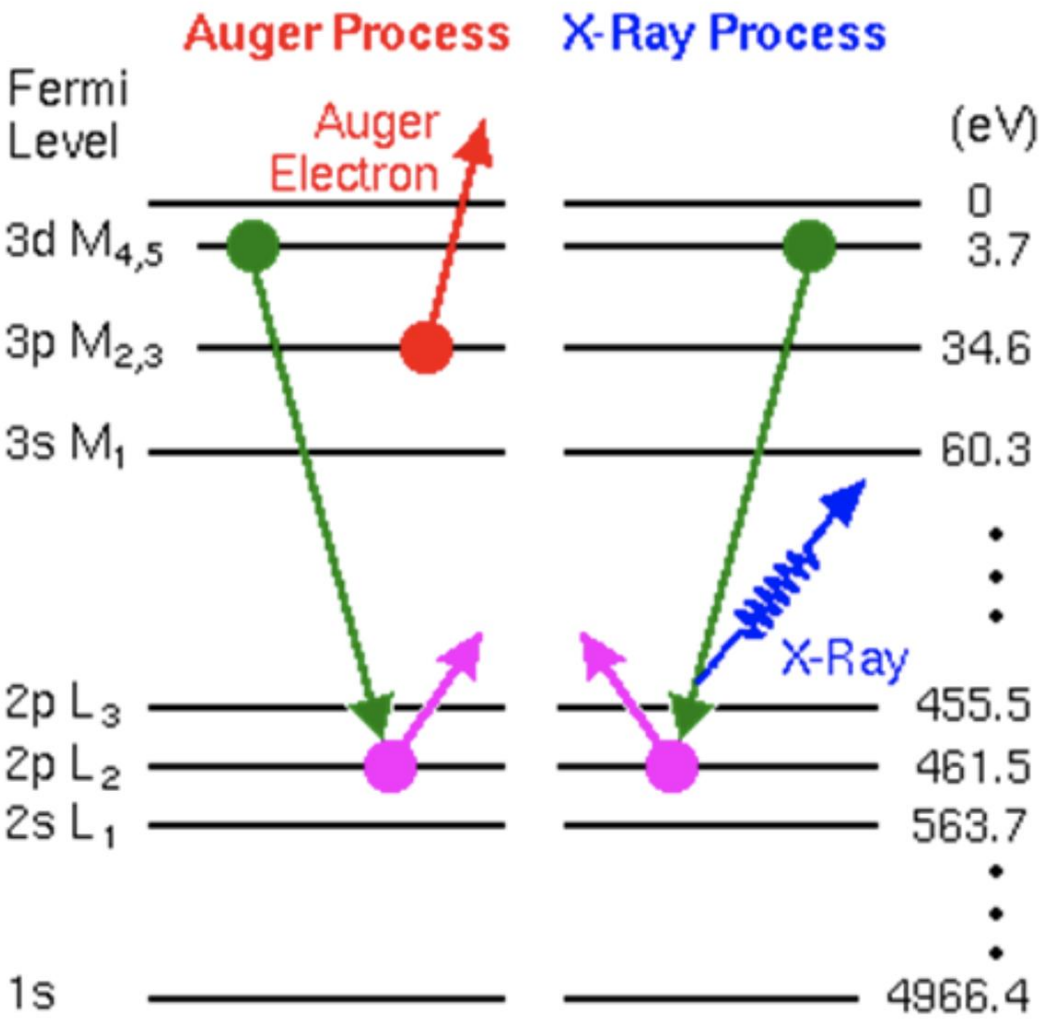
8.1 Energy of Auger electrons and of radiative emission

A core electron (violet arrow) of Ti atoms in a titanium film is excited by an external electron. The two possible relaxation processes are the Auger electron emission or the X-ray emission.

Calculate the energy of the emitted Auger electron and of the emitted photon.
Where necessary, consider a work function = 5 eV.

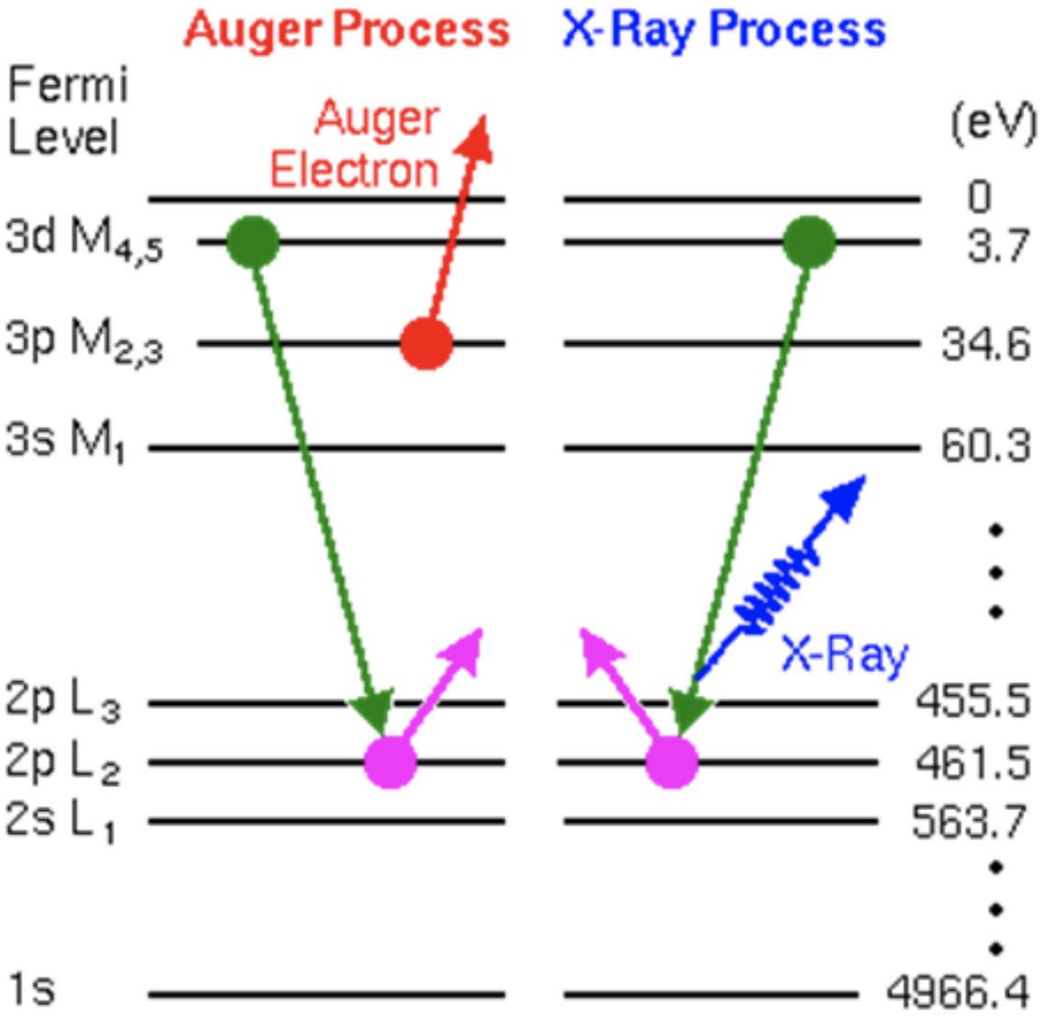


8.1 Energy of Auger electrons and of radiative emission - Solution

The Auger electron energy is

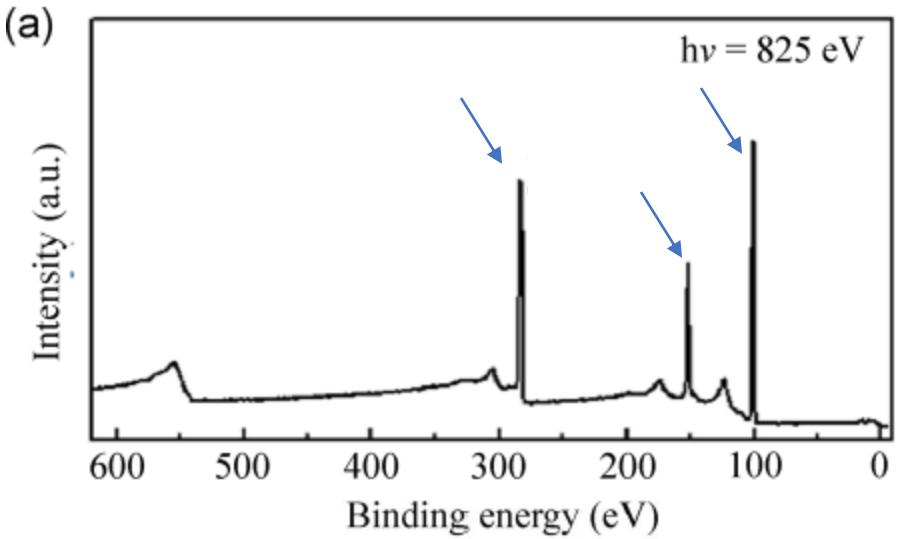
$E_{kin} = E_{L2} - E_{M4} - E_{M2} - \Phi \sim 418$ eV
LMM transition

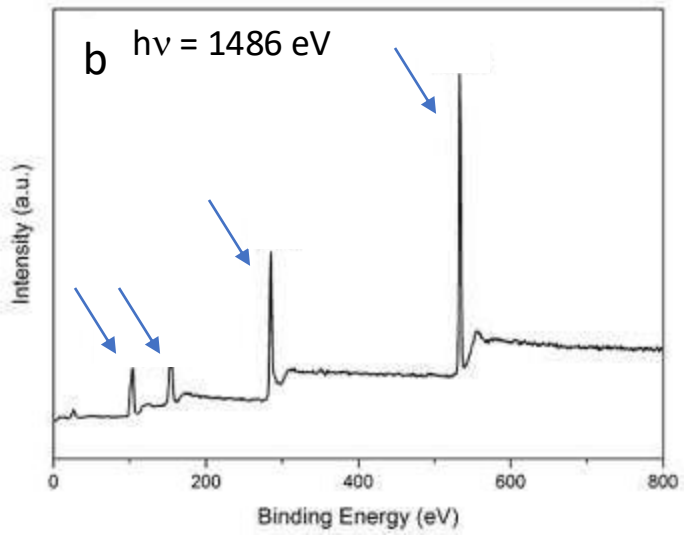
The X-ray photon energy is
$E_{hv} = E_{L2} - E_{M4} \sim 457.8$ eV

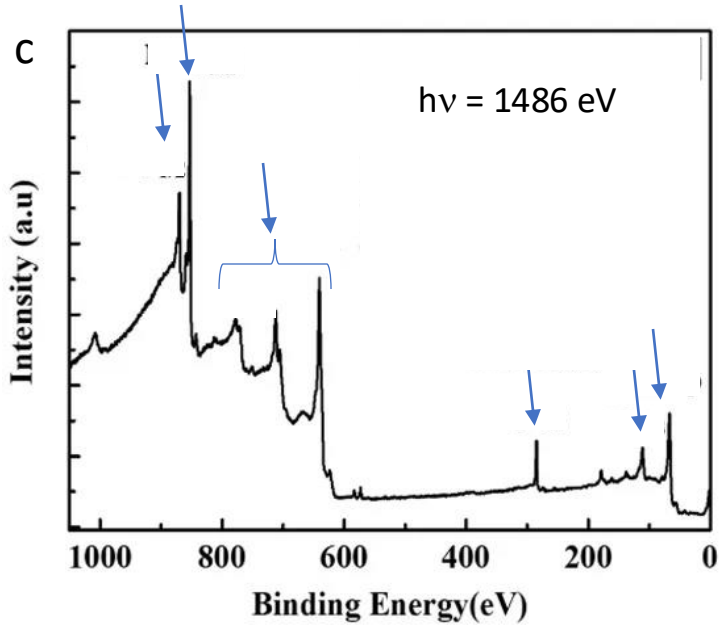


8.2 XPS spectra of graphene on different substrates

The XPS spectra of graphene on three unknown substrates are shown below.
Identify the major peaks marked with arrows and determine the three substrates.
(Use the table of the electron binding energies for potential element candidates provided in the next page)







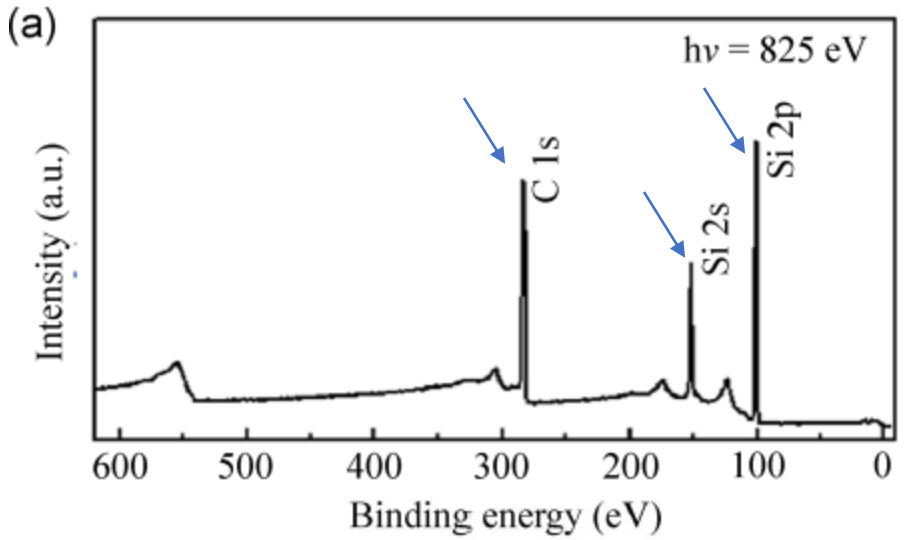
Sources: DOI:10.1039/C6RA05884A; DOI:10.1007/s12274-014-0584-y; doi.org/10.3390/nano11113112

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

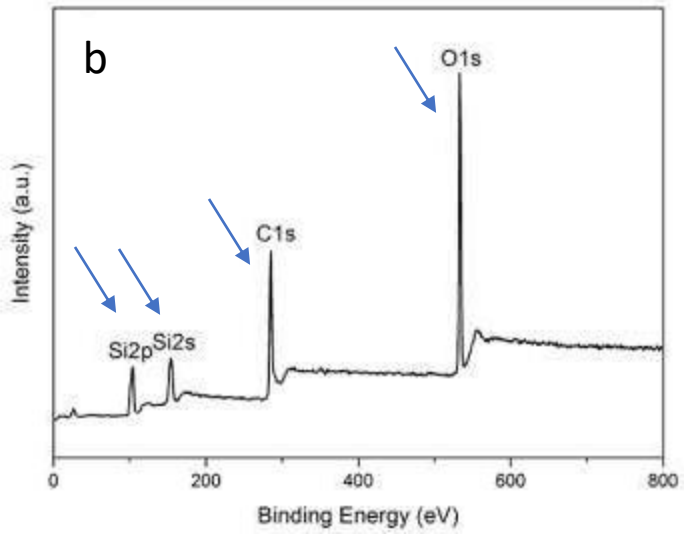
Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$	M_4 $3d_{3/2}$	M_5 $3d_{5/2}$	N_1 4s	N_2 $4p_{1/2}$	N_3 $4p_{3/2}$
1 H	13.6											
2 He	24.6*											
3 Li	54.7*											
4 Be	111.5*											
5 B	188*											
6 C	284.2*											
7 N	409.9*	37.3*										
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†					
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†	159.5†	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*			
36 Kr	14326	1921	1730.9*	1678.4*	292.8*	222.2*	214.4	95.0*	93.8*	27.5*	14.1*	14.1*
37 Rb	15200	2065	1864	1804	326.7*	248.7*	239.1*	113.0*	112*	30.5*	16.3*	15.3 *
38 Sr	16105	2216	2007	1940	358.7†	280.3†	270.0†	136.0†	134.2†	38.9†	21.3	20.1†
39 Y	17038	2373	2156	2080	392.0*b	310.6*	298.8*	157.7†	155.8†	43.8*	24.4*	23.1*
40 Zr	17998	2532	2307	2223	430.3†	343.5†	329.8†	181.1†	178.8†	50.6†	28.5†	27.1†
41 Nb	18986	2698	2465	2371	466.6†	376.1†	360.6†	205.0†	202.3†	56.4†	32.6†	30.8†
42 Mo	20000	2866	2625	2520	506.3†	411.6†	394.0†	231.1†	227.9†	63.2†	37.6†	35.5†
43 Tc	21044	3043	2793	2677	544*	447.6	417.7	257.6	253.9*	69.5*	42.3*	39.9*
44 Ru	22117	3224	2967	2838	586.1*	483.5†	461.4†	284.2†	280.0†	75.0†	46.3†	43.2†
45 Rh	23220	3412	3146	3004	628.1†	521.3†	496.5†	311.9†	307.2†	81.4*b	50.5†	47.3†
46 Pd	24350	3604	3330	3173	671.6†	559.9†	532.3†	340.5†	335.2†	87.1*b	55.7†a	50.9†
47 Ag	25514	3806	3524	3351	719.0†	603.8†	573.0†	374.0†	368.3	97.0†	63.7†	58.3†

8.2 XPS spectra of graphene on different substrates - Solution

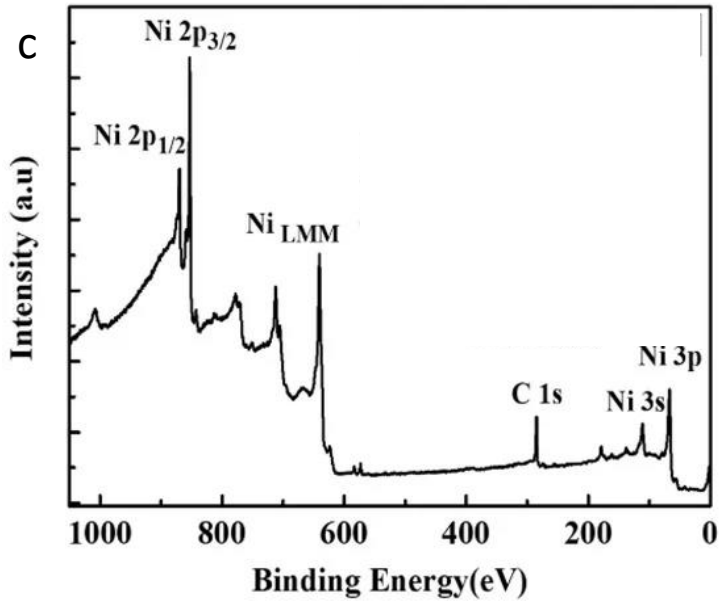
Graphene on Si



Graphene on SiO_2



Graphene on Ni

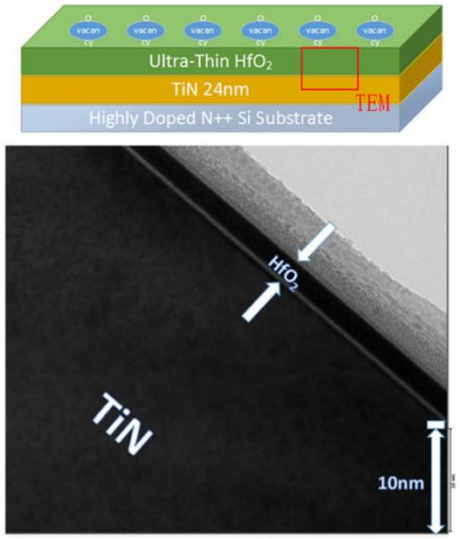


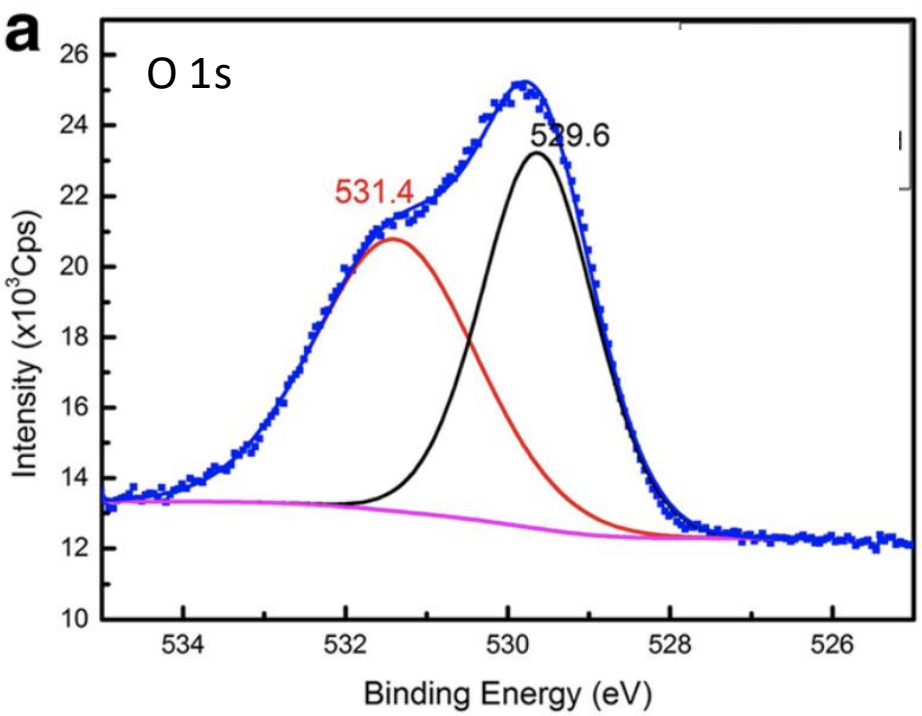
8.3 XPS spectra of HfO_2

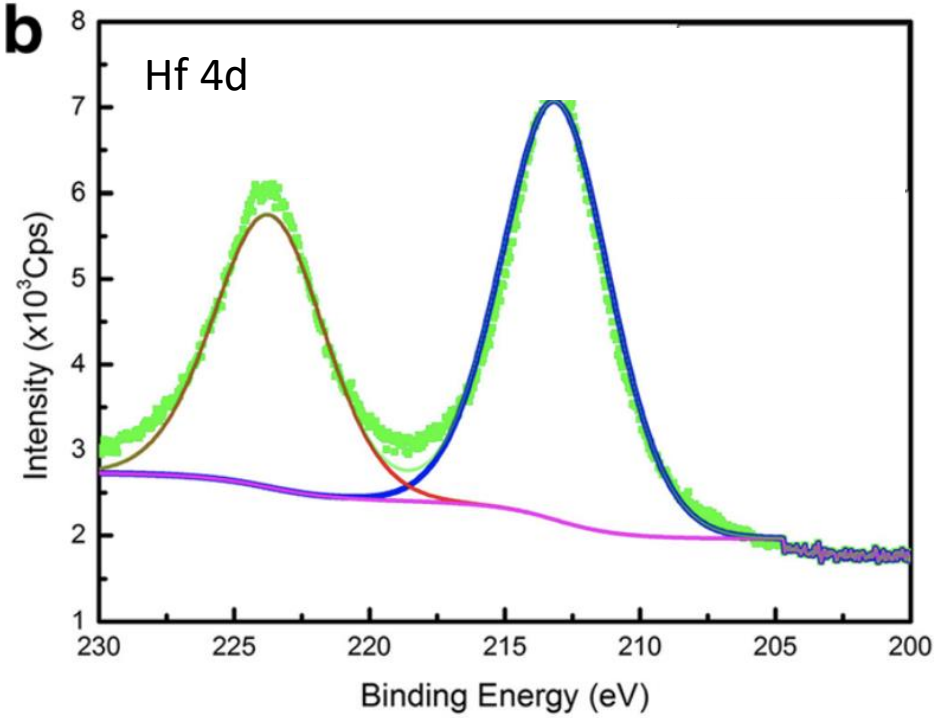
The HfO_2 film grown on a TiN substrate constitutes the gate insulating layer of a FET. It has been characterized by XPS.

a) Why the Hf 4d spectrum shows two peaks? Can you predict the intensity ratio between the two?

b) Why the O 1s peak shows two components?







10.1186/s11671-017-2068-y

8.3 XPS spectra of HfO_2 – Solution

Oxygen 1s: chemical shift, some O atoms are bond to Ti and the charge transfer is different, resulting in different binding energy

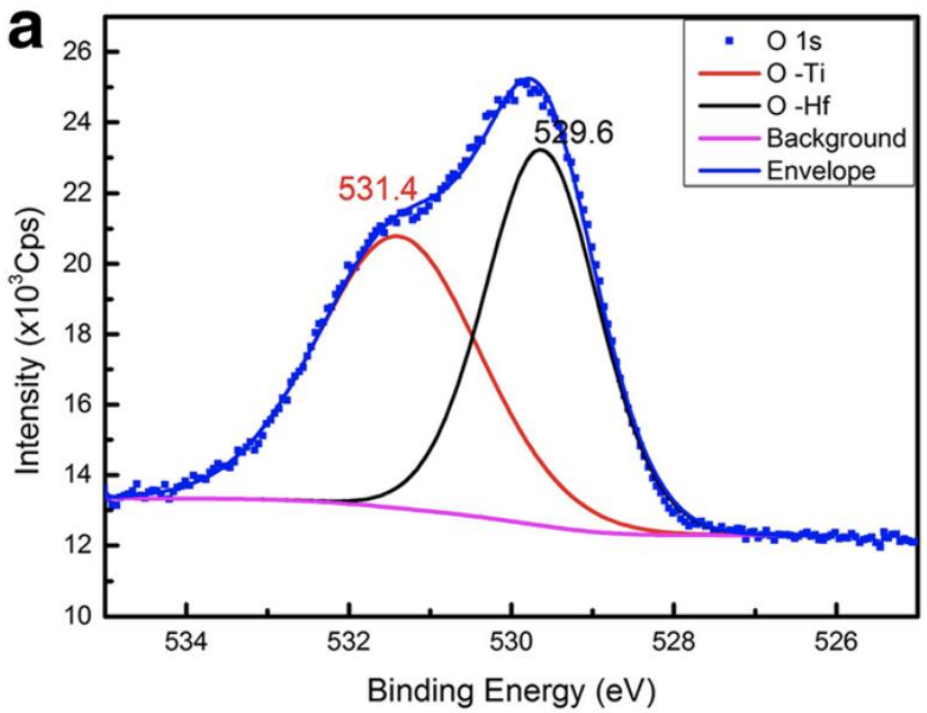
Hf 4d: spin-orbit splitting

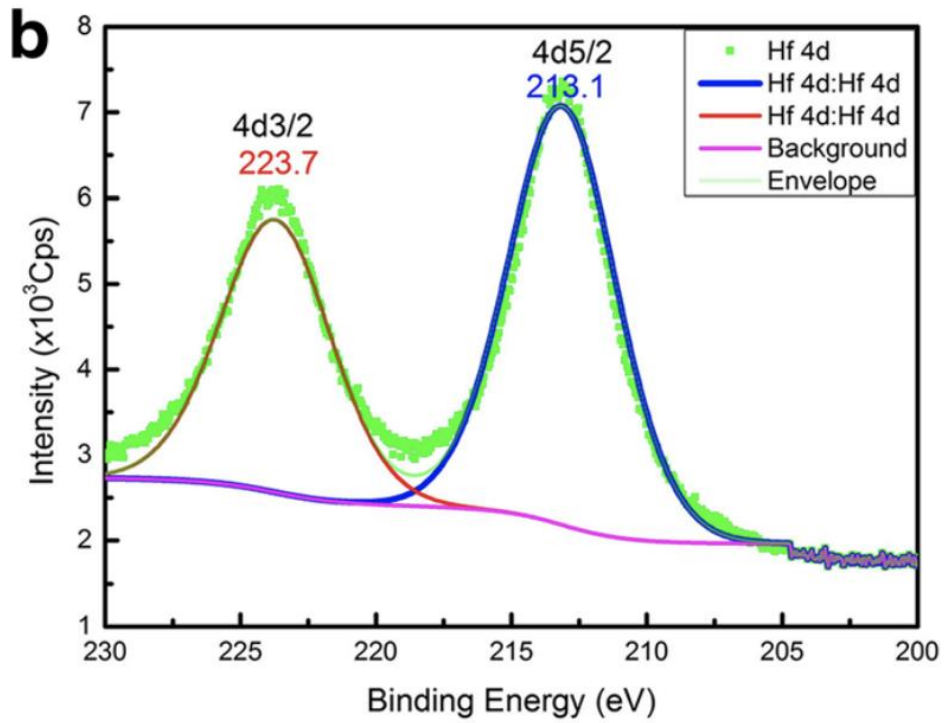
$l = 2$

$s = 1/2$

$j = 5/2, 3/2$

$2d_{3/2} : 2d_{5/2} = 4 : 6 = 2 : 3$





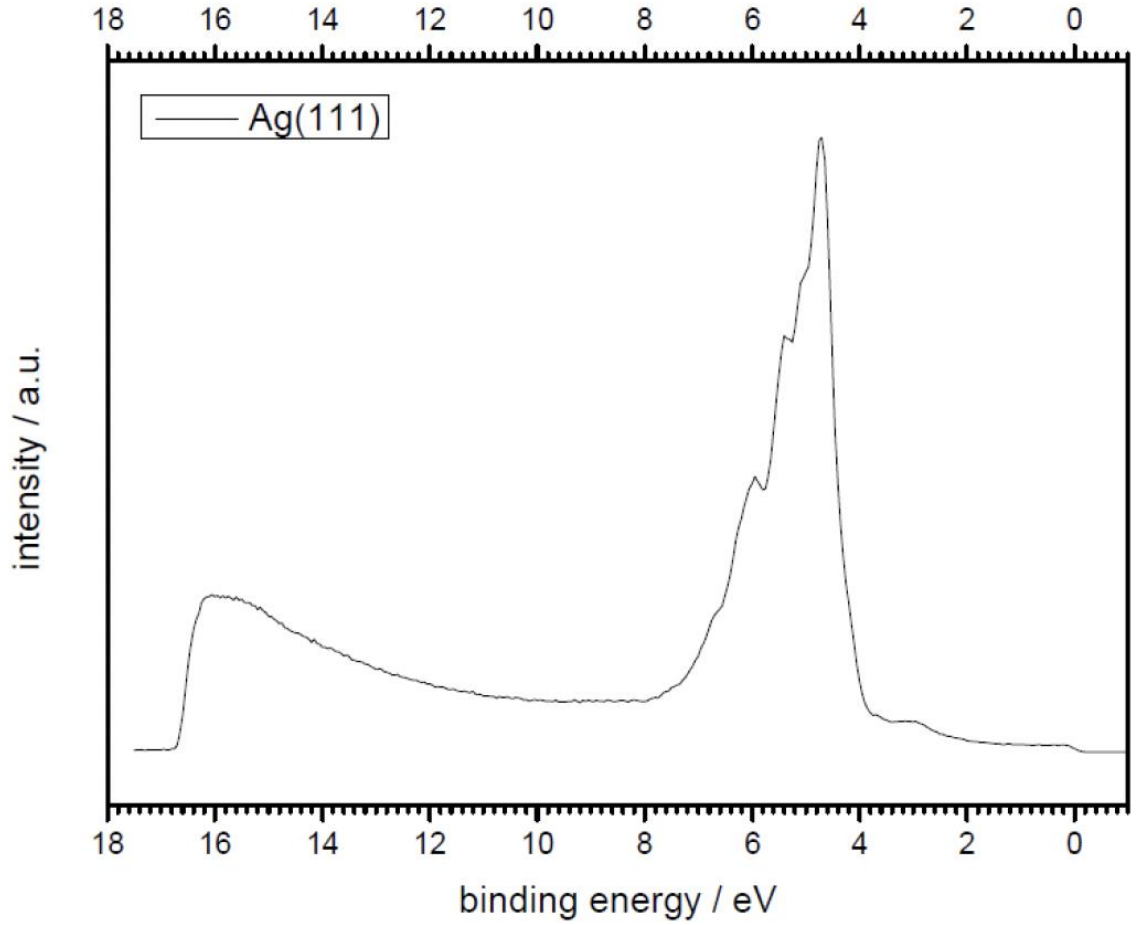
10.1186/s11671-017-2068-y

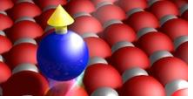
8.4 Ag(111): UPS and work function

The following spectrum was measured on a clean Ag(111) surface using UV-light from a He-I source ($h\nu = 21.22$ eV).

a) Evaluate the work function of Ag(111).

b) What is the origin of the peaks at approximately 5 eV?





8.4 Ag(111): UPS and work function - Solution

a) The electrons with binding energy = 16.5 eV are the last ones that can be emitted from the sample with the used photons. This means that those electrons would have almost zero kinetic energy.

From the relation $E_{kin} = h\nu - E_{bind} - \Phi$, with $E_{kin} = 0$
we deduce $\Phi = h\nu - E_{bind} \approx 21.2 - 16.5 \approx 4.7$ eV

b) This peak originates from the 4d states, that are fully occupied in silver.

8.5 UPS spectra

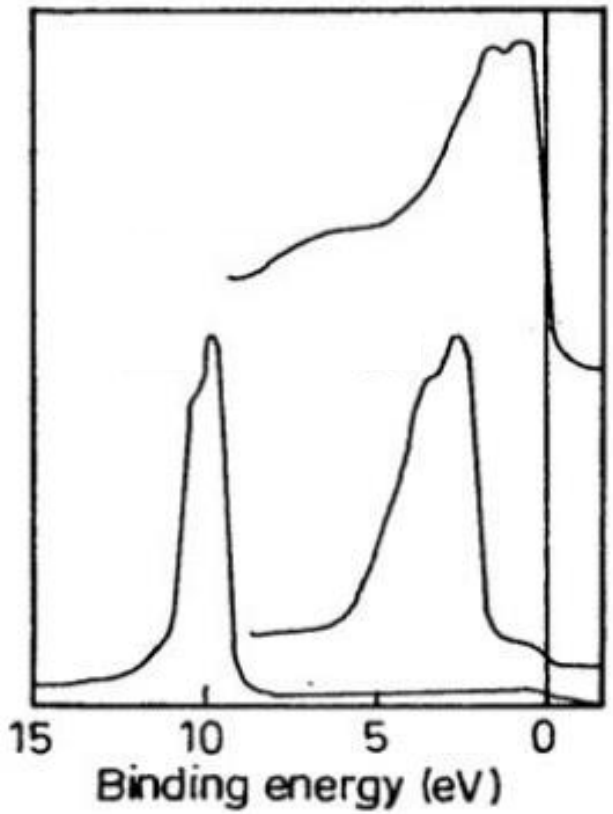
Consider the three UPS spectra shown in the figure, where one has been vertically shifted for clarity.

Using electron configuration given for the three elements (gas phase), identify the spectrum of the solid formed by each element. Justify your answers.

Ni(0): $[Ar]3d^8 4s^2$

Cu(0): $[Ar]3d^{10}4s^1$

Zn(0): $[Ar]3d^{10}4s^2$



8.5 UPS spectra - Solution

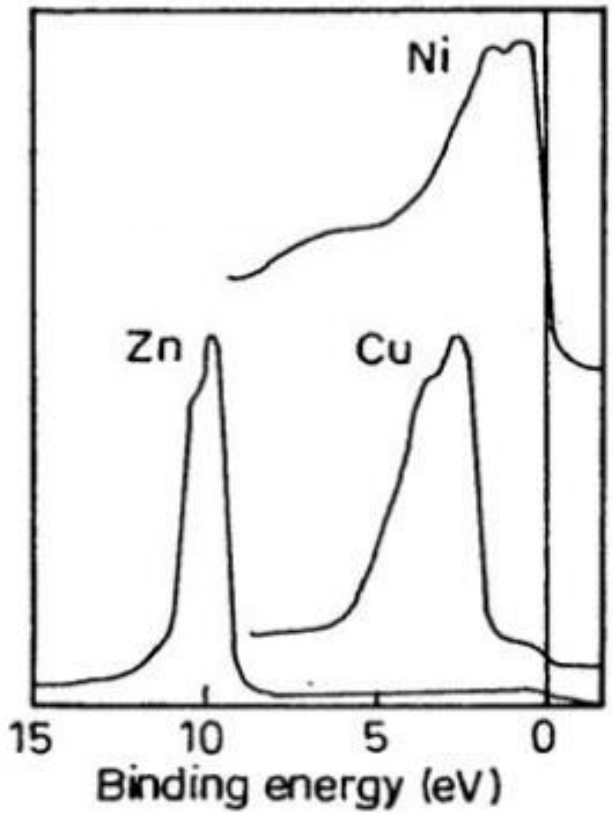
From the filling of the 3d and 4s states, we can deduce that:

- the spectrum with the peak at E_{bind} = 10 eV corresponds to Zn, since the 3d states are fully occupied;
- the spectrum with the peak at E_{bind} = 2-5 eV corresponds to Cu, since the 3d states are fully occupied but we expect the 4s states to be partially occupied;
- the spectrum with the peak at E_{bind} = 0-3 eV corresponds to Ni, since the 3d states are not fully occupied.

Ni(0): $[Ar]3d^8 4s^2$

Cu(0): $[Ar]3d^{10}4s^1$

Zn(0): $[Ar]3d^{10}4s^2$



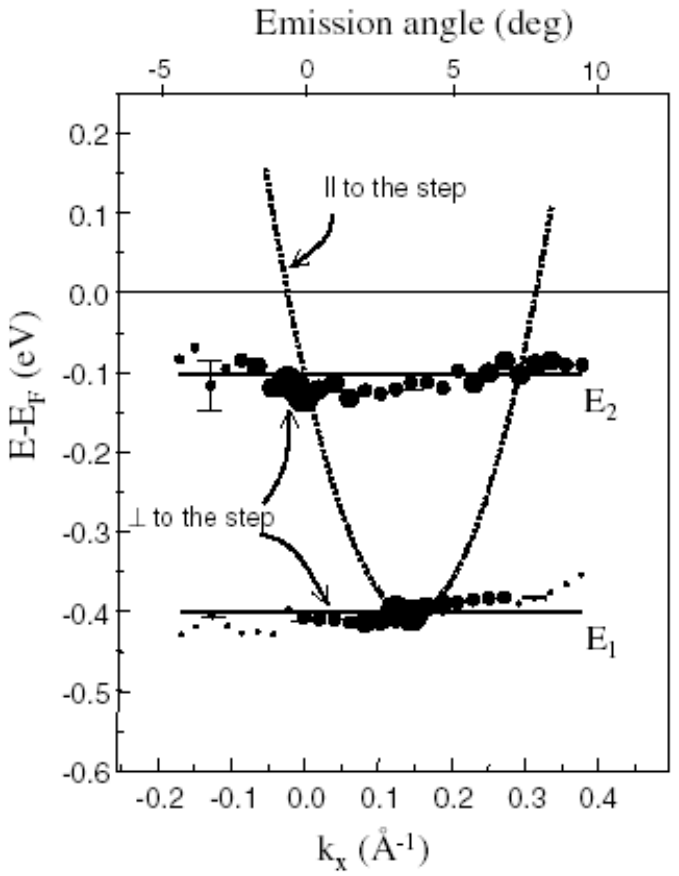
8.6 Surface state confinement

Consider the confinement of the surface state on the Au(788) vicinal surface.

Calculate the energy difference between E_2 and E_1 and compare it to the experimental value.

$L = 3.8$ nm
$m^* = 0.27\, m_e$

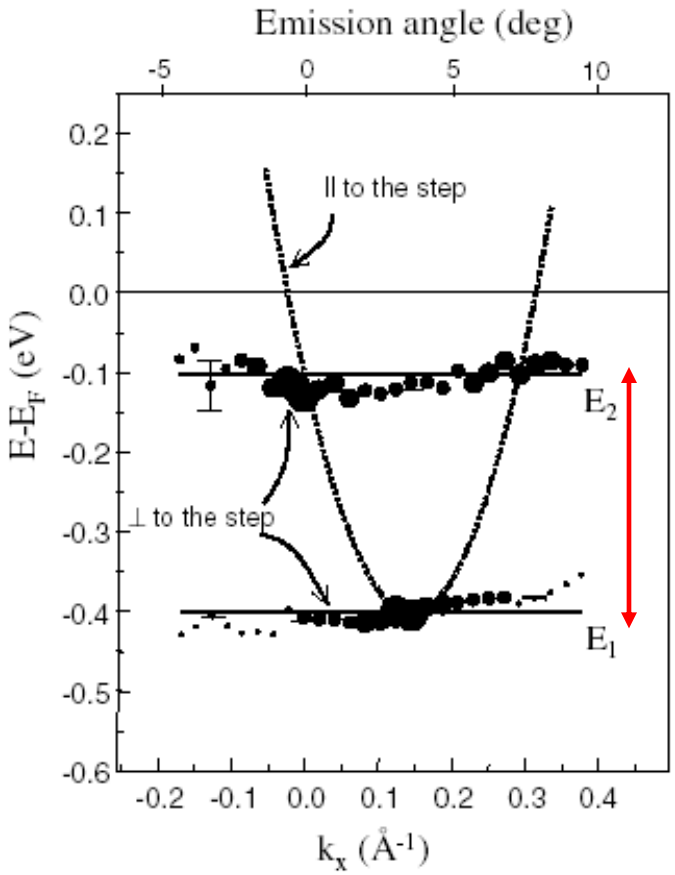
$\hbar = 1.05 \times 10^{-34}$ J·s
$m_e = 9.1 \times 10^{-31}$ kg
$1\,\text{J} = 1.6 \times 10^{19}$eV



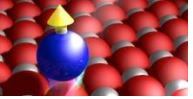
A. Mugarza et al., Phys. Rev. Lett. **87**, 107601 (2001)

8.6 Surface state confinement - Solution

$$E_2 - E_1 = \frac{\hbar^2}{2m^*}\frac{\pi^2}{L^2}(2^2 - 1^2) = 0.46 \times 10^{-19}\text{J} = 0.29\ \text{eV}$$



≈ 0.3 eV

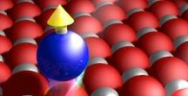


8.7 Density of states of 2D systems

Consider a Au(111) single crystal and a piece of graphene, both with in-plane dimensions $L_x = L_y = L$

a) Find the expression of the Density of states per unit volume corresponding to
the surface state of Au(111)
the π band of graphene

b) What do you expect to observe in UPS measurements for the two systems? And in an STS experiment? Sketch both for both systems.



8.7 Density of states of 2D systems - Solution

a) Density of states per unit volume $g(E) = \frac{D(E)}{L^2} = \frac{1}{L^2}\frac{dN}{dE} = \frac{1}{L^2}\frac{dN}{dk}\frac{dk}{dE}$

For both 2D systems $\frac{dN}{dk} = 2 \cdot 2\pi k \frac{L^2}{(2\pi)^2}$ (factor 2 for the spin, $\frac{L^2}{(2\pi)^2}$ is the volume occupied by each state in k-space)

For the surface state: $E(k) = E_0 + \frac{\hbar^2 k^2}{2m^*} \rightarrow \frac{dE}{dk} = \frac{\hbar^2 k}{m^*} \rightarrow \frac{dk}{dE} = \frac{m^*}{\hbar^2 k}$; $g(E) = \frac{1}{L^2}\, 2 \cdot 2\pi k \frac{L^2}{2\pi^2}\frac{m^*}{\hbar^2 k} = \frac{m^*}{(\pi\hbar)^2}$ for $E \geq E_0$

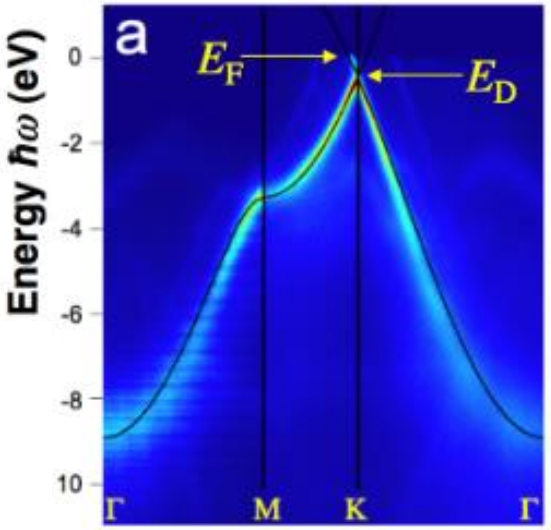
For graphene: $E(k) = \pm\hbar v_F k \rightarrow \frac{dE}{dk} = \pm\hbar v_F \rightarrow \frac{dk}{dE} = \pm\frac{1}{\hbar v_F}$; $g(E) = \frac{1}{L^2}\, 2 \cdot 2\pi \frac{E}{\hbar v_F}\frac{L^2}{(2\pi)^2}\frac{1}{\hbar v_F} = \frac{E}{\pi(\hbar v_F)^2}$

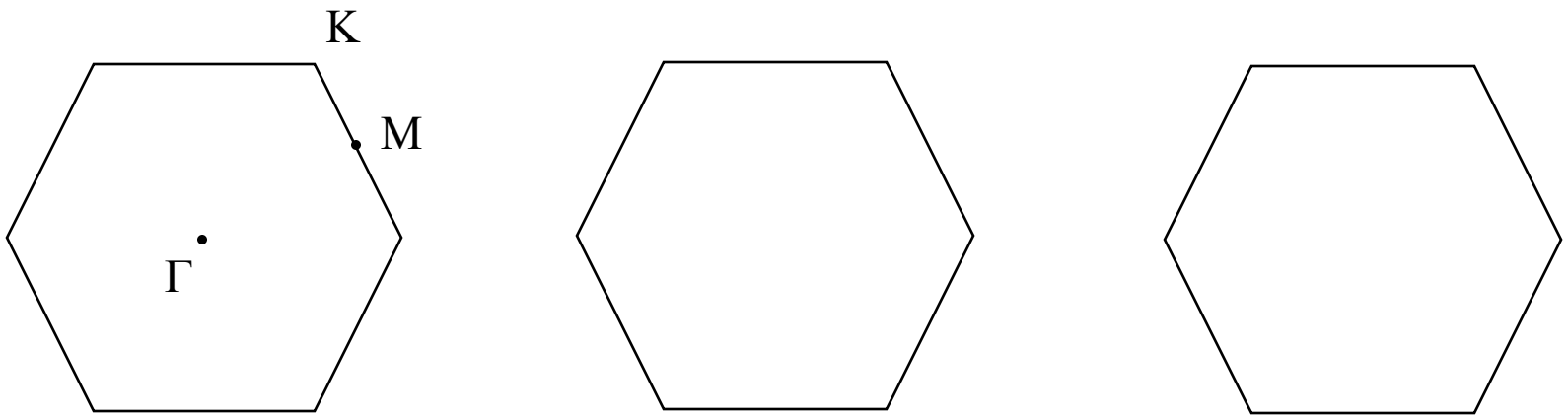
b) In UPS in first approximation the spectrum corresponds to the DOS. For the surface state we expect a constant spectrum (if $E_0 < E_F$) up to E_F. For graphene we expect a linearly decreasing signal, going to zero at E_F.
In STS we can access both occupied (negative bias) and unoccupied (positive bias) states, therefore for the surface we expect to see the constant DOS also above E_F, and for graphene a linearly increasing signal for positive bias, yielding a V-shaped spectrum.

8.8 Graphene: π-band constant energy surfaces

The ARPES spectrum shows the π bands measured on graphene grown on SiC.

Plot qualitatively the constant energy surface at $E = E_D$, at $E = E_F$ (Fermi surface), and at $E = -2$ eV below E_F





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

8.8 Graphene: π-band constant energy surfaces - Solution