4.3: Back to Basics

As energy of the x-ray is increased, progressively more core electrons are excited and a more atomic picture can be constructed. Terminology:

Sub-shells (connected to the angular Momentum Quantum Number): An atom's electron shells are filled according to the following theoretical constraints:

- Each s subshell holds at most 2 electrons
- Each p subshell holds at most 6 electrons
- Each d subshell holds at most 10 electrons
- Each f subshell holds at most 14 electrons
- Each g subshell holds at most 18 electrons

Shells (principal quantum number): Electron shells are labeled K, L, M, N, O, P, and Q; or 1, 2, 3, 4, 5, 6, and 7; going from innermost shell outward:

Shells	s	p	d	f	g	Total
K	2					2
L	2	6				8
M	2	6	10			18
N	2	6	10	14		32
O	2	6	10	14	18	50

As you tune the applied x-ray photons, resonances with different ionization thresholds for electrons will occur resulting in progressively higher energy (higher energy = higher binding energy) electrons being ejected. This is a signature of the nature of the element.

Table 1-1. *Electron binding energies, in electron volts, for the elements in their natural forms.*

Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$	M_4 $3d_{3/2}$	M_5 $3d_{5/2}$	N_1 4s	N_2 $4p_{1/2}$	N_3 $4p_{3/2}$
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†	30.65	30.81								
12 Mg	1303.0†	88.7	49.78	49.50								
13 Al	1559.6	117.8	72.95	72.55								
14 Si	1839	149.7*b	99.82	99.42								
15 P	2145.5	189*	136*	135*								
16 S	2472	230.9	163.6*	162.5*								
17 Cl	2822.4	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†					

Orbital energy levels

Assume there is one electron in a given atomic orbital in a **hydrogen-like** atom (ion). The energy of its state is mainly determined by the electrostatic interaction of the (negative) electron with the (positive) nucleus. The energy levels of an electron around a nucleus are given by :

$$E_n = -hcR_\infty \frac{Z^2}{n^2}$$

(typically between 1 eV and 10^3 eV), where R_∞ is the Rydberg constant, Z is the Atomic number, n is the principal quantum number, h is Planck's constant, and c is the speed of light. For hydrogen-like atoms (ions) only, the Rydberg levels depend only on the principal quantum number n.

For multi-electron atoms, interactions between electrons cause the preceding equation to be no longer accurate as stated simply with Z as the atomic number. Instead an approximate correction may be used where Z is substituted with an **effective nuclear charge** symbolized as Z_{eff}.

$$E_{n,l} = -hcR_\infty \frac{Z_{eff^2}}{n^2} \tag{4.3.1}$$

Hence, different atoms (higher Z) will have different effective Z_{eff} that couple into Equation 4.3.1 to result in different energies for the electrons. Note chance in energies for the S electrons below:

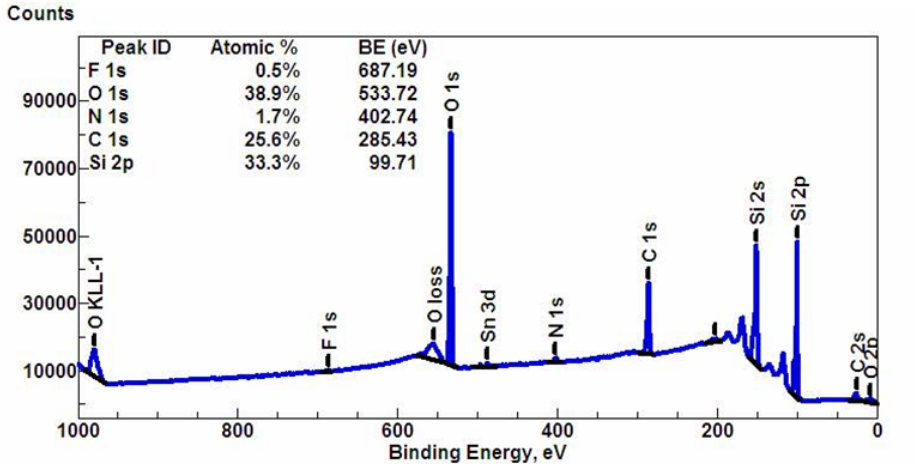
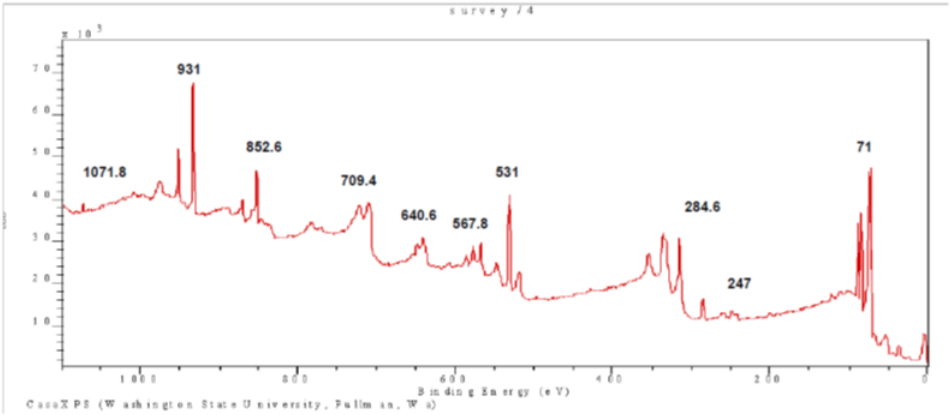


Figure 4.3.1: Wide-scan or survey spectrum of a somewhat dirty silicon wafer, showing all elements present. A survey spectrum is usually the starting point of most XPS analyses. It allows one to set up subsequent high-resolution XPS spectra acquisition. The inset shows a quantification table indicating the atomic species, their atomic percentages and characteristic binding energies. (CC BY-SA 3.0; ; Bvcrist via Wikipedia)

Hence, XPS can be used for elemental analysis of unknown compounds, by measuring and check to known values for the electronic energy levels of elements



Position	FWHM	Raw Area	Library RSF	%At Conc
531.0	2.627	59285	0.736	27.61
284.6	2.410	12081.5	0.318	13.02
1071.8	1.924	2550.56	1.378	0.63
852.6	2.433	39781.1	3.845	3.55
931.8	2.234	112227	4.871	7.90
709.4	9.695	166995	2.947	19.42
71.0	2.227	193937	6.115	10.87
567.8	2.893	53803.5	2.491	7.40
247.0	8.855	13069.7	1.244	3.60
640.6	6.262	47149.5	2.693	6.00

BE Lookup Table for Signals from Elements and Common Chemical Species

1.0	Bi	6p1	3.9	Pt	5d	10.0	P	3p	18.0	At	6s	24.0	Kr	4s	34.0	K	3s	44.0	Ra	6s	52.0	Tm	5s	65.7	V	3s
1.0	Ce	4f	4.0	Ir	5d	10.0	Ti	4s	18.0	Ce	5p	24.0	Sn	4d	35.0	Re	5p3	44.0	U	6s	52.3	Yb	5s	66.0	Ni	3p
1.0	Co	3d	4.0	Pm	4f	10.0	V	4s	18.0	Pr	5p	25.0	Th	6p1	35.2	Mo	4p	44.4	Y	4s	52.6	Fe	3p	66.0	Pt	5p1
1.0	Cr	3d	4.5	Ag	4d	10.0	Zr	5s	18.1	Hf	Ntv Ox	26.0	Bi	5d3	35.2	W	Na2WO4	45.0	Ta	5p1	53.0	Sn	loss	67.8	Ta	5s
1.0	Fe	3d	4.8	Dy	5d	10.5	Bi	6s	18.2	C	2s	26.0	He	1s	35.3	Y	loss	45.1	As	2O3	53.4	Os	4f5	68.0	Ra	5d
1.0	Ga	4p	5.0	B	2p	10.7	Cd	4d5	18.4	Sr	4p	26.0	Rn	6s	35.8	W	O3	45.5	As	Ntv Ox	54.0	Os	5p1	68.0	Tc	4s
1.0	Hf	5d	5.0	Br	4p	11.0	Kr	4p	18.7	Ga	3d5	26.1	Lu	5p	36.0	Ce	5s	45.7	Ge	loss	54.2	Se	CdSe	68.5	Br	3d5
1.0	In	5p	5.0	Ca	3d	11.0	Rn	6p	18.8	Ga	3d	26.8	Ta	2O5	36.0	Gd	5s	46.0	Re	5p1	54.5	Se	GeSe	68.5	Br	KBr
1.0	Na	3s	5.0	Er	4f	11.0	Sc	4s	18.9	Ga	3d3	26.8	Zr	4p	36.6	Sr	4s	46.3	Ga	loss	54.9	Se	3d5	68.8	Cd	4p
1.0	Os	5d	5.0	Po	6p	11.1	Cs	5p3	19.0	Eu	5p	27.0	Br	4s	36.7	V	3p	46.8	Re	2O7	54.9	Li	1s	69.0	Br	3d
1.0	Pb	6p	5.3	Se	4p	11.6	Cd	4d3	19.0	Nd	5p	28.2	Sc	3p	37.0	W	5p3	46.8	W	5p1	54.9	Li	OH	69.5	Br	3d3
1.0	Sn	5p	5.5	Cl	3p	12.0	Cs	5p	19.0	Pb	5d5	28.6	In	loss	37.5	Hf	5p1	47.0	Mn	3p	54.9	Se	3d	70.0	Re	loss
1.2	Yb	4f7	5.8	Au	5d	12.0	Po	6s	19.0	Ra	6p	28.8	Rb	4s	38.0	Pm	5s	47.0	Rh	4p	55.2	Se	GeSe2	71.0	Pt	4f7
1.4	Pd	4d	6.0	Ta	5d	12.0	Te	5s	19.0	Sm	5p	29.0	Dy	5p1	38.0	Pr	5s	47.9	Ru	4p	55.3	Li	CO3	71.8	Mg	loss
1.4	Rh	4d	6.0	Y	4d	12.0	Tl	5d5	19.1	Ga	Sb fract	29.0	Er	5p	38.3	Sn	loss	48.0	Dy	5s	55.6	Nb	4s	72.6	Pt	4f
2.0	Cd	5p	6.2	Hg	5d	12.6	Cs	5p1	19.4	Ga	AlAs etch	29.0	Lu	5p	39.0	Eu	5s	48.0	Rn	5d	55.7	Se	3d3	72.7	Al	2p3
2.0	Mg	3s	6.9	Eu	4f	13.0	Tl	5d	19.5	N	2s	29.1	Ge	3d5	39.0	Nd	5s	48.0	Sb	loss	56.8	Au	5p3	72.9	Al	2p
2.0	Mo	4d	7.0	O	2p	13.2	Rb	4p	19.7	Ga	P fract	29.2	F	2s	39.0	Tc	4p	48.5	I	4d	56.8	Lu	5s	73.1	Tl	5p3
2.0	Nb	4d	7.0	Sm	4f	13.2	Rb	4p	19.7	Ga	As fract	29.4	Ge	3d	39.5	Tm	5p	49.5	Ho	5s	57.4	Er	5s	73.2	Al	2p1
2.0	Nd	4f	7.0	Sn	5s	14.0	Ne	2p	20.0	U	6p	29.5	Ho	5p1	40.0	At	5d	49.5	Mg	CO3	58.0	Ag	4p	73.8	Al	N
2.0	Ni	3d	7.0	Xe	5p	14.0	Sc	3d	20.2	Zn	loss	29.7	Ge	3d3	40.0	Ba	5s	49.6	Mg	(OH)2	58.0	Fr	5d	74.0	Au	5p1
2.0	Pr	4f	7.1	Lu	4f7	14.2	Hf	4f7	20.5	Gd	5p	30.2	Ge	Se	40.0	In	loss	49.6	Mg	2p3	58.0	Hg	5p3	74.2	Cr	3s
2.0	Sb	5p	7.1	Tb	4f	15.0	Fr	6p	20.7	Ga	2O3	30.3	Na	2p	40.0	Tb	5s	49.7	Mg	O	58.1	W	loss	74.3	Al	2O3
2.0	Sc	4p	7.7	Gd	4f	15.0	H	1s	21.0	Pb	5d3	30.9	Nb	4p	40.1	Te	4d	49.8	Mg	2p	58.2	Ti	3s	74.3	Al	2O3-nH2O
2.0	Tc	4d	7.8	Dy	4f	15.0	Hf	4f	21.6	Ta	4f7	30.9	Pb	loss	40.2	Re	4f7	49.9	Mg	2p1	58.3	Te	loss	74.4	Pt	4f5
2.0	Ti	3d	8.0	At	6p	15.0	Rb	4p1	21.8	Tb	5p	31.0	Hf	5p3	41.0	Ne	2s	50.0	Mg	CO3	58.6	Ag	4p	74.4	Al	(OH)3
2.0	V	3d	8.0	S	3p	15.0	Tl	5d3	22.0	Dy	5p3	31.0	Po	5d	41.0	Sm	5s	50.0	Sr	loss	58.9	Y	loss	74.9	Cu	3p
2.0	Yb	4f	8.3	Ho	4f	15.7	Cl	3s	22.0	Pm	5p	31.3	W	4f7	41.2	Re	4f	50.3	Zr	4s	59.0	Co	3p	74.9	Se	loss
2.0	Zr	4d	8.3	Lu	5d	15.9	Hf	4f5	22.3	Ar	3s	31.5	Ge	Se2	41.4	Re	Ntv Ox	50.4	Mg	NtvOx1	59.2	As	loss	75.0	Cs	4d5
2.5	Yb	4f5	8.4	Lu	2O3	15.9	I	5s	22.7	Ta	4f	31.7	Sb	4d	41.5	As	3d5	50.7	Os	4f7	60.8	Ir	4f7	75.1	Pt	O2-nH2O
2.6	Te	5p	8.5	Tm	4f7	16.0	K	3p	23.0	Cs	5s	32.1	Ga	loss	41.8	As	3d	50.7	Pd	4p	61.0	Mg	loss	75.1	W	5s
2.8	Cu	3d	8.6	Lu	4f5	16.0	P	3s	23.1	O	2s	32.3	W	4f	42.0	As	S	50.7	Sc	3s	62.0	Ir	4f	75.5	Al	Ntv Ox
2.8	Mn	3d	8.9	Ar	3p	16.0	S	3s	23.3	Ho	5p3	32.4	Ti	3p	42.0	Th	6s	50.9	Mg	reoxid	62.0	Ir	O2	76.0	Cs	4d
2.8	Re	5d	9.0	F	2p	16.9	In	4d	23.3	Y	4p	32.6	Ta	5p3	42.1	Ca	3s	51.0	Ir	5p3	62.0	Ir	5p1	77.8	Ni	loss
2.8	Si	3p	9.0	Ru	4d	17.0	La	5p	23.4	Ta	S2	33.0	La	5s	42.1	Cr	3p	51.0	Mg	NtvOx2	62.0	Mo	4s	78.3	In	4p
2.8	W	5d	9.0	Sb	5s	17.0	Th	6p3	23.5	Ca	3p	33.2	Ge	O2	42.2	As	3d3	51.4	Os	4f	62.0	Xe	4d	79.0	Cs	4d3
3.0	Ge	4p	9.0	Si	3s	17.0	Xe	5s	23.5	Yb	5p	33.4	Lu	5p	42.7	Re	4f5	51.5	Pt	5p3	62.3	Hf	5s	80.0	Ru	4s
3.0	I	5p	9.1	As	4p	17.1	Hf	O2	23.8	Bi	5d	33.5	W	4f5	42.7	Ta	loss	51.5	Mg	reoxid	62.7	Ir	Ntv Ox	80.7	Rh	4s
3.0	Pb	6s	9.7	Zn	3d	17.7	Pb	5d	24.0	Ta	4f5	33.8	Ge	Ntv Ox	43.0	As	2S3	51.7	Re	loss	63.3	Na	2s	81.0	Hg	5p1
3.2	Bi	6p3	10.0	Ba	5p	17.9	Ga	InAs (ar)	24.0	Bi	5d5	34.0	Fr	6s	44.0	Os	5p3	51.9	Mg	NtvOx3	63.8	Ir	4f5	81.8	Re	5s

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