Photoemission spectroscopy

From Naturejobs Blog

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Outline

- ✓ Introduction

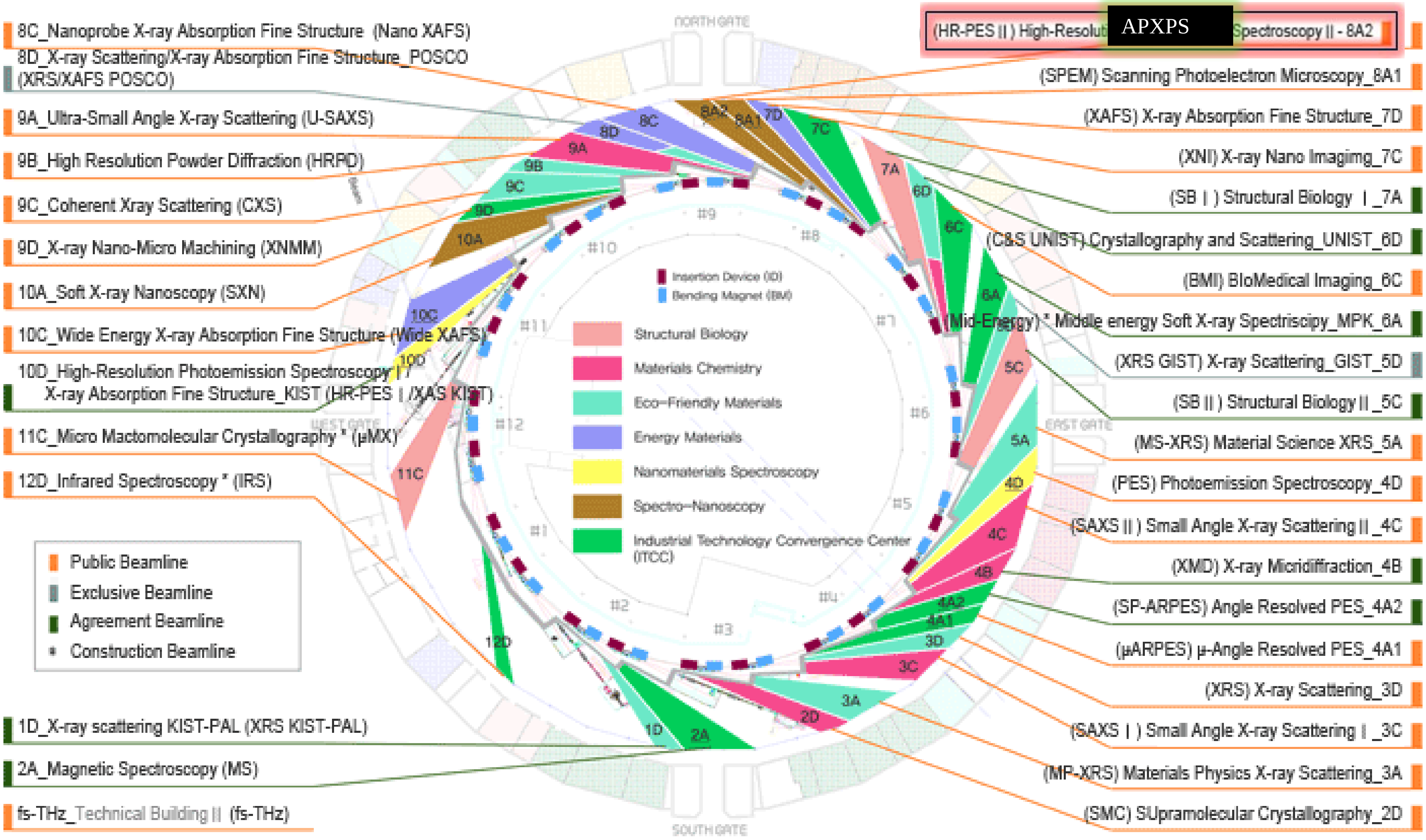
- ✓ Photoemission Spectroscopy
- - Principle
- - Specialized Exp.
  - - ARPES, APXPS, HAXPES…

- ✓ Science

- ➢ Summary

Pohang Accerator Loboratory
Phang, Korea

PLS II Beamlines



PAL-XFEL

X-ray coherence imaging/ Crystallography

Soft X-ray imaging/ Absorption

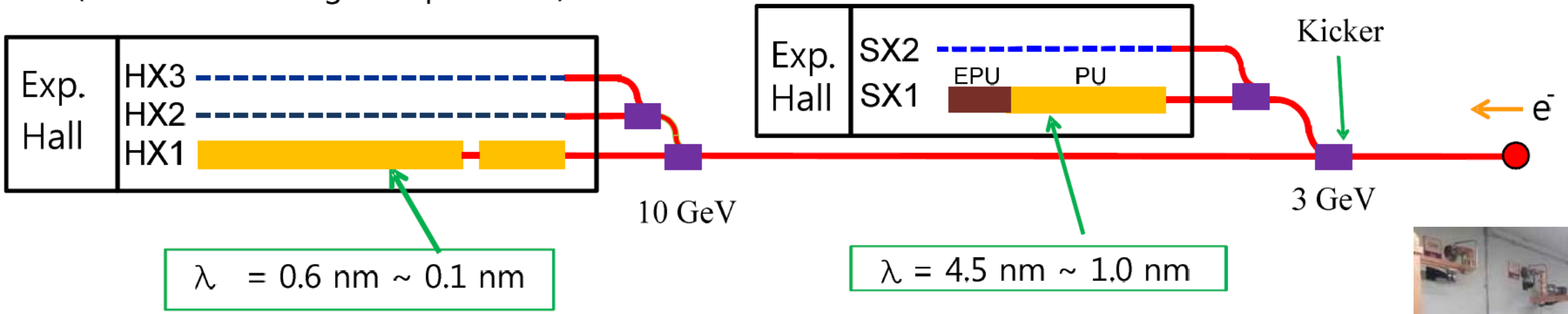
Hard X-ray Endstation II

Hard X-ray Endstation I

Soft X-ray Endstation I

Hard X-ray Undulator Hall
(~225 m including Dump section)

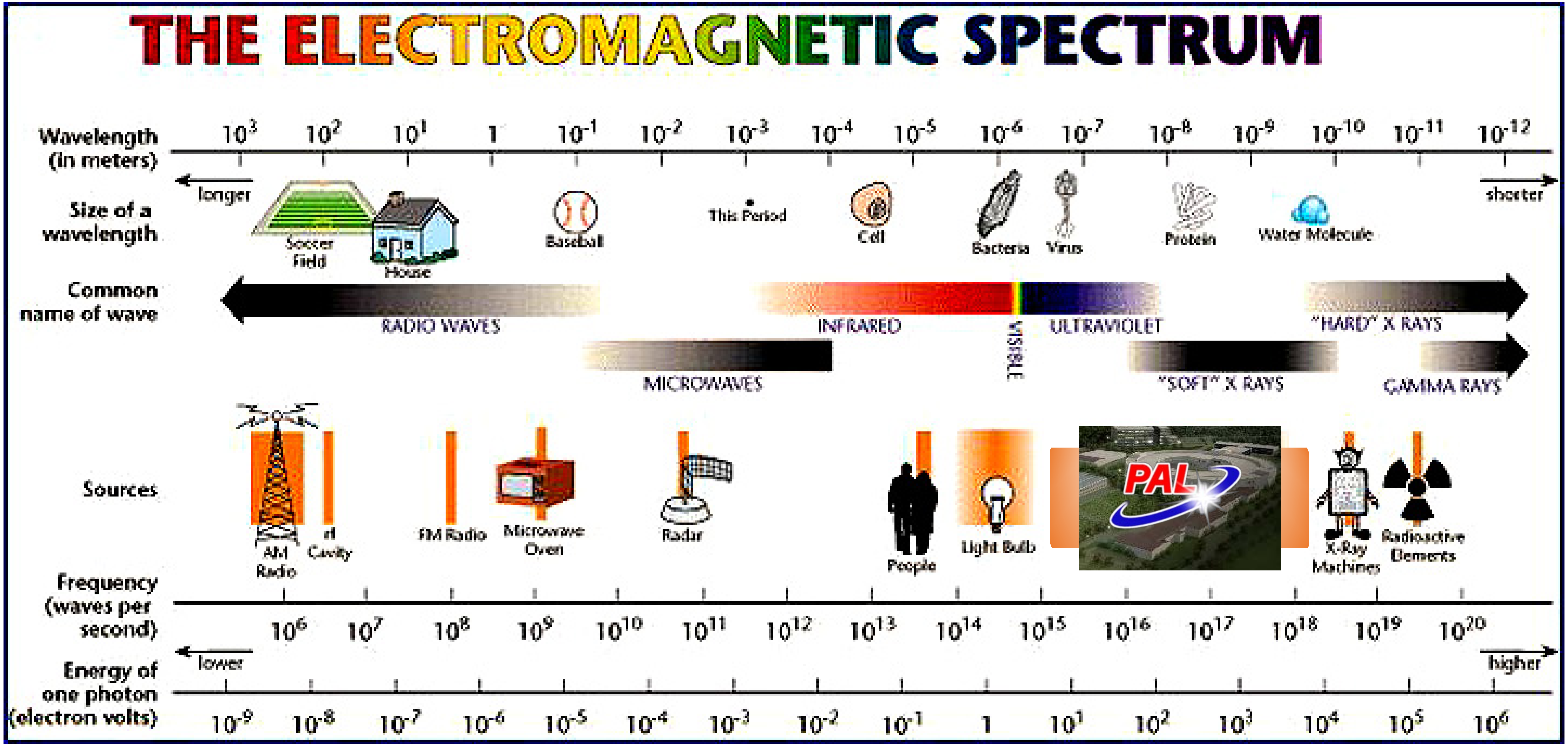
Soft X-ray Undulator Hall
(~110 m including Dump section)



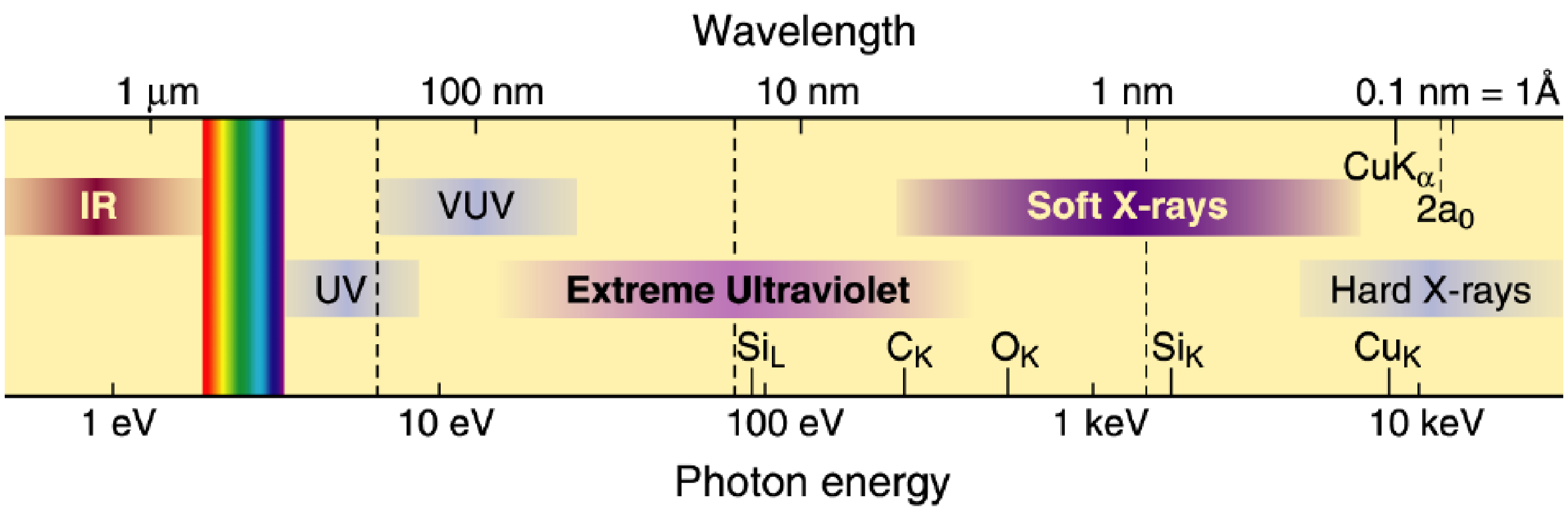
Courtesy of H.S. Kang

Photon!

- Electromagnetic wave



Synchrotron Radiation



- **See smaller features**
- **Write smaller patterns**
- **Elemental and chemical sensitivity**

$$\hbar\omega \cdot \lambda = hc = 1239.842 \text{ eV nm}$$

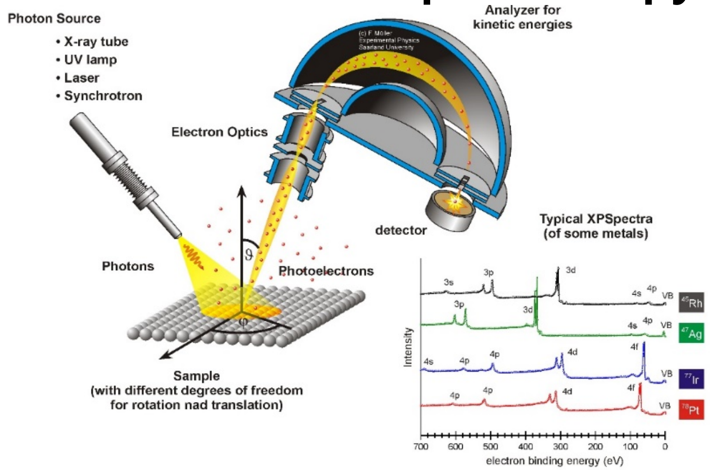
$$n = 1 - \delta + i\beta \qquad \delta, \beta << 1$$

PLS II Beamlines

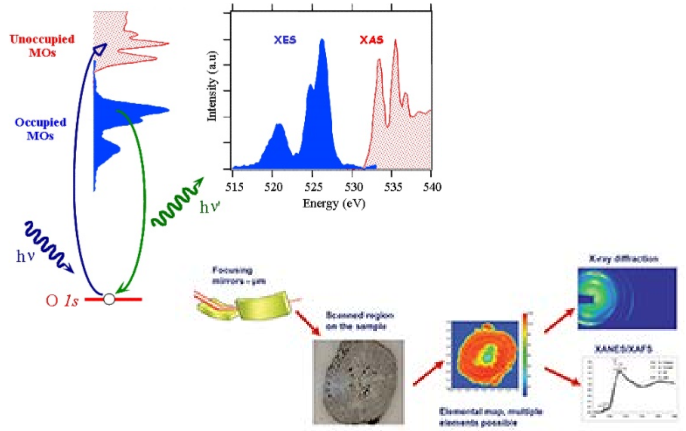
Classify of Beamline Expriments

- ✓ Photoemission Spectroscopy
- ✓ Magnetic Spectroscopy
- ✓ (Soft) X-ray Imaging
- ✓ X-ray Absorption Spectroscopy
- ✓ X-ray Imaging
- ✓ Small Angle X-ray Scattering
- ✓ Protein Crystalography
- ✓ Lithography
- ✓ Infrared Spectroscopy

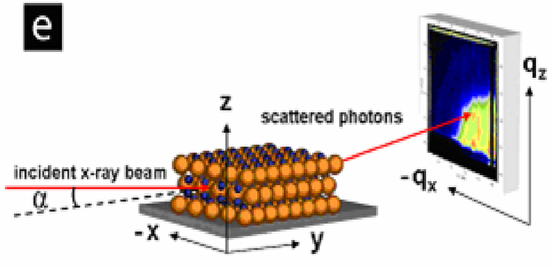
Photoemission Spectroscopy



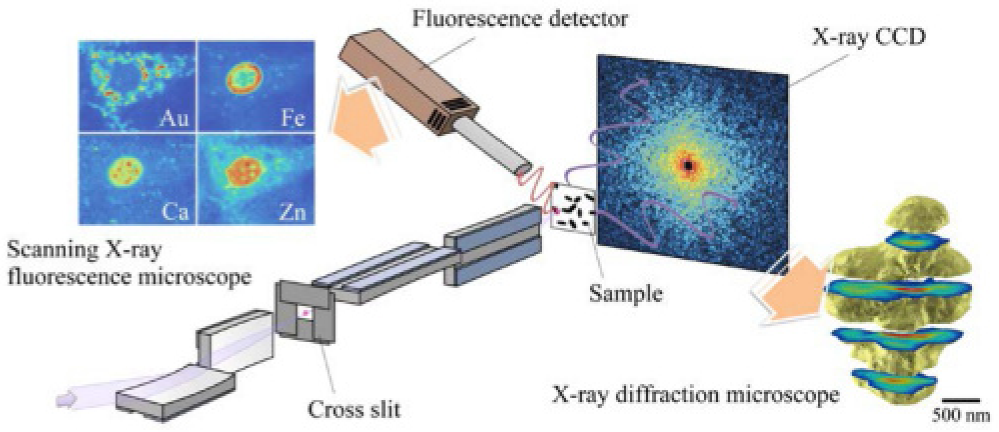
X-ray Absorption Spectroscopy



X-ray Imaging



X-ray Imaging



Photoemission Spectroscopy

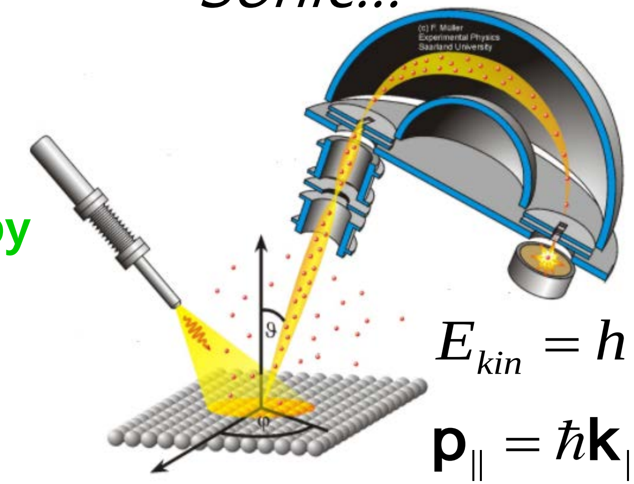
To probing the properly of samples

Stimulate **Respond**

Source → *Sample* → *Detector*

Source	Sample	Detector
Photon	*Solid*	*Photon*
Electron	*Liquid*	*Electron*
Ion	*Gas*	*Ion*
Neutron	*All of things in the world*	*Neutron*
Sonic		*Sonic…*
Heating & Cooling		
Chemical		
Physical….		

Photoemission spectroscopy (PES)



$$E_{kin} = h\nu - \phi - |E_B|$$

$$\mathbf{p}_{\parallel} = \hbar \mathbf{k}_{\parallel} = \sqrt{2mE_{kin}} \cdot \sin\vartheta$$

History

Albert Einstein's theory of the "photoelectric effect" says that a light particle (photon) can liberate an electron from an atom if it has sufficient energy.

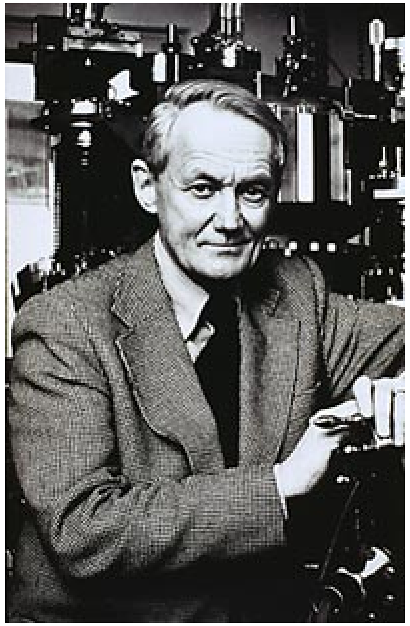
1950s **Kai Siegbahn** : **Developed methods for achieving highly accurate measurements of energy levels in atoms**

Precision Method for Obtaining Absolute Values of Atomic Binding Energies

CARL NORDLING, EVELYN SOKOLOWSKI, AND KAI SIEGBAHN
Department of Physics, University of Uppsala, Uppsala, Sweden
(Received January 10, 1957)

WE have recently developed a precision method of investigating atomic binding energies, which we believe will find application in a variety of problems in atomic and solid state physics. In principle, the method

Phys. Rev. **1957**, *105*, 1676



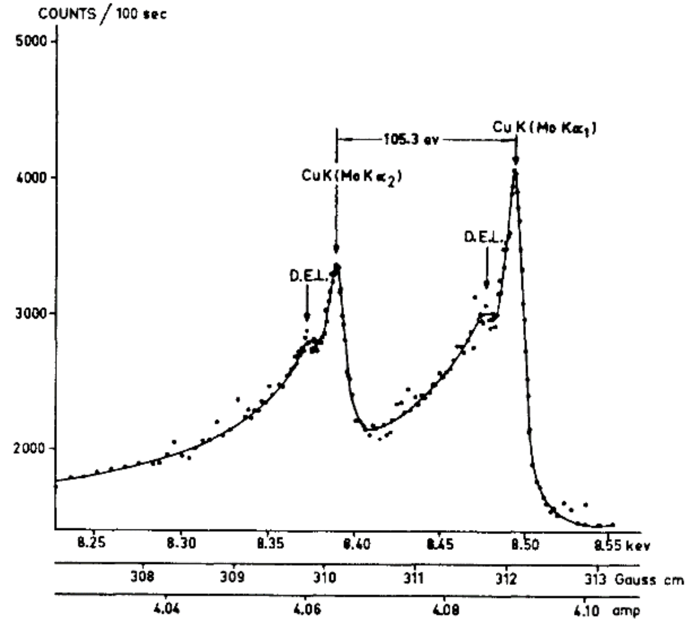
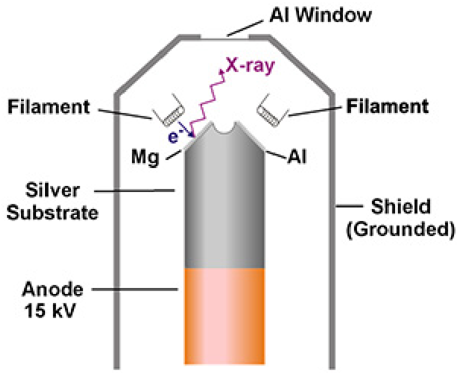
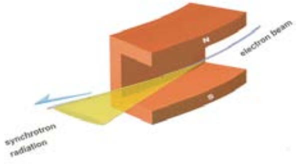


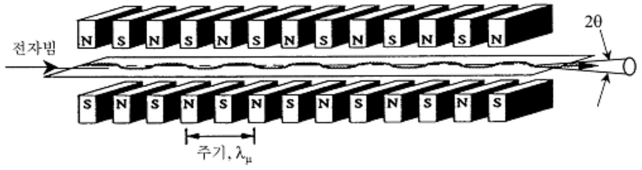
FIG. 1. Lines resulting from photoelectrons expelled from Cu by Mo $K\alpha_1$ and Mo $K\alpha_2$ x-radiation. The satellites marked D.E.L. are interpreted as due to electrons which have suffered a discrete energy loss when scattered in the source.

Nobel Prize in Physics 1981
: for his contribution to the development of high-resolution electron spectroscopy.

Light Sources







Type	Available photon energies	Polarization
Laser	6-11 eV; not much variation for a given laser	Variable polarization
Gas (He, Xe, Ne, Ar…) discharge lamp	21.2, 40.8, 8.4, 9.6, 11.6 eV (and more)	random polarization
Solid(Mg, Al, Ag, Cr…)	1253.6, 1486.7, 2984.2, 5400 eV ….	random polarization
Synchrotron	Variable; different synchrotrons and en dstations specialize in different energy ranges	Variable polarization

Intense, highly *collimated,*
continuous, polarized, *time structure…*

Principle

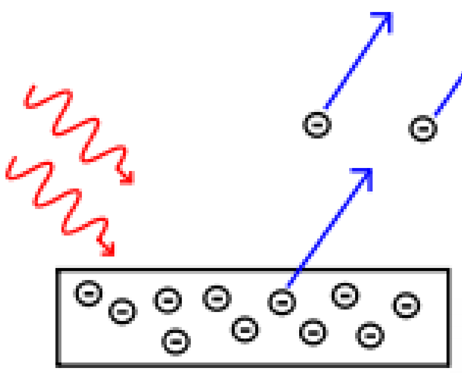
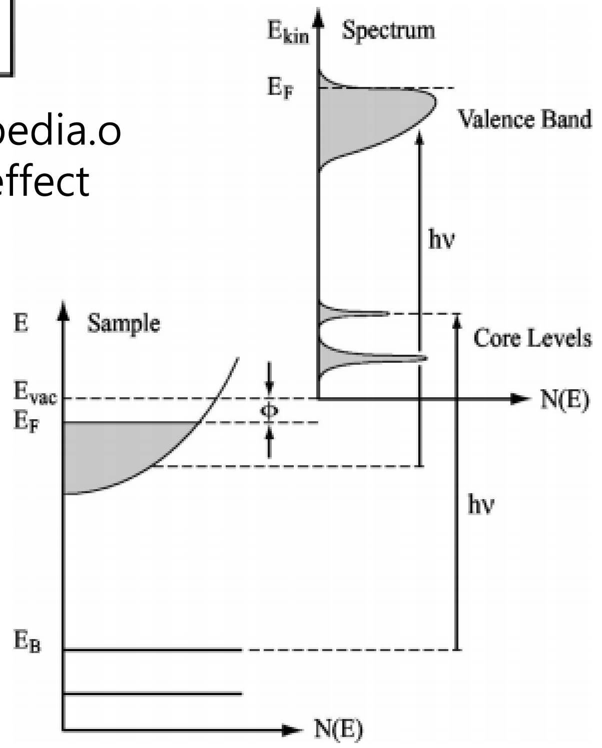


Image: https://en.wikipedia.org/wiki/Photoelectric_effect



Hufner. *Photoelectron Spectroscopy* (2003)

3 step model

1. Optical excitation of electron in the bulk
2. Travel of excited electron to the surface
3. Escape of photoelectrons into vacuum

Probability of transition related to Fermi's golden rule:

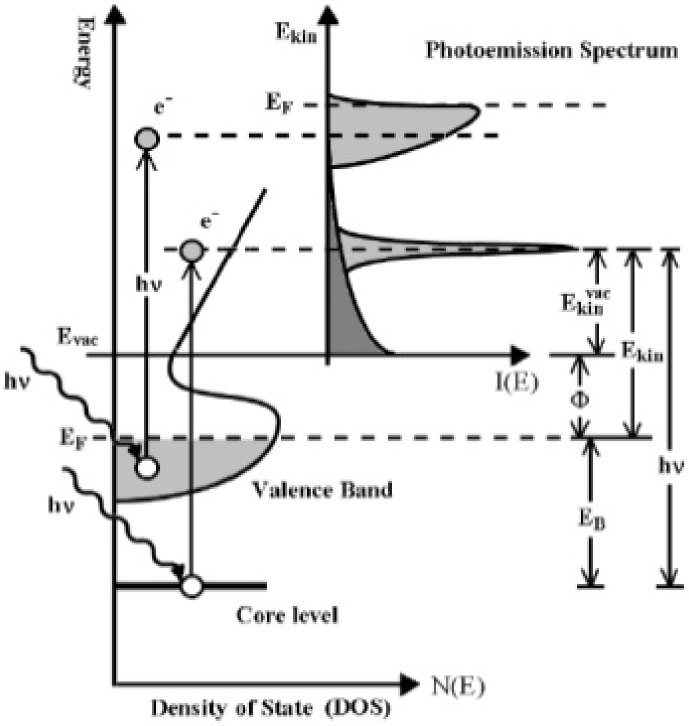
$$w_{fi} = \frac{2\pi}{\hbar}\left| < \Psi_f^N \right| - \frac{e}{mc}\boldsymbol{A}\cdot\boldsymbol{p}\left|\Psi_i^N > \right|^2 \delta(E_f^N - E_i^N - h\nu)$$

p=electron momentum
A=vector potential of photon

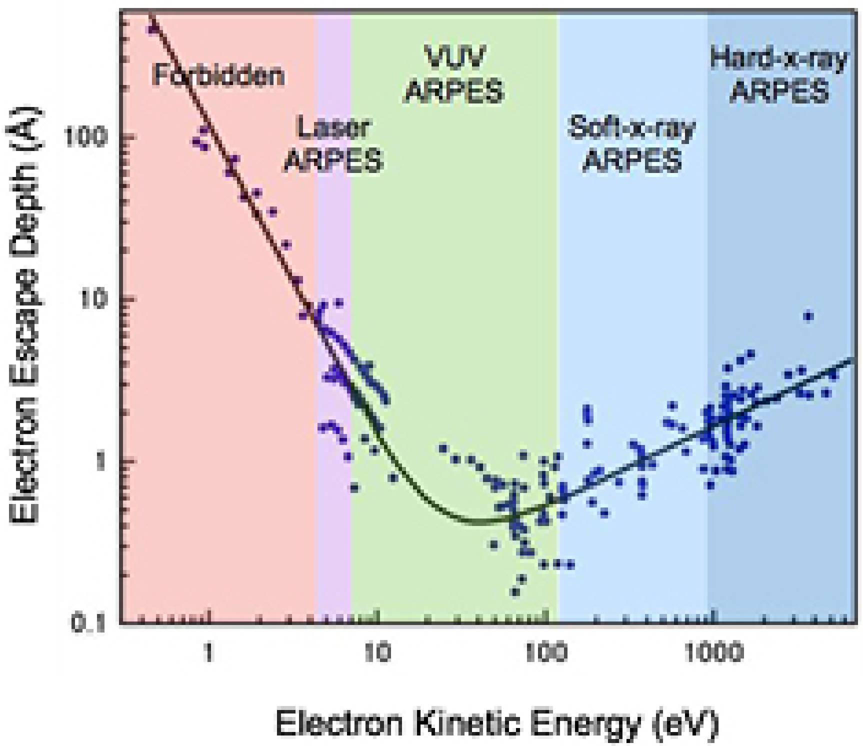
$$E_{kin} = h\nu - \phi - |E_B|$$

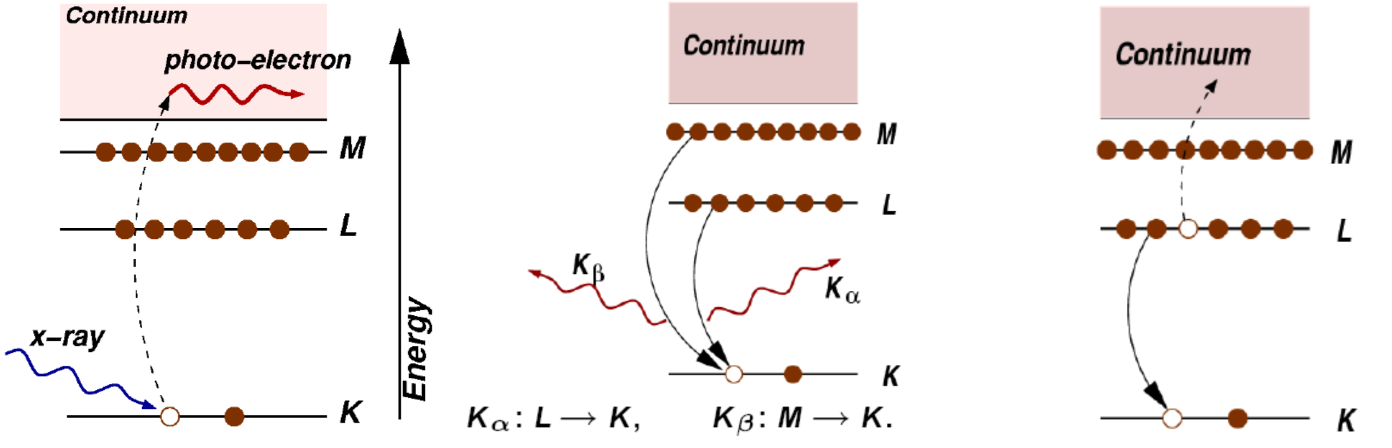
$$\mathbf{p}_{\parallel} = \hbar\mathbf{k}_{\parallel} = \sqrt{2mE_{kin}}\cdot\sin\vartheta$$

Electron Escape Depth



$$E_B = h\nu - E_k - \phi$$





Photoelectron

Fluorescent

Auger electron

Experimental Configuration for PES

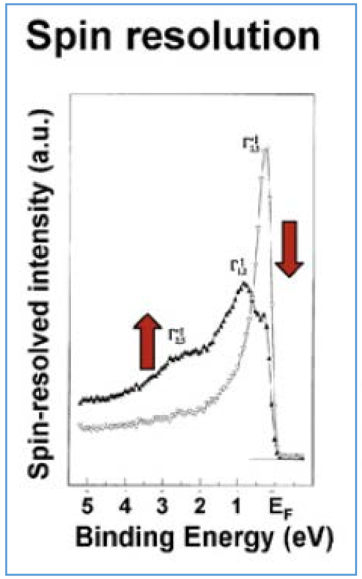
Available Photon Energy
: up to several keV
Exp. Environments
: UHV → Multi. Torr
Space & Time Resolution

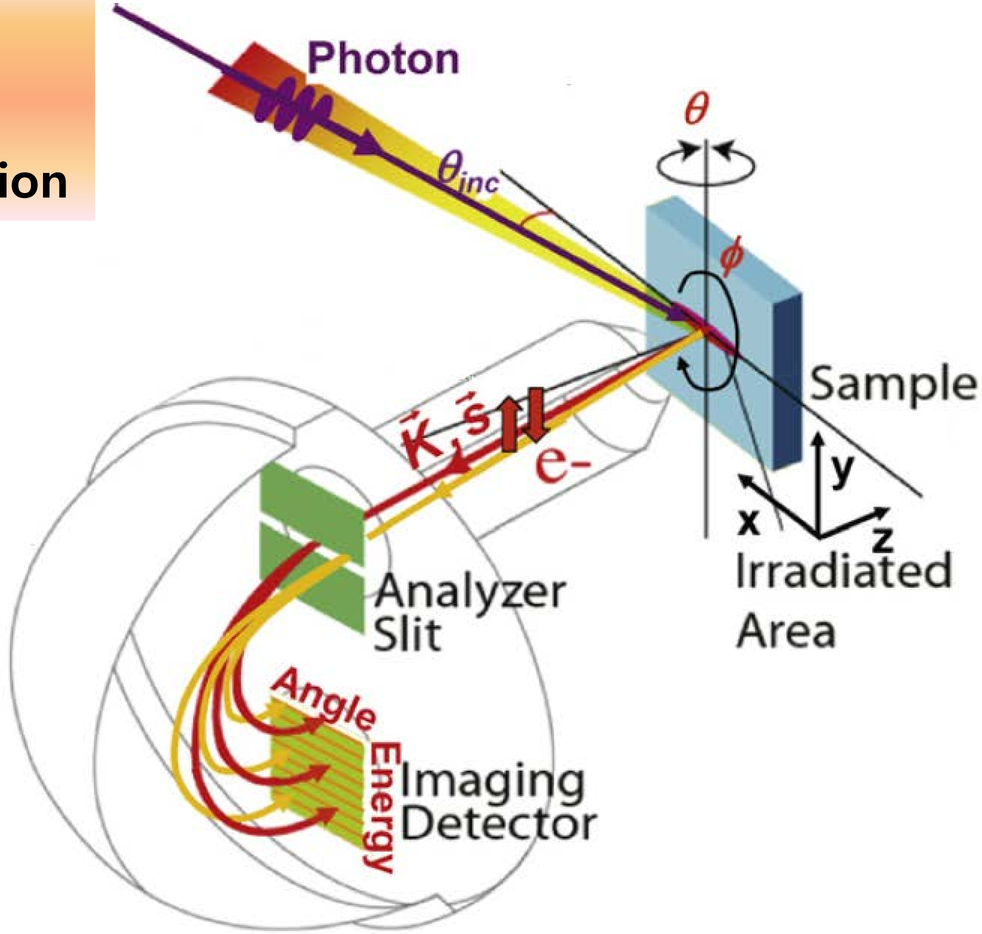
Energy Conservation

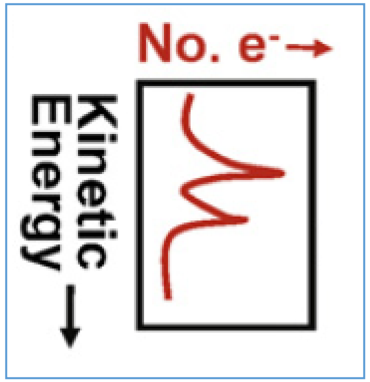
$$E_{kin} = h\nu - \phi - |E_B|$$

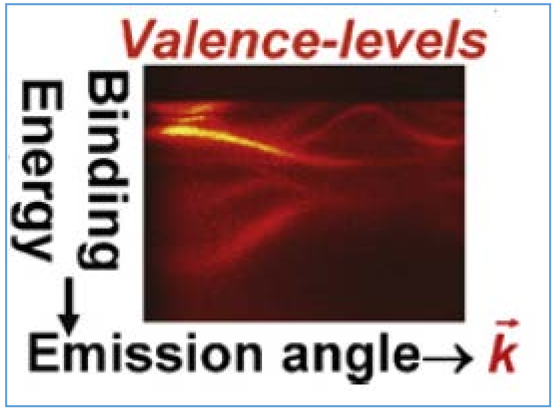
Momentum Conservation

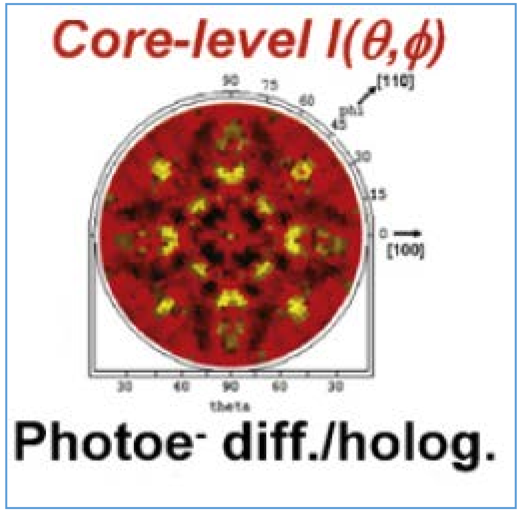
$$\mathbf{p}_{\|} = \hbar \mathbf{k}_{\|} = \sqrt{2mE_{kin}} \cdot \sin\vartheta$$









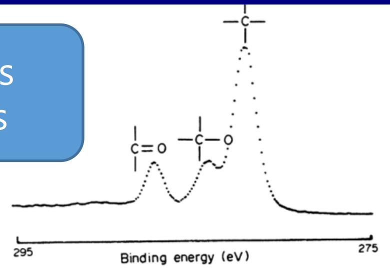


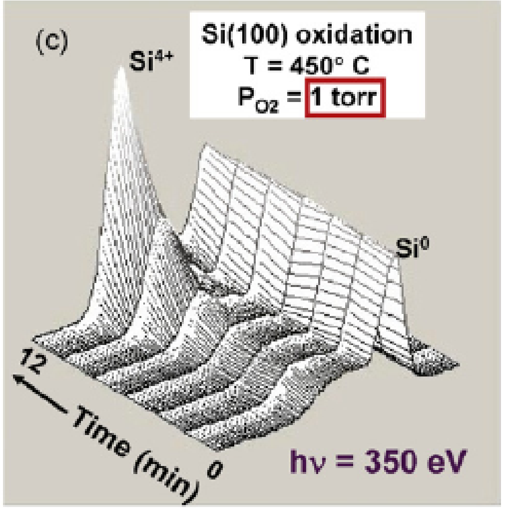
C.S. Fadley / J. of Elec. Spectroscopy and Related Phenomena *178–179 (2010) 2–32*

How to prepare a sample surface?

-Ex. Situ. Sample

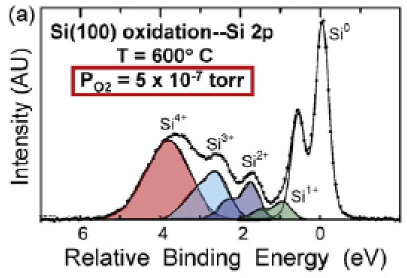
Sample Transfer to Vacuum Chamber → Analysis as it is



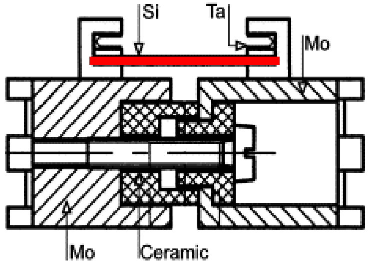


-In Situ. Sample

Sample Transfer to Vacuum Chamber → Sample Cleaning & Reconstruction → Analysis



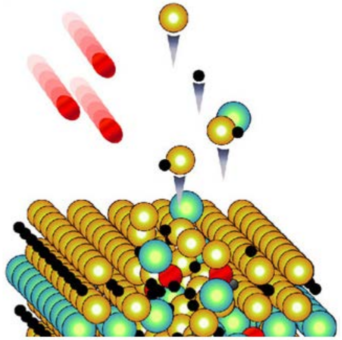
Annealing & Flashing



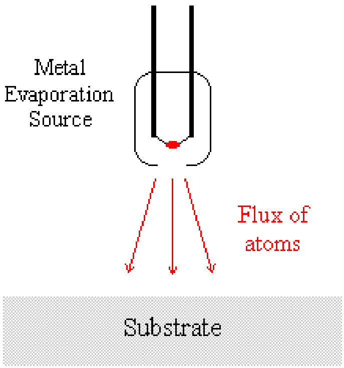
Cleaving

Sputtering & annealing

ion beam



Evaporation

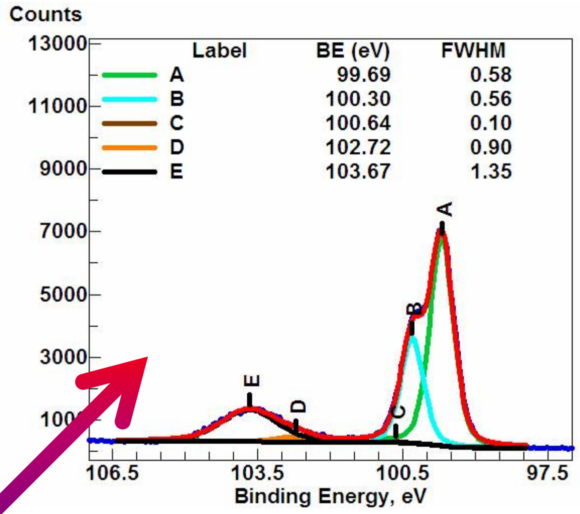


What information is learned from PES?

- Elemental identification (peak position)
- Atomic concentration (peak intensity)
- Chemical environment (core level shift)
- Atomic structure (soft x-ray & angle-resolved)
- Band structure (UV & angle-resolved)
- Symmetry of electronic state (polarization)

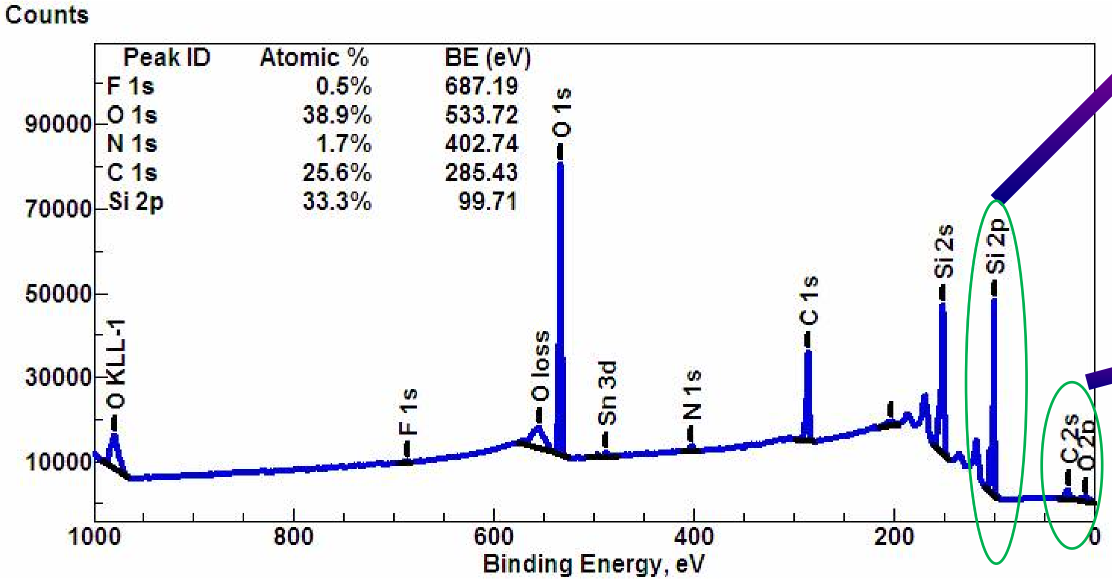
Core-level spectrum

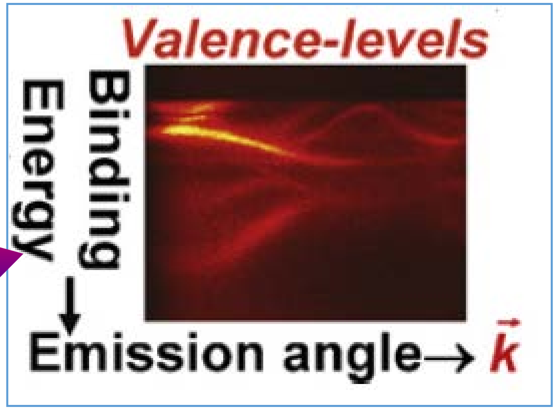
→ Chemical environments



Survey

→ Elemental identification on the surface





ARPES

→ Band Structure

Elemental Identification

References

- Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data, John F. Moulder, Physical Electronics Division, Perkin-Elmer Corporation, 1992

- https://srdata.nist.gov/xps/

NIST X-ray Photoelectron Spectroscopy Database

NIST Standard Reference Database 20, Version 4.1

Data compiled and evaluated
by

Alexander V. Naumkin, Anna Kraut-Vass, Stephen W. Gaarenstroom, and Cedric J. Powell

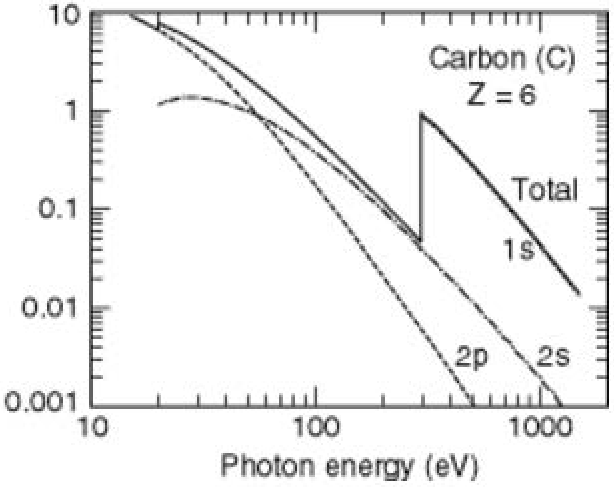
Table 1-1. *Electron binding energies, in electron volts, for the elements in their natural forms.*

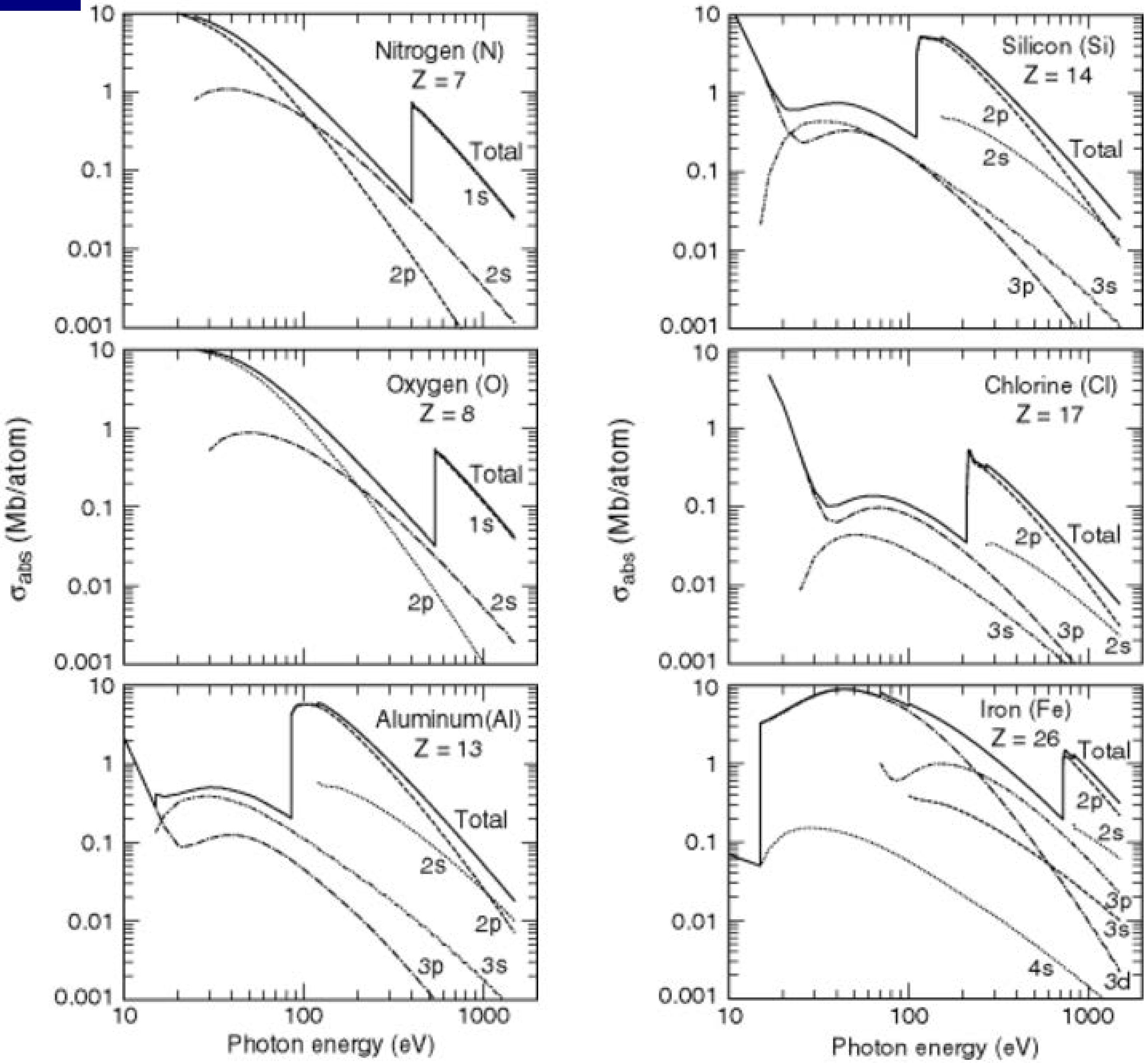
Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$	M_4 $3d_{3/2}$	M_5 $3d_{5/2}$	N_1 4s	N_2 $4p_{1/2}$	N_3 $4p_{3/2}$
1 H	13.6											
2 He	24.6*											
3 Li	54.7*											
4 Be	111.5*											
5 B	188*											
6 C	284.2*											
7 N	409.9*	37.3*										
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†

....

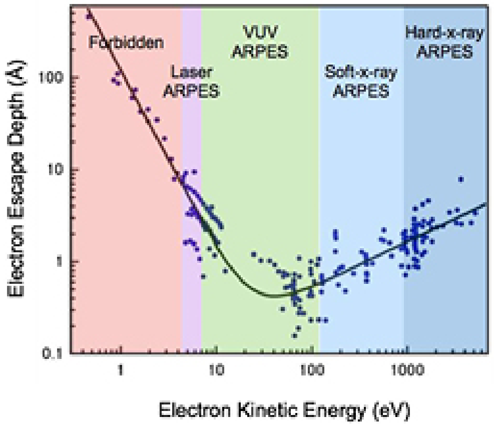
Photoionization Cross Section

1. J.-J. Yeh and I. Lindau, "Atomic Subshell Photoionization Cross Sections and Asymmetry Parameters: 1 < *Z* < 103," *At. Data Nucl. Data Tables* **32**, 1 (1985).
2. J.-J. Yeh, *Atomic Calculations of Photoionization Cross Sections and Asymmetry Parameters* (Gordon and Breach, Langhorne, PA, 1993).

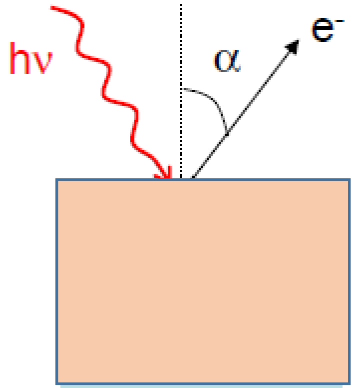




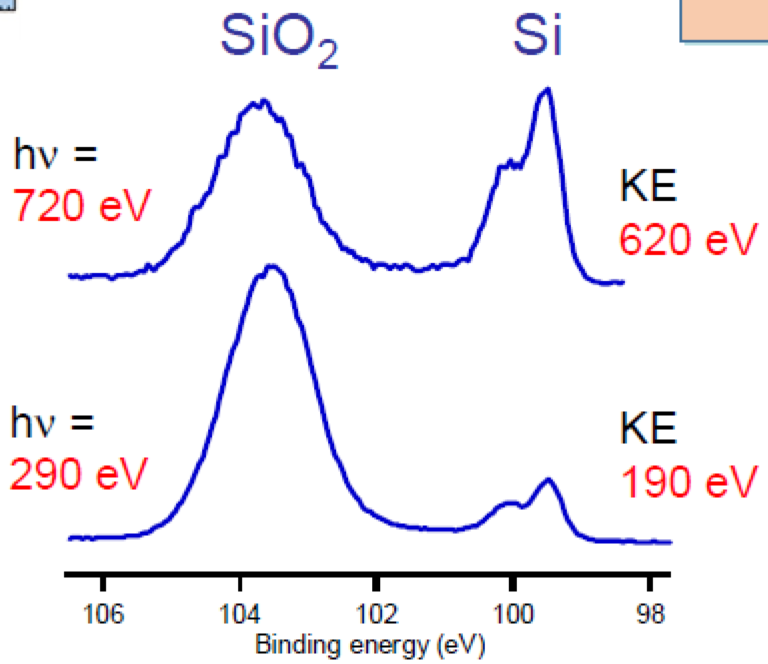
Depth profiling

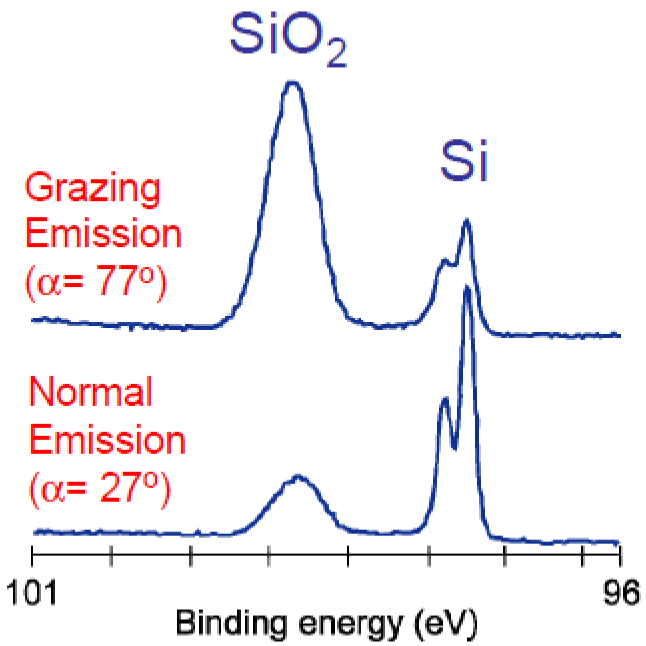


Electron Energy



Emission Angle





K. Siegbahn,
Phil. Trans. R. Soc. Lond. A, 318, 3 (1986).

Lower electron energy and at grazing emission
→ Greater surface sensitivity

Workfunction change

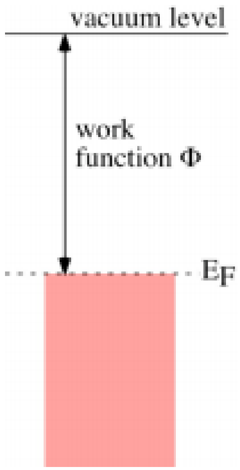


Fig.1: Schematic energy diagram of a metal.

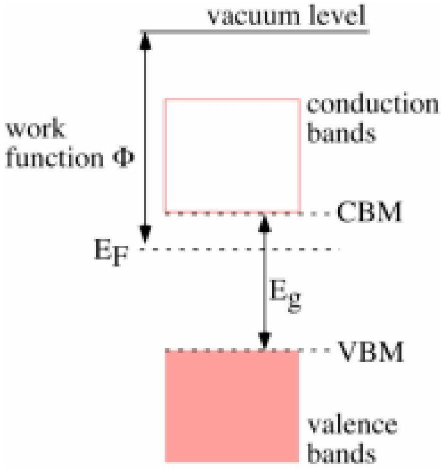


Fig.2: Schematic energy diagram of a semiconductor.

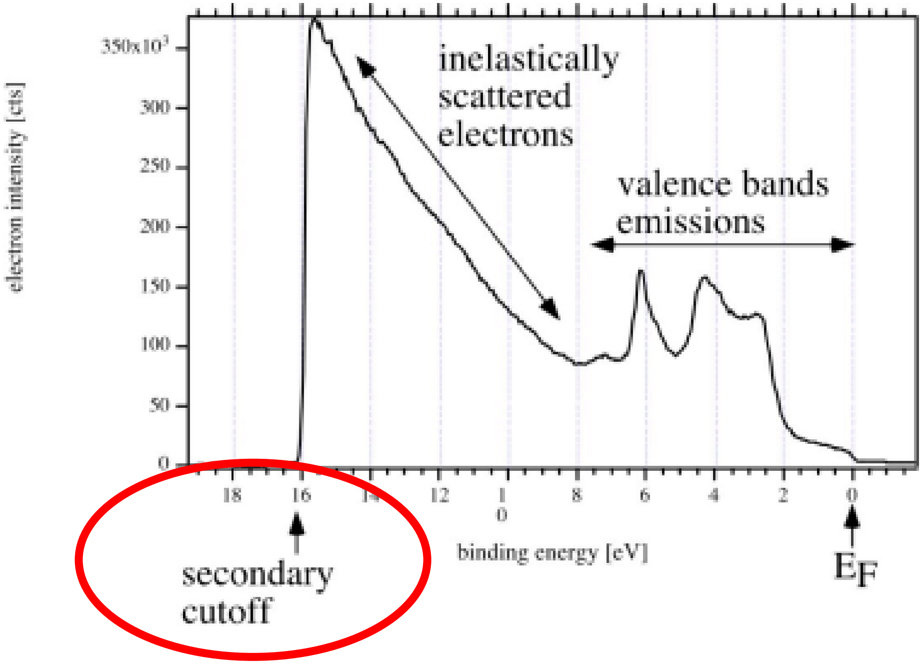


Fig.3: UP-spectrum of Au surface.

ΦAu = 21.21 eV – 15.9 eV=5.3 eV

New Science enabled by....

Powerful Synchrotron
Technology developments

Advanced tools?
...

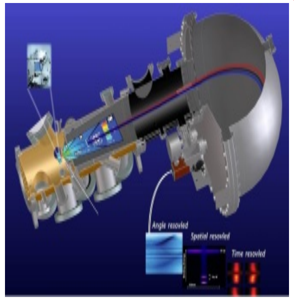
- New Battery and Solar cell materials
- Photosynthesis
- Drug discovery
- Catalysis
- ....

PES under evolution

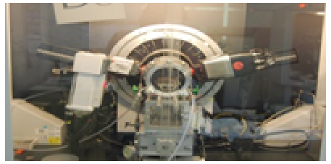
Experimental environments
: UHV → Ambient Pressure
Space
: 2D → 3D
Polarization
: →Spin resolved PES
Angle
: Angle integrated → Angle resolved
Time
: Static → dynamic

AP-XPS for in-situ and operando Science

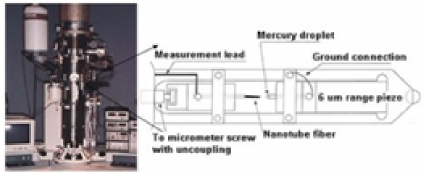
AP-XPS



in-situ XRD

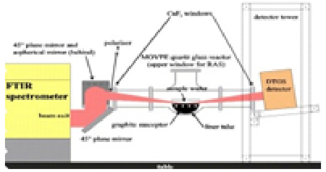


in-situ TEM

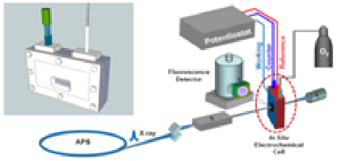


Operando
&
in-situ
Technology

in-situ FT-IR



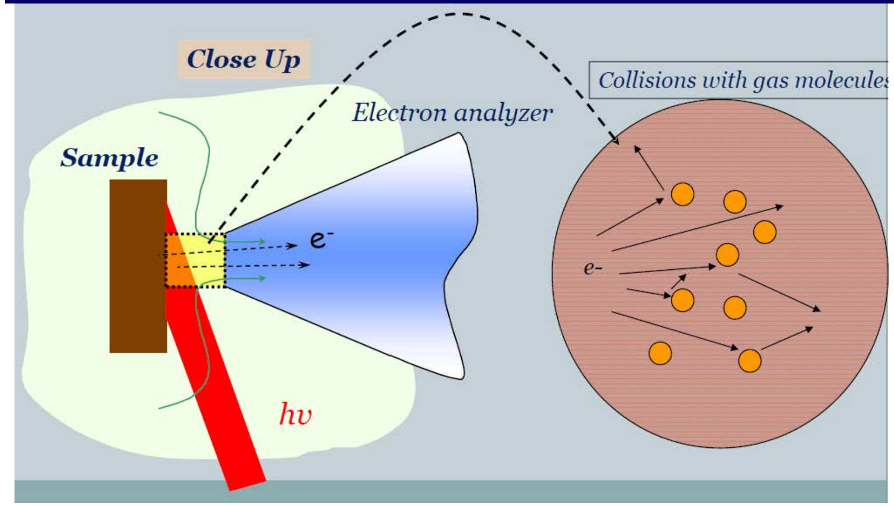
in-situ XAFS

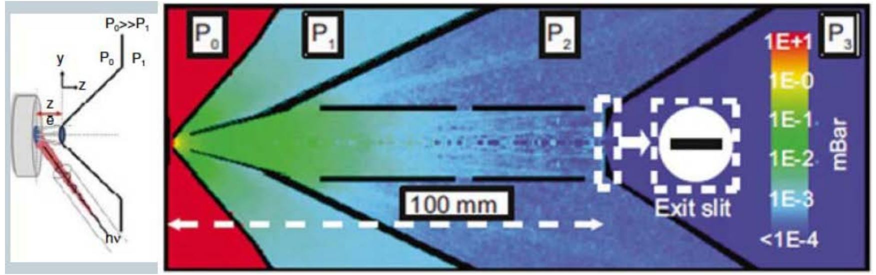


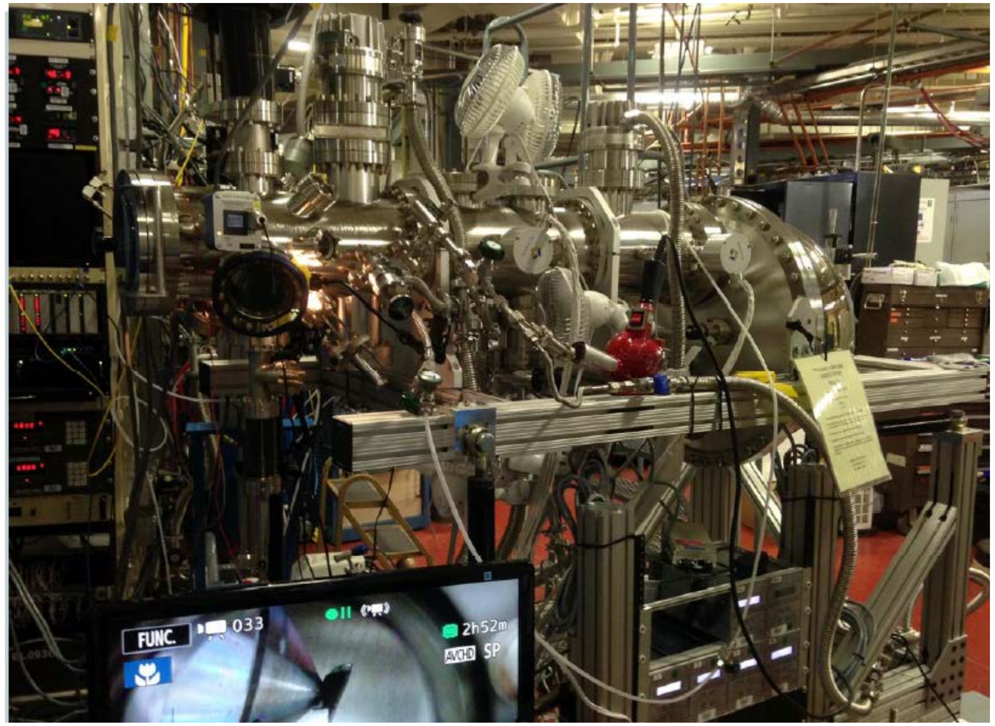
Science

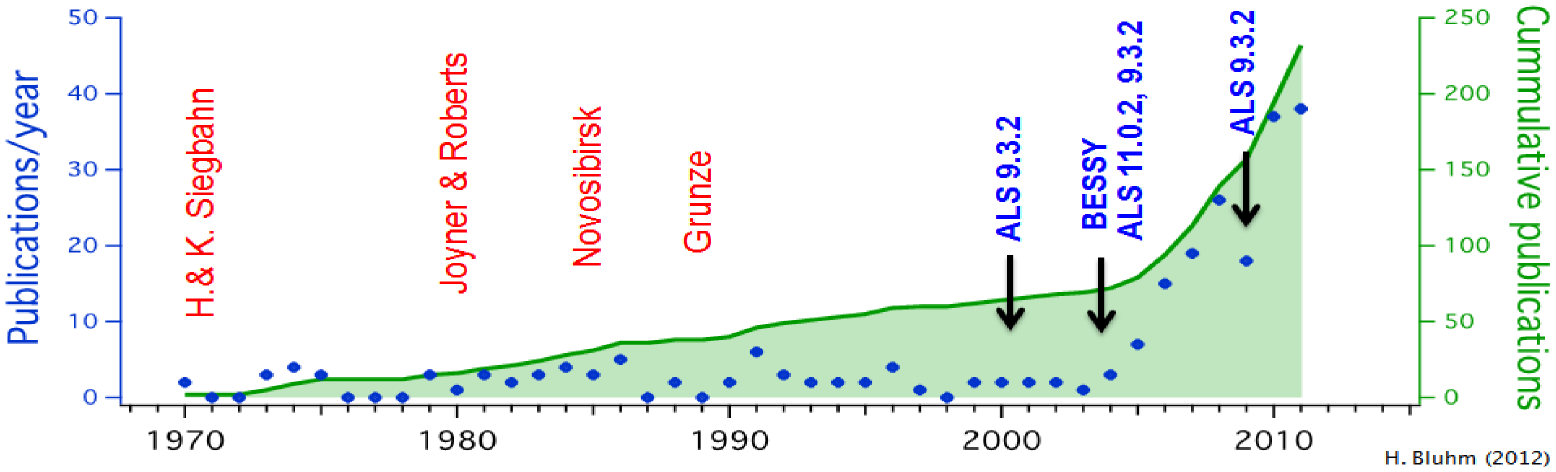
- -Physics at surface and interface
- -Catalysis,
- -Fuel cells,
- -Photovoltaic,
- -Environmental science
- -Corrosion,
- -Biological systems
- -…

Ambient Pressure X-ray Photoemission Spectroscopy

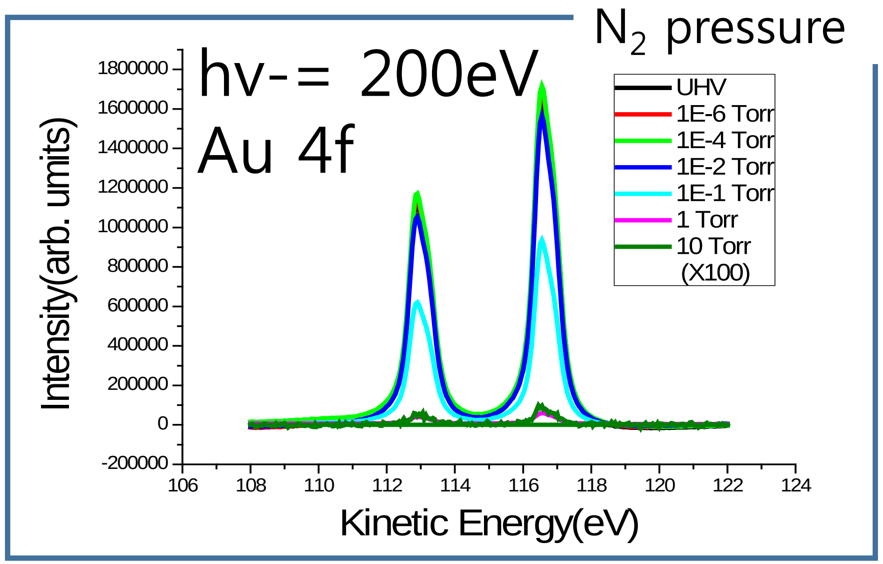


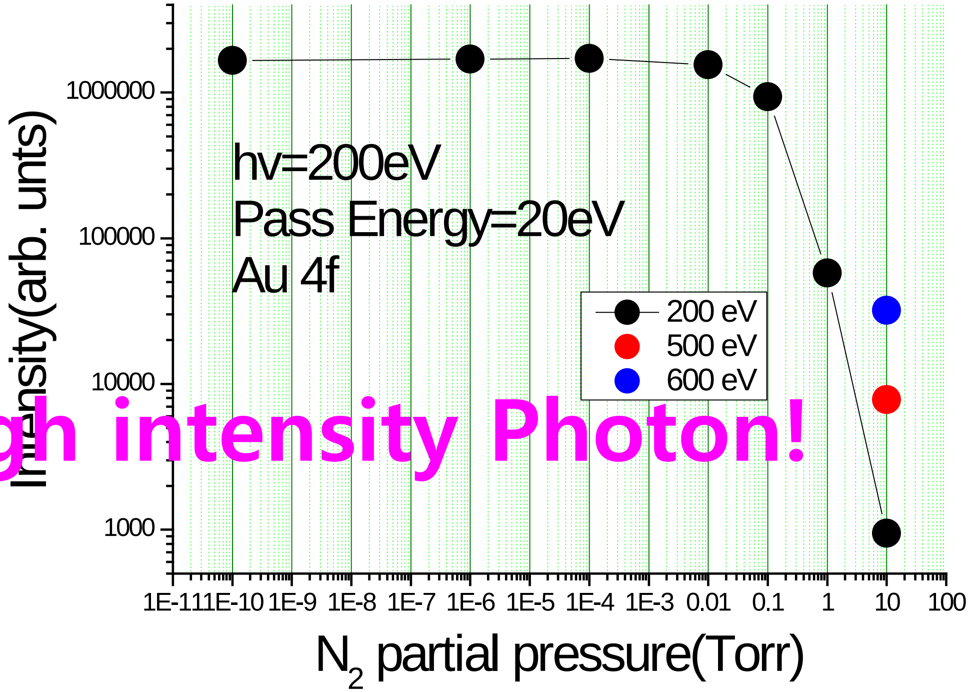


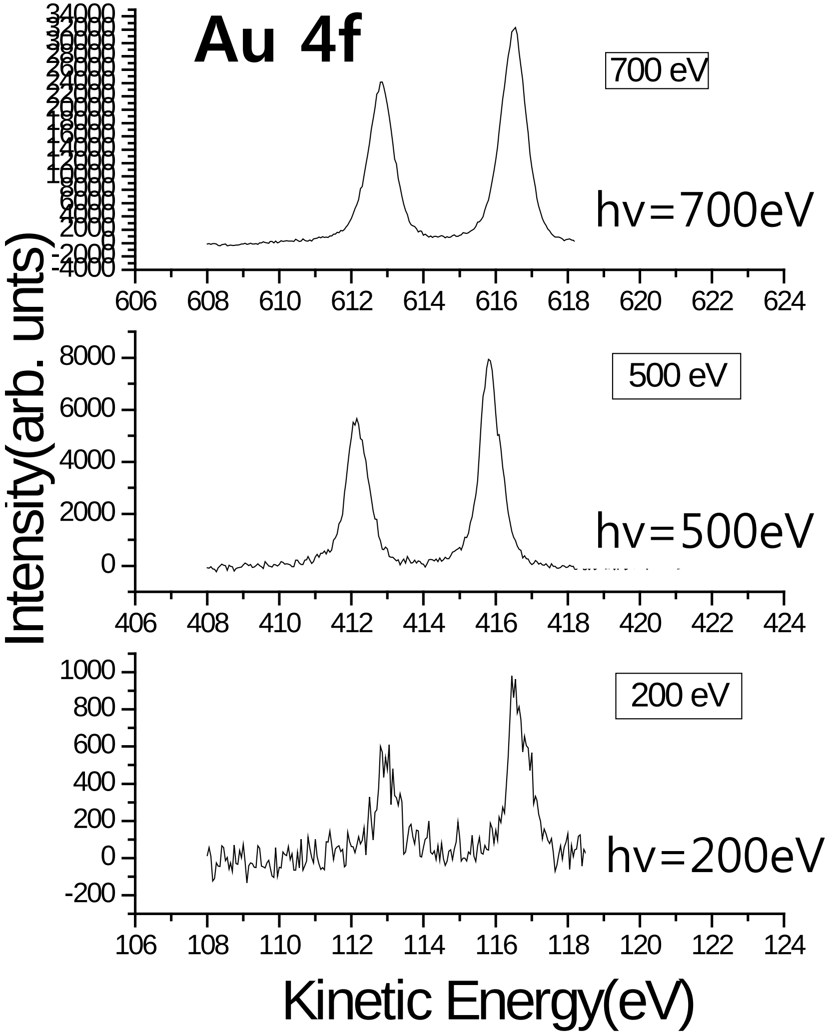




AP-XPS Exp. at TEMPO beamline







High intensity Photon!

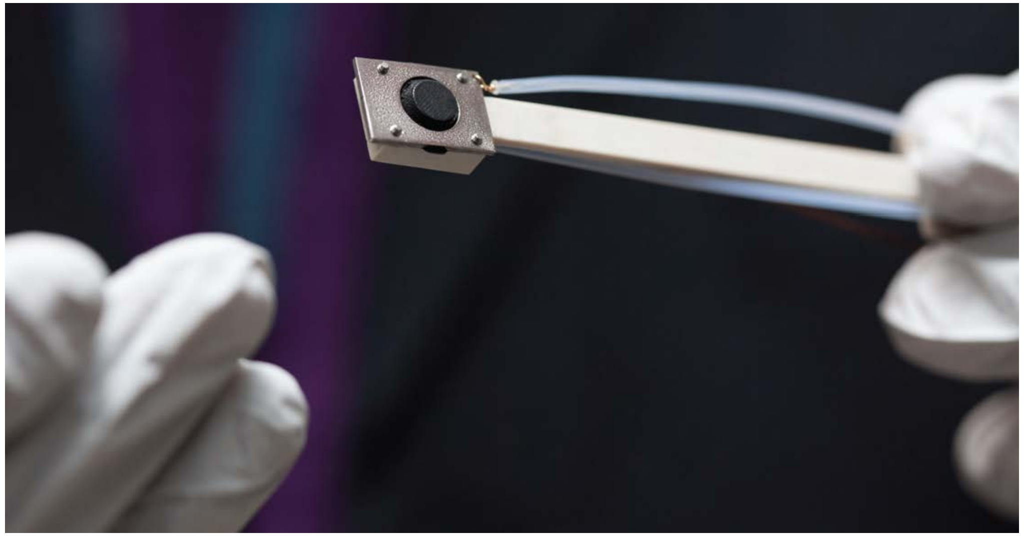
High Photon Energy!

Direct observation of the oxygenated species during oxygen reduction on a platinum fuel cell cathode

APPES

: Mimic the real world condition

Provide a closer look at the chemical bonds that form



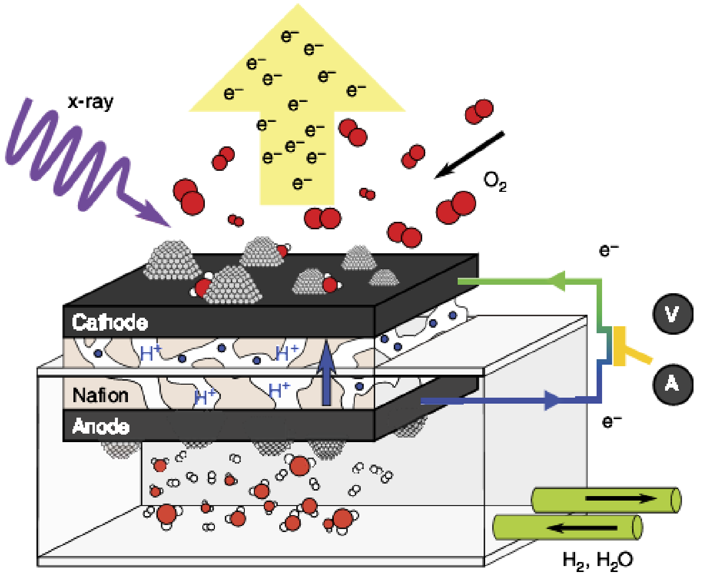
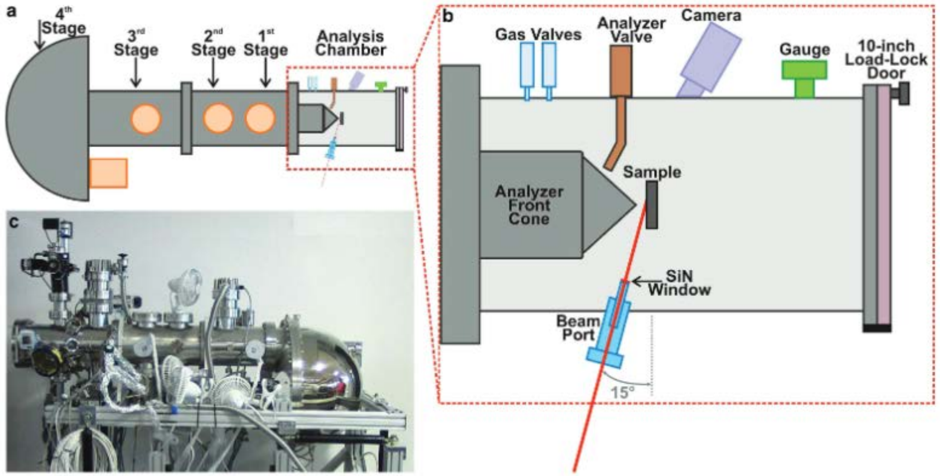
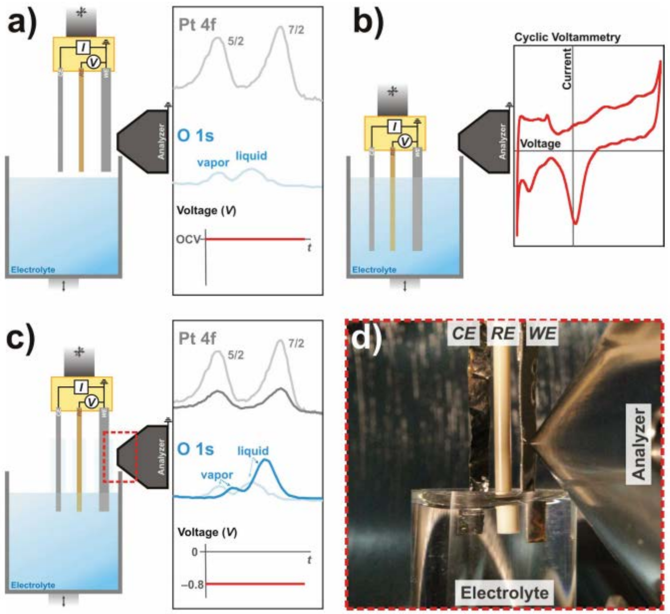


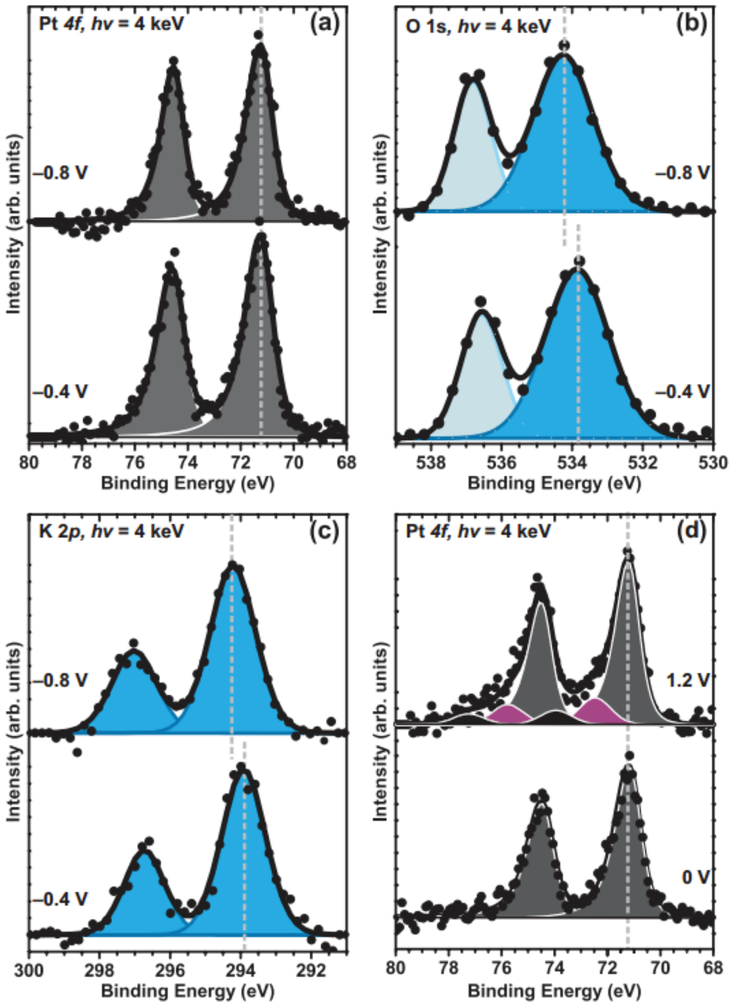
Figure 1 | Electrochemical cell for photoelectron spectroscopy. Schematic drawing of a PEM fuel cell set-up for APXPS investigations: the electrochemical cell has a Nafion membrane coated on both sides with a mixture of Nafion and carbon-supported Pt nanoparticles with catalyst loading of 4 mg cm^{-2} (particle size 10–20 nm), which serve as anode and cathode. The cathode side of the assembly was exposed to the APXPS gas cell, which was filled with oxygen gas. The anode chamber was filled with humidified forming gas (95% N_2/5% H_2, saturated H_2O). The voltmeter and galvanometer used for measurements are denoted by V and A, respectively. By connecting both electrodes to an external voltmeter or galvanometer, we can simultaneously record both XPS and either cell voltage or cell current.

H. Sanchez, H. Ogasawara et. al., Nat. com. (2013)

Using “Tender” X-ray Ambient Pressure X-Ray Photoelectron Spectroscopy as A Direct Probe of Solid-Liquid Interface



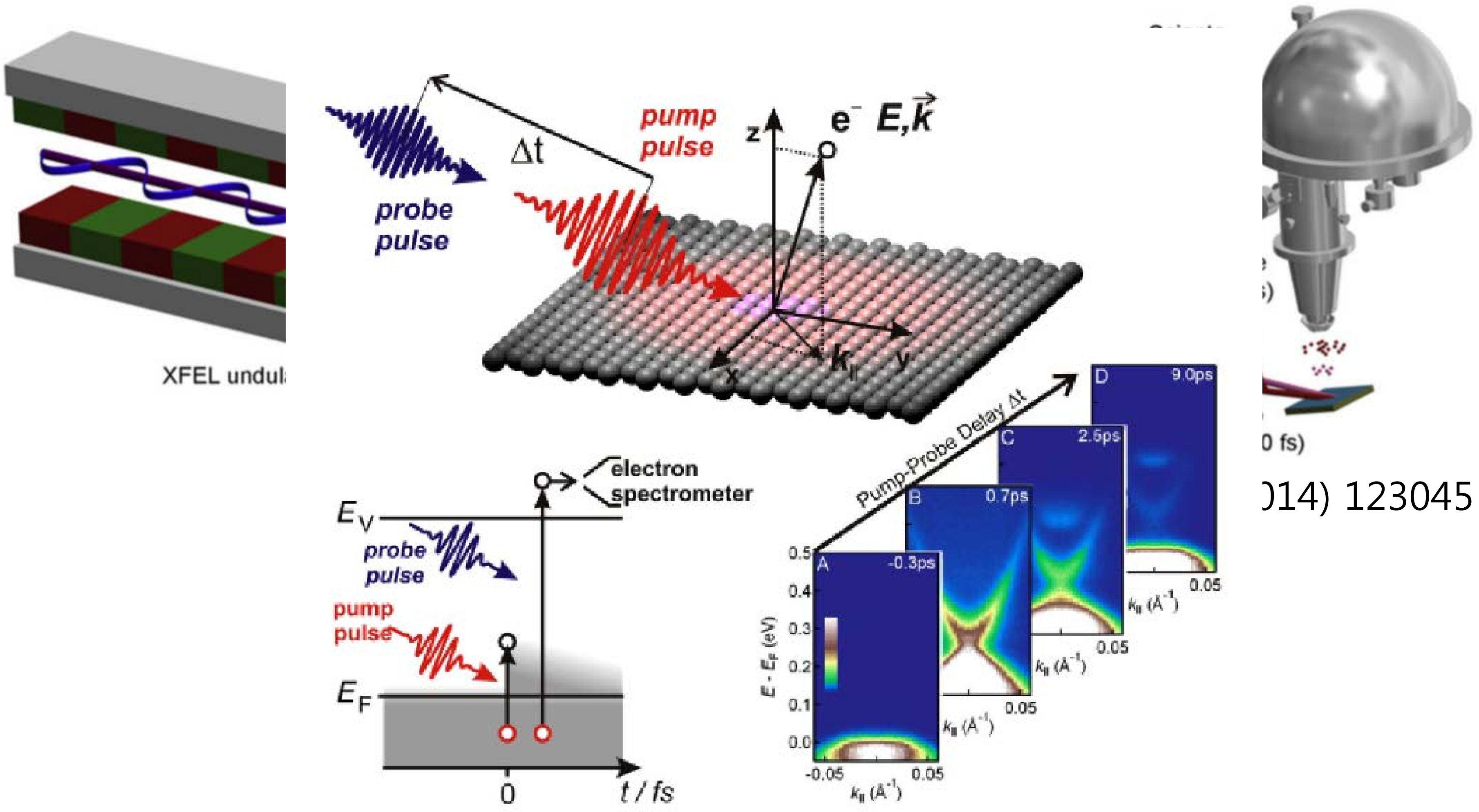




Dip and pulled methods

X. Axananda, et al., Scientific Reports(2015)

tr-(HAX)PES



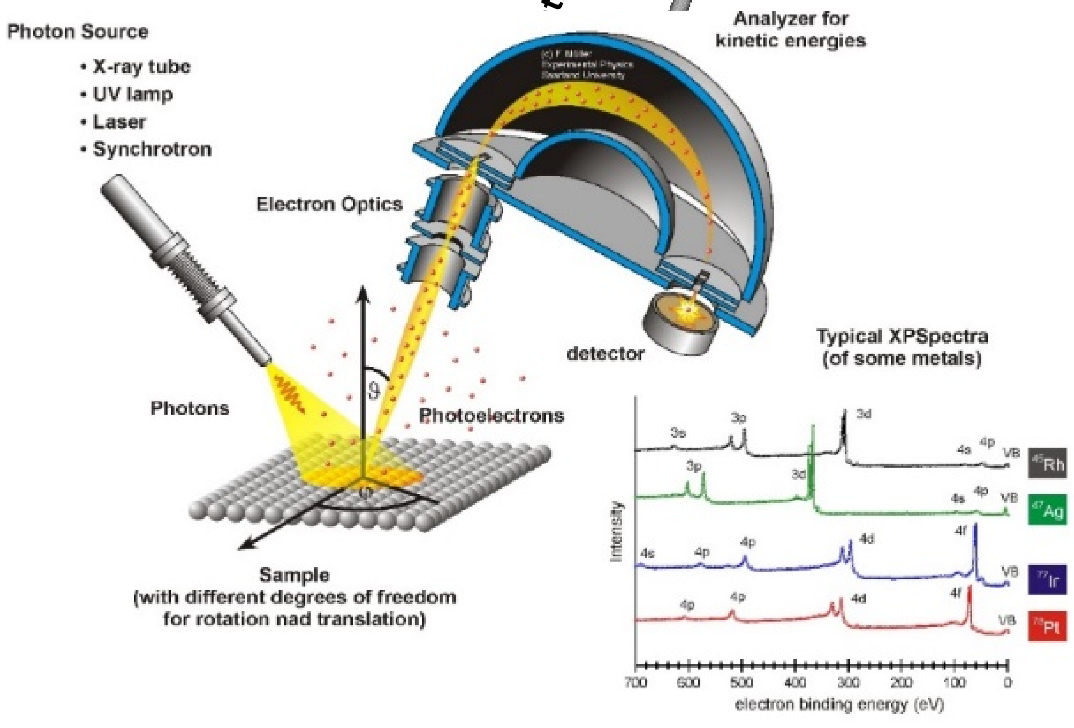
XFEL undul
probe pulse
Δt
pump pulse
z
e⁻ E,k
x
y
k∥
electron spectrometer
E_V
probe pulse
pump pulse
E_F
0
t / fs
Pump-Probe Delay Δt
A -0.3ps
B 0.7ps
C 2.5ps
D 9.0ps
E - E_F (eV)
k∥ (Å⁻¹)
0 fs)
)14) 123045

Science examples

8A2 High-Resolution Photoemission Spectroscopy (HR-PES) Beamline

Aim

- Adequate for surface and material science.
- PES and NEXAFS
- Easy to experiments.
- Good data quality.



Beamline Specification

Light Source

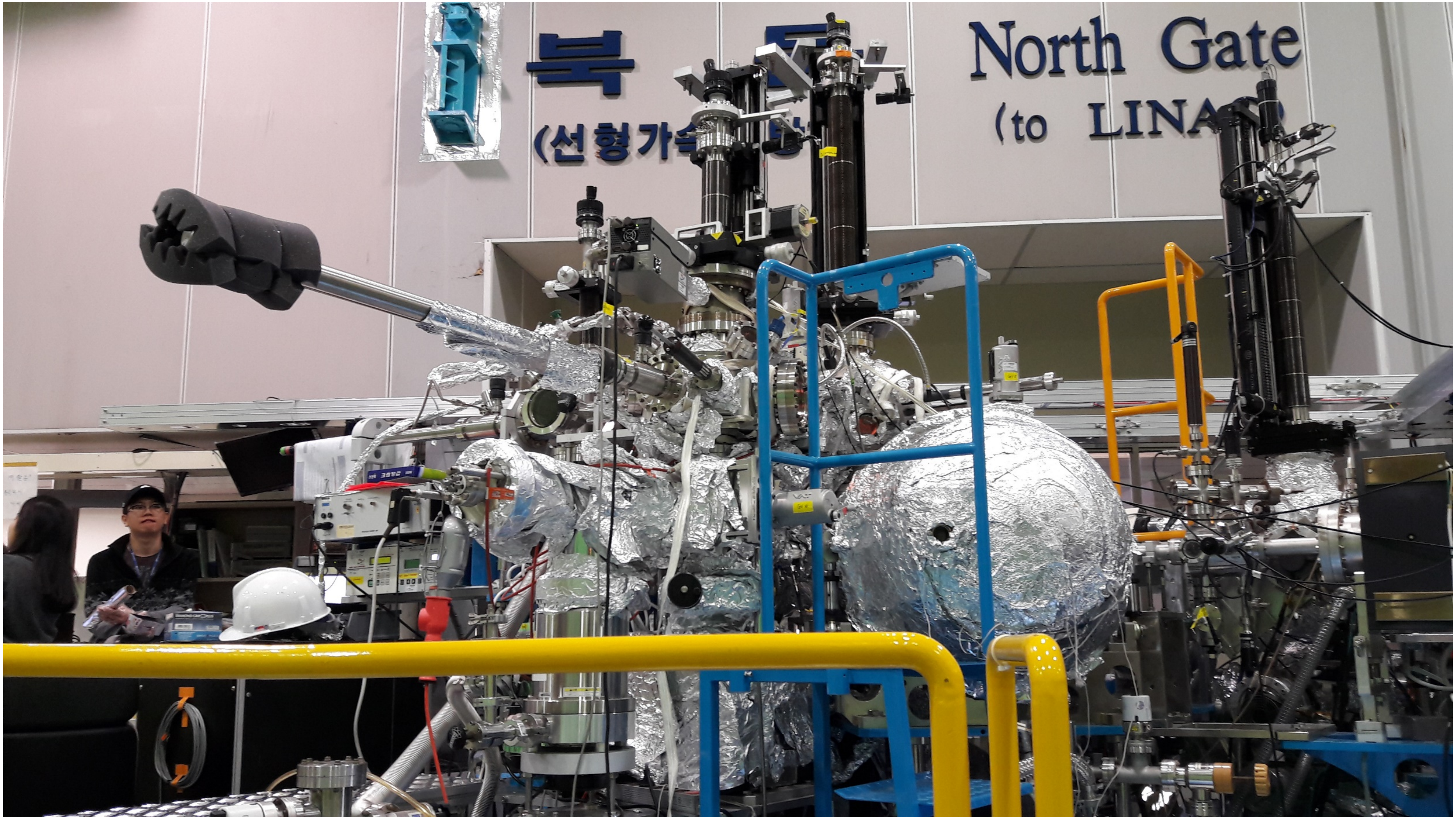
- Type : Undulator U6.8
- 1st harmonics at 3 GeV: 60 ~ 1000 eV

Photons at Sample

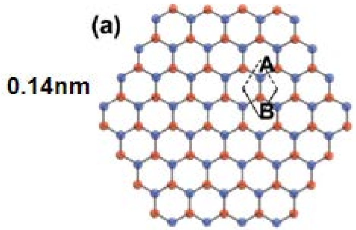
- Energy rnge: 100 ~ 1600eV
- Energy Resolution : E/ΔE ≥ 5000
- Photon Flux : >10^{11} photons/sec
- Beam size : 300 μm x 300 μm

Equipments

- Electron analyzer(Sceinta 2002).
-Partial electron yield (PEY) detector for NEXAFS.
-Low energy electron diffraction(LEED)
- Electron gun (Omicron).
-Ion gun(PSI 3000).
- Residual Gas Analyzer(RGA)
- Sample Heating up to 2000 °C
- Sample cooling system using LN_2
-Base pressure of main chamber : ~1 x 10^{-10} Torr.


북
North Gate

Functionalization of graphene

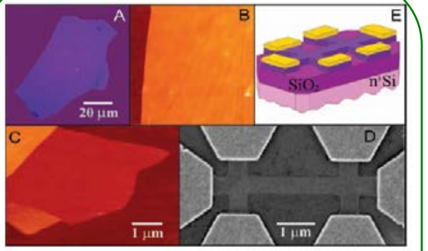


P. Avouris
Nano. Lett. 10 4285(2010)

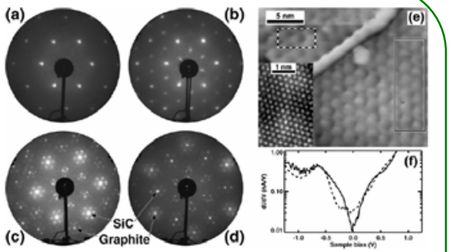
Issues

Band gap control
Inertness
→ Functionalize

Uniform Graphene and mass production



K. S. Novoslov, et al.,
Science 306, 666(2004)



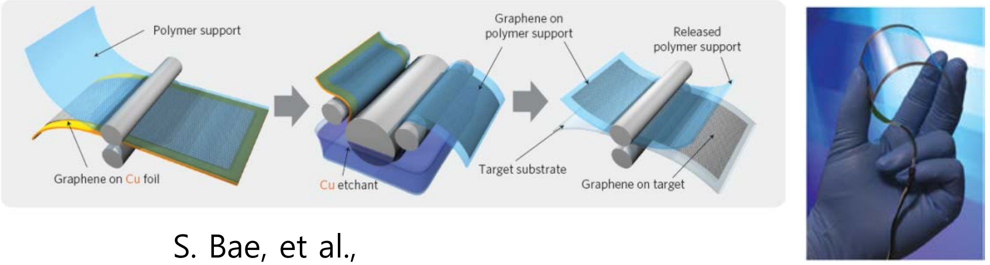
C. Berger et al.,
J. Phys. Chem. B, 108, 19913(2004).

Interest

→Surface modify and probing its electrical property changes!

Organic molecules
Photon
Electron, Ion….
Gases, Metals

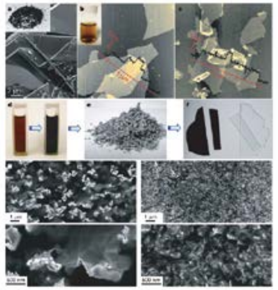
…..



S. Bae, et al.,
Nature Nanotech. 5, 574 (2010)

We……

→ Characterize the surface properties.
→ Growth geometry of Graphene on SiC.
→ Functionalize the Graphene surface.

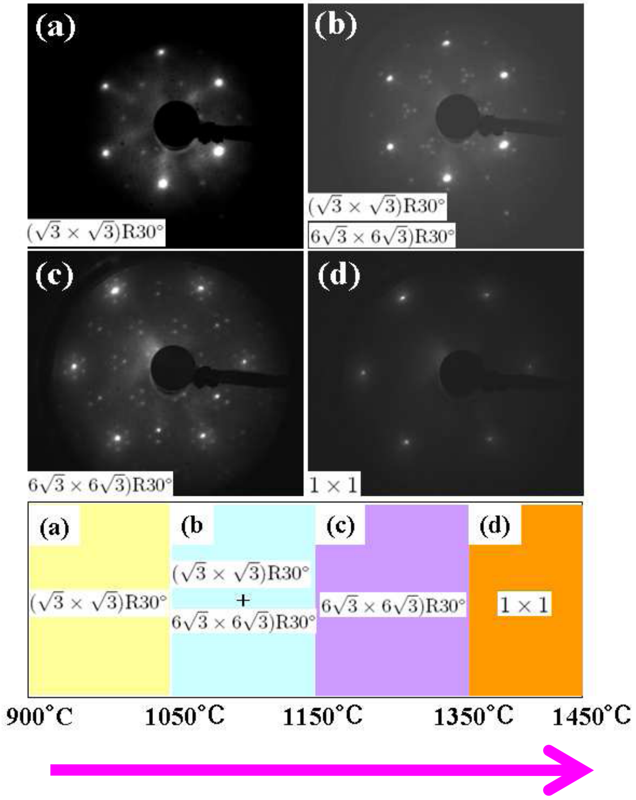


S. Stankovich, et al.,
Nature,442,282(2007)

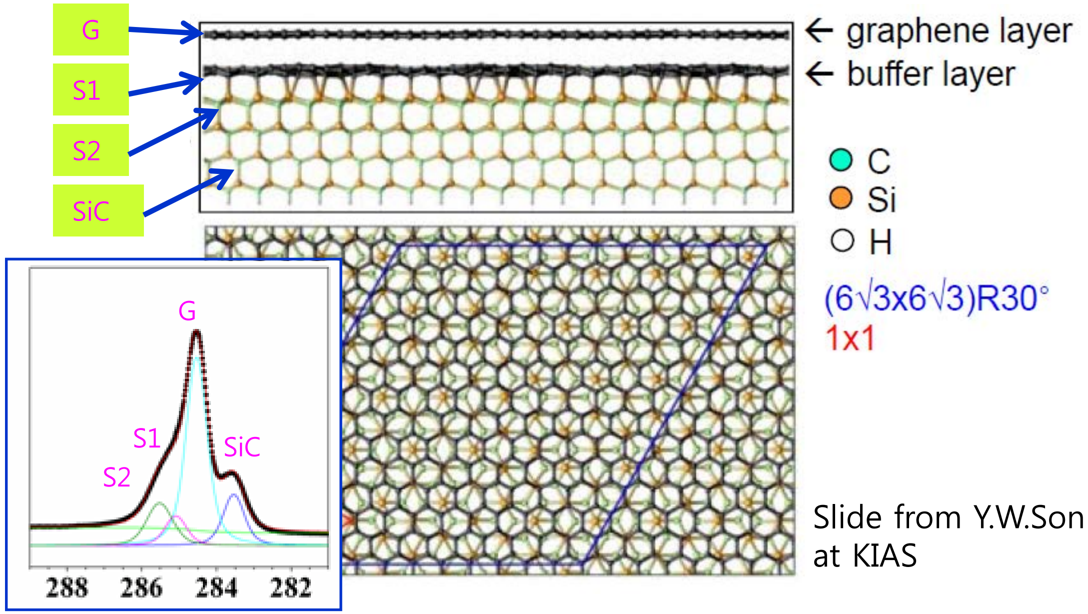
Graphene on SiC

Surface reconstruction

LEED

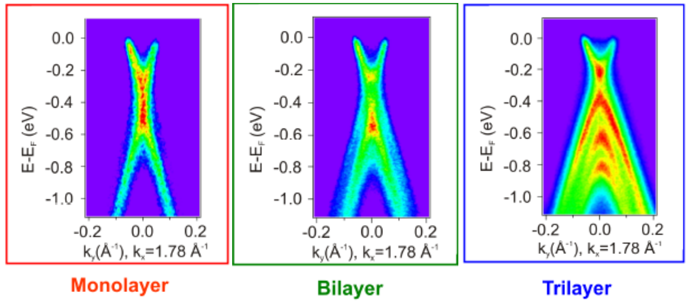


Model structure of Graphene/SiC

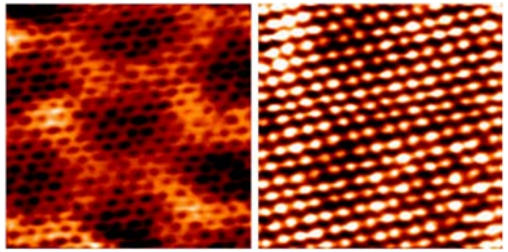


Slide from Y.W.Son at KIAS

ARUPS



STM



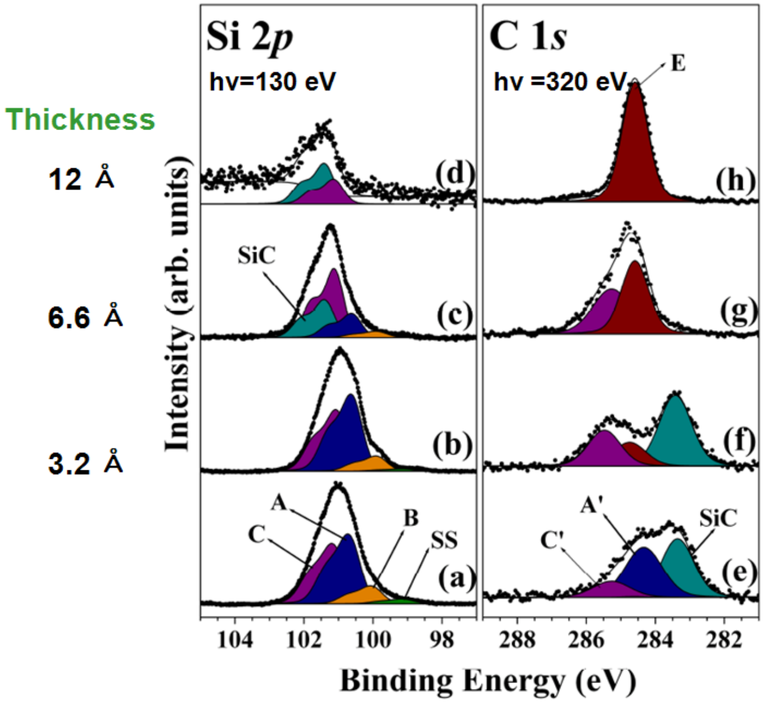
Monolayer Multilayer

K. J. Kim, et. Al.

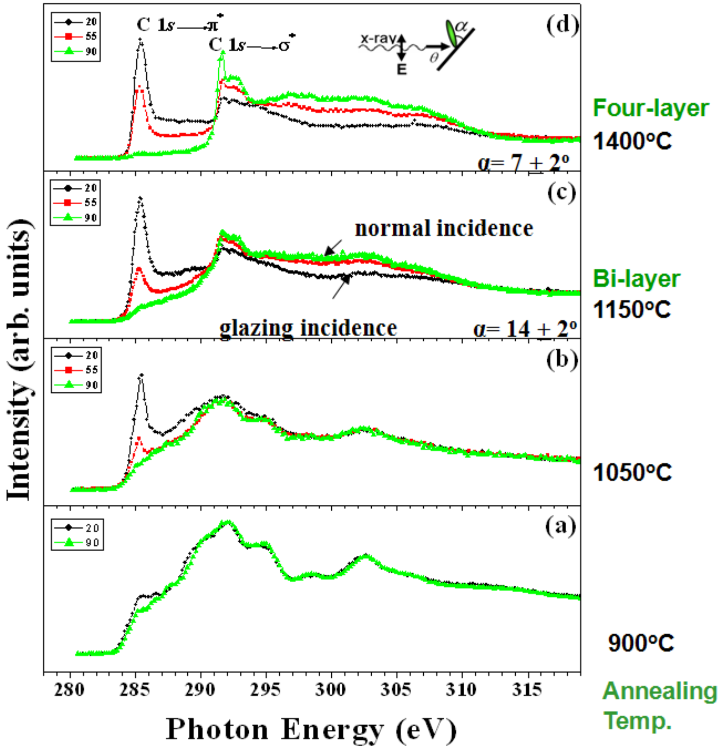
J. Phys.: Condens. Matter 20 (2008) 225017

Surface change of 6H-SiC(0001) upon a thermal treatments

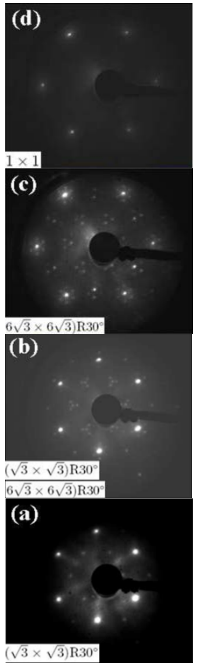
PES



NEXAFS



LEED



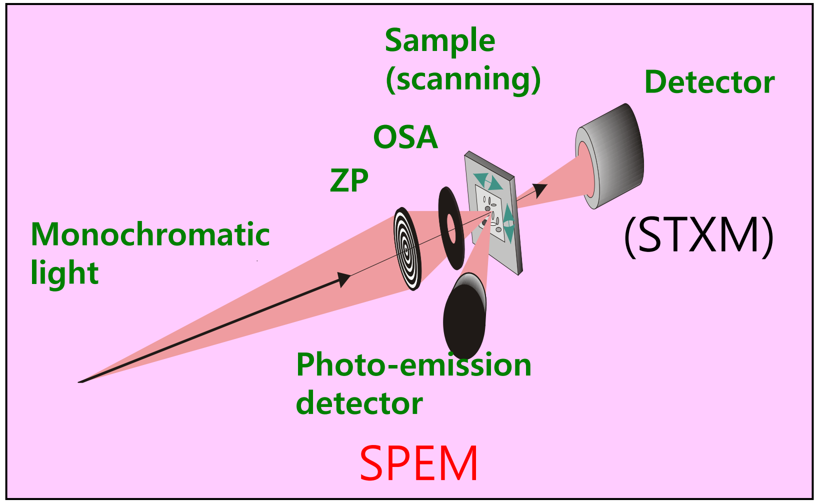
-The tilting angle of the graphene sheet was estimated to be 14±2° at 1150°C. As the thickness of the graphene layers increased, this angle gradually decreases to 7±2° at 1400°C.

- The existence of the interface influenced more on the thin layer than on the thick layer.

K.J.Kim, et al.,
J. Phys.: Condens. Matter 20 (2008) 225017

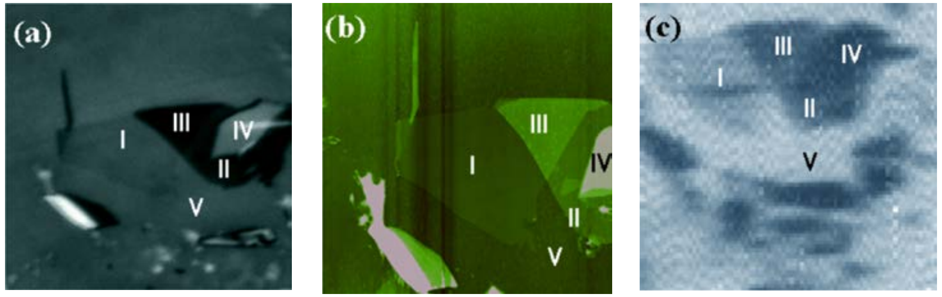
Chemical Image of Graphene Flakes

Photoemission Spectroscopy
⊗
Microscopy



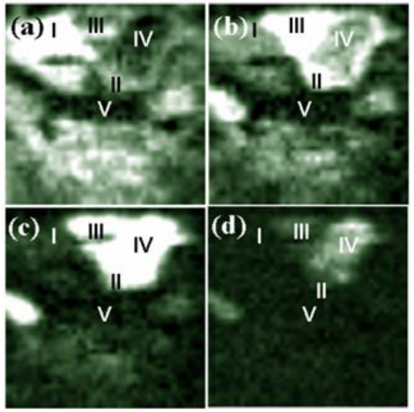
SPEM
- Spatially resolved elemental and chemical mapping.
- Chemical information of the local area of the surface.

Graphene Sheets on SiO_2

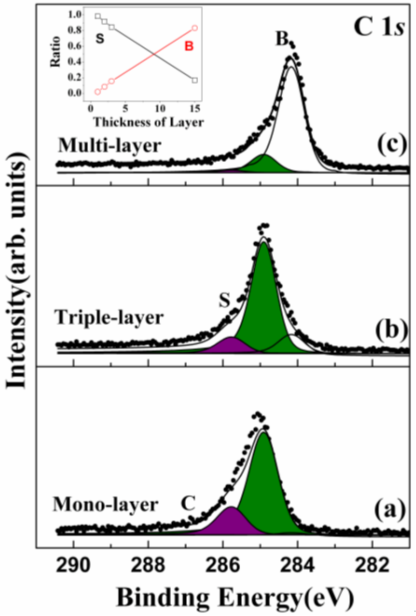


Optical Microscope | AFM | SPEM

I: Monolayer,
II: Double-layer,
III: Triple-layer
VI: Multilayer,
V: SiO_2 substrate

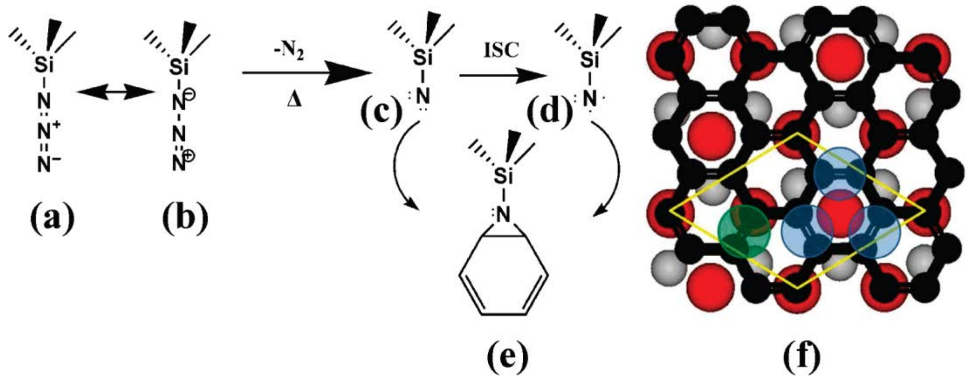


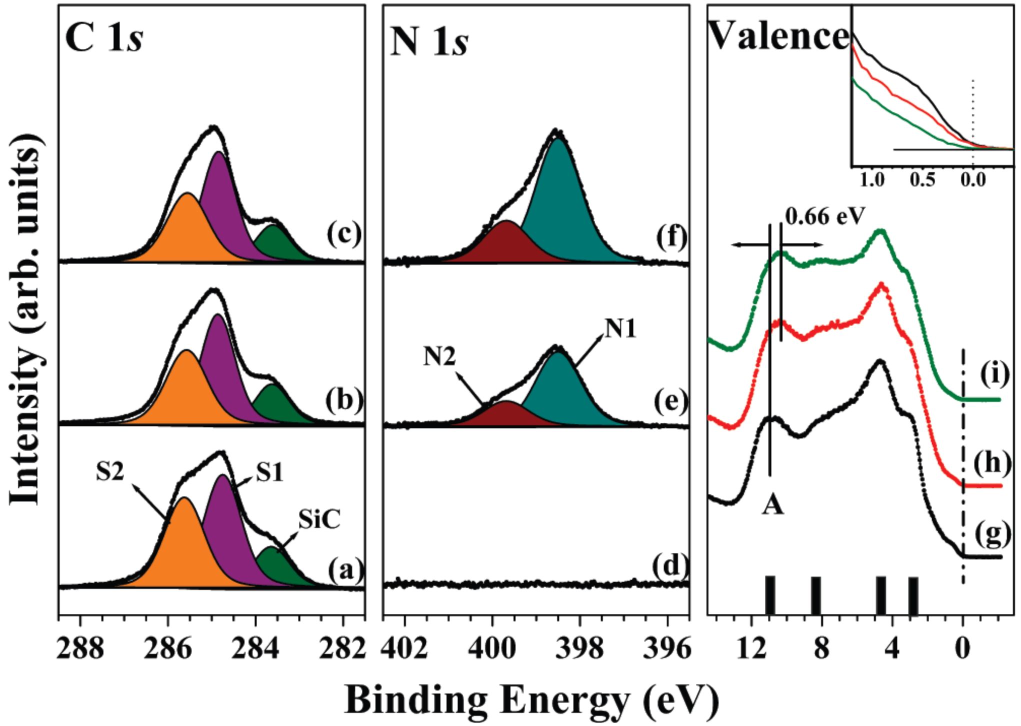
Binding energy of
(a) 285.2, (b) 284.8,
(c) 284.4, and (d) 284 eV



K. J. Kim et al., Adv. Mat. 2008

Chemical Modification of Epitaxial Graphene by Azidotrimethylsilane





- Thermally generated nitrene radicals adsorb on EG

- N 1s peaks due to the adsorption of nitrene at two different adsorption sites in the interface layer

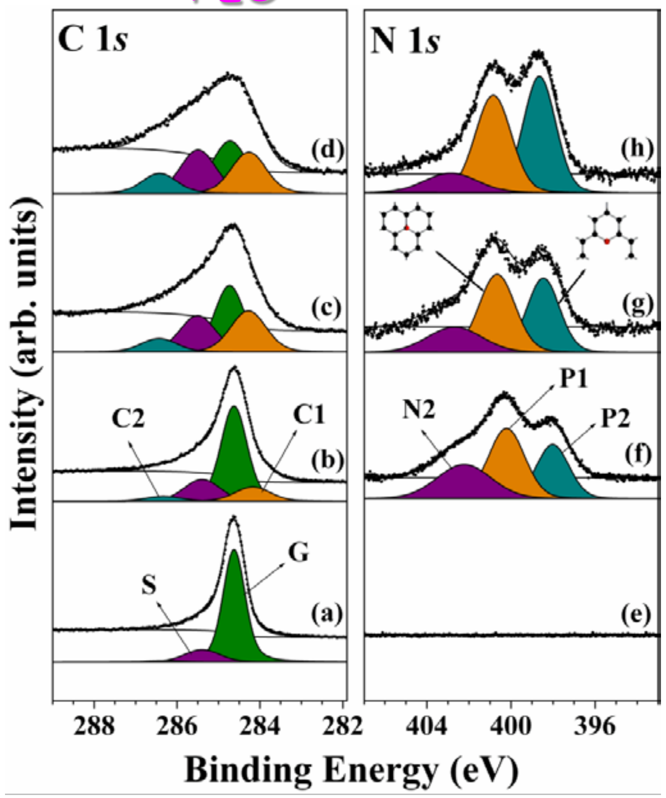
- Gap opening with the increase in the coverage of ATS from valence band spectra -> adsorption on graphene

C 1s , N 1s core-level spectra and Valence band spectra
(a), (d), and (g) 0.5 ML of graphene
(b), (e), and (h) ATS deposition (7200 L) at 100 °C,
(c), (f), and (i) 36 000 L at 100 °C.

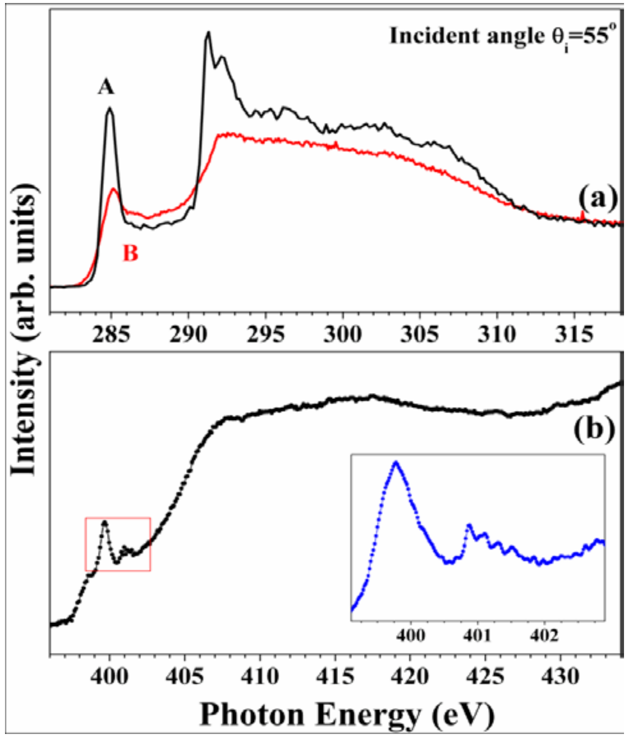
J. Choi et al. *J. Phys. Chem. C* 113 9433-9435 (2009)

Surface composition change after N_2^+ ion doping on 4-layer Graphene

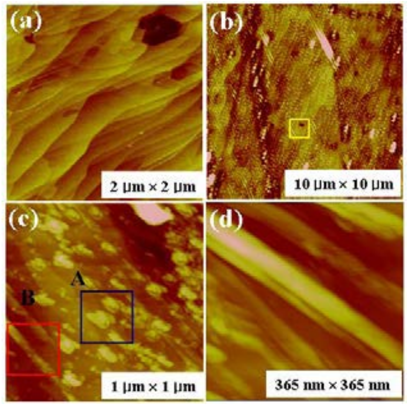
PES



NEXAFS



AFM



- After N_2^+ ion beam(E_{ion}=100 eV) irradiation on graphene

: C=C π* was decreased.

N_2, Pyridine-like, Graphite-like species were appeared.

Layer structure was destroyed.

K. J. Kim, et. al.,
J. Phys.: Condens. Matter 22 045005(2010)

Morphological changes in the surface structures by Nitrogen Ion

❖ **Graphene/SiC**

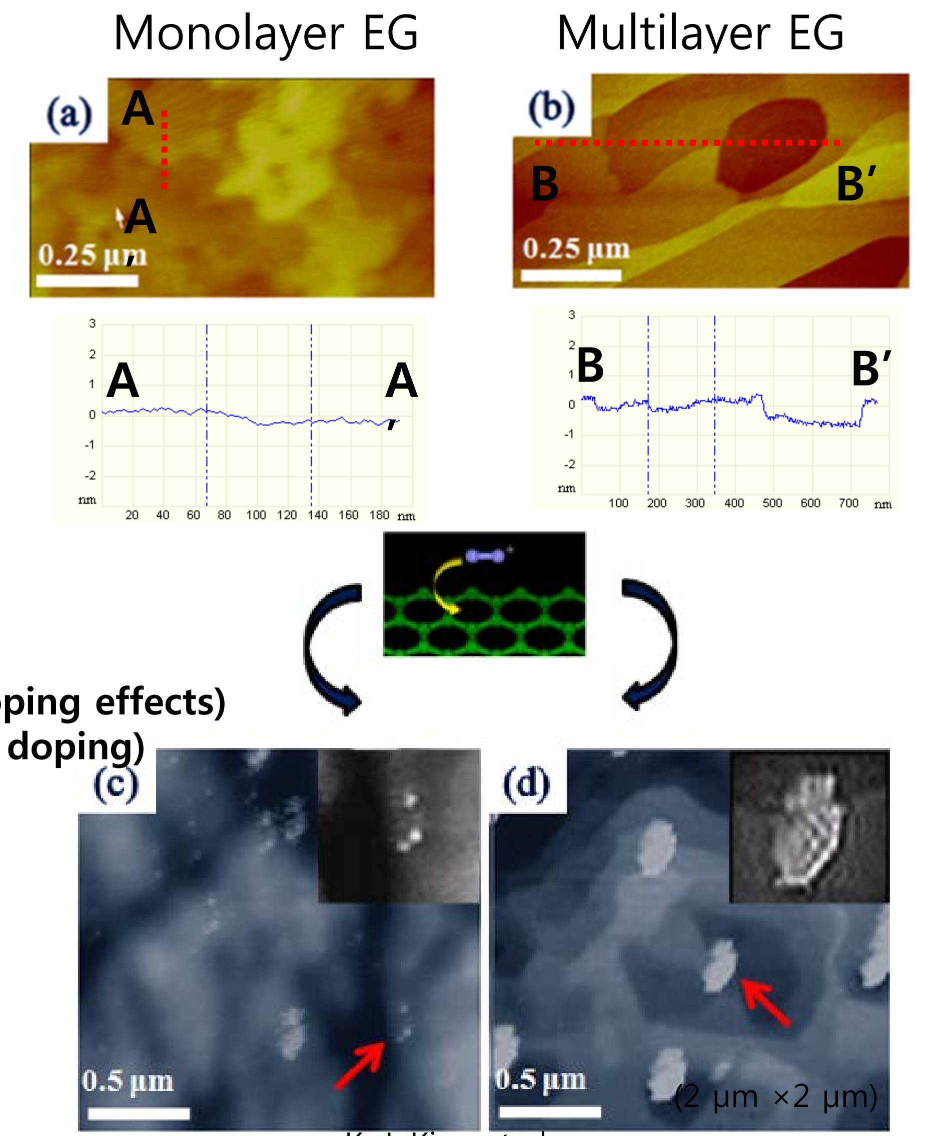
- Hydrogen plasma treatments
- Si flux at 900 °C
- Annealin…

What happen after annealing?

- Irradia… …n

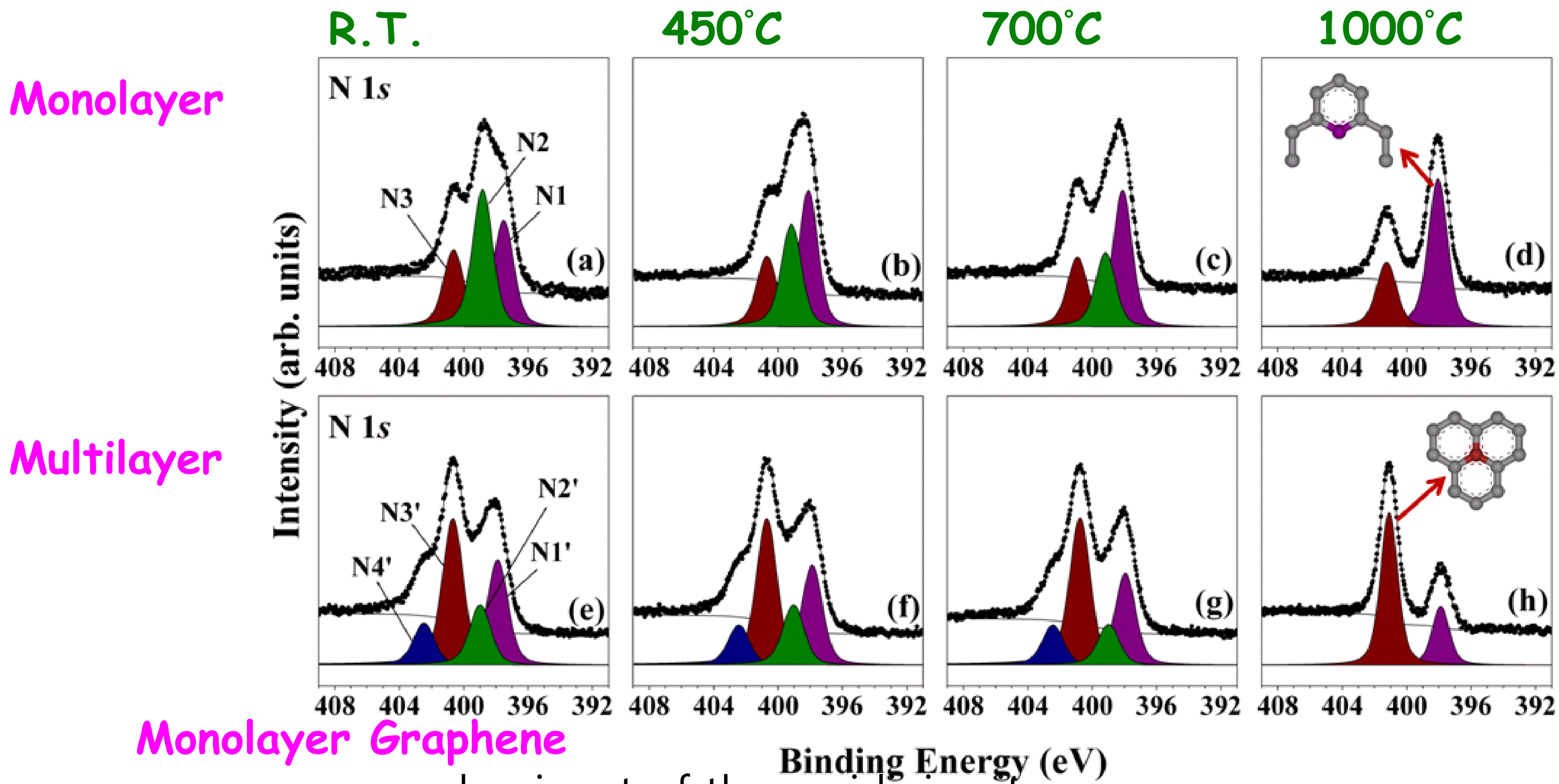
❖ **After 1000 °C for 2 minute**

- Mono. Graphene : pyridinic nitrogen (no doping effects)
- Multi. Graphene : graphitic nitrogen(n-type doping)



K. J. Kim, et al.,
J. Phys. Chem. C , 117 , 2129-2134 (2013)

N 1*s* CLPES spectra measured at photon energy of 500 eV.



Monolayer Graphene

; dominant of the pyridinic nitrogen

p-type doping property, $\phi_{N2\ on\ mG}$ ~ 4.34 eV

Multilayer Graphene

; dominant of the graphytic nitrogen

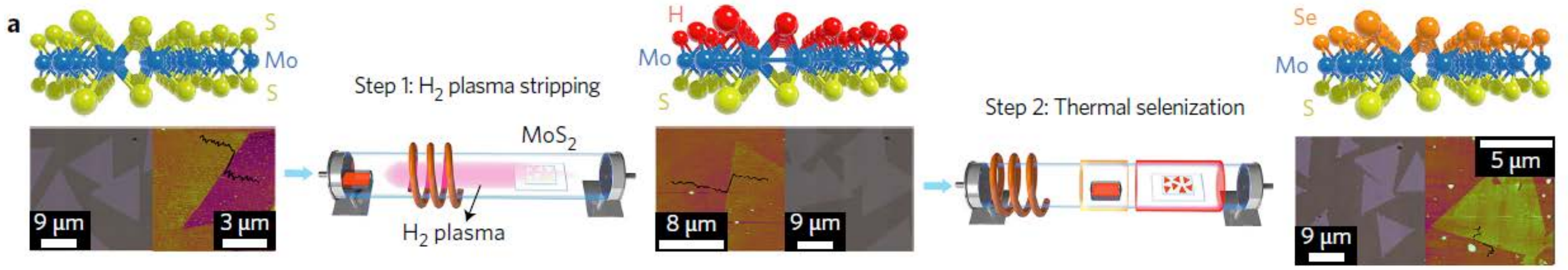
n-type doping property, $\phi_{N2\ on\ MG}$ ~ 3.93 eV

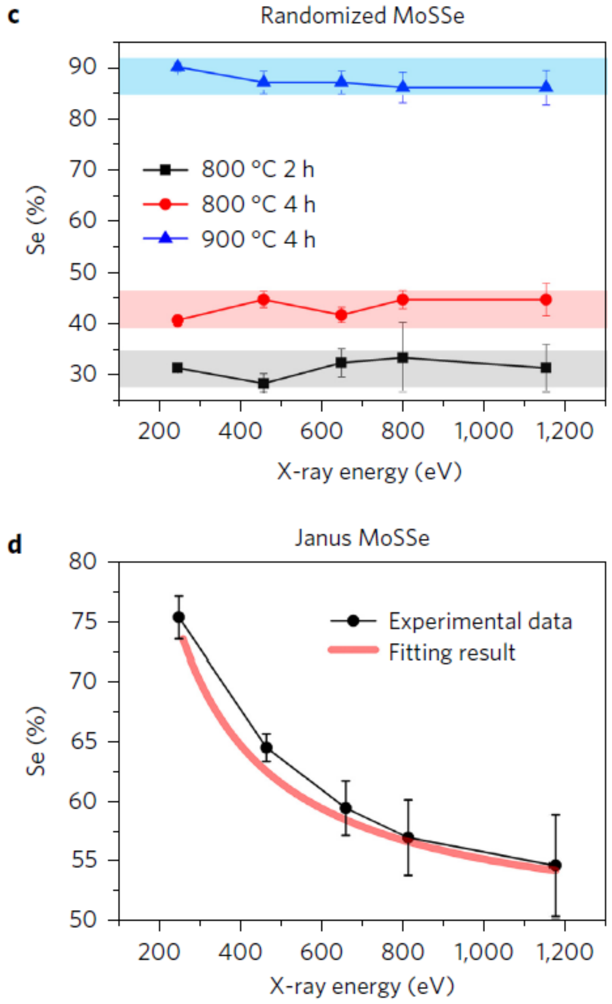
K. J. Kim, et al.,
J. Phys. Chem. C , 117 , 2129-2134 (2013)

Janus monolayers of transition metal Dichalcogenides(MoSSe)

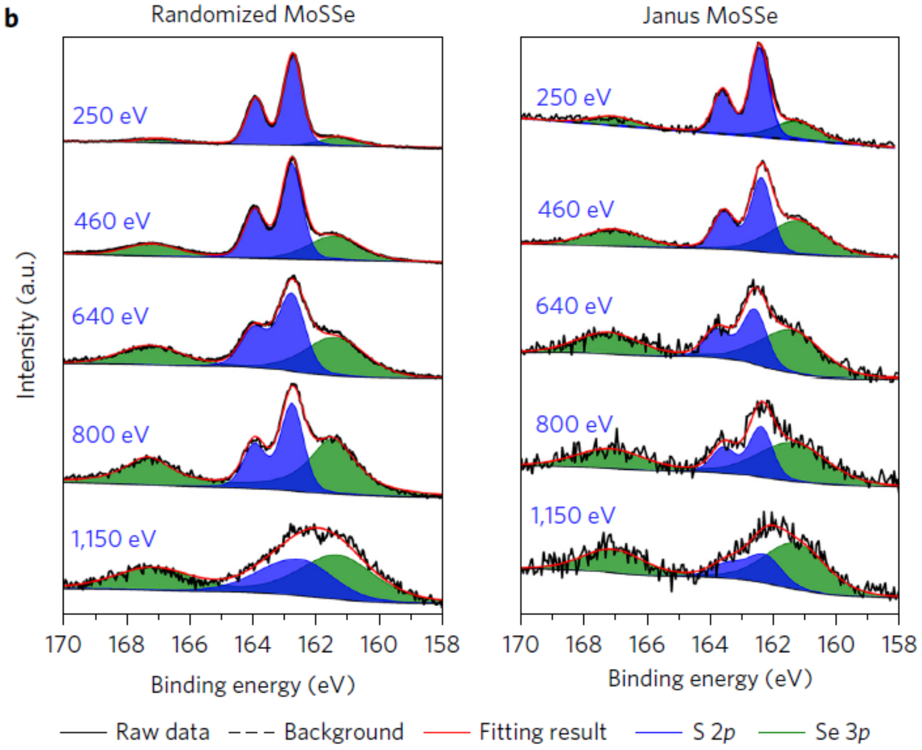
Transition metal dichalcogenide monolayers
: semiconductors with intrinsic in-plane asymmetry,
: leading to direct electronic bandgaps, distinctive optical properties
: great potential in optoelectronics

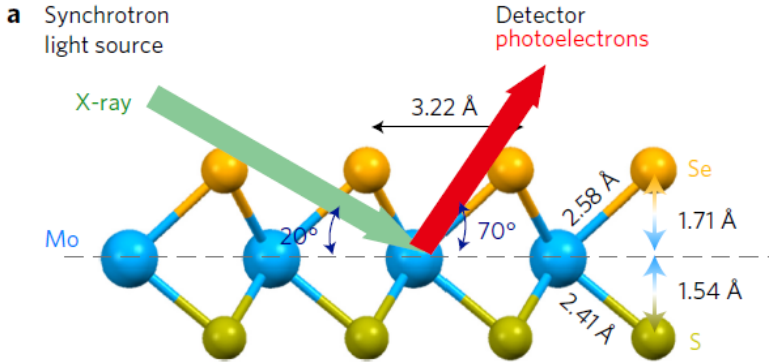
Spin manipulation





Energy-dependent X-ray photoelectron spectroscopy





Nature Nanotech.(May 2017)
DOI: 10.1038/NNANO.2017.100

Summary

✓ Photoemission Spectroscopy

→ A unique tool to understand the electronic and chemical structure at surface and interface

$$E_{kin} = h\nu - \phi - |E_B|$$

$$\mathbf{p}_{\|} = \hbar \mathbf{k}_{\|} = \sqrt{2mE_{kin}} \cdot \sin\vartheta$$

- Elemental identification
- Atomic concentration
- Chemical environment
- Atomic structure
- Band structure

  Symmetry of electronic state (polarization)

✓ Evolution of PES

Experimental environments
- **UHV → Ambient Pressure**

Space
- **2D → 3D**

Polarization
- **→Spin resolved PES**

Angle
- **Angle integrated → Angle resolved**

Thank you for your attentions!