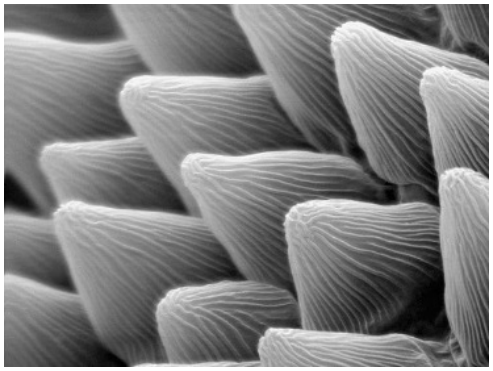
XPS & Scanning Auger Principles & Examples

Shared Research Facilities Lunch Talk

Contact info: Sidhu Pujari & Han Zuilhof
Lab of Organic Chemistry
Wageningen University

E-mail:
Sidharam.Pujari@wur.nl
Han.Zuilhof@wur.nl

Surface Properties are Crucial

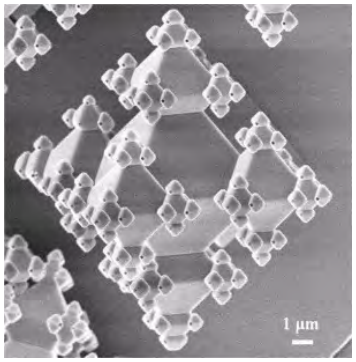


Effects of miniaturization:

If size ↓, then: surface area/volume ↑

⇒ In micro/nanometer-sized objects:
control over surface properties is ‘everything’

Surface determines: - wettability
- chemical inertness/catalysis
- sticking behavior
- density of (bio-)active groups
- presentation of (bio-)active groups

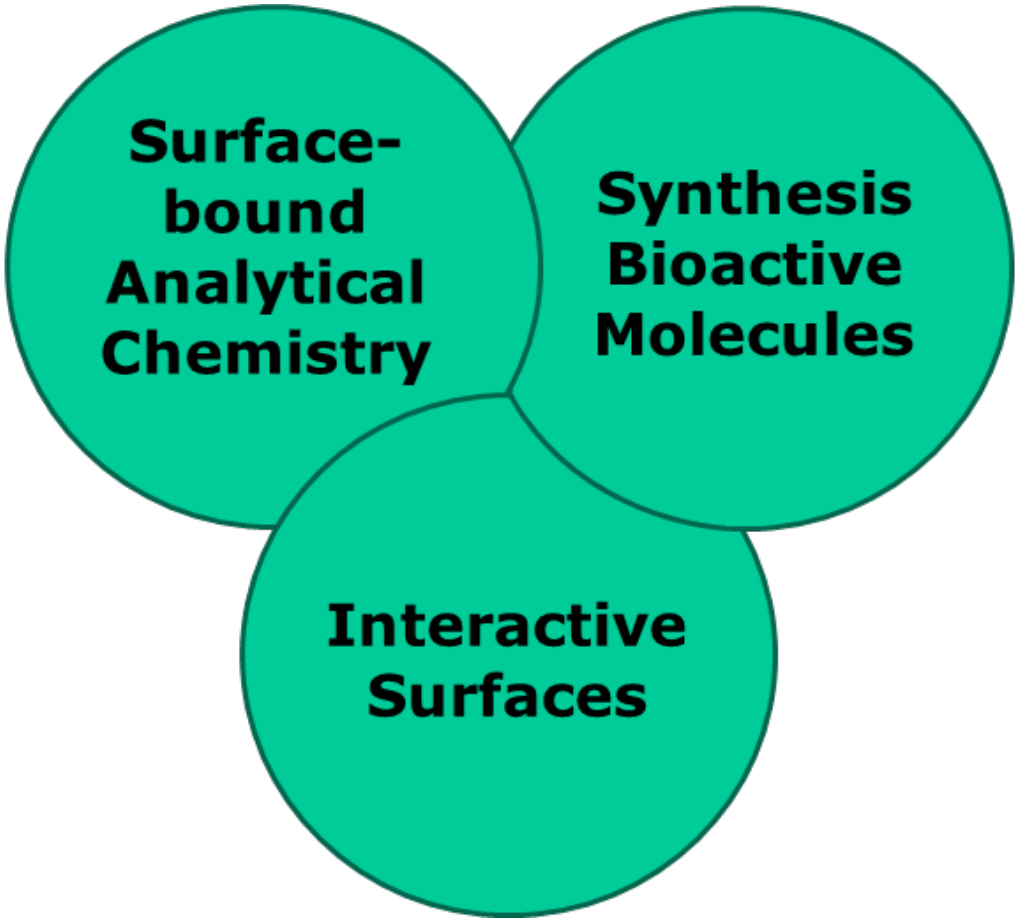


(>80% of all biological reactions take place @ surface!)

Research Focus of Chair Group Organic Chemistry

Bio-organic Surface Chemistry

Surface-bound biological moieties find increasing use – however, resulting surfaces are highly complex



X-Ray Photoelectron Spectroscopy & Scanning Auger Microscopy

XPS & SAM are surface analysis techniques.
Sampling depth: ca. 10 nm & ca. 3 nm, respectively.

Information provided:

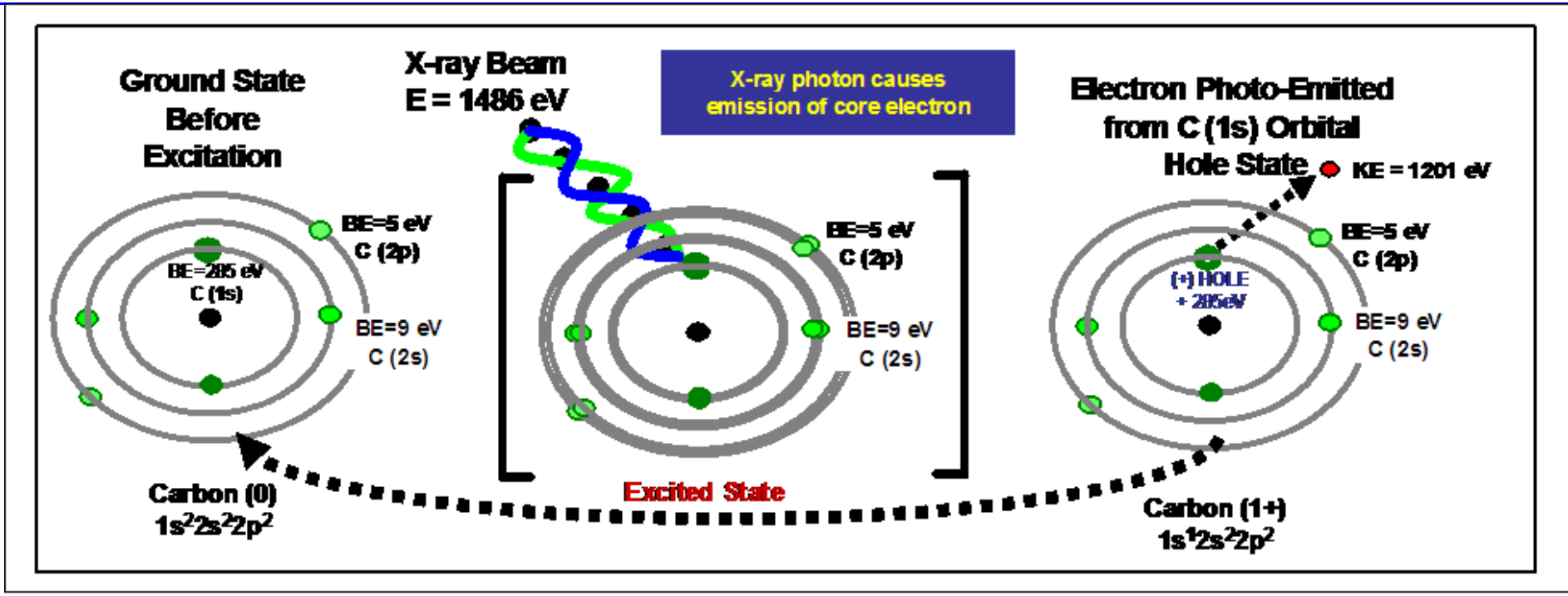
1) Surface composition in terms of elements
2) Some more info on chemical environment
3) Mapping: elemental composition in x-y direction (to some degree: z direction)
4) Thickness of layer

Biggest differences:

Penetration depth (XPS probes deeper; SAM more 'surface-sensitive')

Lateral resolution (SAM < 30 x 30 nm; XPS more 30 x 30 μm XPS more chemical info)

X-Ray Photoelectron Spectroscopy
The Basics

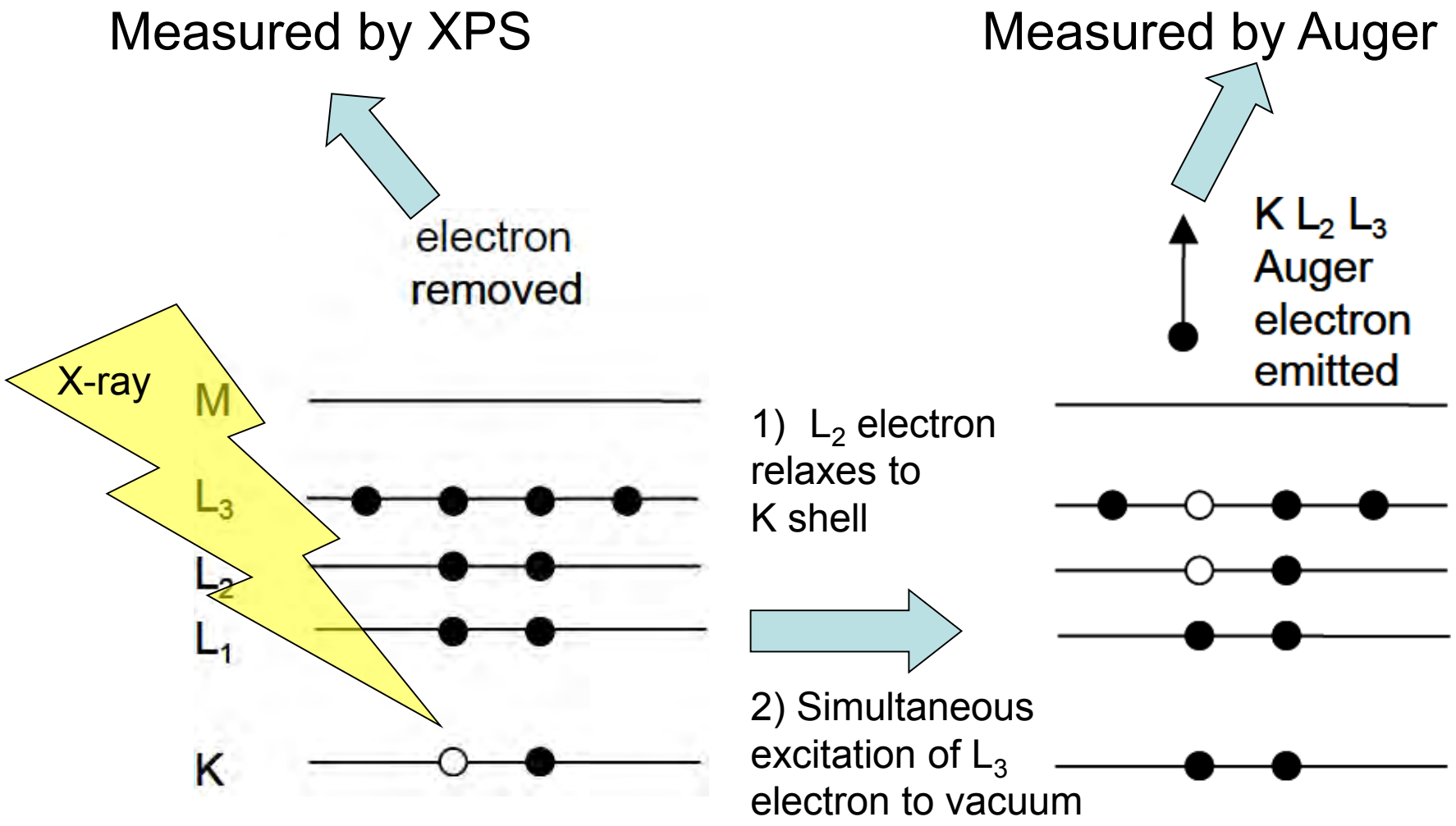


Usually electrons of core orbitals measured:
1s for C, N, F, and 2s or 2p for Si, S, etc.

$E_{kinetic} = E_{photon} - E_{binding} - \Phi$

E_{photon} is known; Φ = *electric potential; ideally 0, but ~constant for all* e^-*'s* $\Rightarrow E_{kinetic}$ is measured, to derive $E_{binding}$

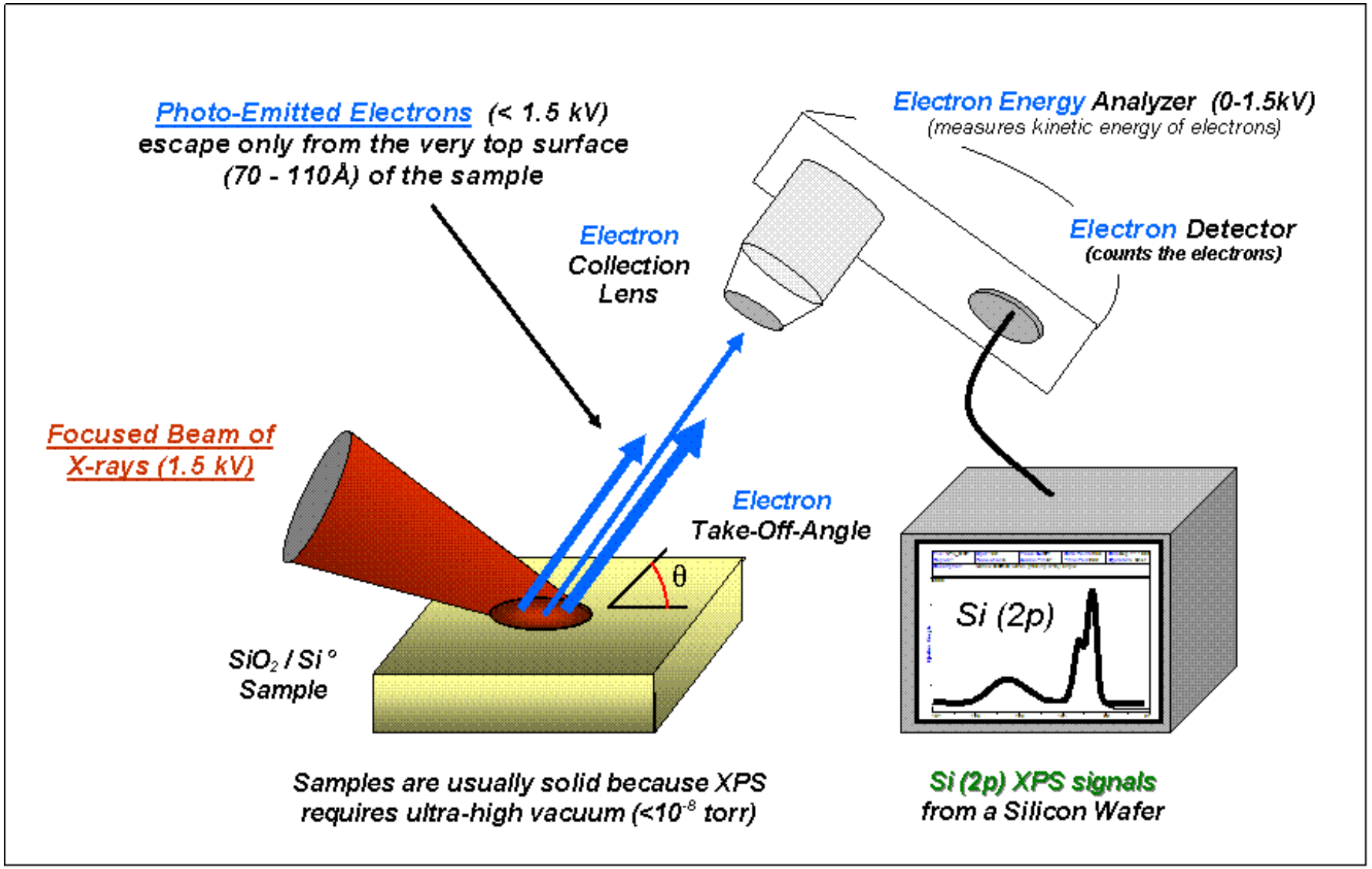
Auger spectroscopy versus XPS



In XPS: Excitation by X-rays

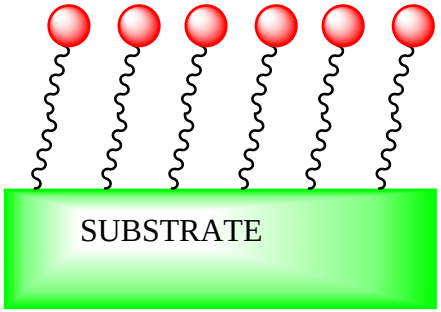
In SAM: Excitation by electron beam

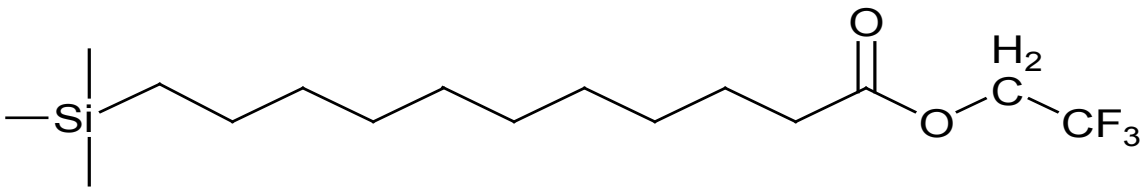
Schematic Set-Up of XPS machine

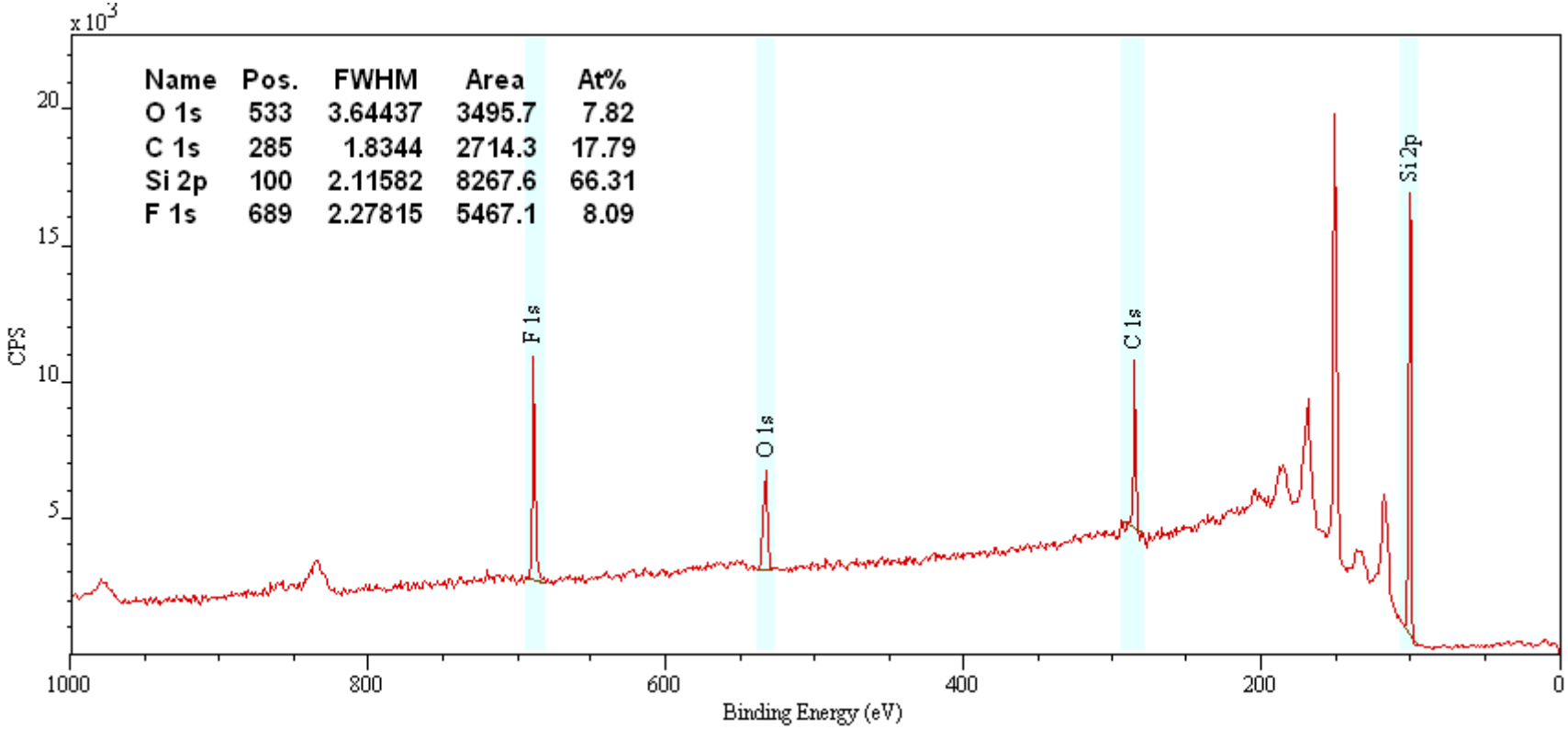


1) Determination of Elemental Composition

Wide scan survey spectrum: Peaks for several elements.

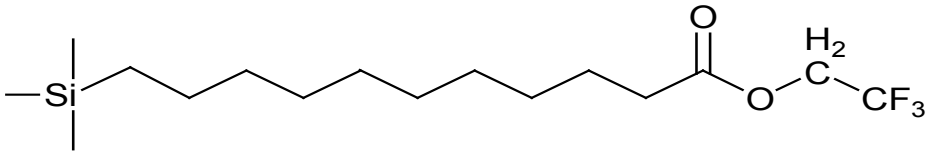




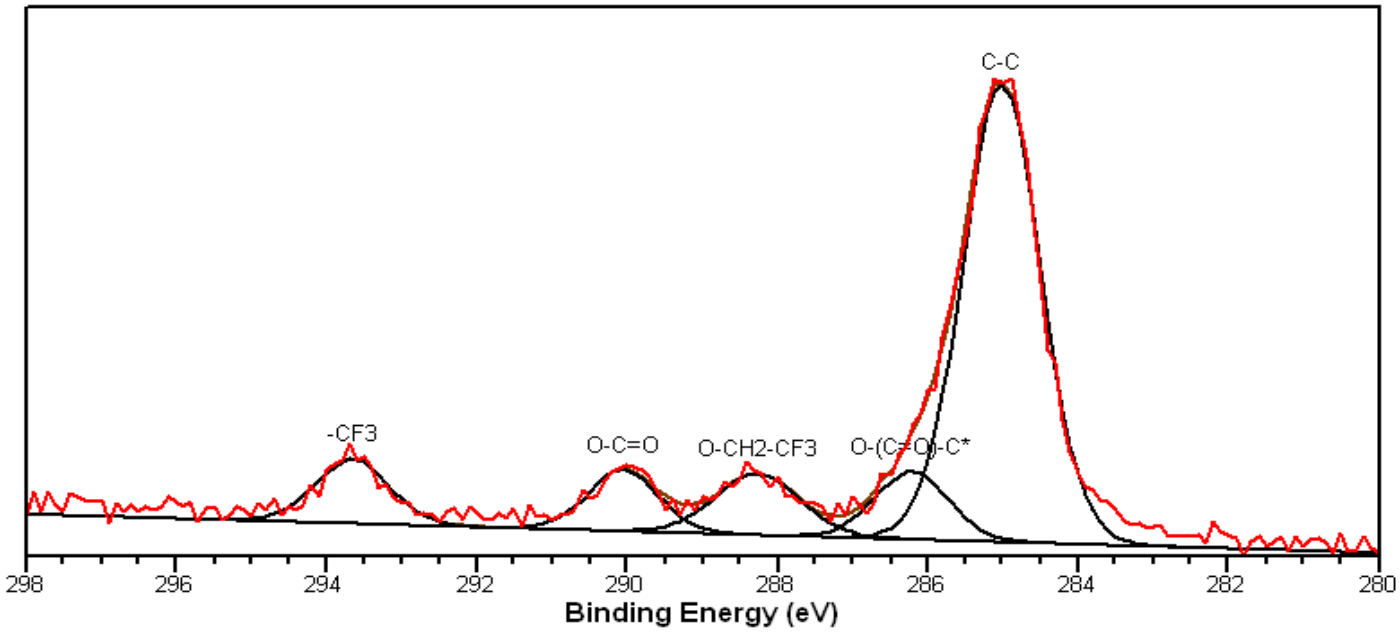


2) Chemical or Electronic State of Each Element

Narrow scan shows variation in electronic properties



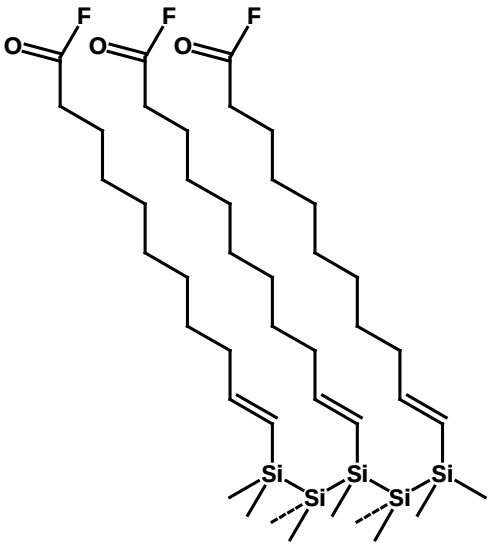
Ratios are correct for same element if layer is thin:
In this case 1 : 1 : 1 : 1 : 9



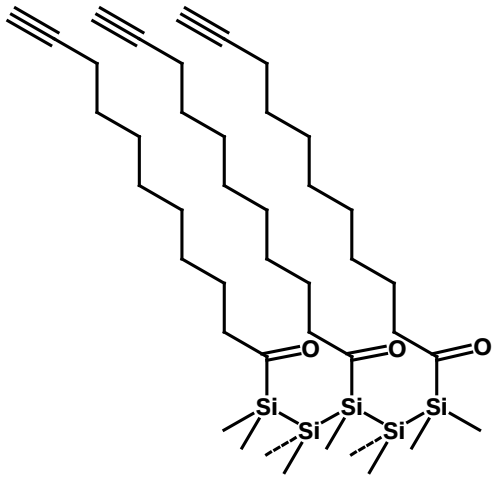
Chemical Shift Analysis shows Monolayer Structure

Alternative to NHS chemistry:

Acid Fluoride termination: Highly amine-reactive endcap

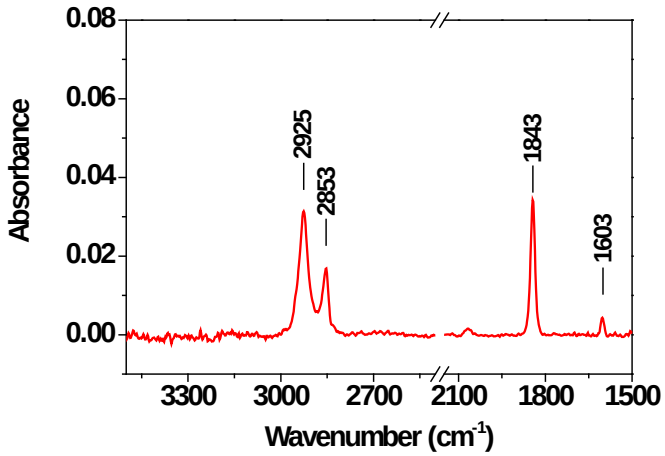


or



XPS & IR:
only C(=O)F !

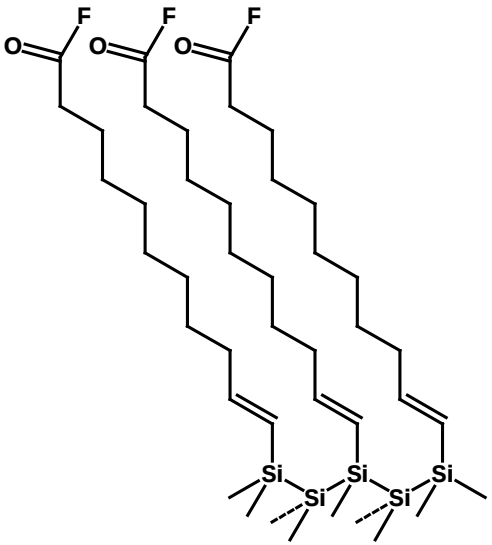
(confirm by calc of alternatives)



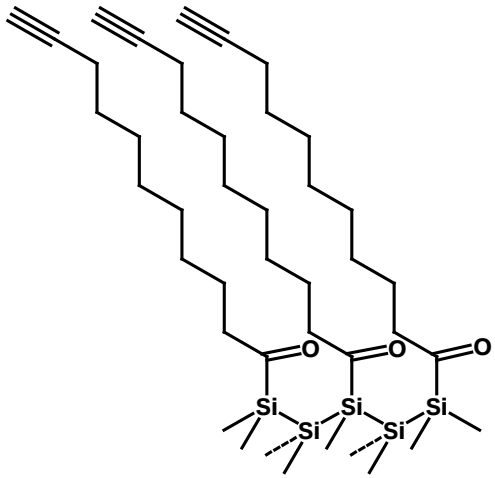
Chemical Shift Analysis shows Monolayer Structure

Alternative to NHS chemistry:

Acid Fluoride termination: Highly amine-reactive endcap

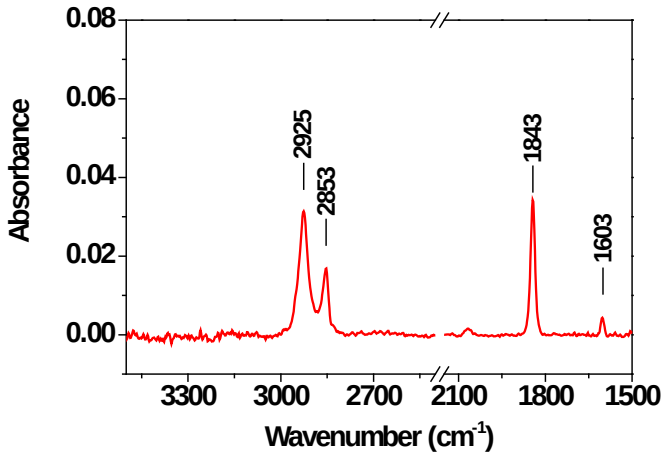


or



XPS & IR:
only C(=O)F !

(confirm by calc of alternatives)

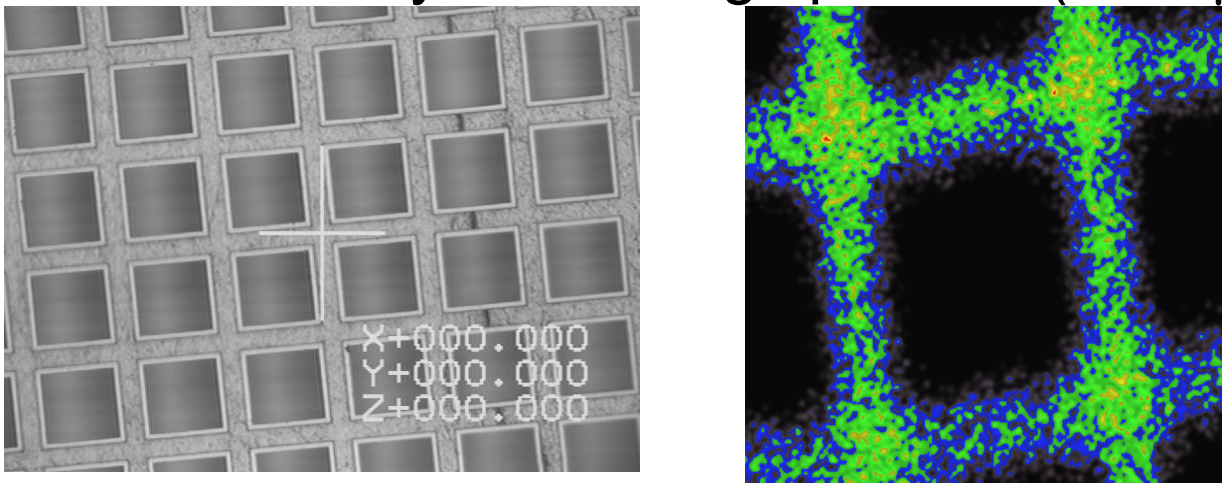


3) Elemental Composition Across Top Surface: Mapping

Direct information on relative amounts of elements at different spots

This can be used to “map” elements pixel by pixel

Resolution limited by measuring spot size (~ 30 μm^2)

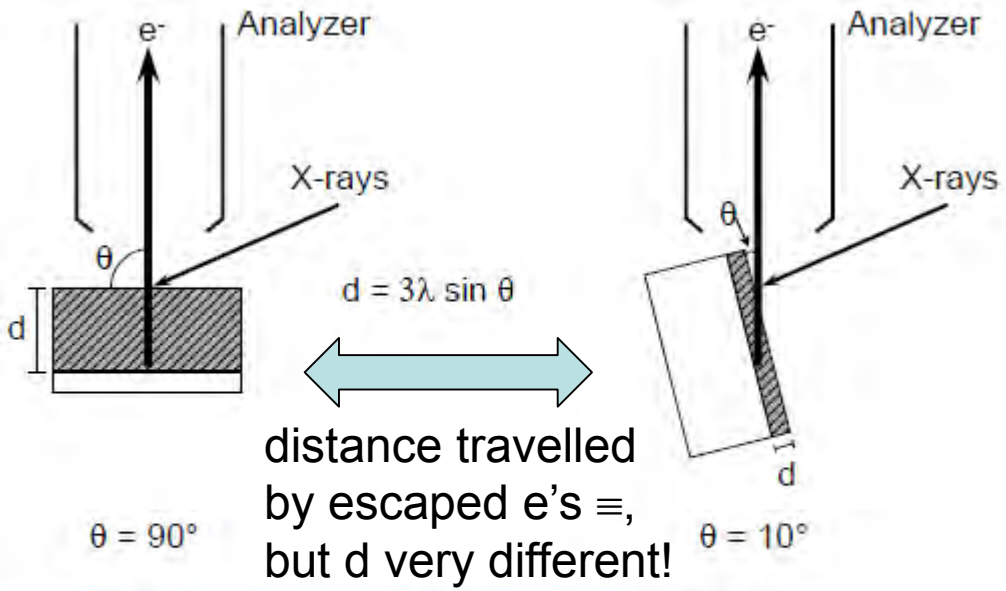


Cu-grid on Si wafer: left AFM; right XPS mapping

NB: 1) XPS imaging can test uniformity of surface modification

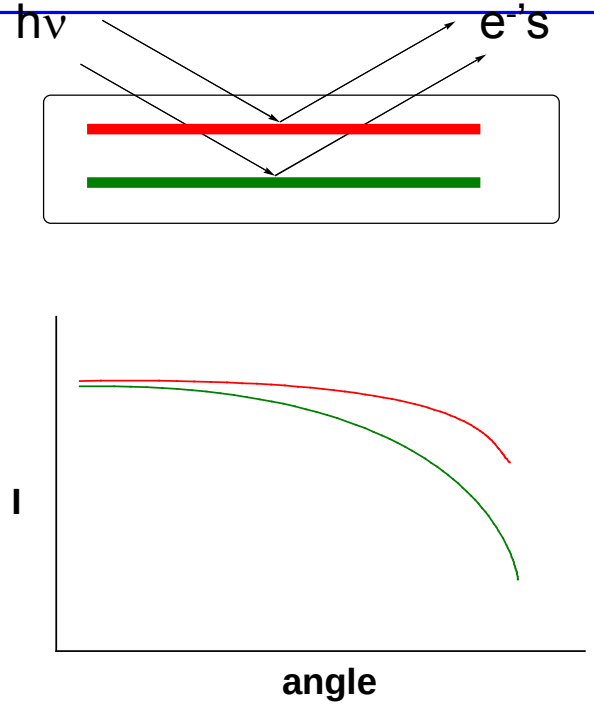
2) Mapping resolution of Auger spectroscopy much better

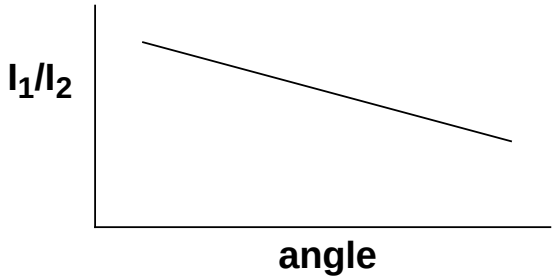
4) Depth Information: Angle-resolved XPS



d = analysis depth, λ = electron attenuation length

θ = take-off angle = 90° - emission angle





Due to scattering, e⁻'s can only travel limited distance thru material ⇒ by tilting sample that distance can only be reached from nuclei near surface

Depth profiles: Angle-resolved XPS
Layer of SiN on Si

No unique method to obtain depth info from angle info, but several semi-quantitative methods available:

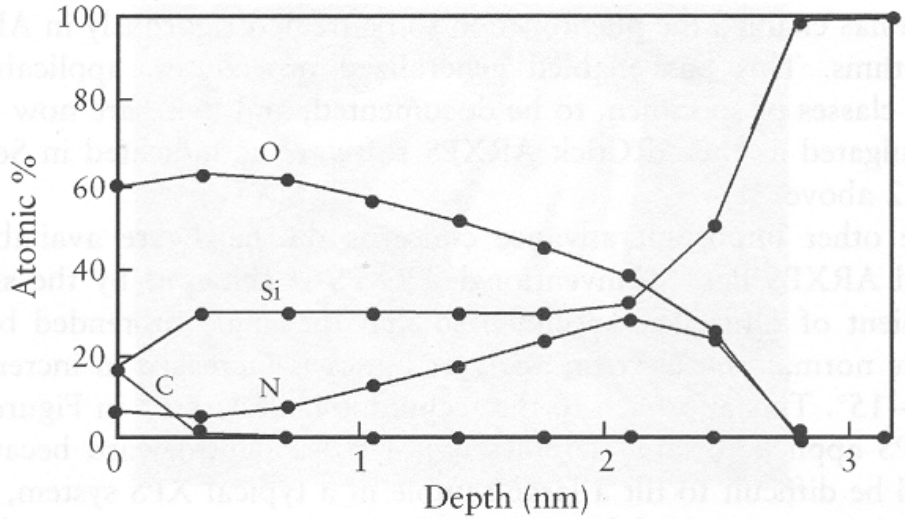
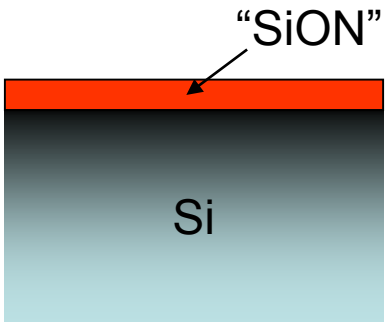


Figure 4.8 Depth profile through an ultra-thin layer of silicon oxynitride reconstructed from ARXPS data using the maximum entropy method

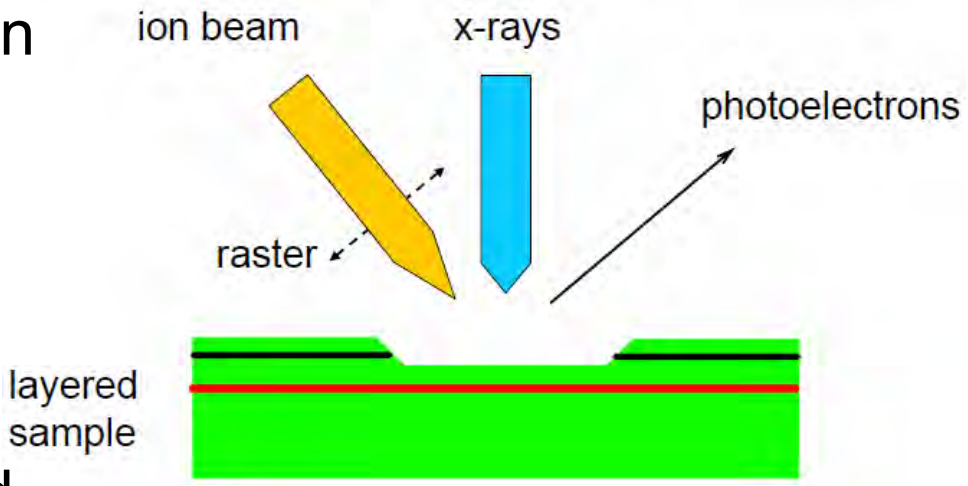


⇒ SiN slightly oxidized; most oxidized on surface

⇒ slight C-based contamination present

4) Depth Information: Ion Sputtering

- Used to determine composition as function of depth from original surface.
- Surface layers removed by sputtering with inert gas ions (e.g. Ar) or C_{60}
- XPS analysis of newly created surface is used to determine composition at that depth
- Process is repeated to get composition at series of depths



NB: to obtain depth info, sputter rate should be known!
(differs e.g. for organic materials vs SiC vs metals..)

Surface Sensitivity

Determined by electrons, not by X-rays

- Intensity X-ray: slow ↓ with depth
- Still significant intensity 1000's of atomic layers into sample
- Photoelectrons produced near surface: higher probability of escape from surface without E loss (= producing peak in spectrum), than those produced deeper in sample.
- Photoelectrons that lose energy:

  appear in background @ E_{kin} ↓ (looks like $E_{binding}$ ↑)
- Analysis depth:

  determined by 'electron inelastic mean free path'.

XPS is real surface technique
Information Depth

- Information Depth = sample thickness from which specified % (e.g. 95% or 99%) of detected signal originates.

- 95% ID ≈ 3 x IMFP ($3\lambda_i$), if elastic scattering effects neglected

Typical ID: ~ 10 nm ⇒
well suited for analysis
of monolayers, polymer brushes,
thin coatings

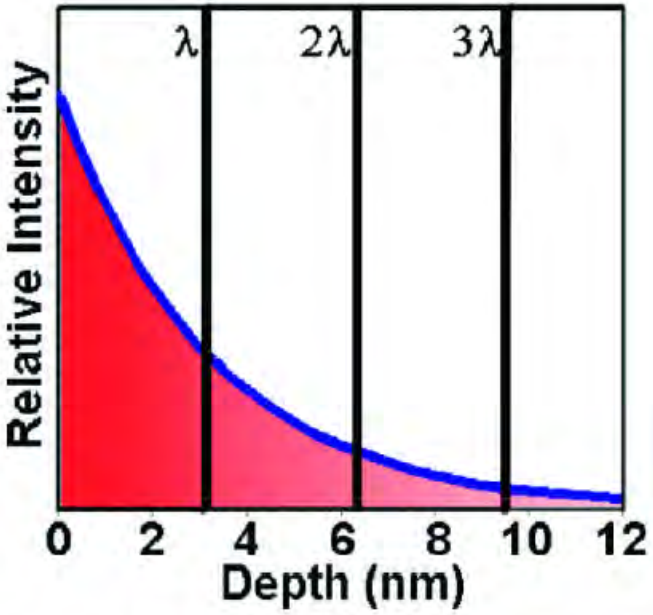


Figure 3 Relative intensity as a function of depth.

Scanning Auger Electron Microscopy

- Measures Auger electrons
- Excitation not by X-rays, but by (narrow) electron beam

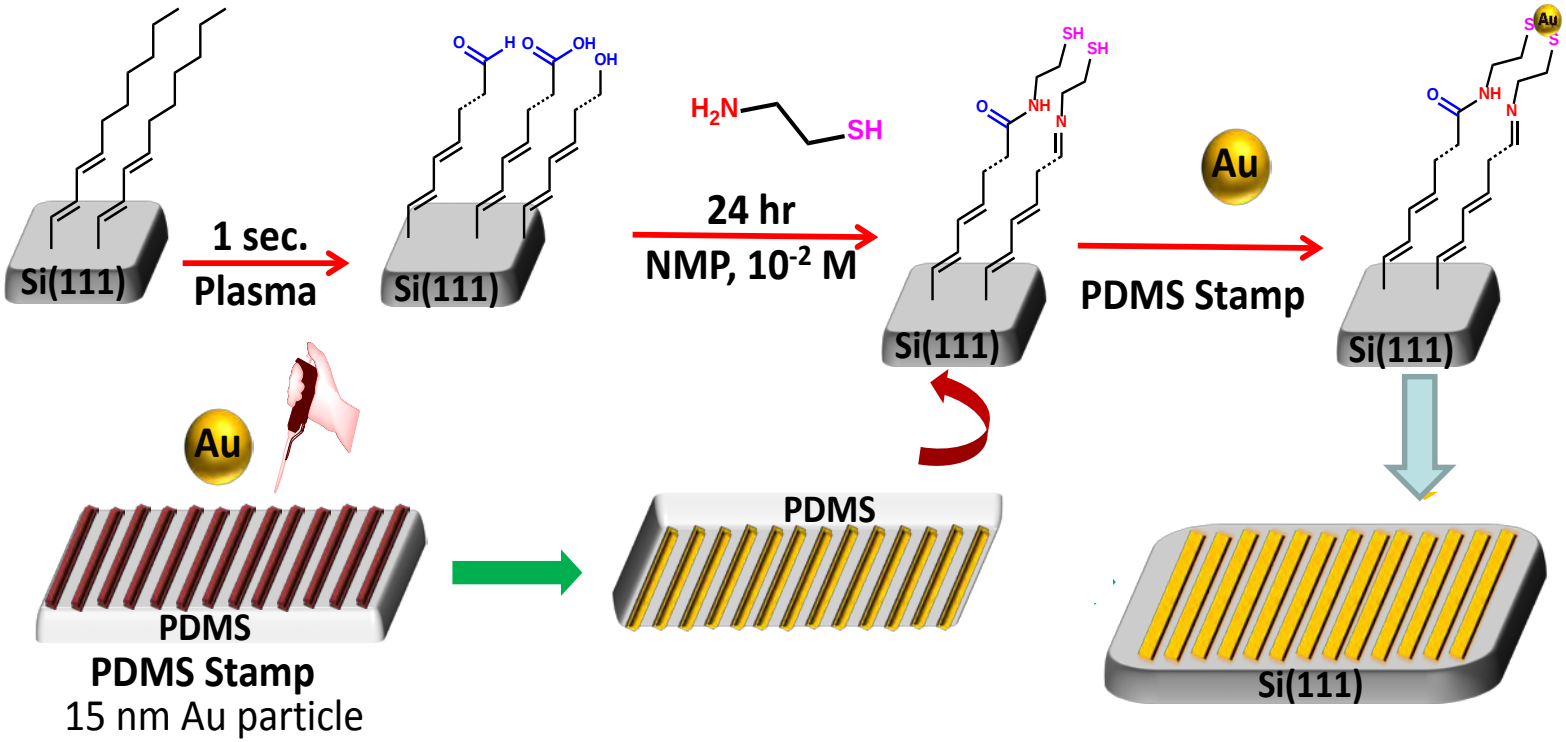
- MUCH higher spatial resolution

- SAM is like a SEM with special detector.
- The “SEM” in the SAM has lower spatial resolution than dedicated SEMs, but provides elemental composition.
- Conductive samples required.

JAMP-9500F offers highest spatial resolution available in microprobe:
8 - 10 nm for Auger analysis

Scanning Auger Electron Microscopy

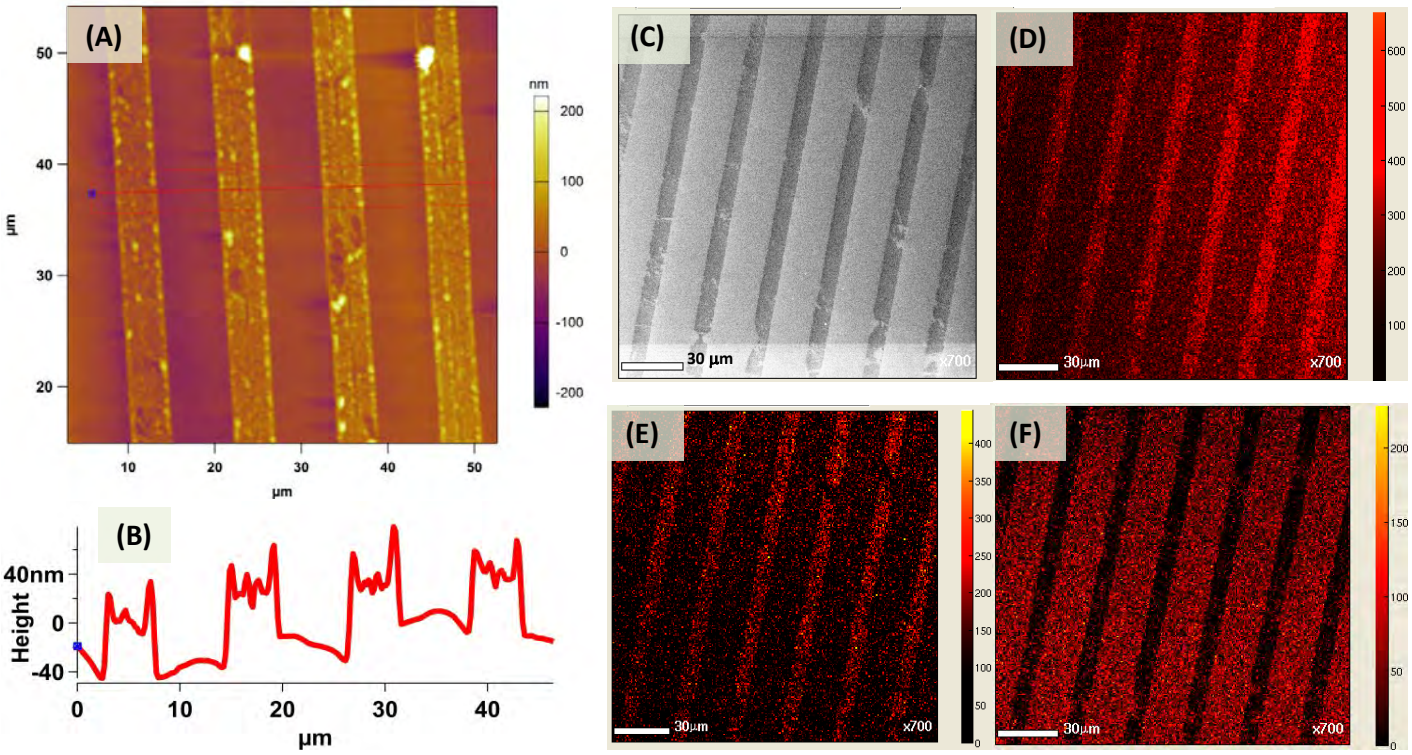
Analysis of Surface Patterning



⇒ Patterned surface with lines of Au nanoparticles

Scanning Auger Electron Microscopy

Analysis of Surface Patterning

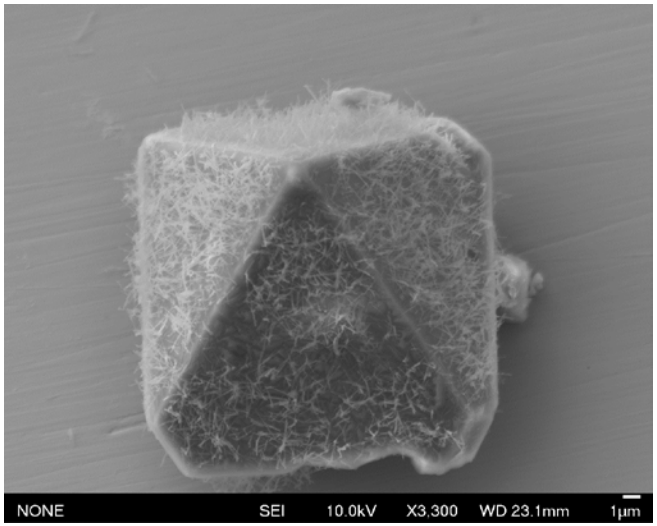


Patterned surface with lines of Au nanoparticles

A: AFM (height)
B: AFM (profile)
C: SEM
E: O mapping
D: C mapping
F: Au mapping

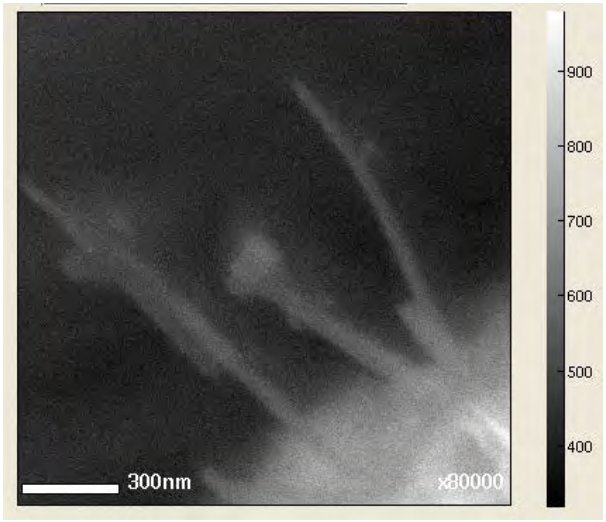
Scanning Auger Electron Microscopy

Analysis of Metal Organic Frameworks

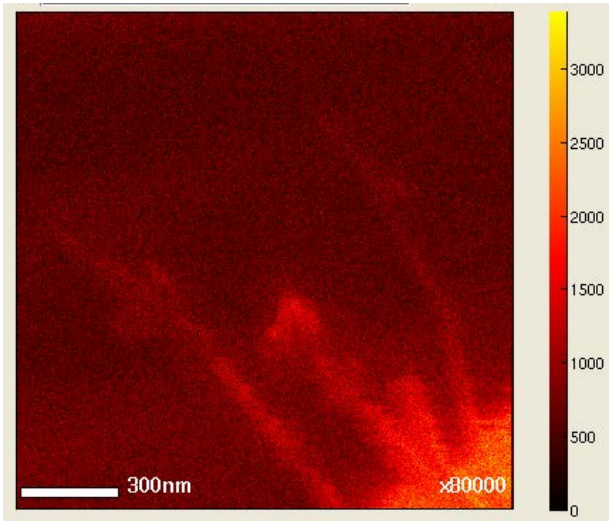


Zoom in

SEM

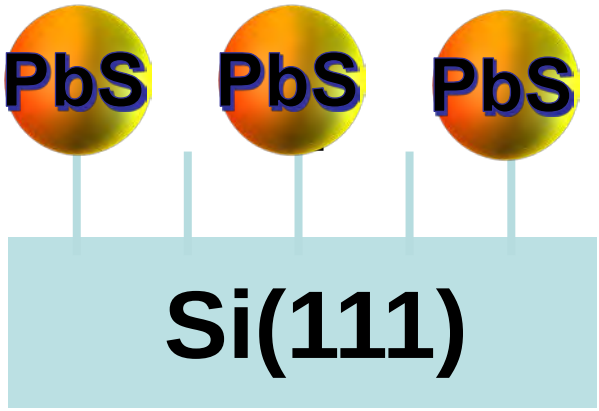


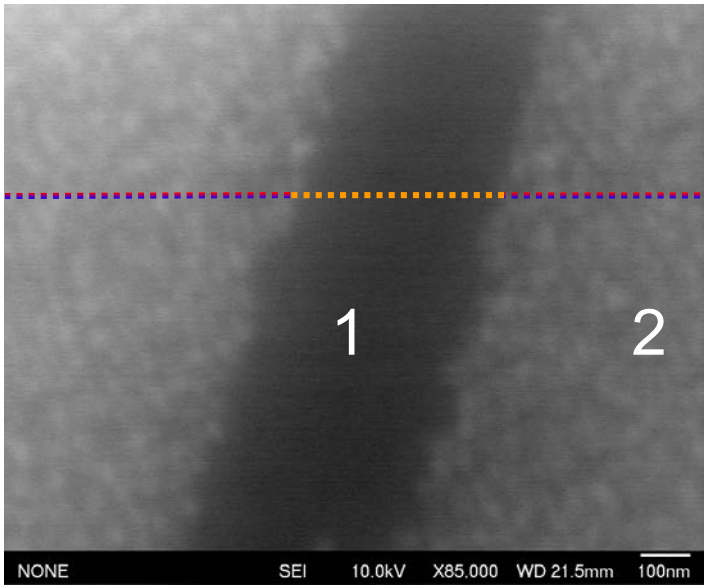
C

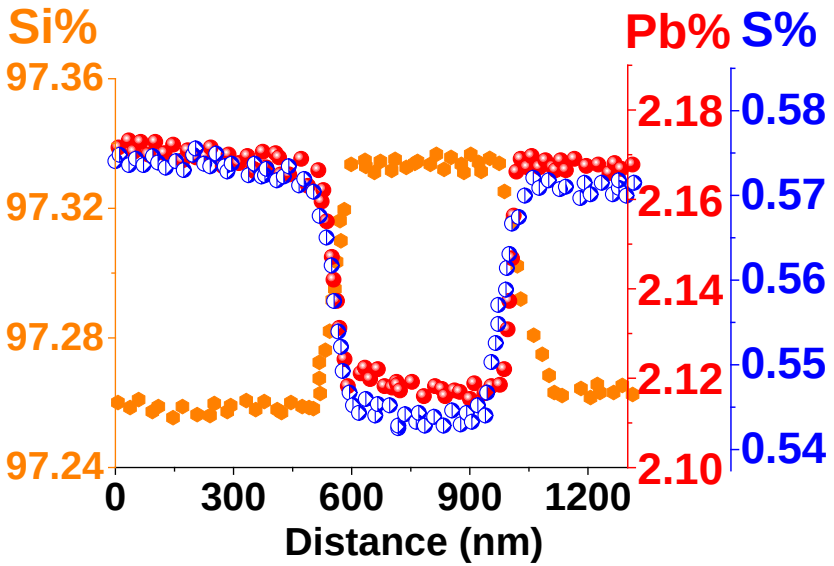


Scanning Auger Electron Microscopy

Thin lines of PbS nanoparticles







SEM

Auger Electron Spectroscopy

Point analysis (8 - 200 nm):

- chemical shift is complex
- broader peak
- presence of loss features
- more difficult to interpret than XPS

Line scan

- monitors Auger peak intensity as function of position

Elemental mapping

- AES has excellent spatial resolution

Depth profiling

- surface etching by Ar ion or angle resolved

XPS & Scanning Auger

Further info:
Dr. Sidhu Pujari

(Sir Fraser agrees ☺)

Thanks to:
Shared Research Facilities
Dr. Marcel Giesbers (who helped selection of SAM)
Global collaborators