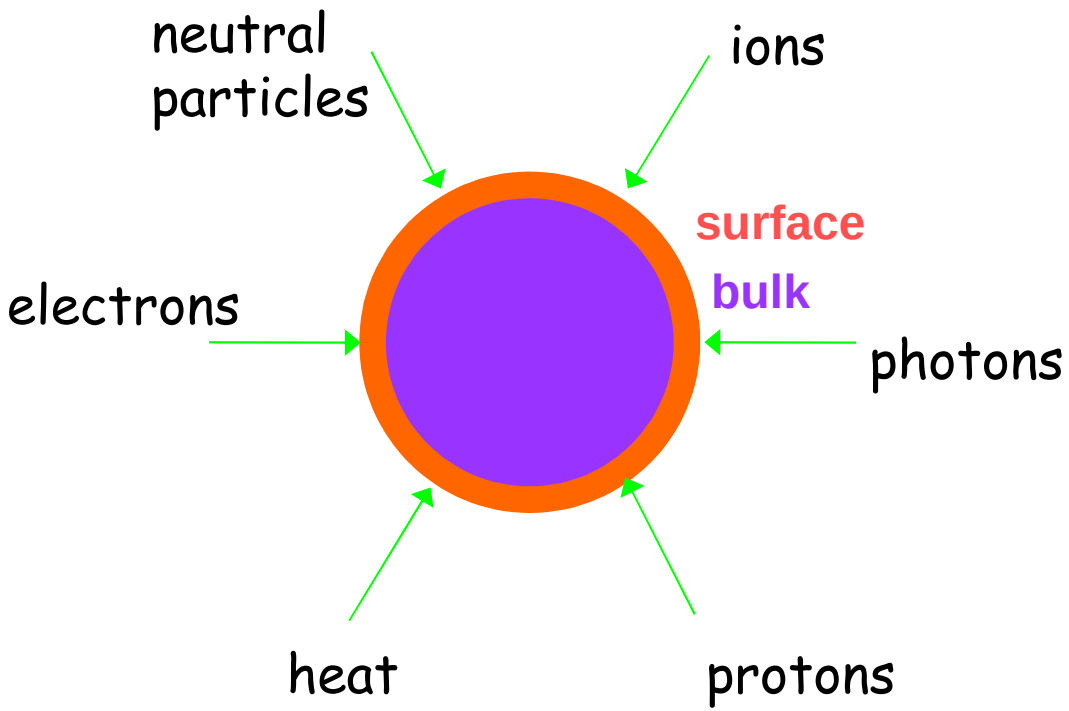
XPS SPECTROSCOPY



Rosanna Larciprete
CNR-ISC and LNF-INFN

Surface science

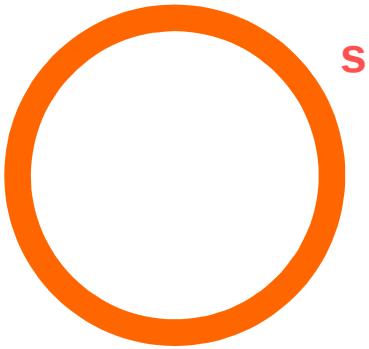


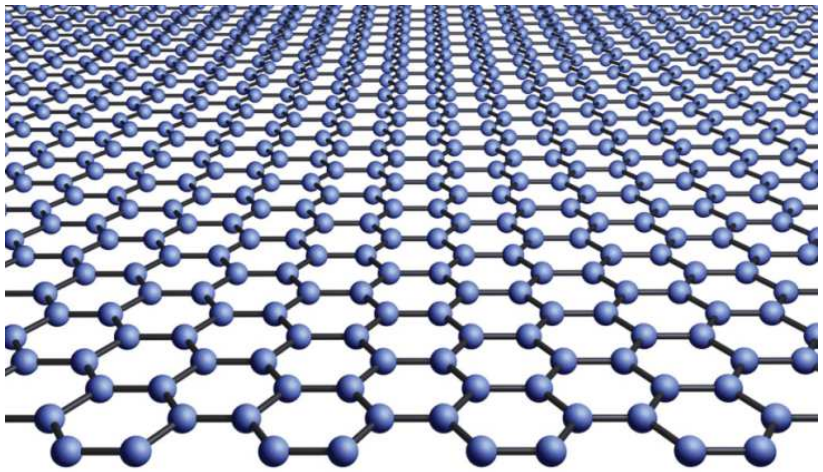
INFORMATION

- Chemical
- Electronic
- Structural
- Magnetic
- Transport
- Thermic
- ……

Surface science

Chemical composition of a surface
Surface reactions (oxidation, catalysis)
Surface diffusion
Surface states
Epitaxy, thin film growth, self-assembly of nanostructures

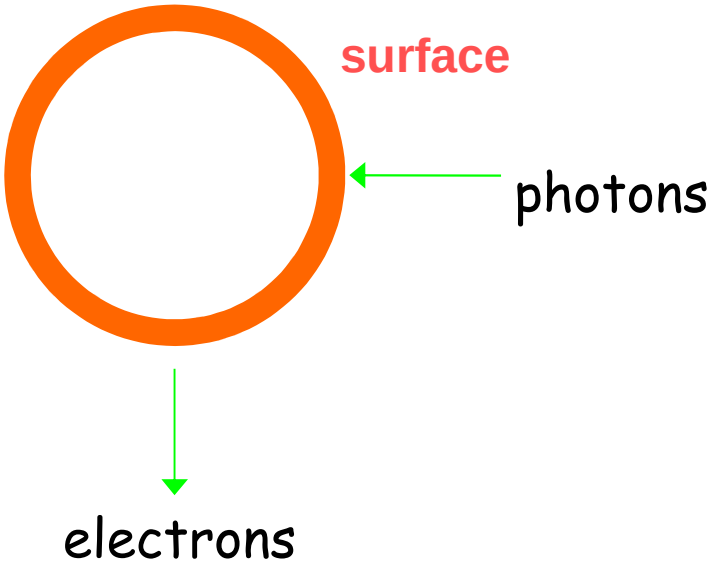




graphene

Surface science

Chemical composition of a surface
Surface reactions (oxidation, catalysis)
Surface diffusion
Surface states
Epitaxy, thin film growth, self-assembly of nanostructures

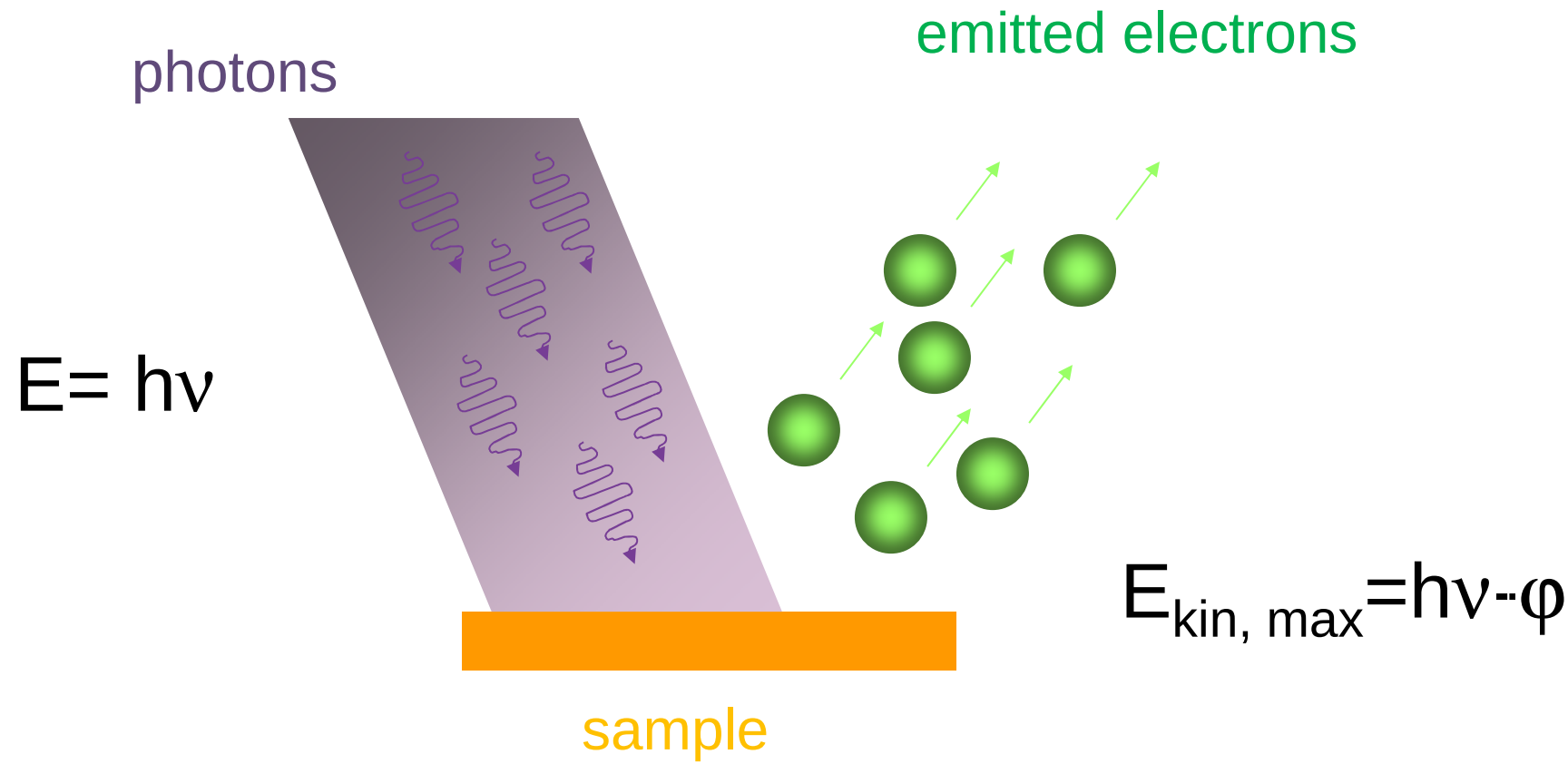


INFORMATION

Chemical

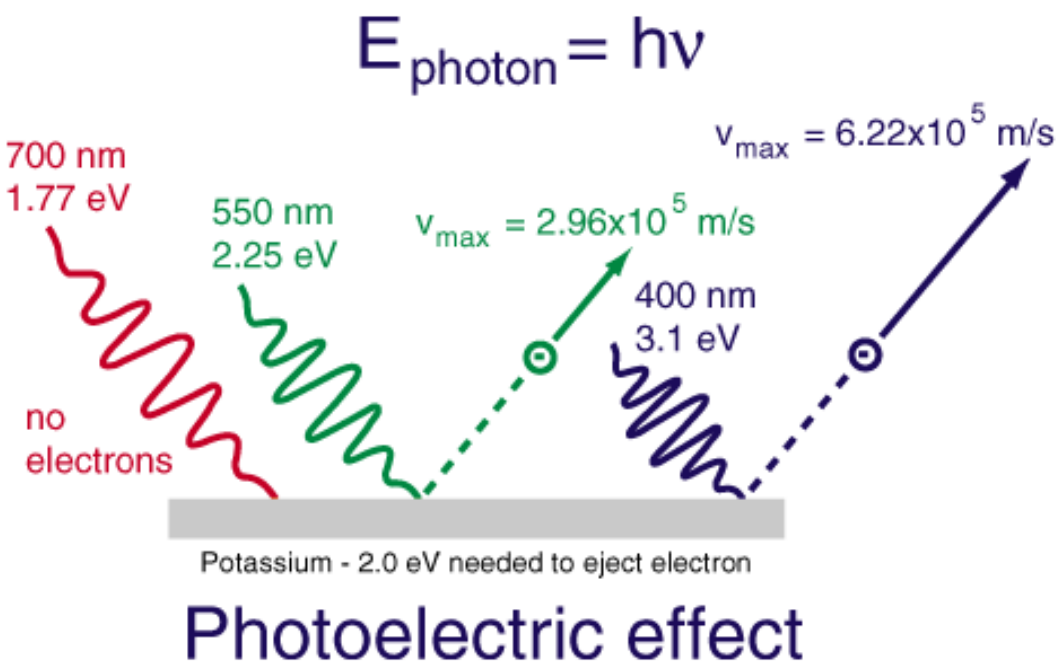
Electronic

Photoelectric effect



E_{kin} does not depend on the intensity of the photon beam

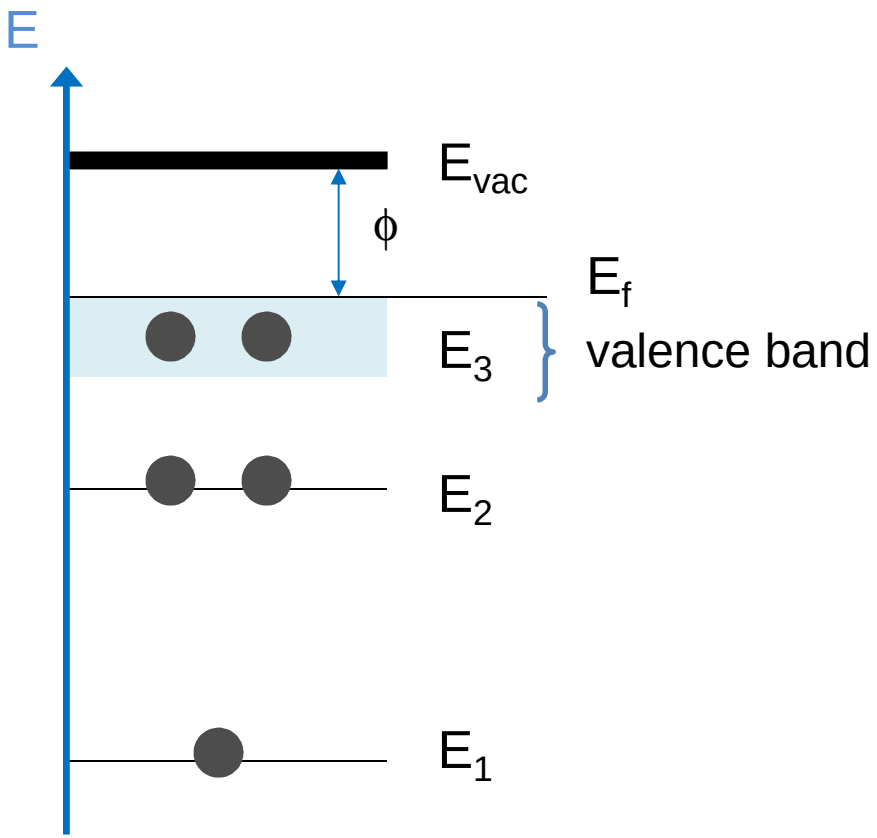
Photoelectric effect

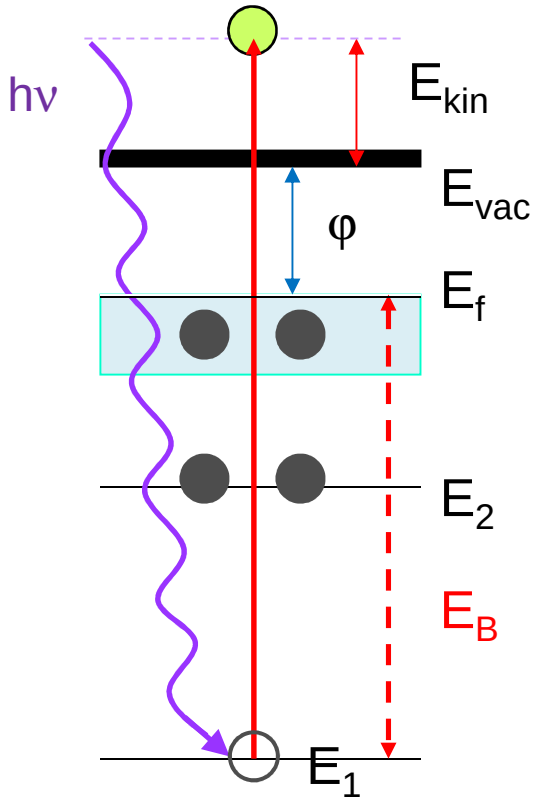


The work function φ is the energy needed to to remove an electron from a solid to a point in the vacuum immediately outside the solid surface

Element	Work Function(eV)
Aluminum	4.08
Beryllium	5.0
Cadmium	4.07
Calcium	2.9
Carbon	4.81
Cesium	2.1
Cobalt	5.0
Copper	4.7
Gold	5.1
Iron	4.5
Lead	4.14
Magnesium	3.68
Mercury	4.5
Nickel	5.01
Niobium	4.3
Potassium	2.3
Platinum	6.35
Selenium	5.11
Silver	4.73
Sodium	2.28
Uranium	3.6
Zinc	4.3

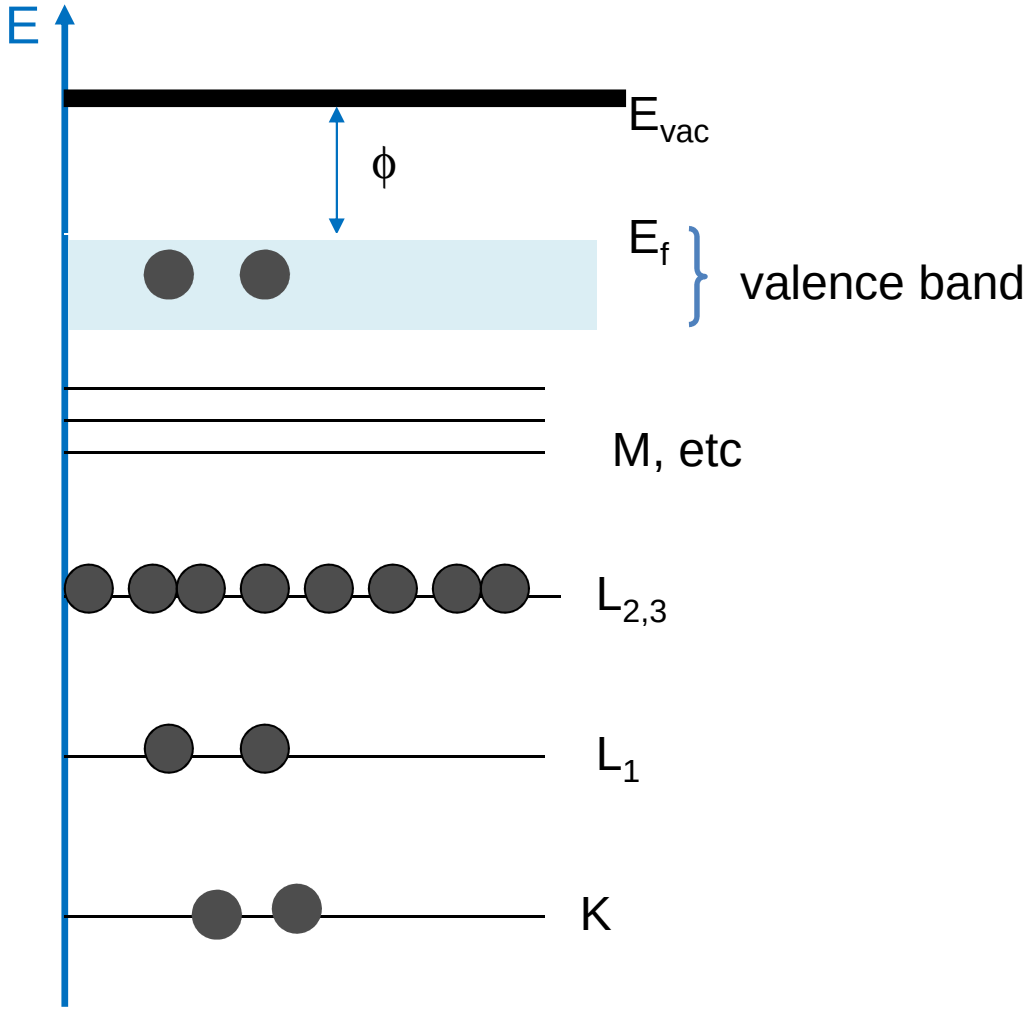
The photoemission process



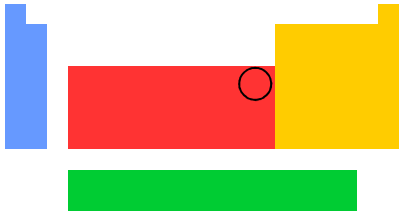


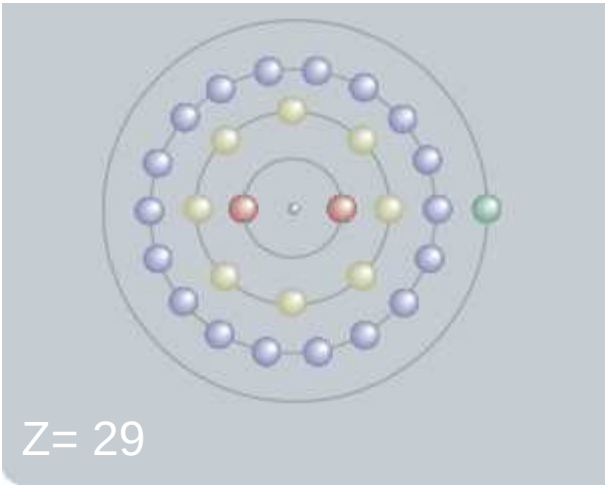
$$E_{Kin} = h\nu - E_B - \varphi$$

Atomic energy levels



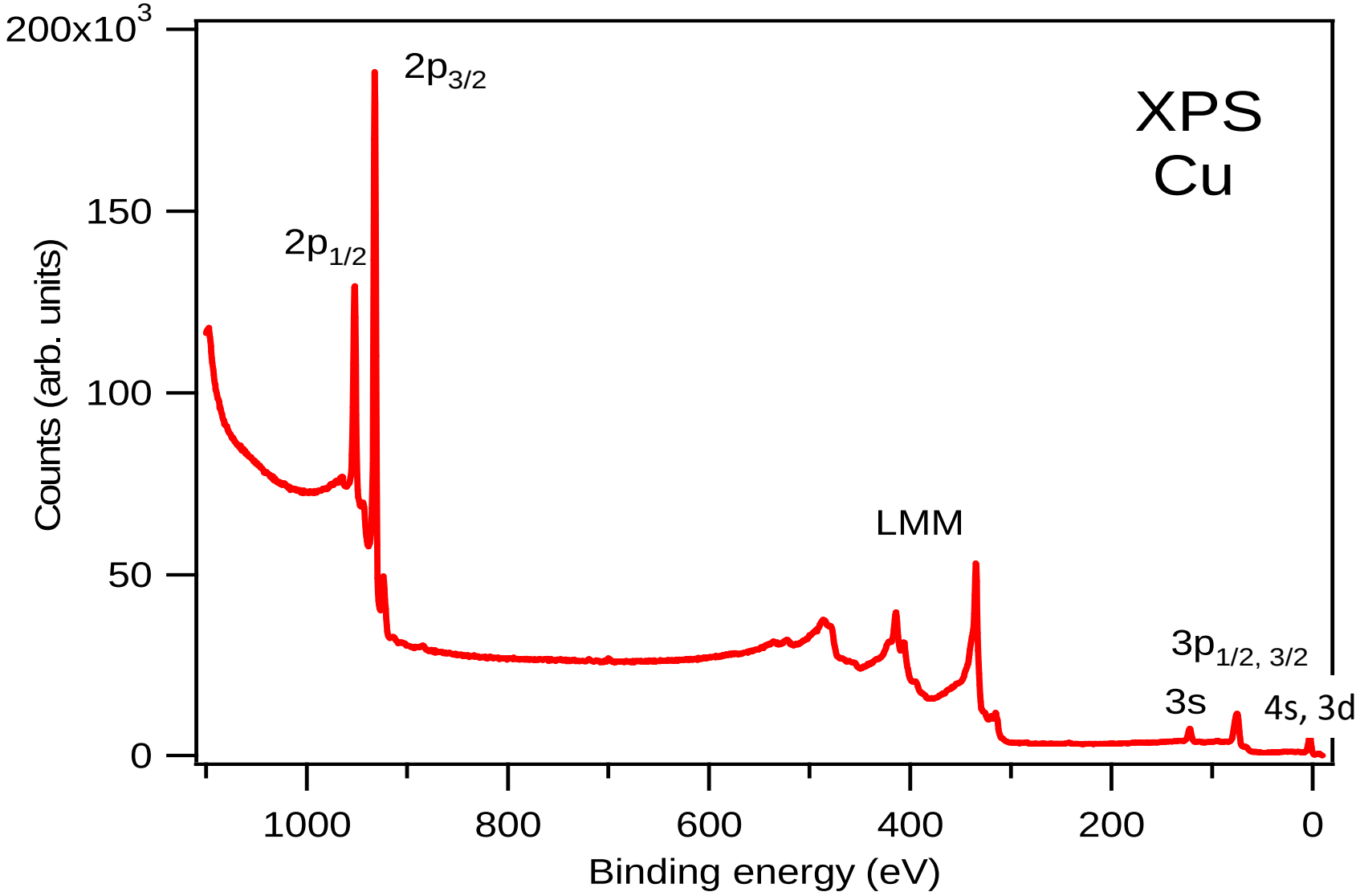
Cu





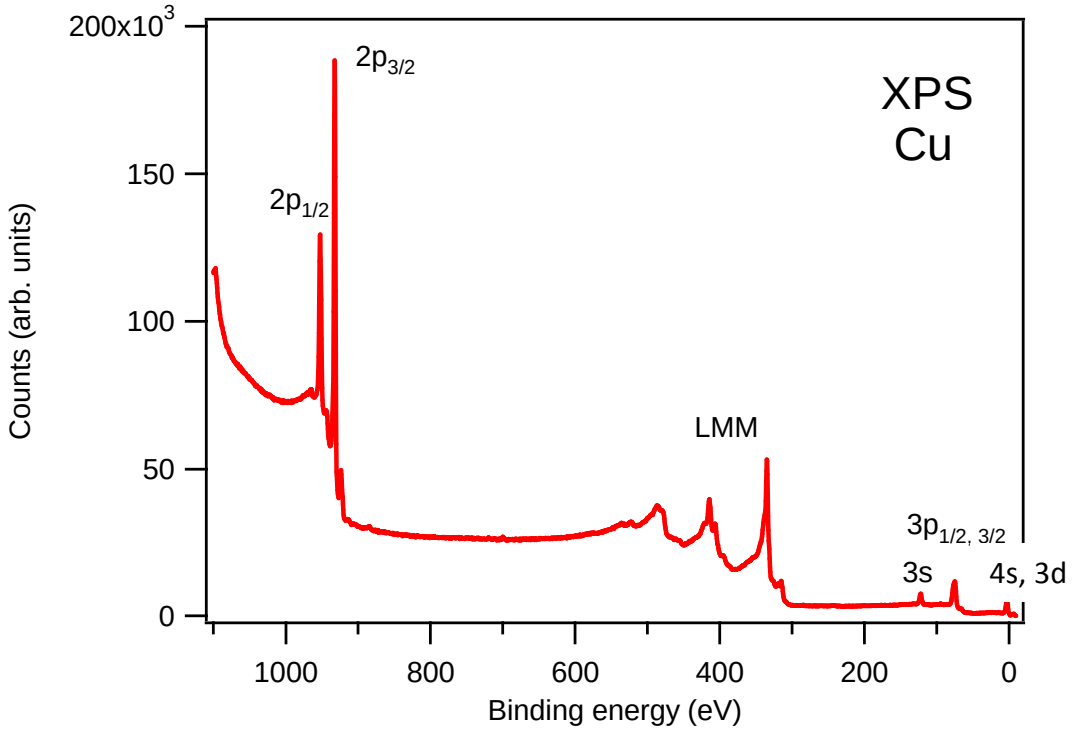
$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 3d^{10}\ 4s^1$

XPS spectrum

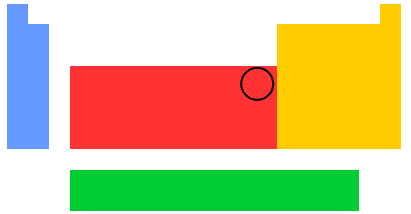


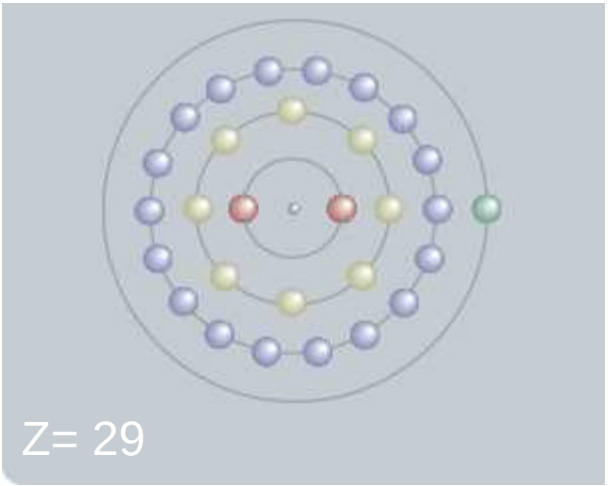
XPS spectrum

Label	Orbital	eV
K	1s	8979
L I	2s	1096.7
L II	2p1/2	952.3
L III	2p3/2	932.7
M I	3s	122.5
M II	3p1/2	77.3
M III	3p3/2	75.1



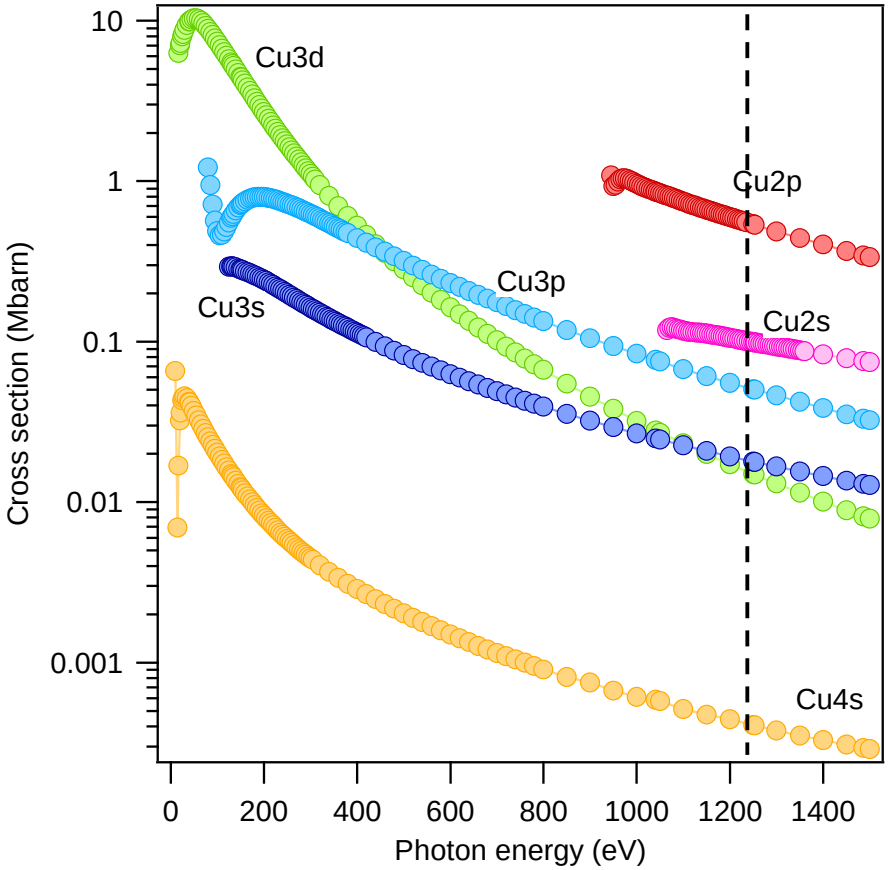
Cu

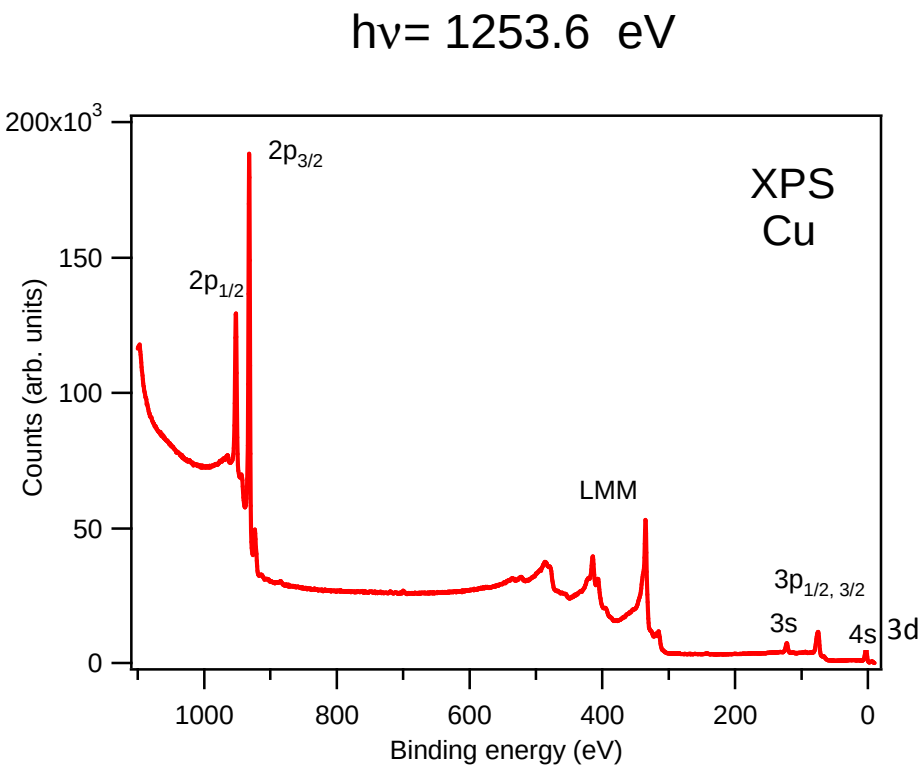




$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 3d^{10}\ 4s^1$

Photoionization cross section

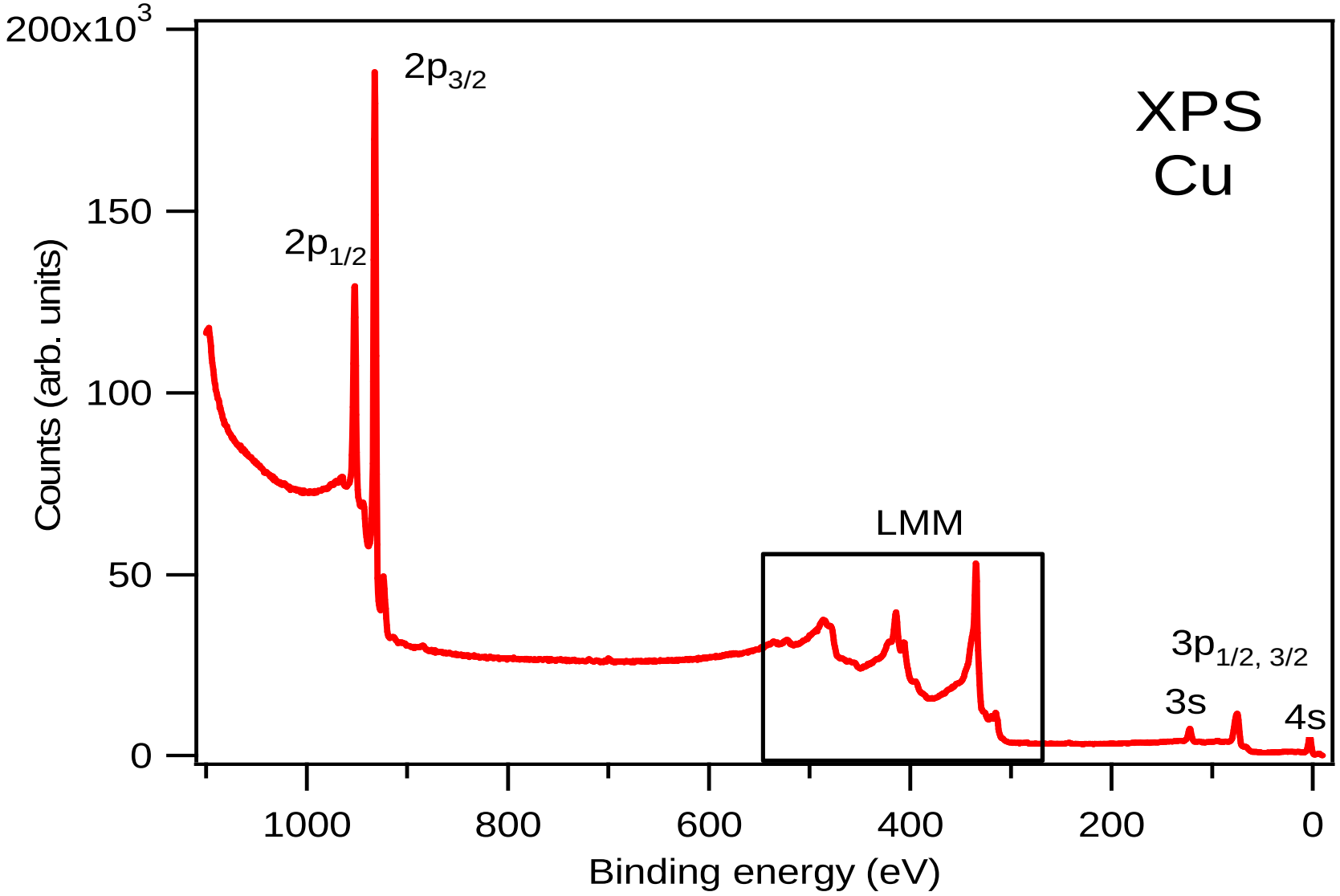




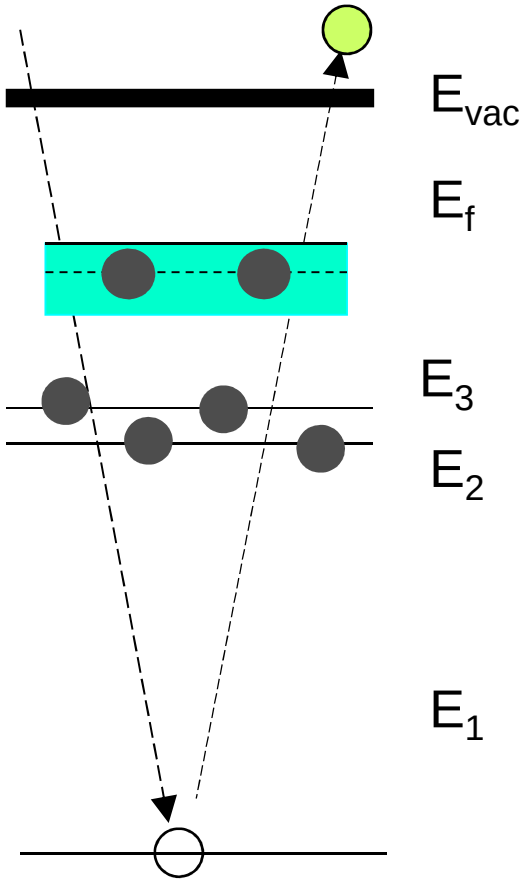
Core level binding energies

		K 1s	L-I 2s	L-II 2p1/2	L-III 2p3/2	M-I 3s	M-II 3p1/2	M-III 3p3/2	M-IV 3d3/2	M-V 3d5/2
1	H	13.6								
2	He	24.6*								
3	Li	54.7*								
4	Be	111.5*								
5	B	188*								
6	C	284.2*								
7	N	409.9*	37.3*							
8	O	543.1*	41.6*							
9	F	696.7*								
10	Ne	870.2*	48.5*	21.7*	21.6*					
11	Na	1070.8+	63.5+	30.4+	30.5*					
12	Mg	1303.0+	88.6*	49.6+	49.21					
13	Al	1559	117.8*	72.9*	72.5*					
14	Si	1839	149.7*b	99.8*	99.2*					
15	P	2145.5	189*	136*	135*					
16	S	2472	230.9	163.6*	162.5*					
17	Cl	2822	270*	202*	200*					
18	Ar	3205.9*	326.3*	250.6+	248.4*	29.3*	15.9*	15.7*		
19	K	3608.4*	378.6*	297.3*	294.6*	34.8*	18.3*	18.3*		
20	Ca	4038.5*	438.4+	349.7+	346.2+	44.3+	25.4+	25.4+		
21	Sc	4492	498.0*	403.6*	398.7*	51.1*	28.3*	28.3*		
22	Ti	4966	560.9+	460.2+	453.8+	58.7+	32.6+	32.6+		
23	V	5465	626.7+	519.8+	512.1+	66.3+	37.2+	37.2+		
24	Cr	5989	696.0+	583.8+	574.1+	74.1+	42.2+	42.2+		
25	Mn	6539	769.1+	649.9+	638.7+	82.3+	47.2+	47.2+		
26	Fe	7112	844.6+	719.9+	706.8+	91.3+	52.7+	52.7+		
27	Co	7709	925.1+	793.2+	778.1+	101.0+	58.9+	59.9+		
28	Ni	8333	1008.6+	870.0+	852.7+	110.8+	68.0+	66.2+		
29	Cu	8979	1096.7+	952.3+	932.7	122.5+	77.3+	75.1+		
30	Zn	9659	1196.2*	1044.9*	1021.8*	139.8*	91.4*	88.6*	10.2*	10.1*
31	Ga	10367	1299.0*b	1143.2+	1116.4+	159.51	103.5+	100.0+	18.7+	18.7+
32	Ge	11103	1414.6*b	1248.1*b	1217.0*b	180.1*	124.9*	120.8*	29.8*	29.2*
33	As	11867	1527.0*b	1359.1*b	1323.6*b	204.7*	146.2*	141.2*	41.7*	41.7*
34	Se	12658	1652.0*b	1474.3*b	1433.9*b	229.6*	166.5*	160.7*	55.5*	54.6*
35	Br	13474	1782*	1596*	1550*	257*	189*	182*	70*	69*

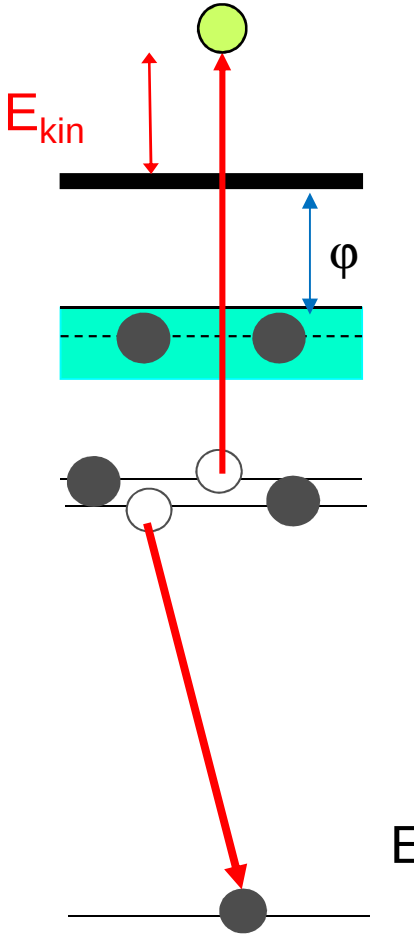
XPS spectrum



Auger process



Auger ($C_1C_2C_3$)



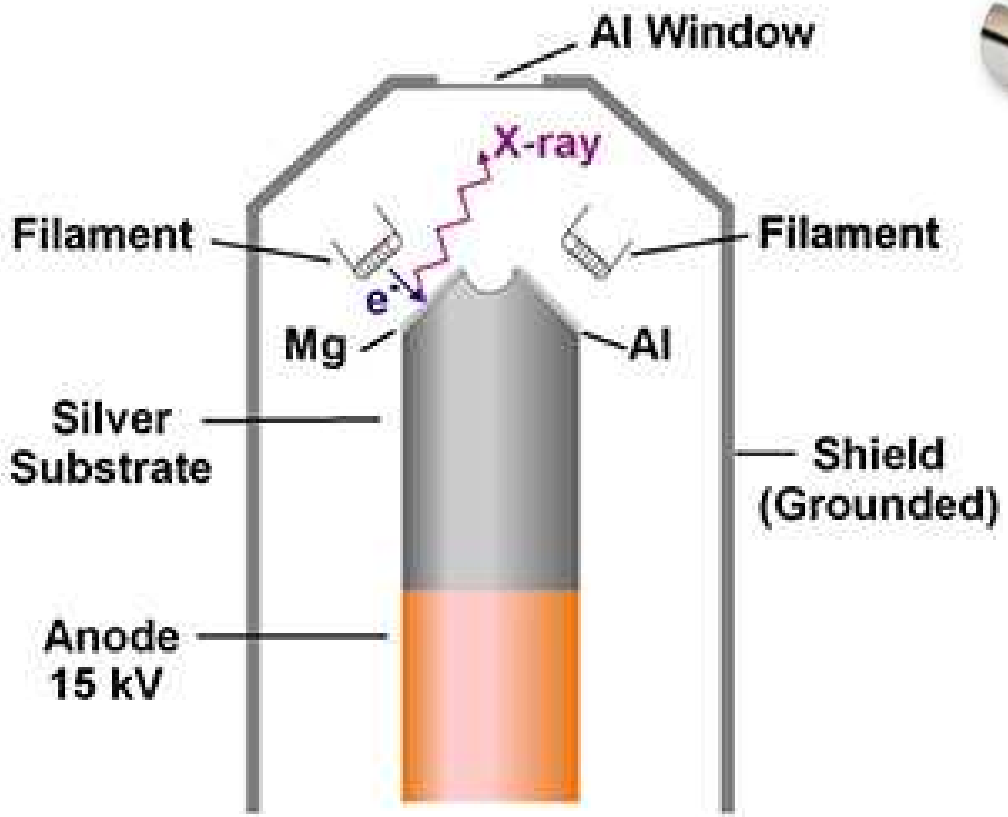
$E_2-E_1= E_3+\varphi+ E_{kin}$

$E_{kin}=E_2-E_1-E_3- \varphi$

What do we need?

- **Ultra High Vacuum**
- **X-ray source**
- **Electron energy analyser**
- **Data acquisition system**

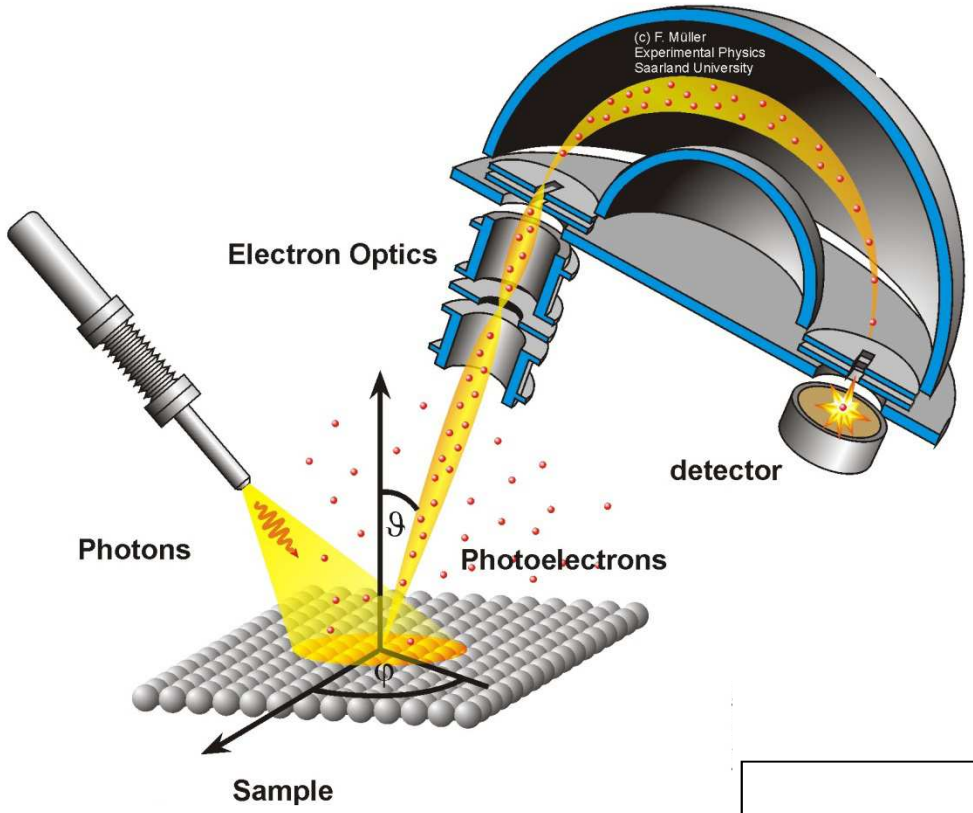
X-ray source



Mg Kα 1253.6 eV

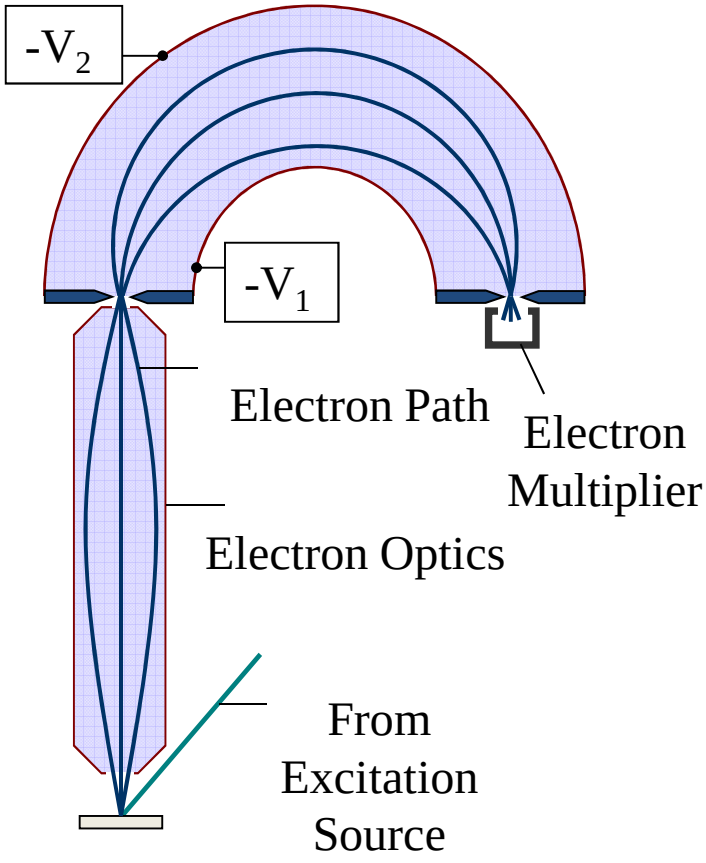
Al Kα 1486.7 eV

Electron energy analyser

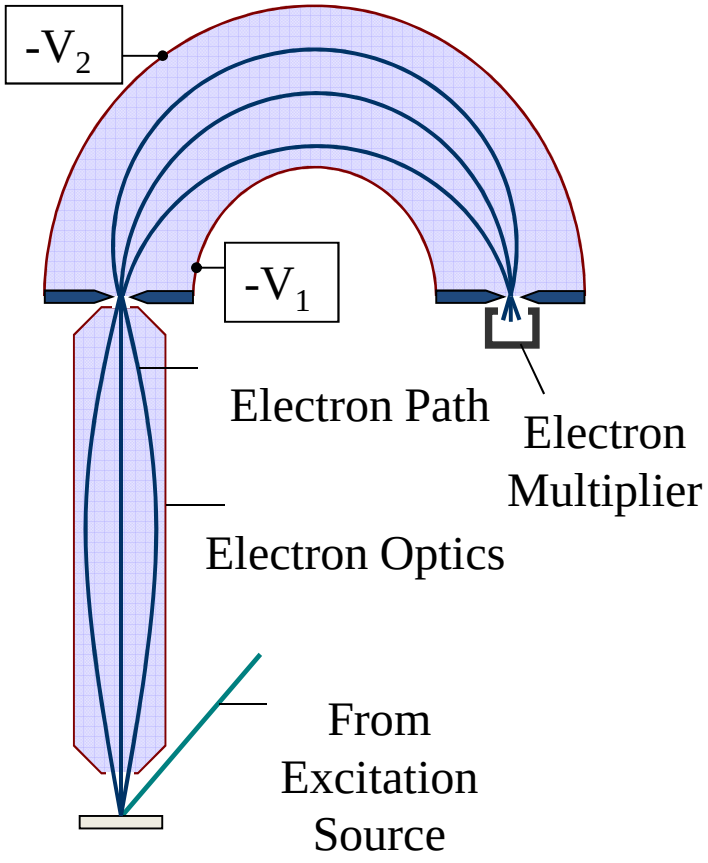


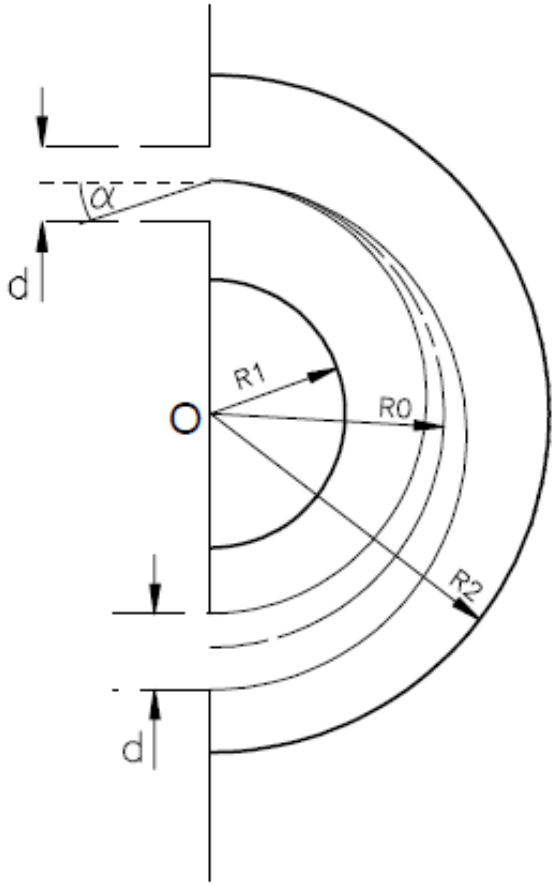
$$E_B = h\nu - E_{Kin} - \varphi$$

Electron energy analyser



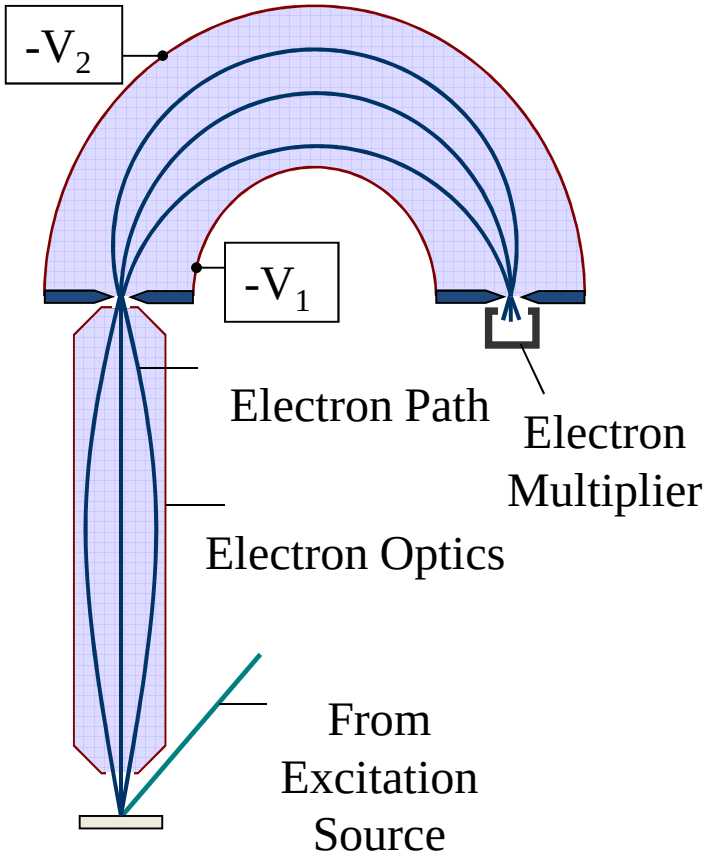
Electron energy analyser

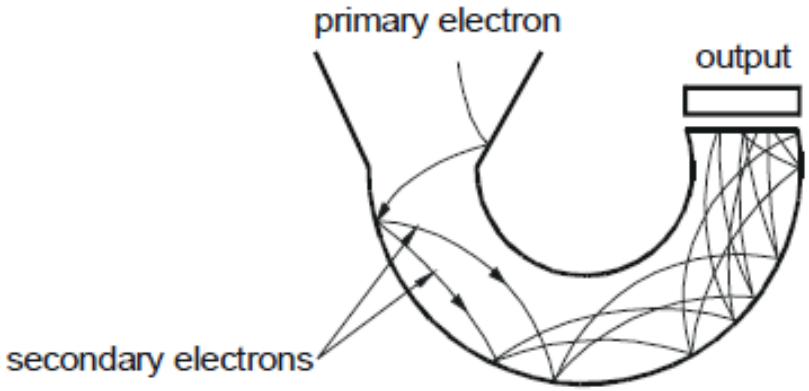




$$eV_0 = E_p \cdot \left(\frac{R_2}{R_1} - \frac{R_1}{R_2}\right)$$

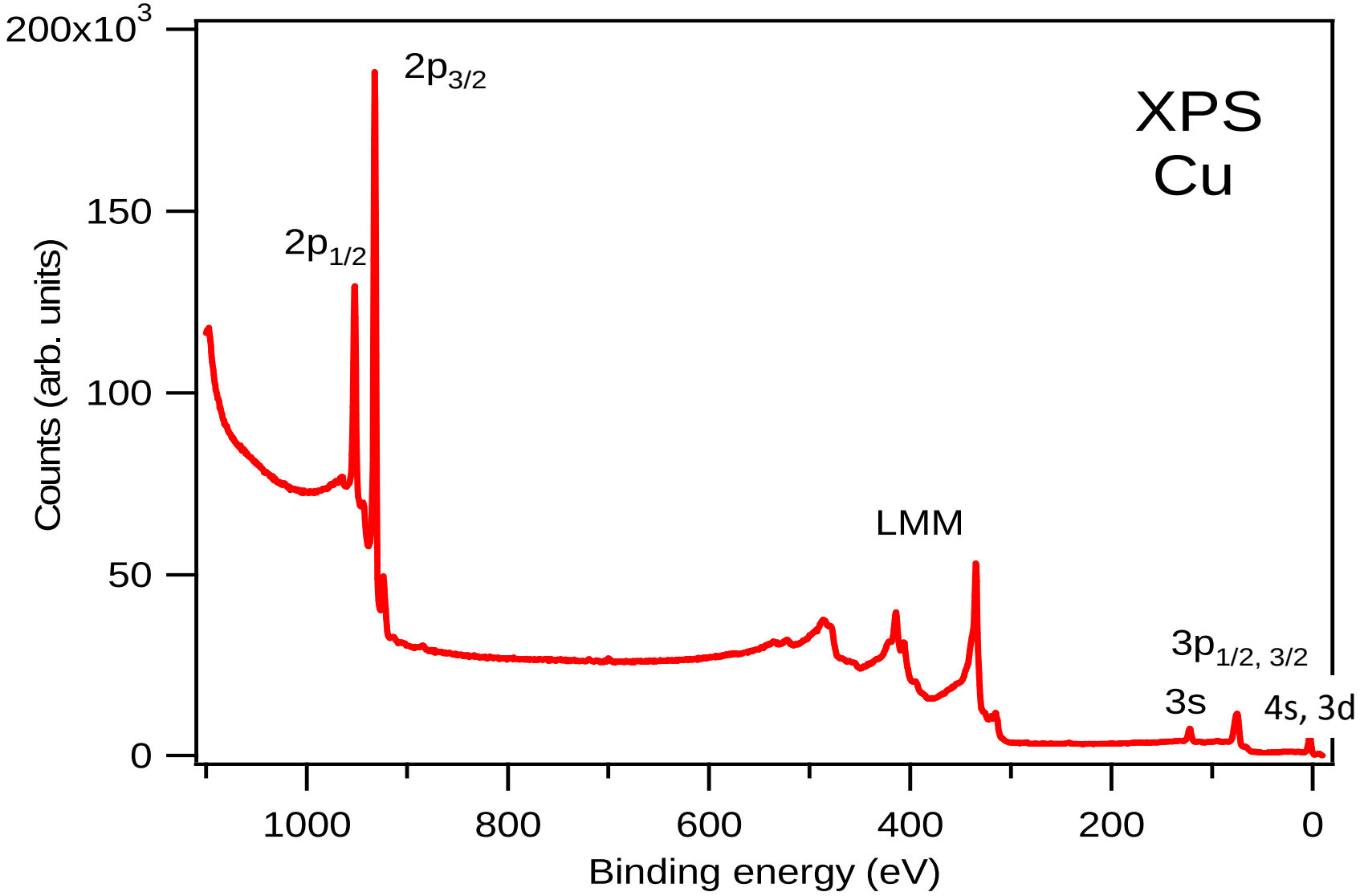
Electron energy analyser



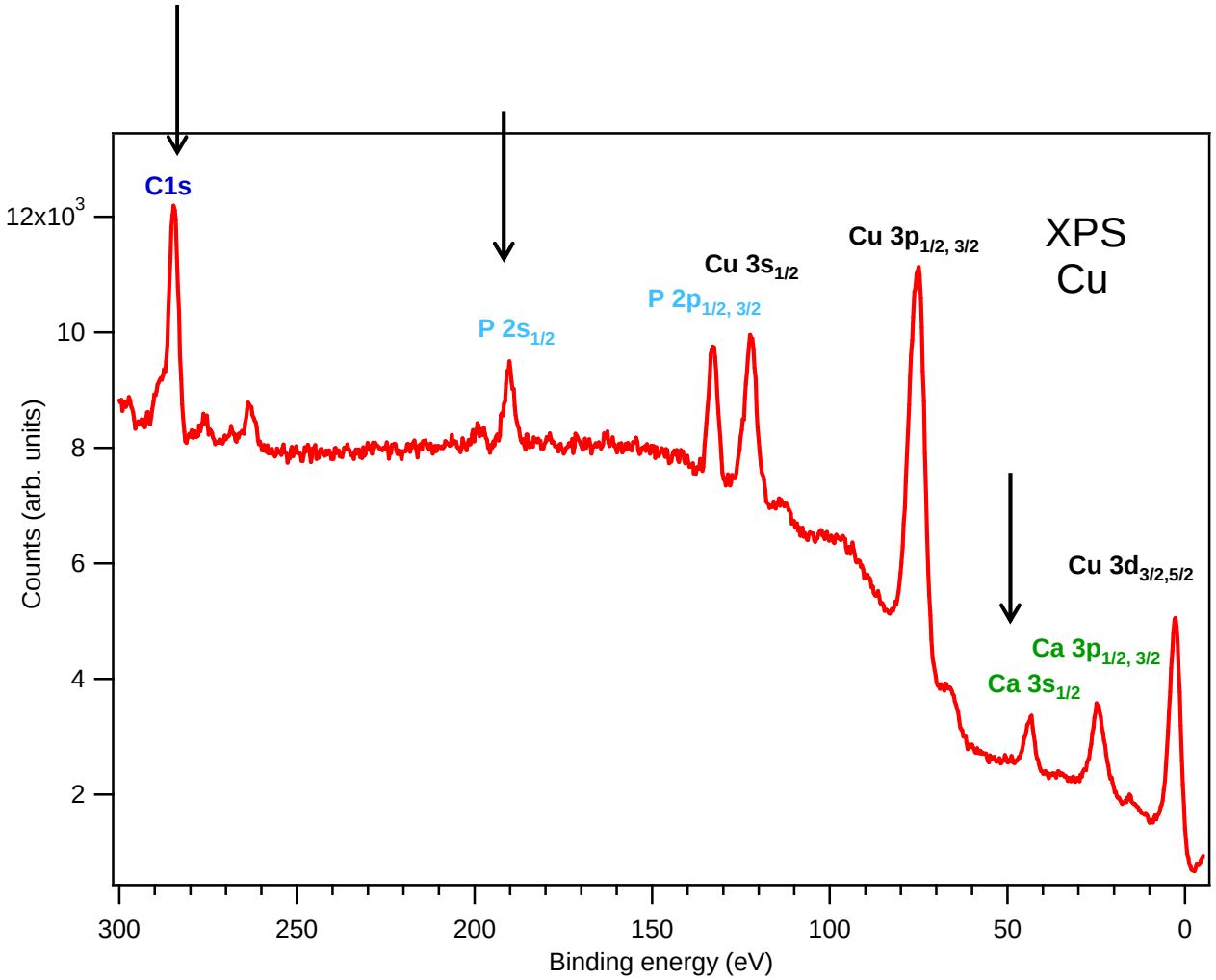


Channeltron multiplier

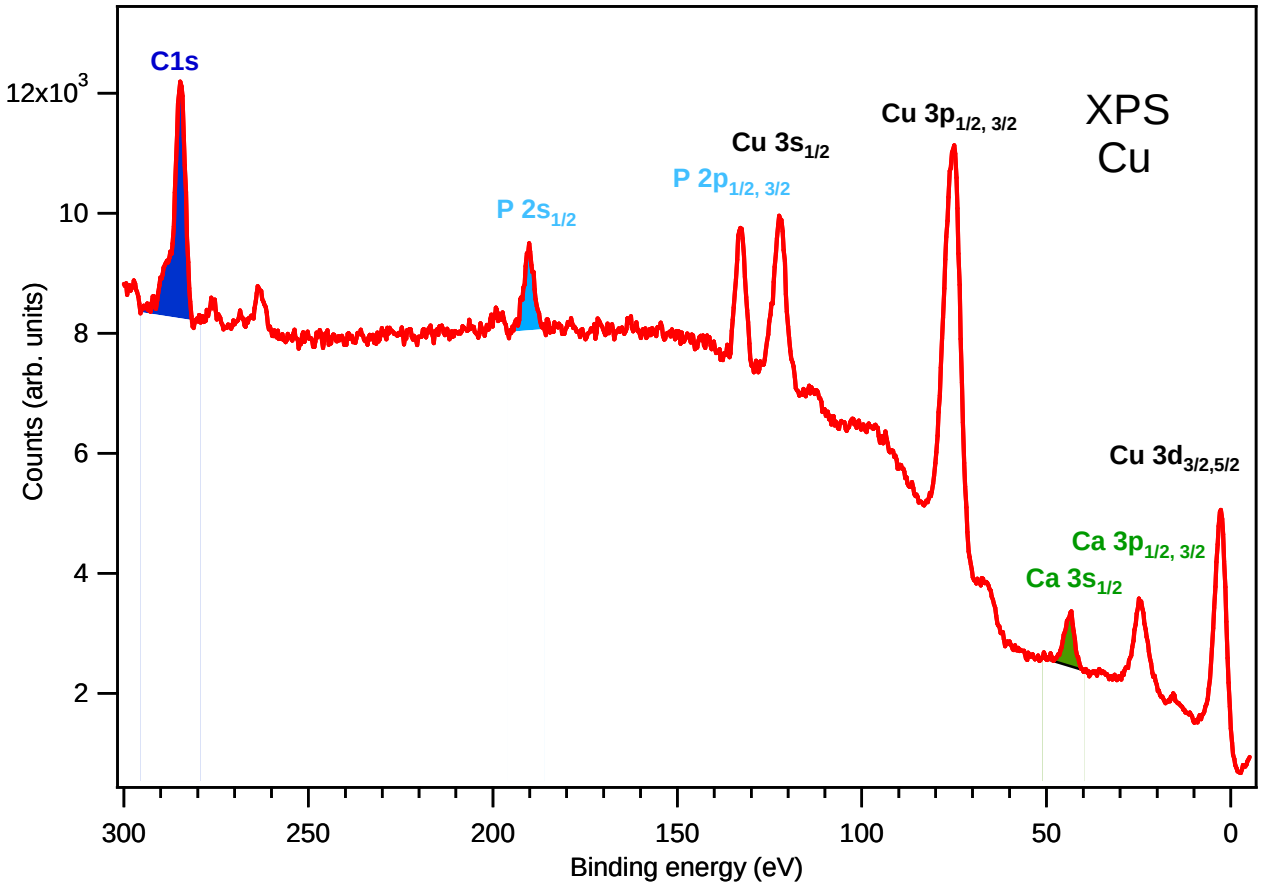
XPS spectrum



Quantitative analysis



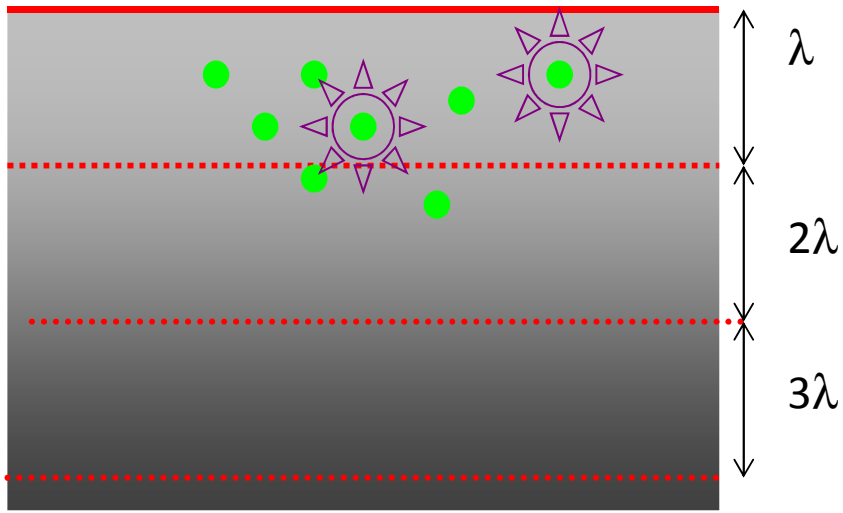
Quantitative analysis

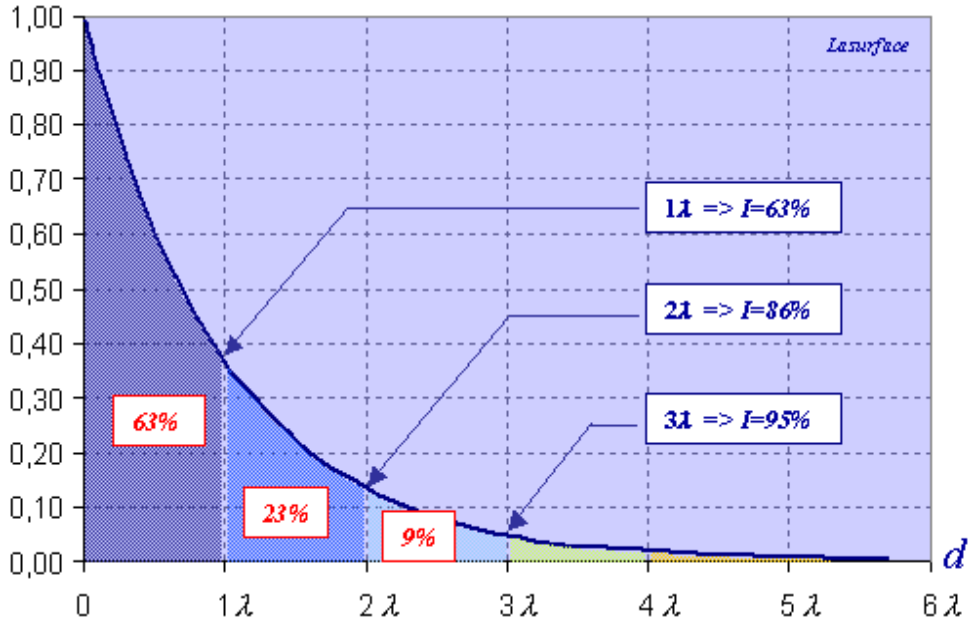


Photoionization
Cross sections

C 1s	0.02
Ca 3s	0.0068
P 2s	0.023

Electron escape depth



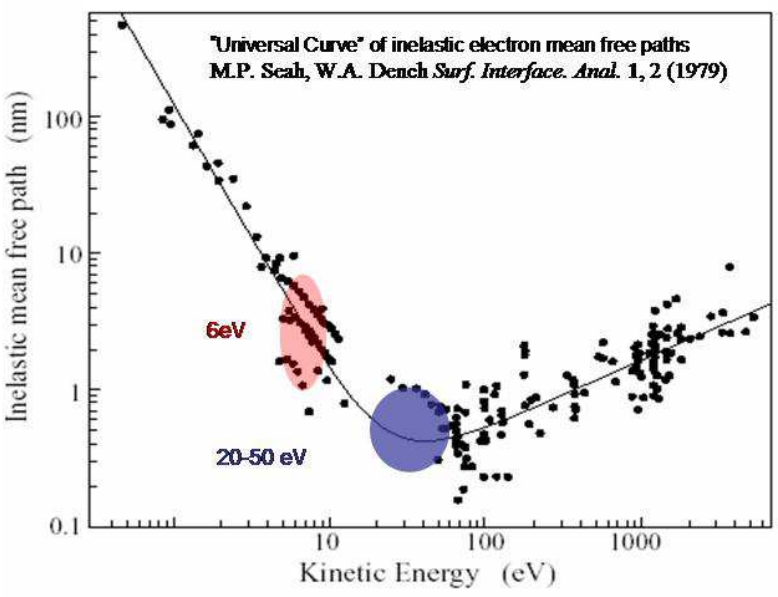


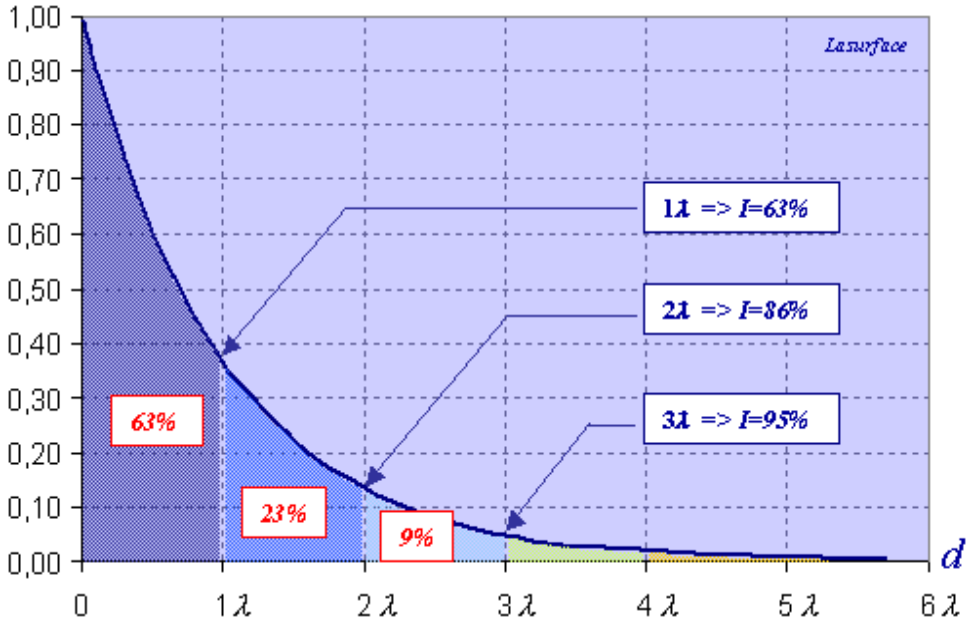
$P(d) = \exp(-d/\lambda)$

λ= inelastic electron mean free path

λ depends on the electron kinetic energy

Electron escape depth





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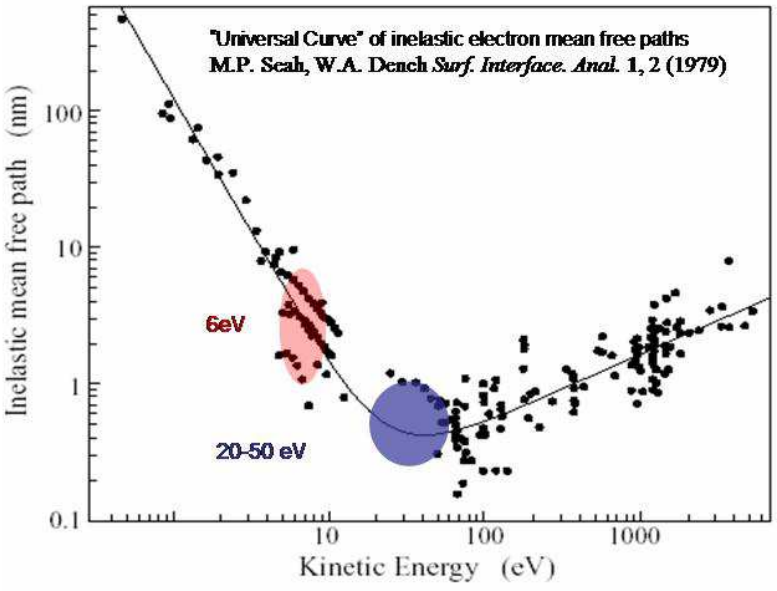
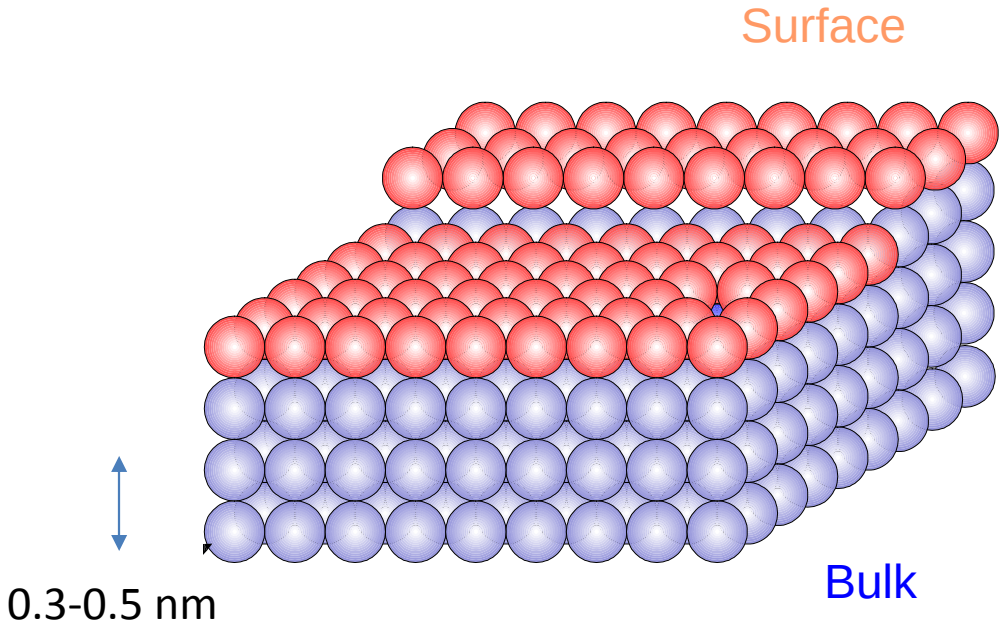
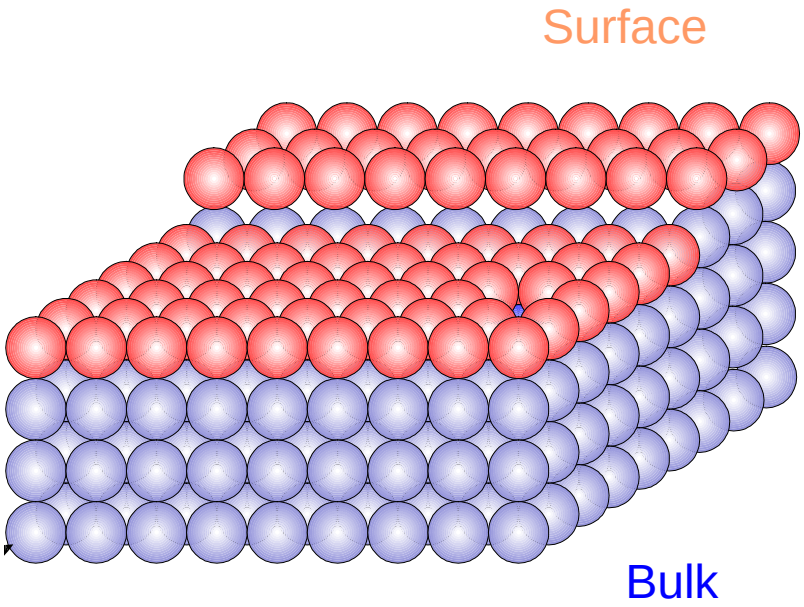
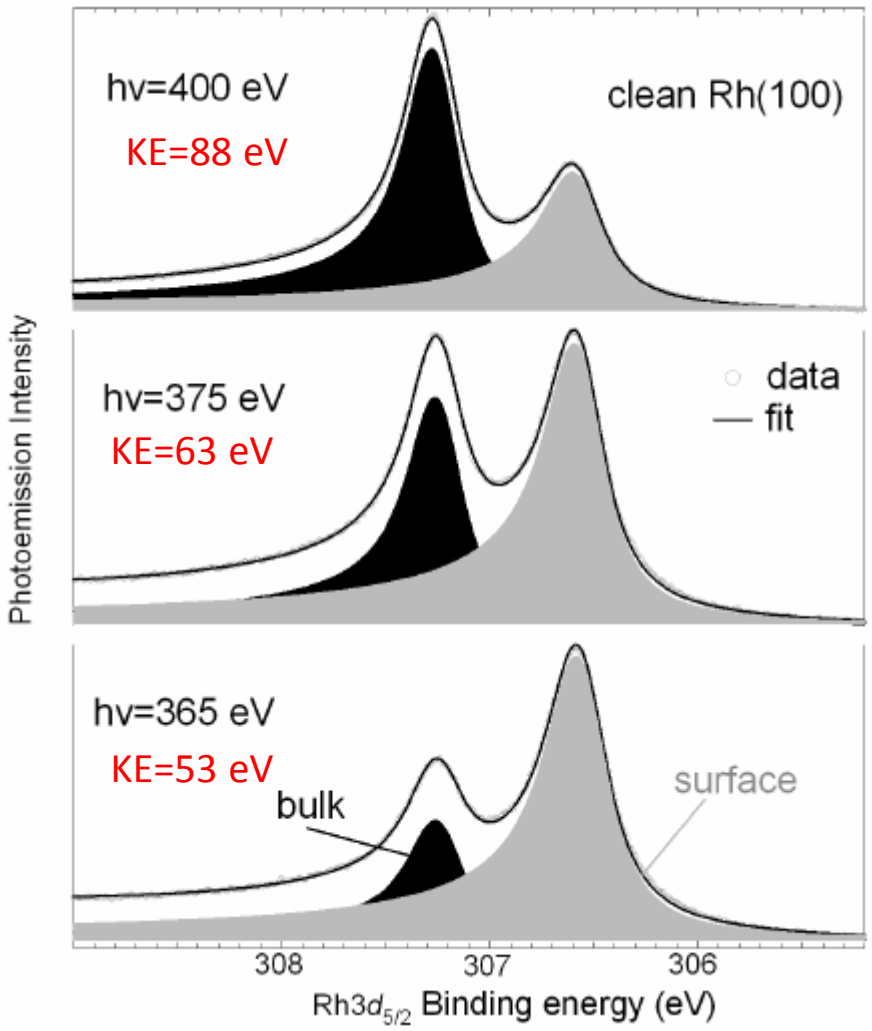


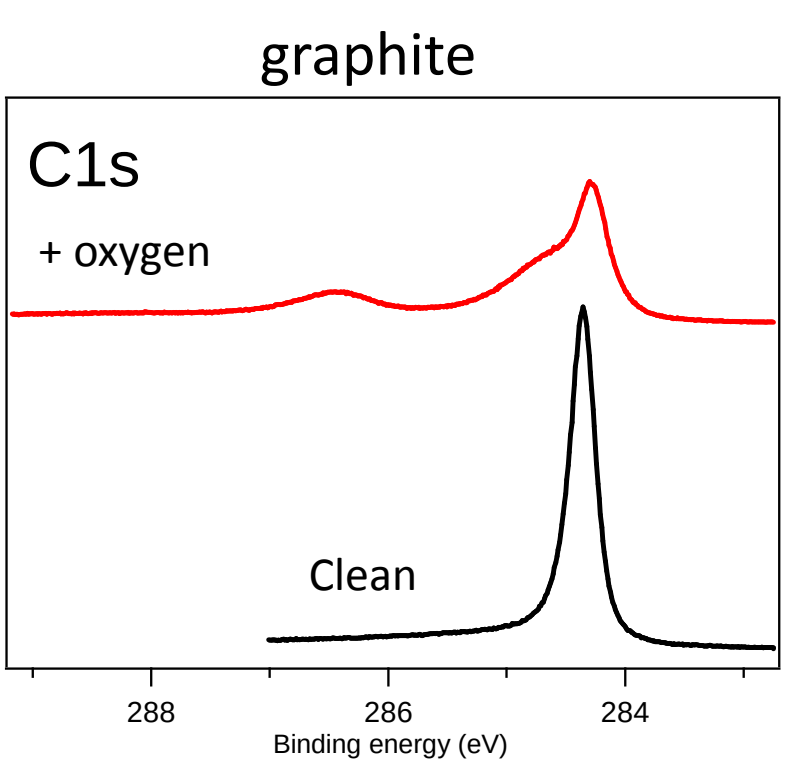


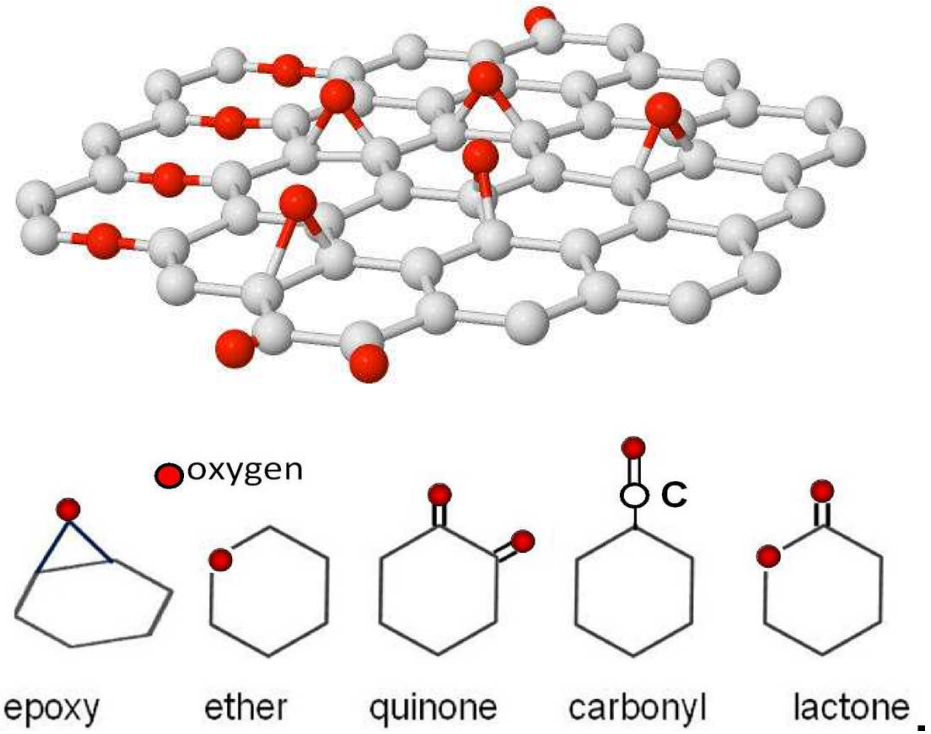
Surface sensitivity



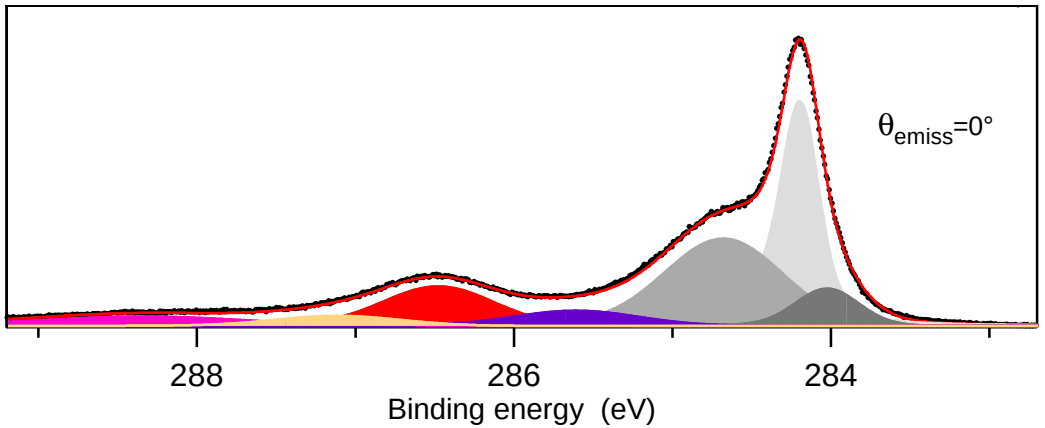


Chemical shift

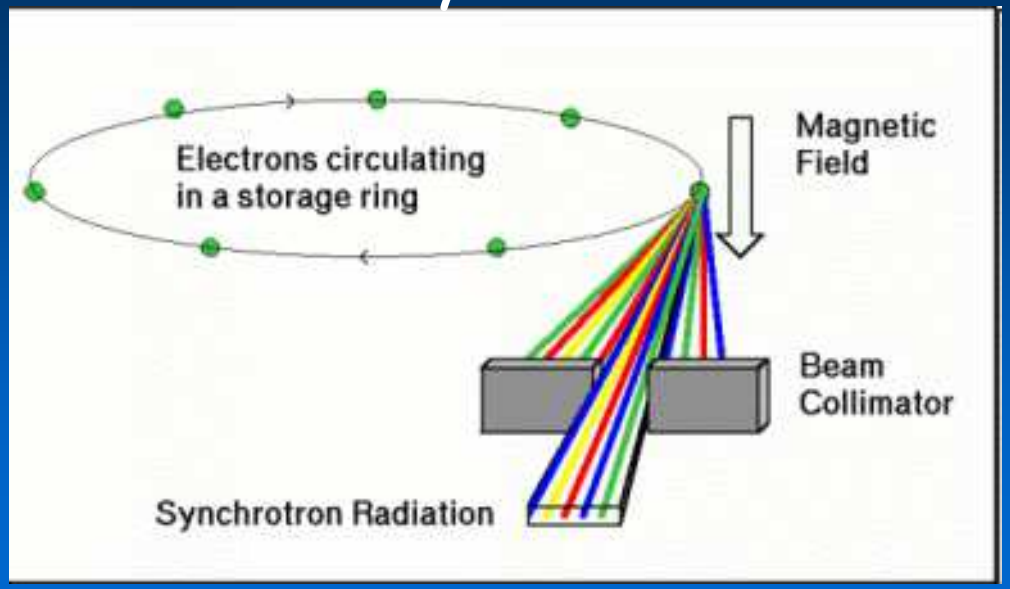


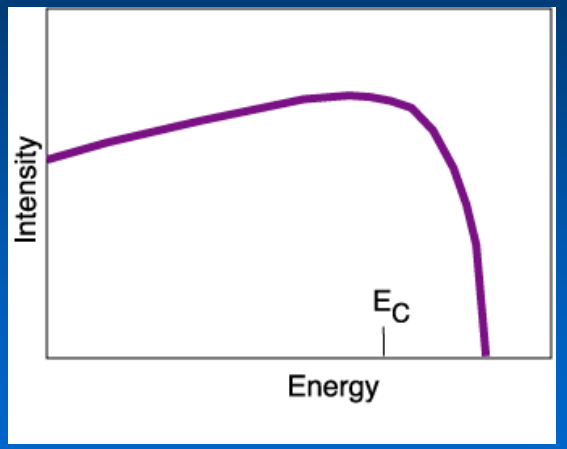


Chemical shift

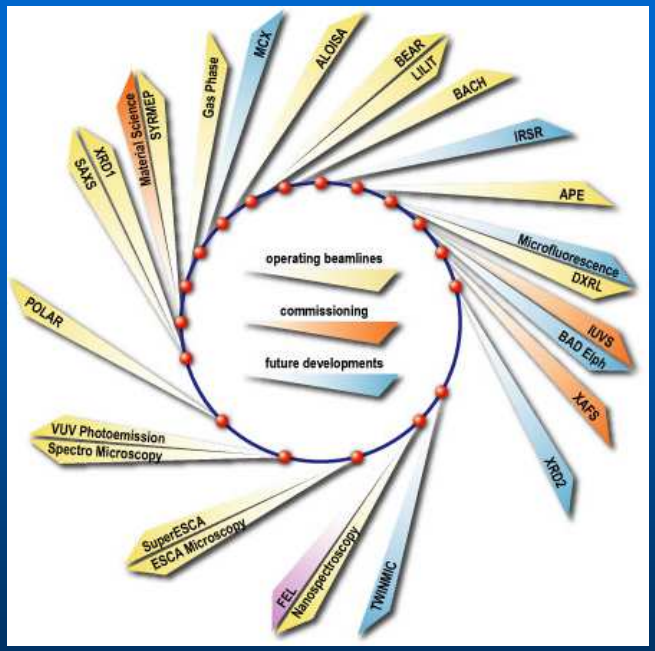


Synchrotron radiation

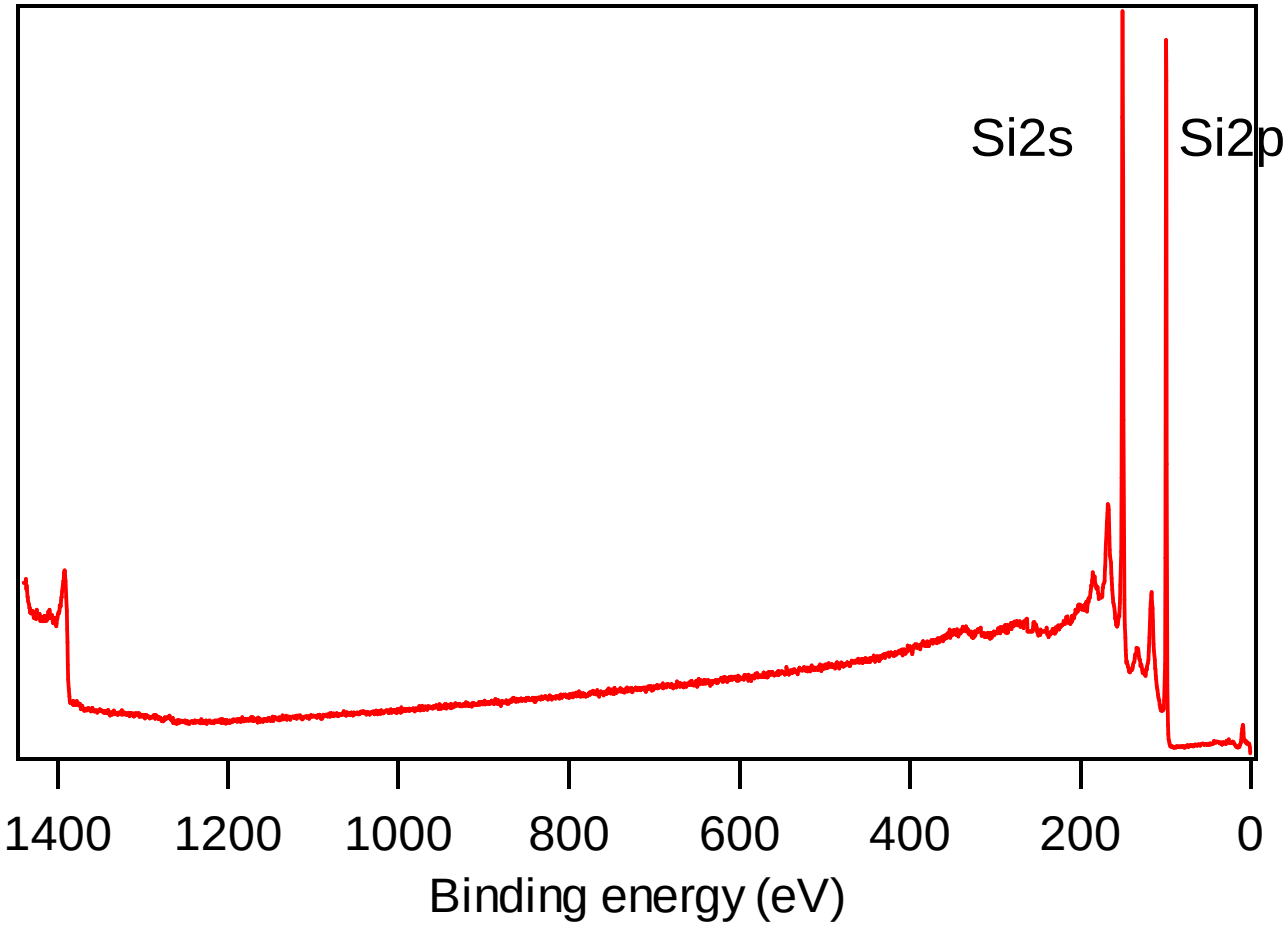




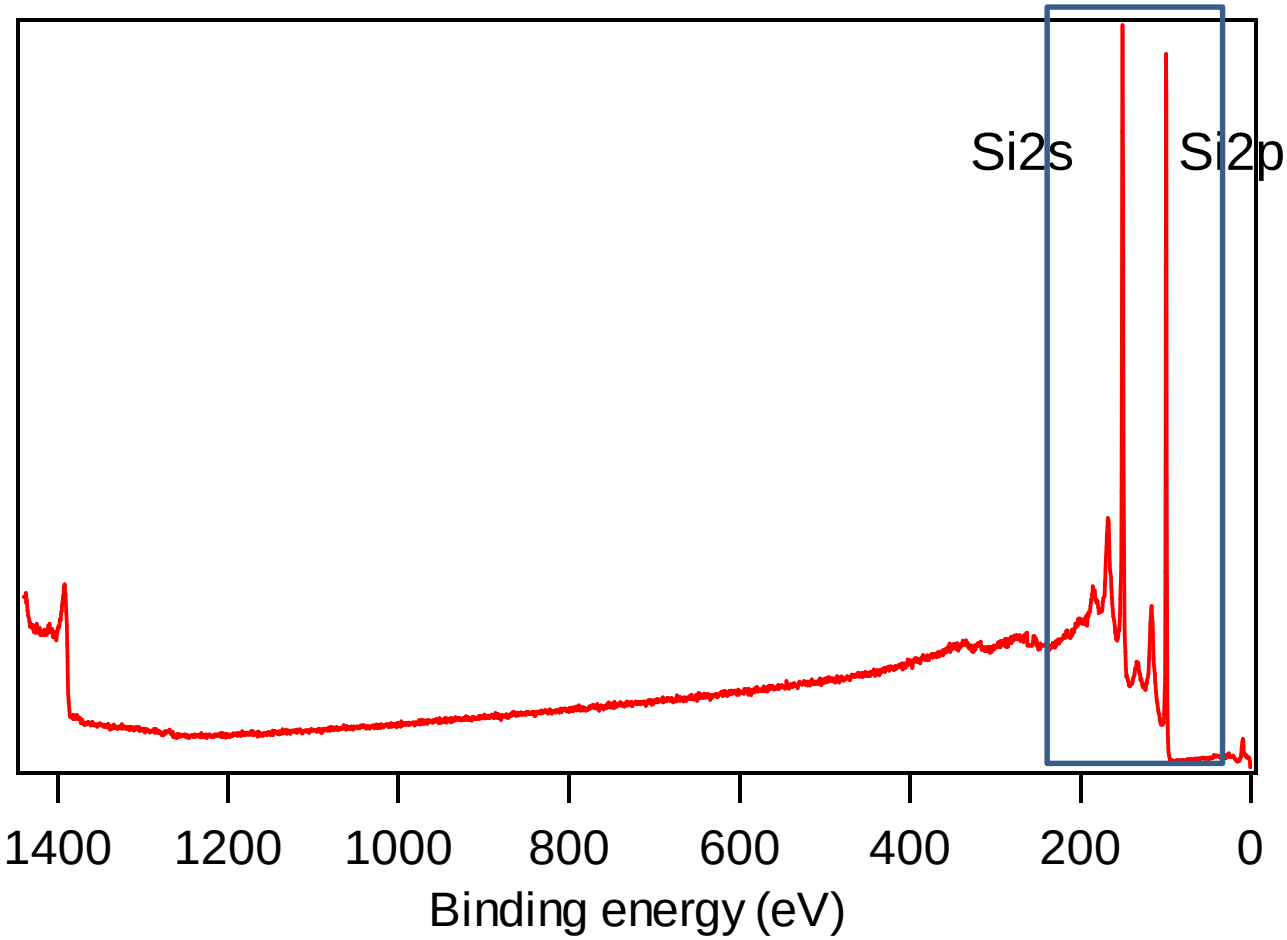
ELETTRA Trieste



Spectral resolution

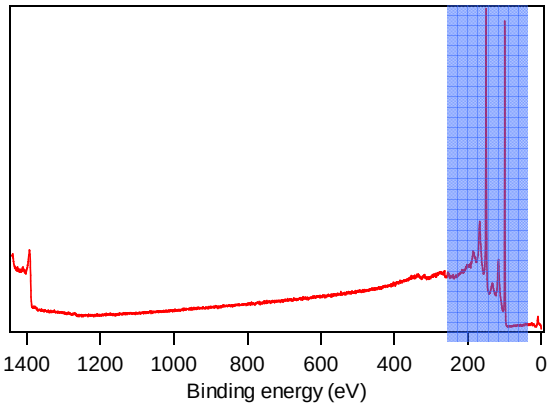


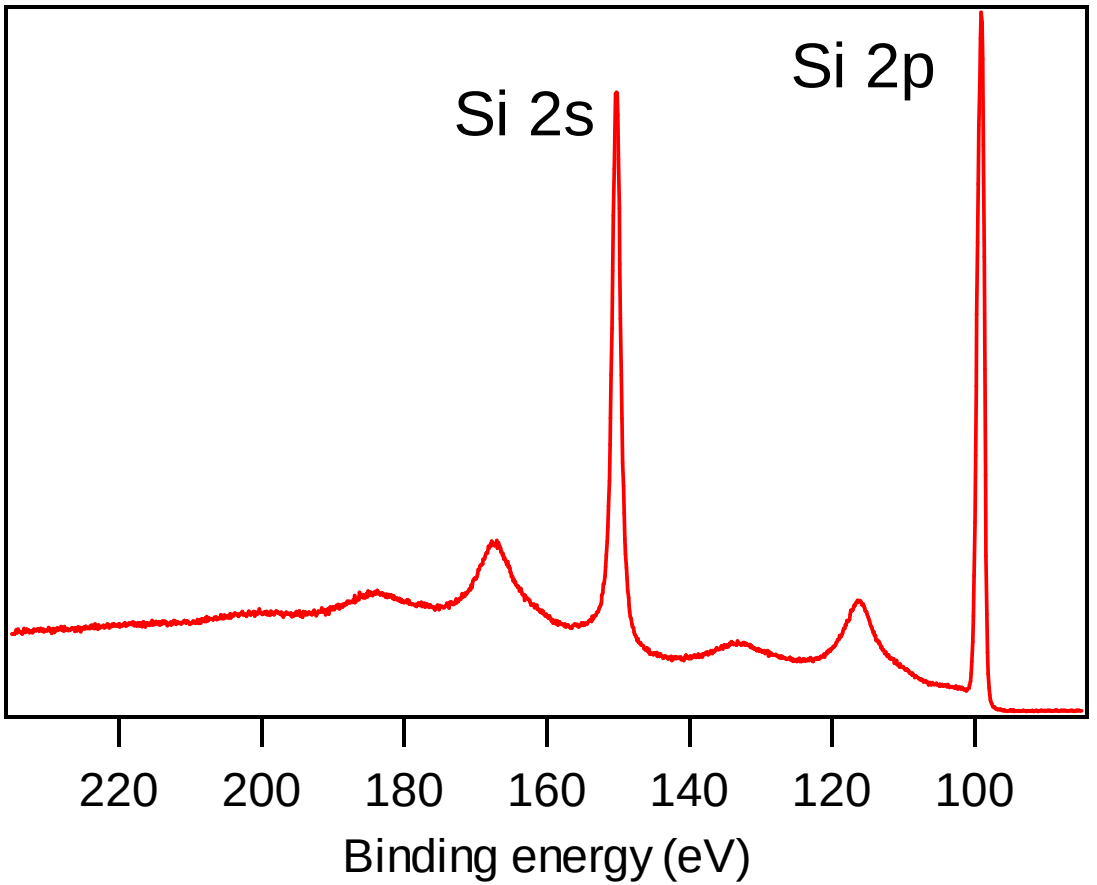
Spectral resolution



λ= 1486.6 eV ΔE = 0.9 meV

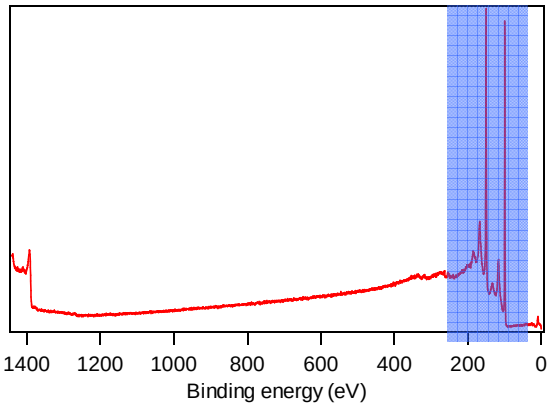
Spectral resolution

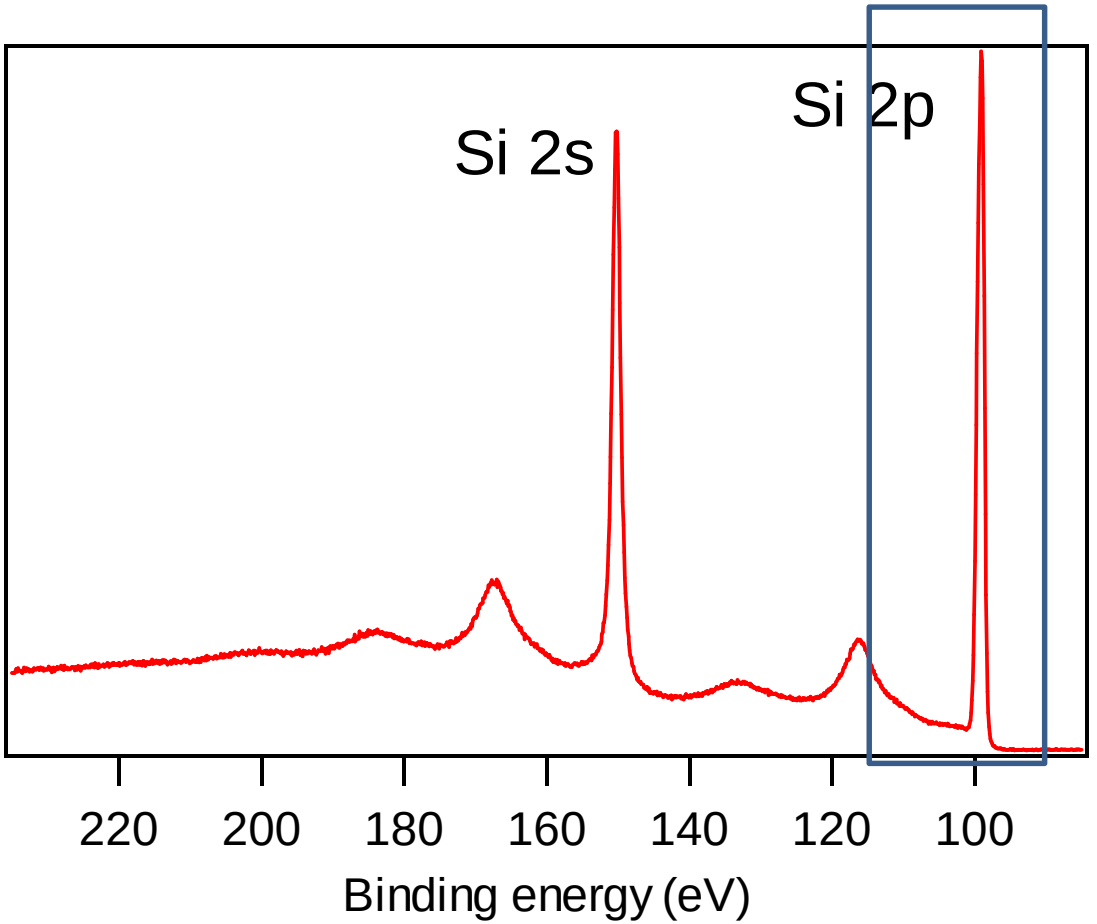




λ= 1486.6 eV ΔE = 0.9 meV

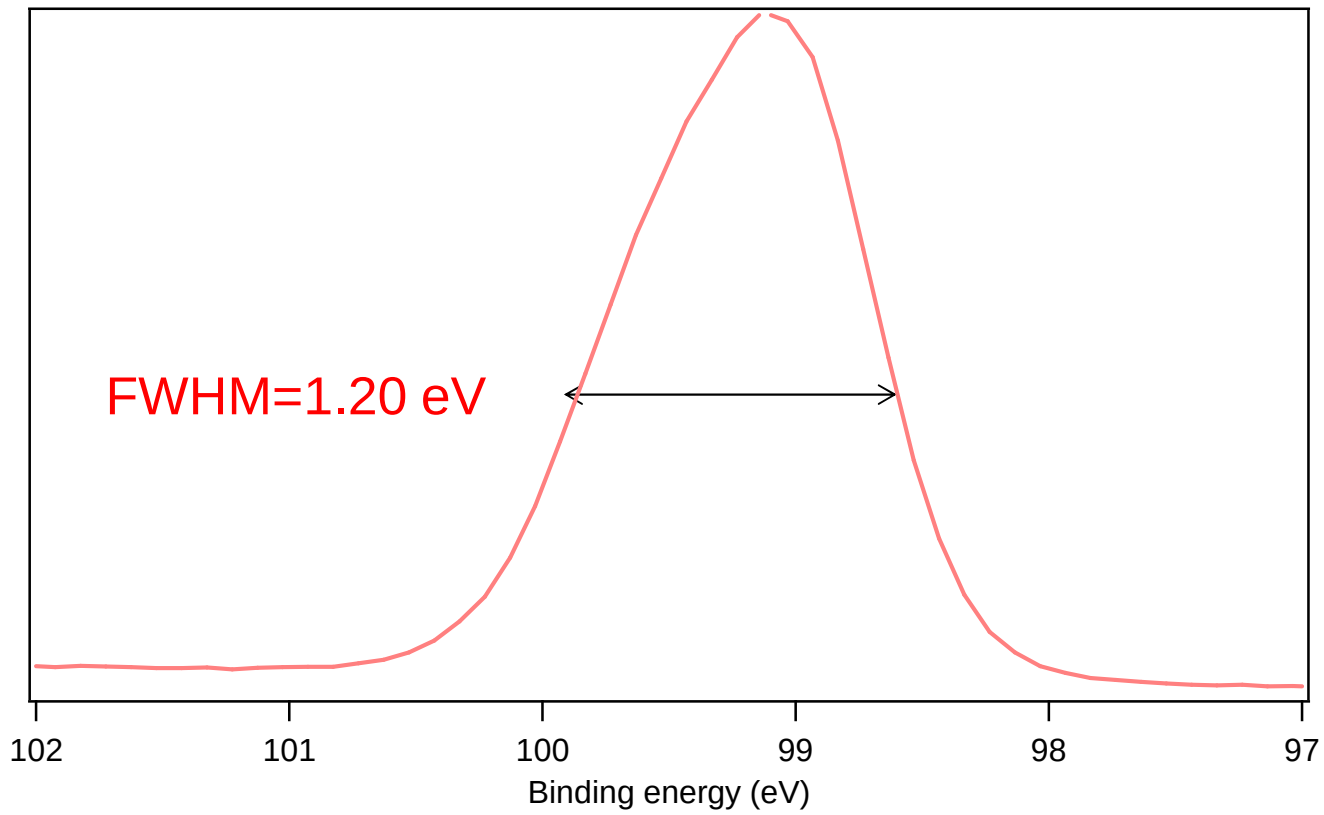
Spectral resolution





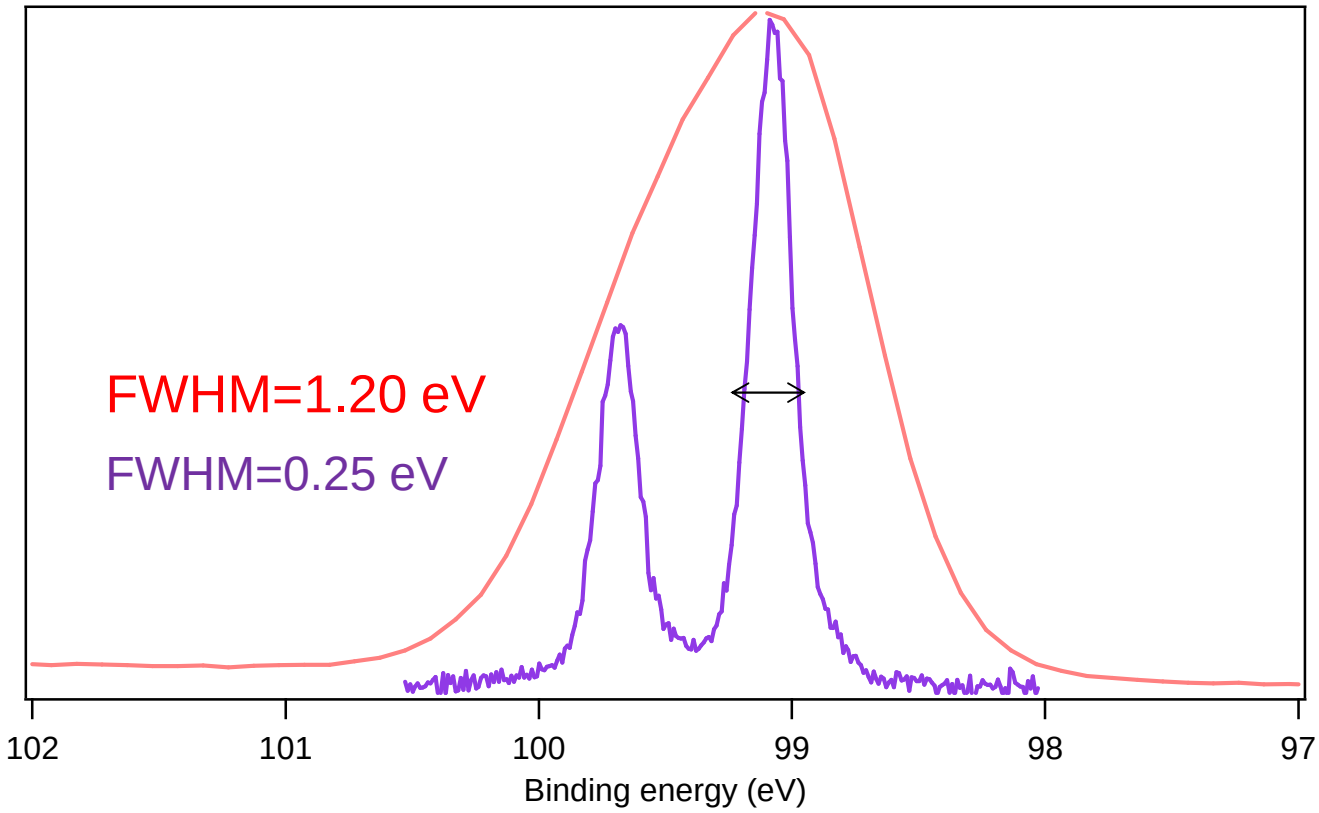
λ= 1486.6 eV ΔE = 0.9 meV

Spectral resolution



λ= 1486.6 eV ΔE = 0.9 meV

Spectral resolution



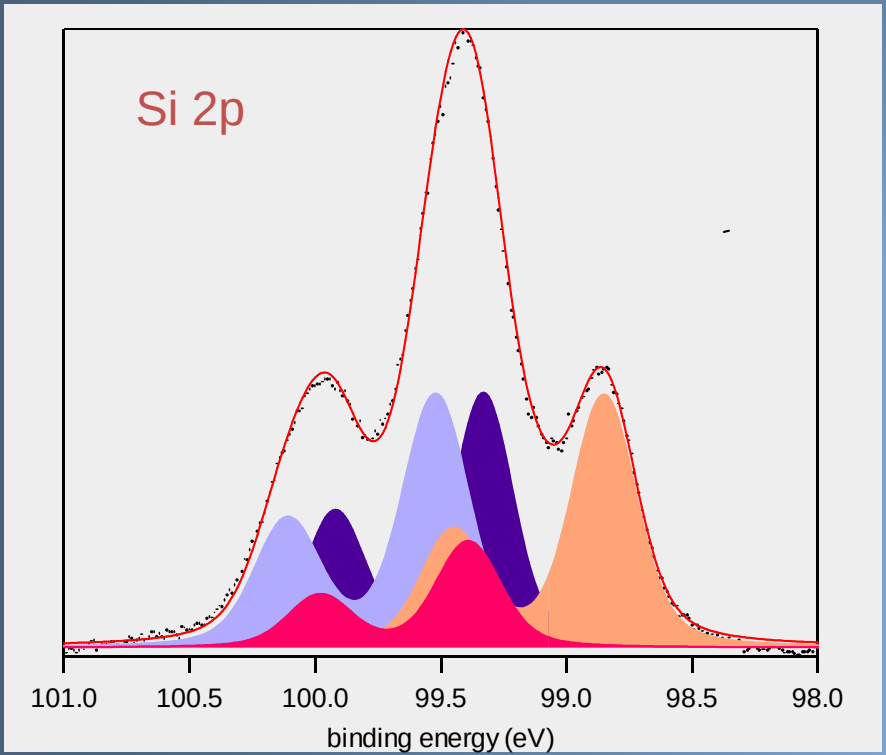
λ= 1486.6 eV ΔE = 0.9 meV

λ= 130 eV ΔE = 50 meV

Si(100)

(2x1) reconstruction

hν=130 eV



Si(001) (2x1)