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Extraction of Depth Information from ARXPS Data

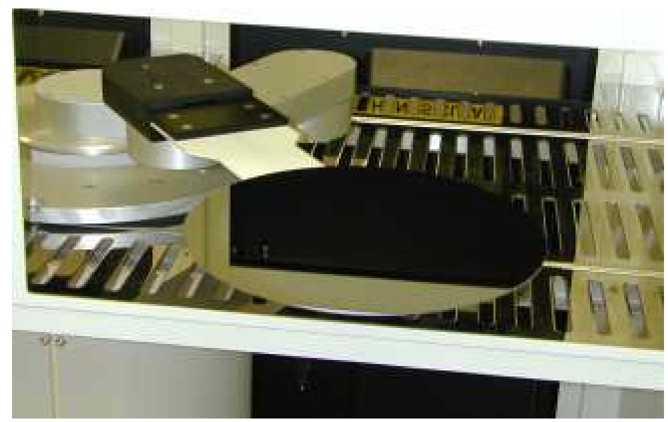
John Wolstenholme

Theta Probe Features

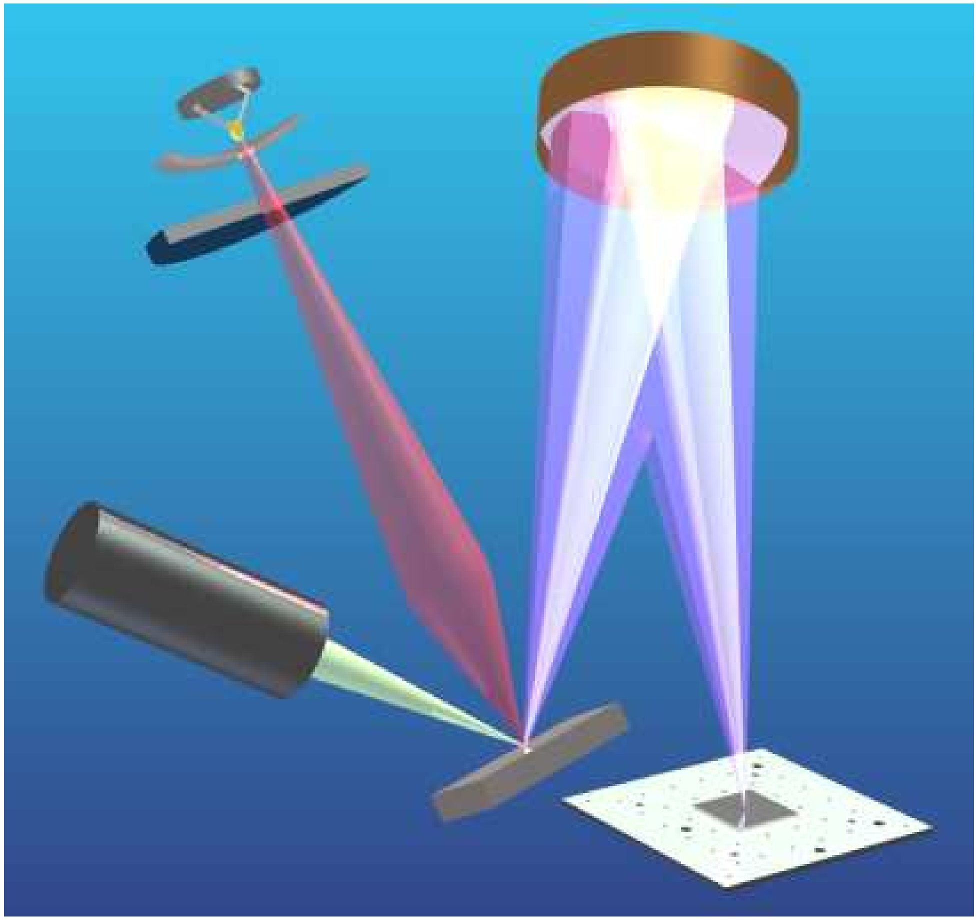
- X-ray monochromator with spot size from 15 µm to 400 µm
- Real time angle resolved XPS analysis without sample tilting

Theta 300XT

- **Parallel ARXPS from 300 mm wafers**

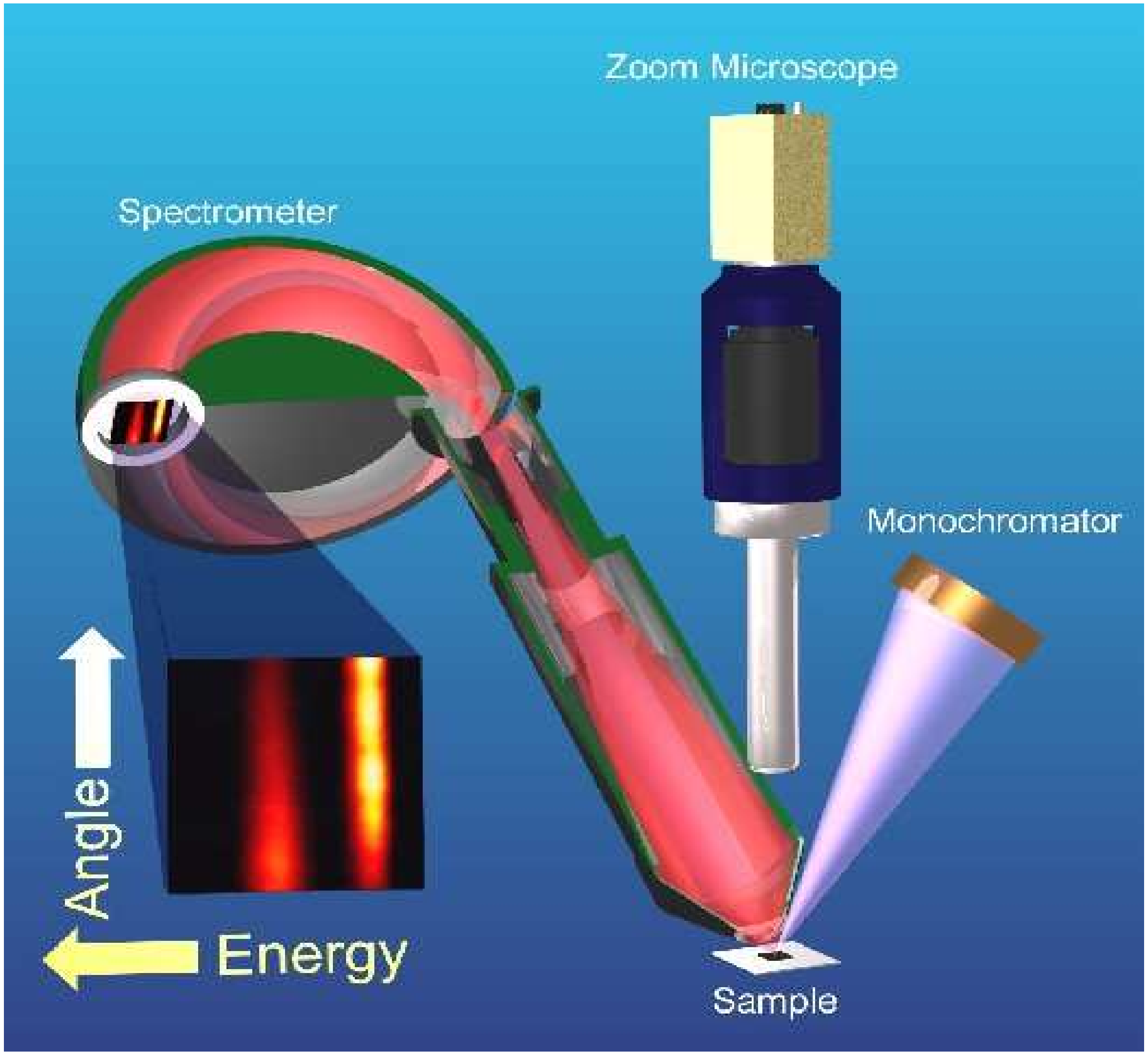


Microfocusing Monochromator



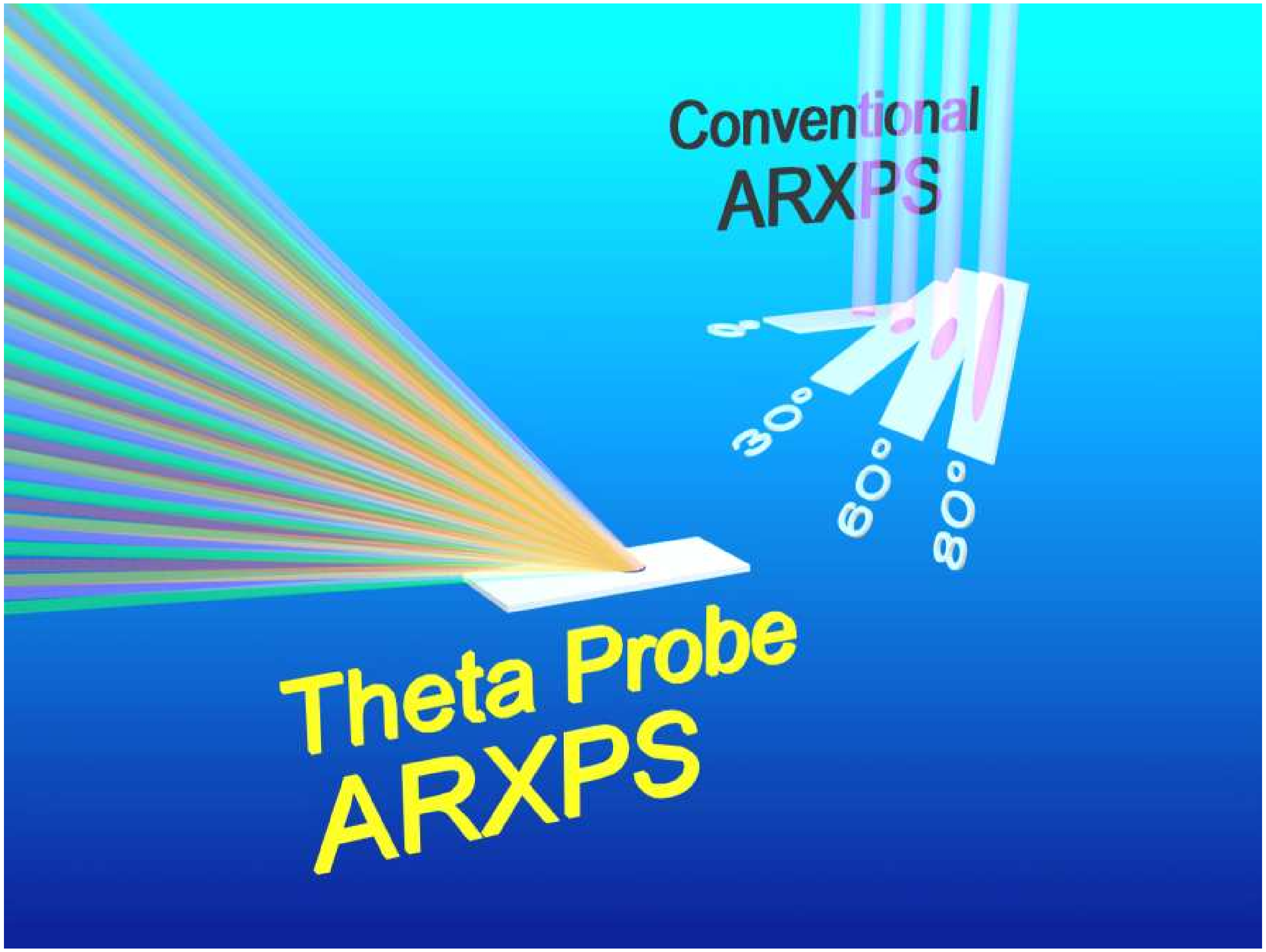
15 µm – 400 µm spot size

Geometry

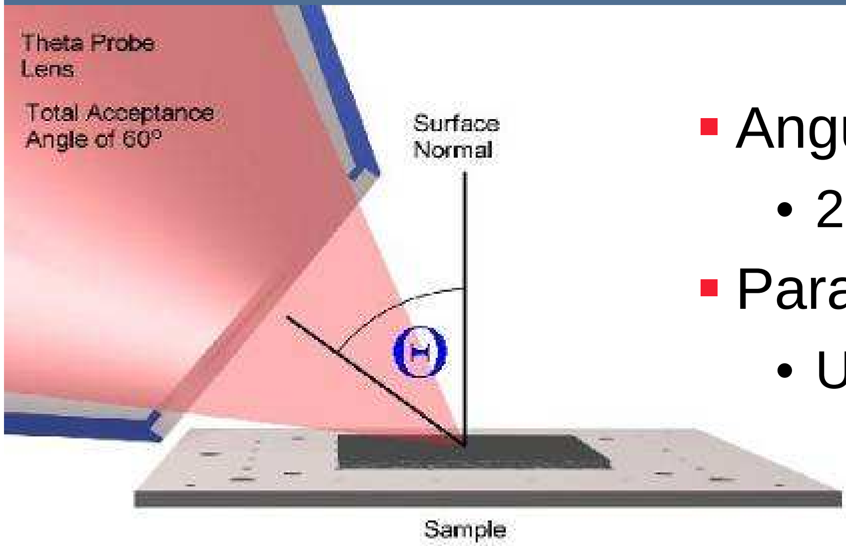


Zoom Microscope
Spectrometer
Monochromator
Angle
Energy
Sample

Theta Probe



Collection Conditions

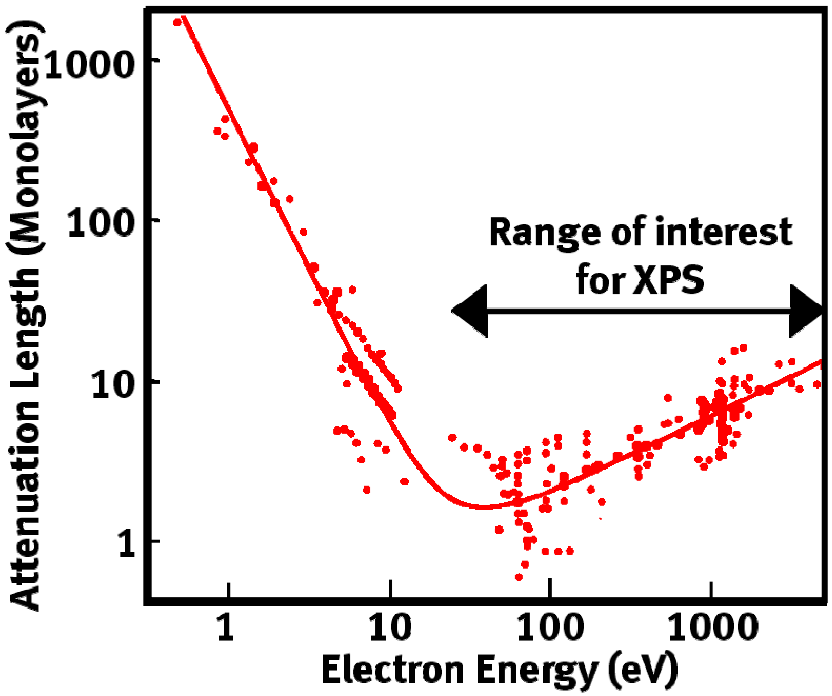


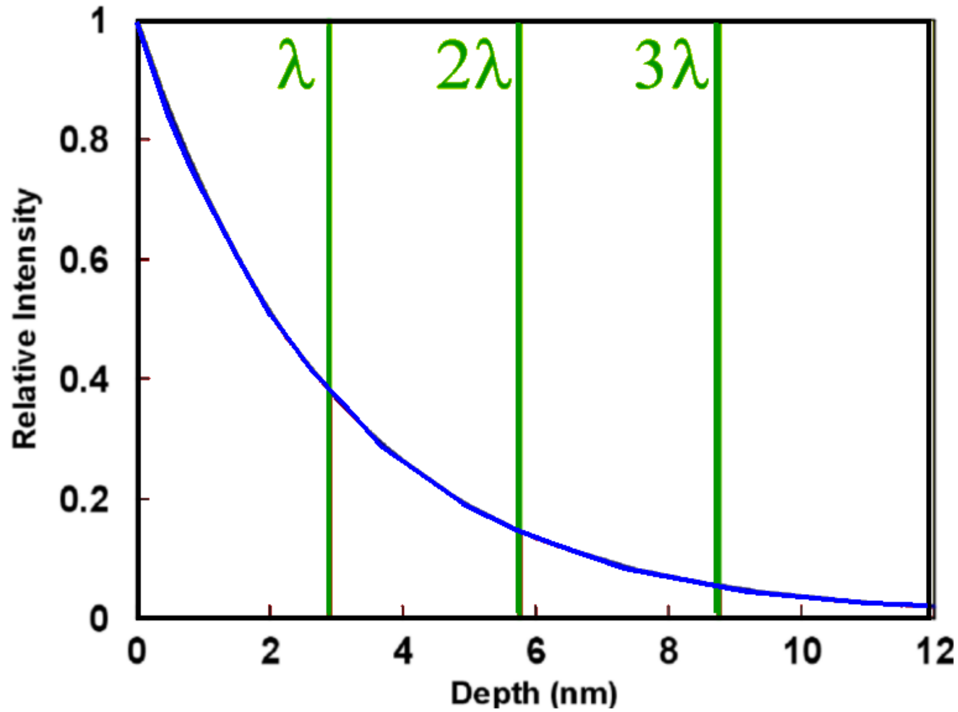
- Angular Range
  - 20° to 80°
- Parallel collection
  - Up to 96 channels in angle
    - Generally, 16 angles are used giving an angular resolution of 3.75°
  - Up to 112 channels in energy
- Parallel collection allows rapid ‘snapshot acquisition’
  - Excellent for ARXPS maps
  - Thickness maps
  - Dose maps

Data Acquisition

- Binding energy
  - Parallel (snapshot) or scanned
- Angle
  - Always parallel
- Video of snapshot acquisition
  - SiO_2 on Si
- Advantages of Parallel ARXPS
  - Fast
  - ARXPS from small features is possible
  - Mapping possible
  - Analysis area is constant
  - ARXPS from large samples

Attenuation Length





- Each data point represents a different element or transition

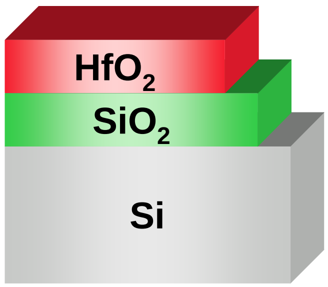
$$\lambda \propto\sim E^{0.5}$$

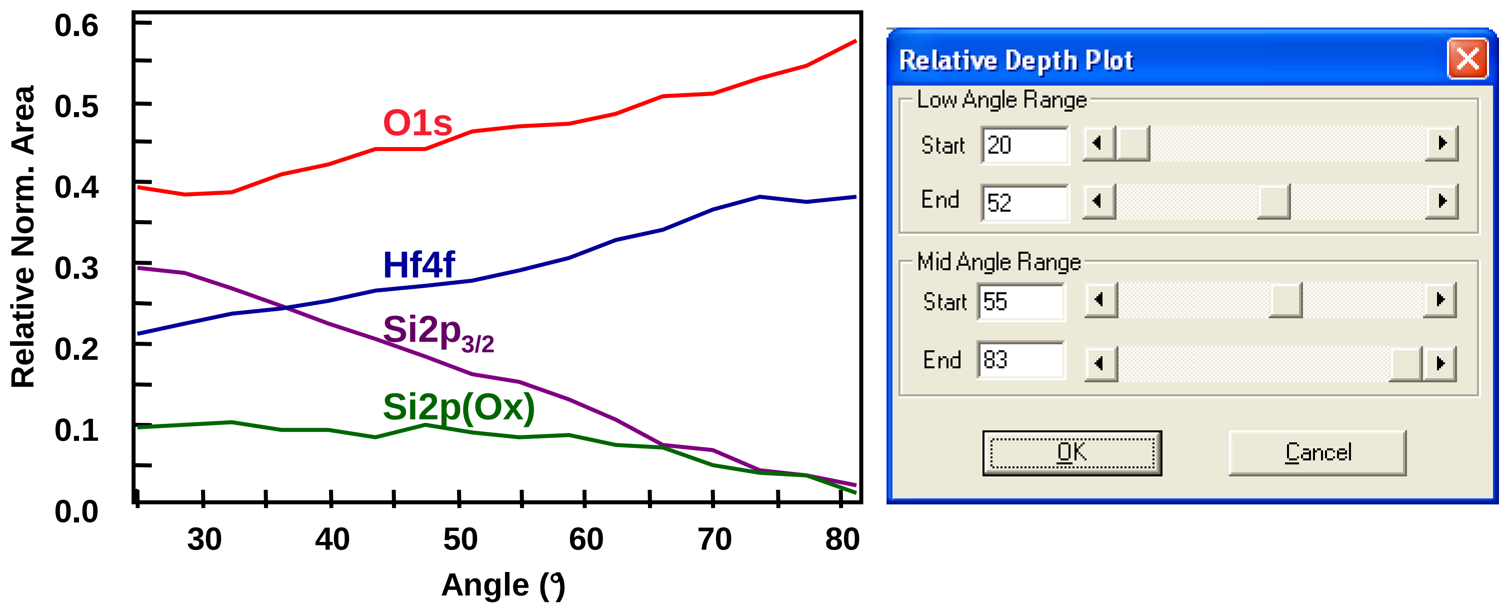
- Intensity as a function of depth
  - 65% of the signal from <λ
  - 85% from <2λ
  - 95% from <3λ

M. P. Seah and W.A. Dench, Surface and Interface Analysis 1 (1979) 2

Relative Depth Plot (RDP)

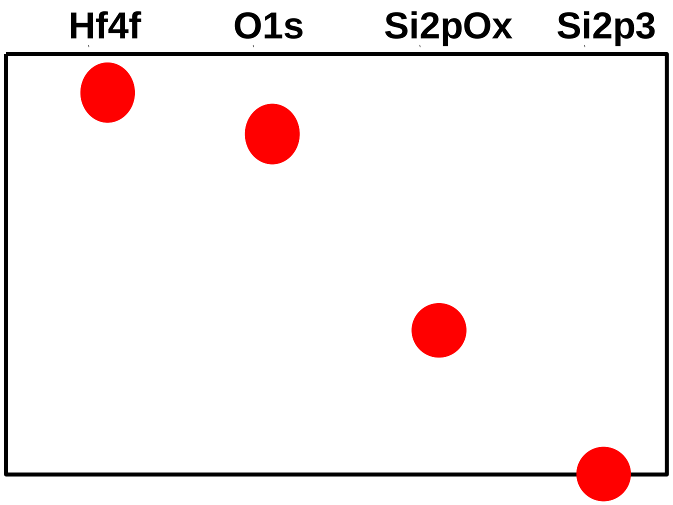
- Select range of bulk sensitive angles (I_{bulk})
- Select range of more surface sensitive angles ($I_{surface}$)
- Ln ($I_{surface}$ / I_{bulk})
- Provides qualitative species depth distribution



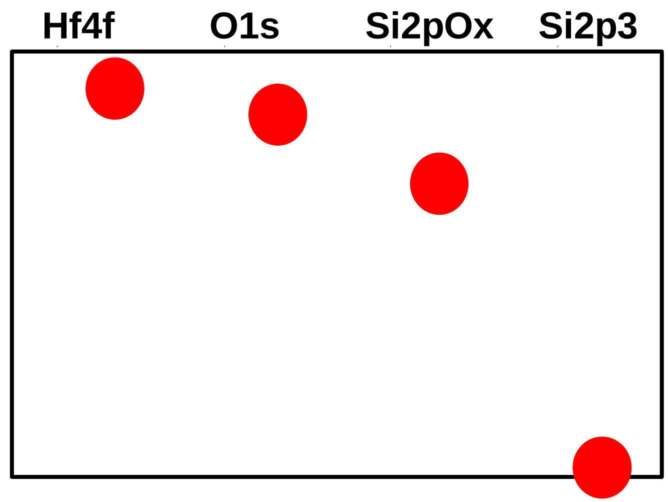


RDP – HfO_2 Grown by ALD

- 30 Cycles ALD on thermal SiO_2



- 30 Cycles ALD on HF-last Si

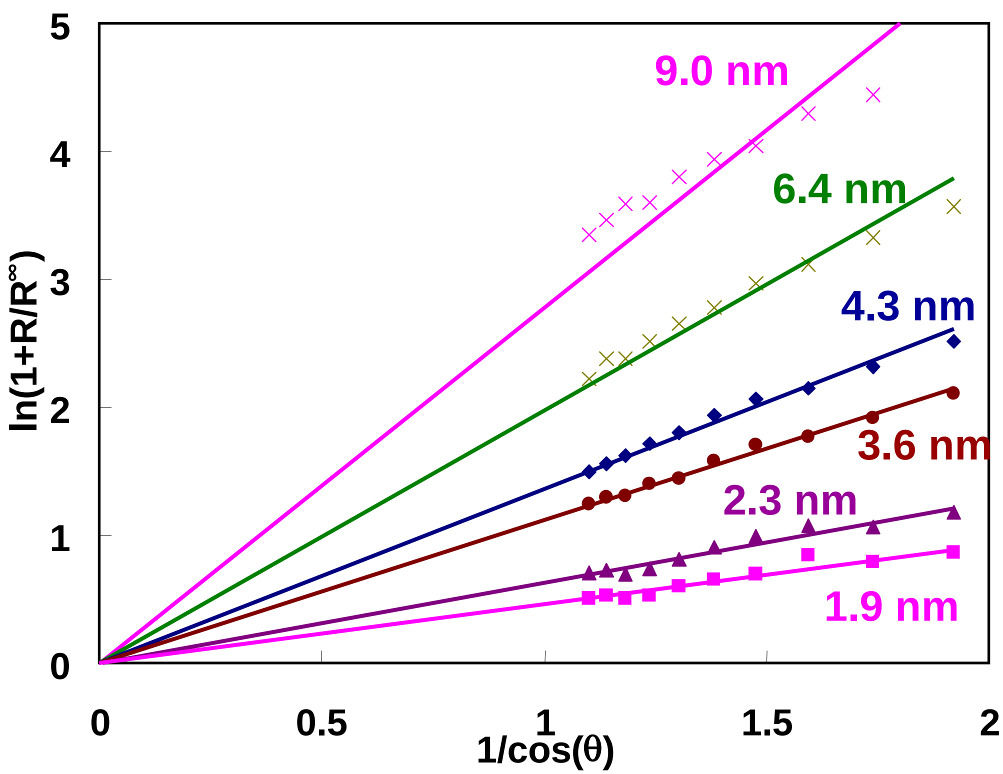


- Advantages
  - Excellent for showing the ordering of the layers
  - Shows gross differences between samples
  - Does not rely on mathematical models
  - Does not require a knowledge of the material properties

- Disadvantages
  - No quantitative data
  - No means to interpret the differences between samples
  - Subtle differences not apparent

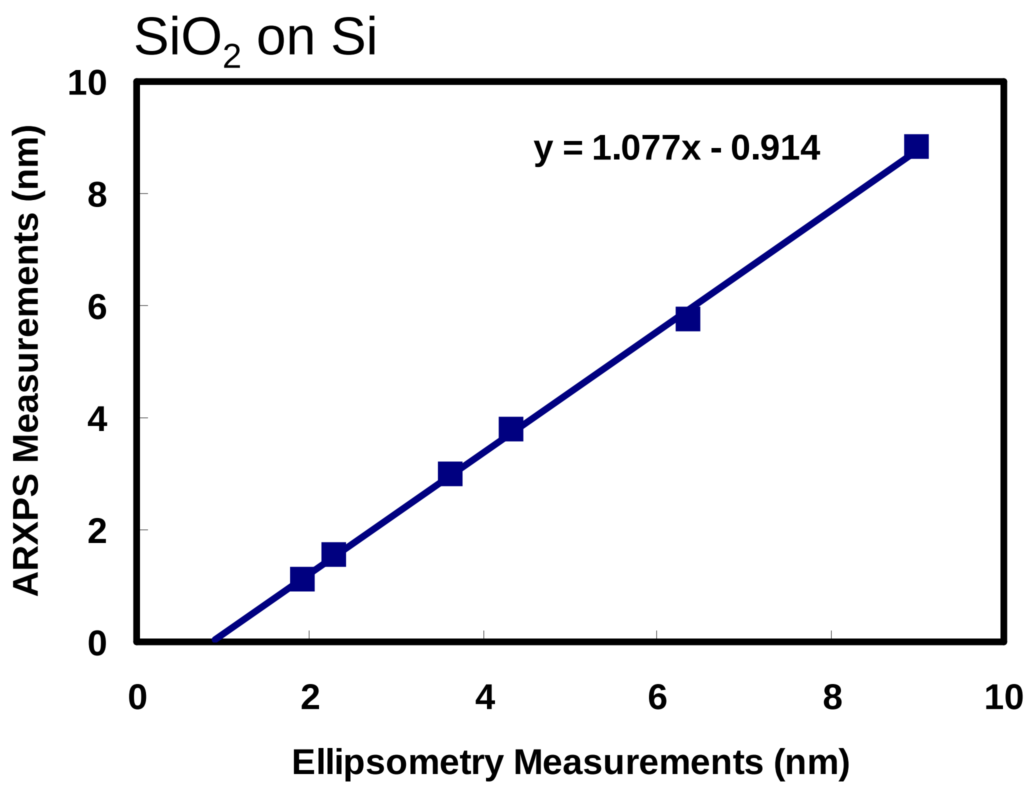
Thickness Measurement

- Equations
  - Photoemission from a thin film
    - $I = I_0 [1-\exp(-d/\lambda\cos\theta)]$
  - Attenuation by a thin film
    - $I = I_0 \exp(-d/\lambda\cos\theta)$
  - Where
    - I_0 = Emission from bulk material
    - θ = Emission angle (with respect to sample normal)
    - d = Film thickness
    - λ = Attenuation length
- Silicon dioxide on silicon
- Plot:
  - $\ln[1+R/R^{\infty}]$ vs. $1/\cos(\theta)$
- Gradient
  - d/λ



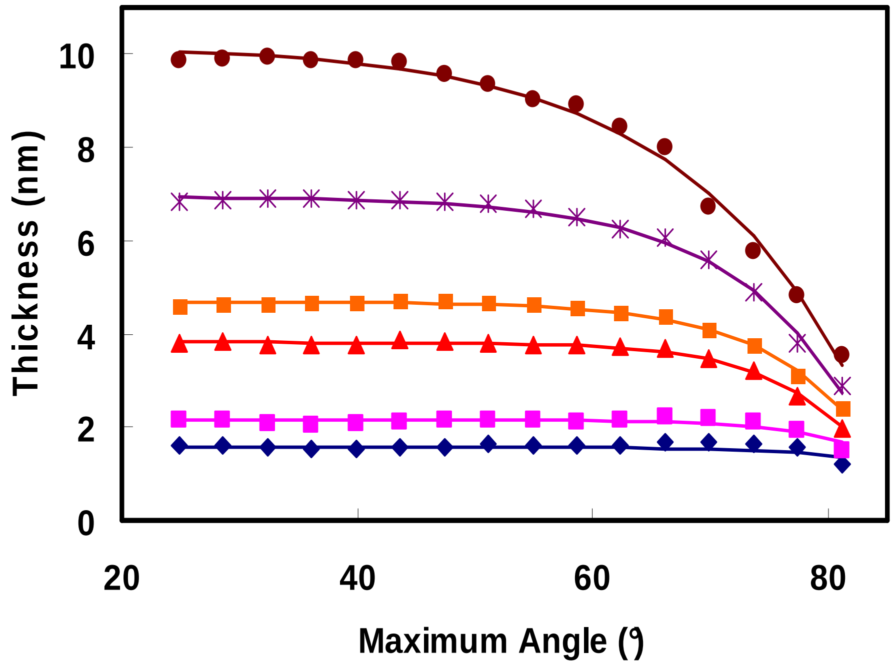
Thickness Measurements –Single Layer

- Equations
  - Photoemission from a thin film
    - $I = I_0 [1-\exp(-d/\lambda\cos\theta)]$
  - Attenuation by a thin film
    - $I = I_0 \exp(-d/\lambda\cos\theta)$
  - Where
    - I_0 = Emission from bulk material
    - θ = Emission angle (with respect to sample normal)
    - d = Film thickness
    - λ = Attenuation length
- For thickness calculation
    - $\ln[1+R/R_0] = d/(\lambda_A \cos\theta)$

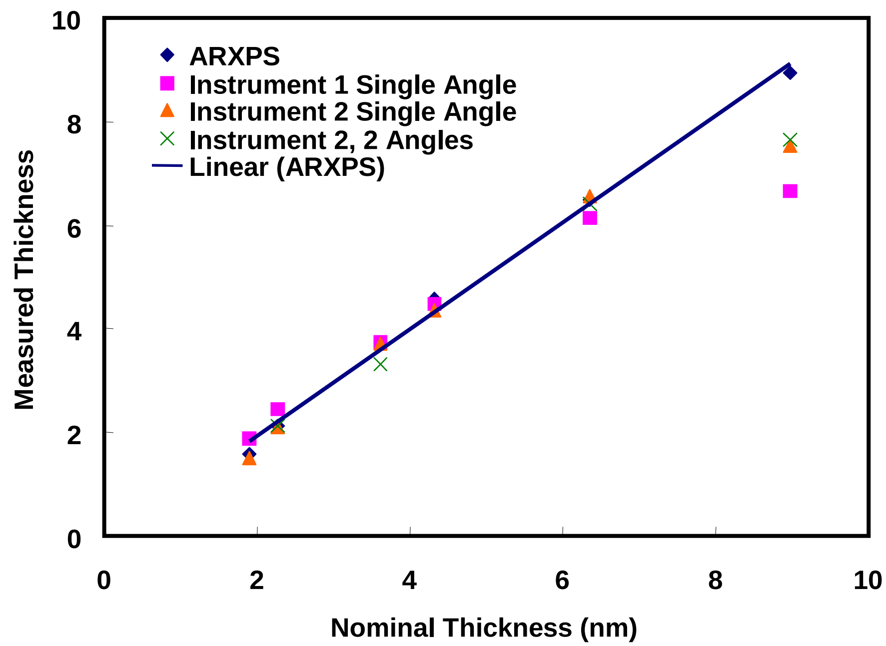


- Beware of R_0
  - For SiO_2/Si experimental value is very different from calculated value

XPS Measurements of SiO_2 Thickness

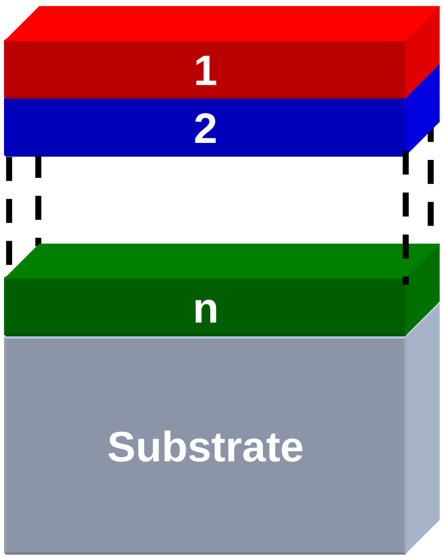


- Comparison of ARXPS with fixed angle XPS
  - Good agreement except at large thickness
  - Single angle measurement samples large angular range.



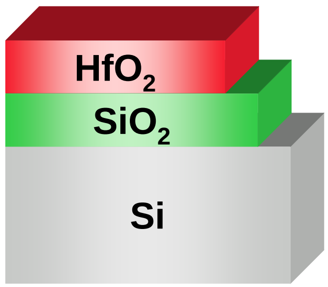
- ARXPS measurements
  - Effect of angular range upon measured thickness
  - Minimum angle is 23° in all cases
  - Highest usable maximum angle depends upon oxide thickness

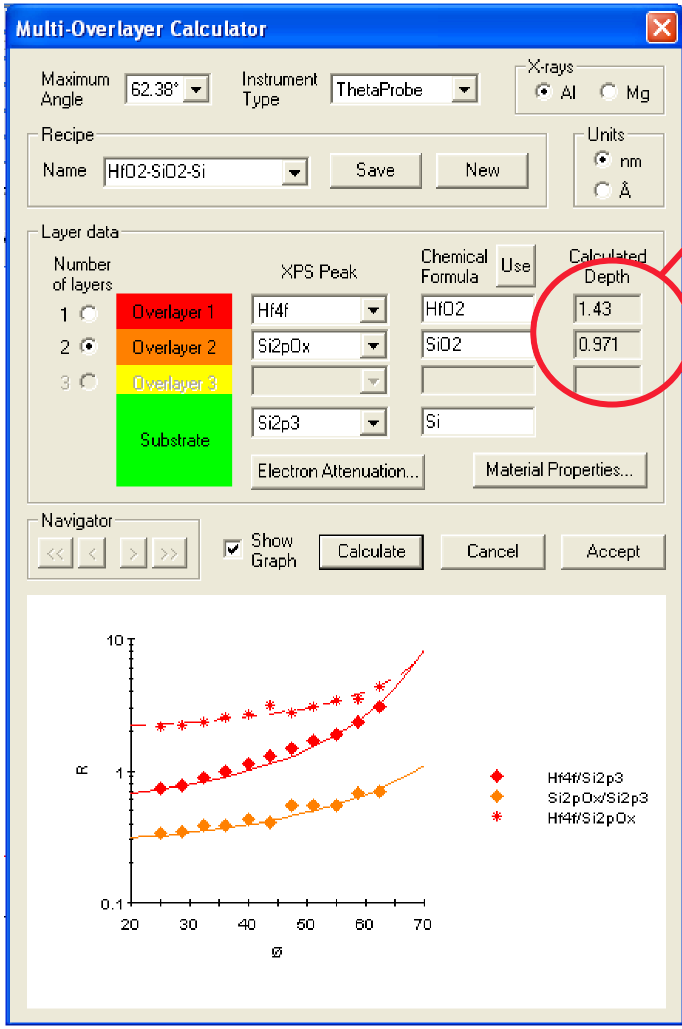
Multiple Overlayers



- Choose XPS transitions representing the composition of each layer
- Measure signals as a function of angle
- Determine intensity ratios
  - $I_j(\theta)/I_{j+1}(\theta)$
  - $I_j(\theta)/I_{sub}(\theta)$
  - $I_j(\theta)$ is the XPS signal from layer j as a function of angle
- Fit theoretical ratios to measured ratios using layer thickness as fitting parameter
- Best results are obtained by finding the best fit to all of the data simultaneously

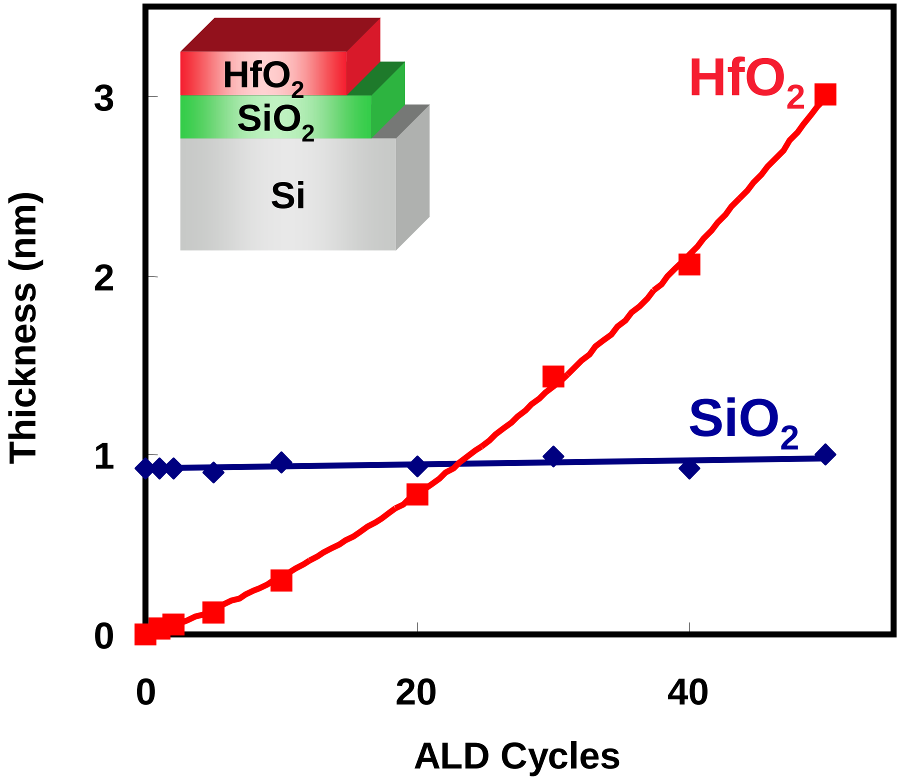
Layer Thickness Calculation



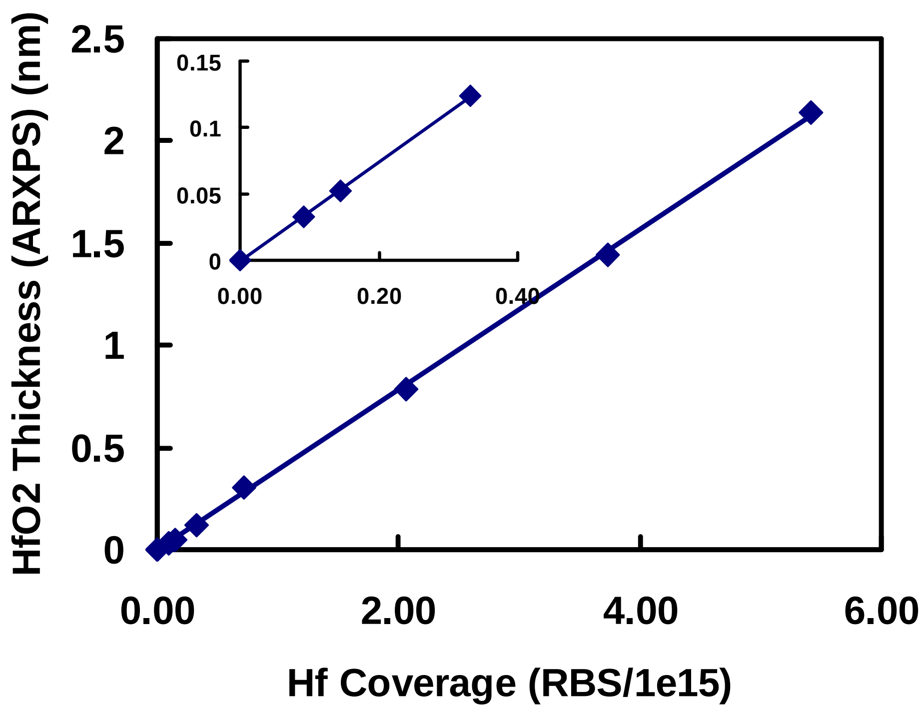


Layer Thickness (nm)

HfO_2 Growth on Thermal SiO_2

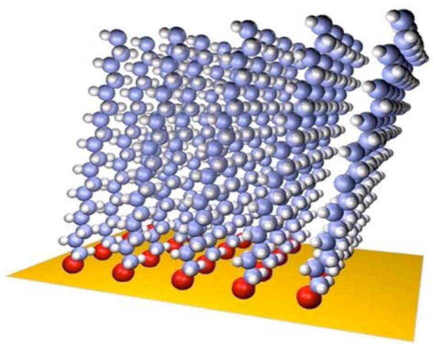


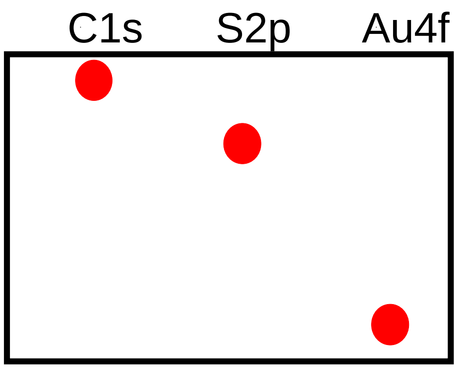
- Thickness calculated from PARXPS data using multi-layer thickness calculator
- Increasing growth rate
- Constant SiO_2 thickness

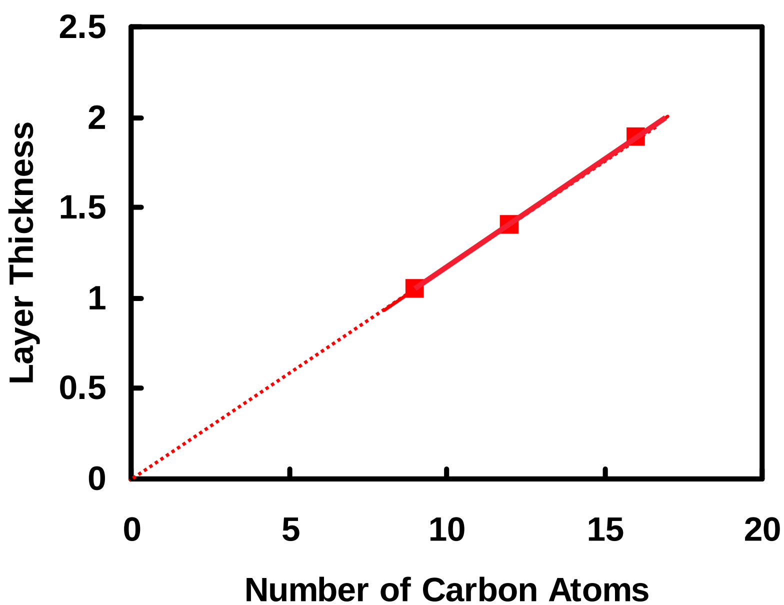


Thickness Measurement of SAMs Using PARXPS

- Measurements from 3 Alkanethiols deposited on gold
  - $C_9H_{19}SH$
  - $C_{11}H_{23}SH$
  - $C_{16}H_{33}SH$



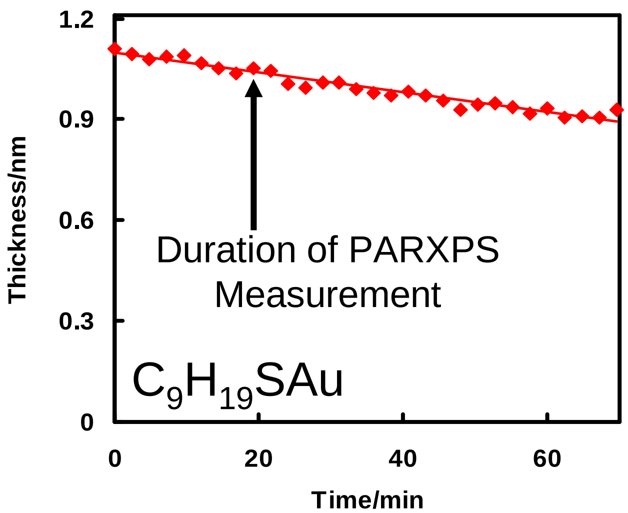


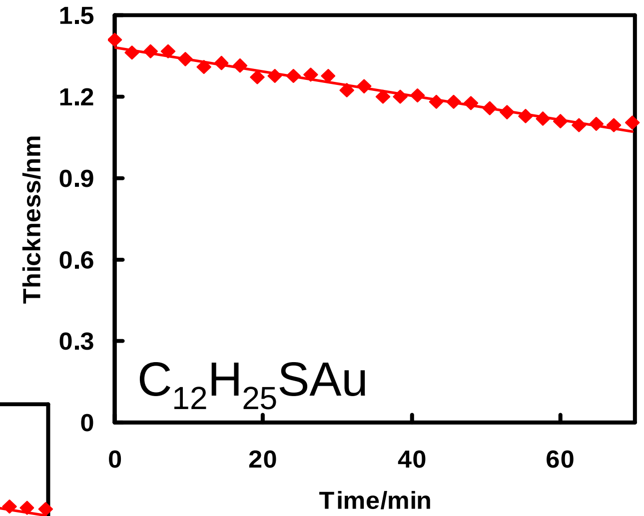


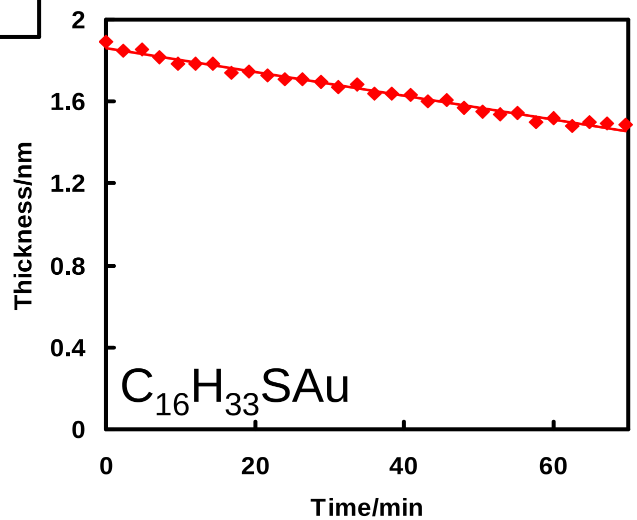
- Acquisition Times
  - C 1s 3 min
  - Au 4f 1 min
  - S 2p 15 min

Thickness Measured as Function of Time

- Conditions
  - Angle integrated
  - Acquisition time per point = 1.25 min.



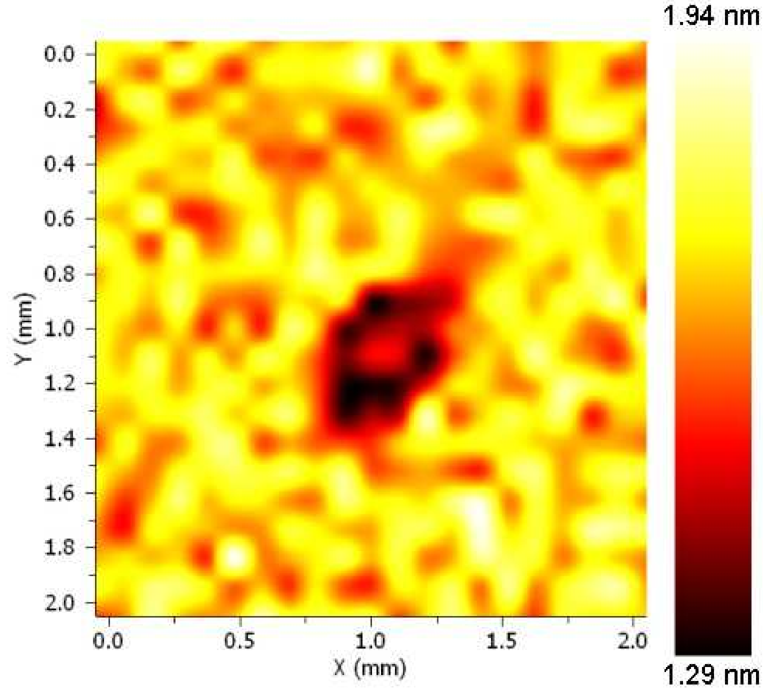




~20% Decrease in 70 minutes

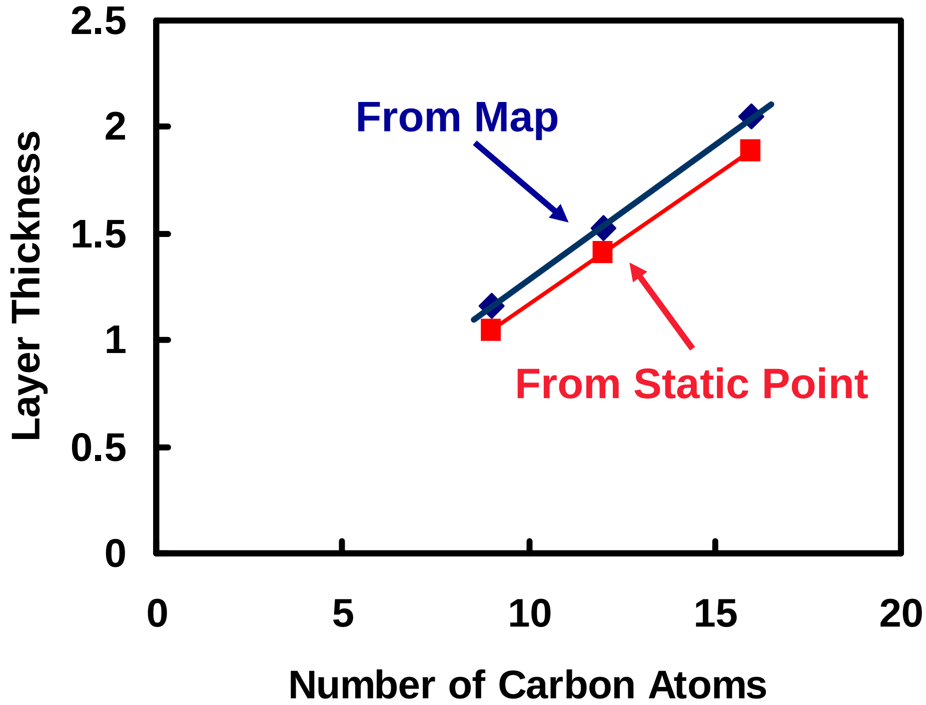
Thickness Map

- Conditions
  - Sample $C_{16}H_{33}SAu$
  - Angle integrated
  - Snapshot
  - 20 x 20 pixels
  - 100 µm spot size
  - Time per point 3 seconds



- Clear evidence for X-ray damage caused during ARXPS measurement

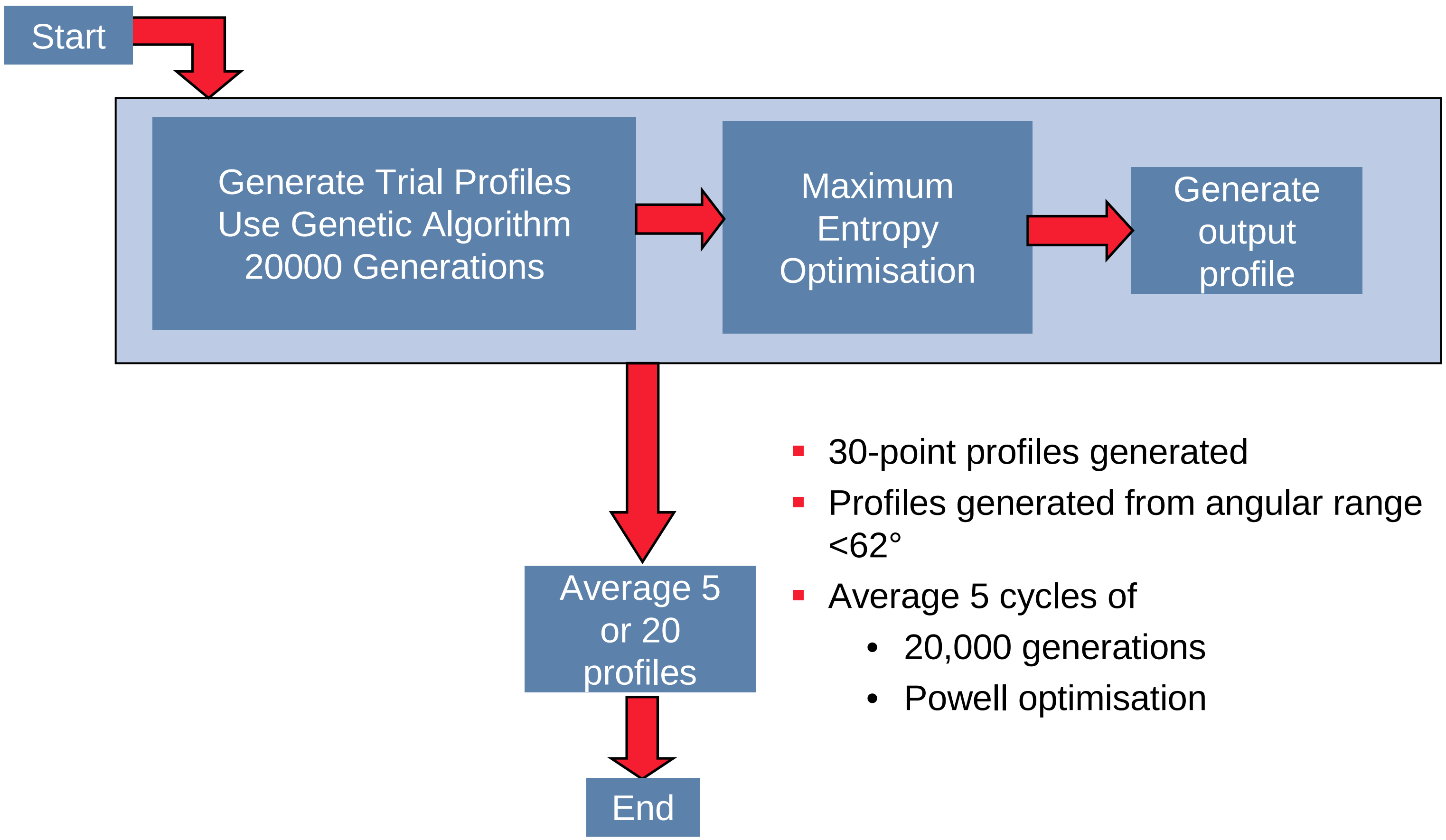
Thickness Measurement



- ARXPS can be applied to delicate samples by mapping the sample and summing the data.
- Only feasible with PARXPS

Generation of Depth Profiles

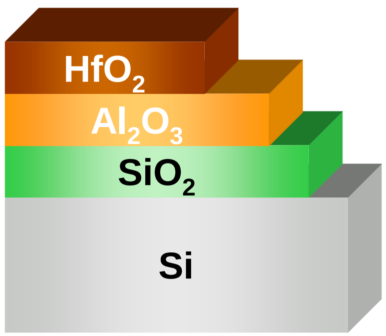
- Summary of the Maximum Entropy method



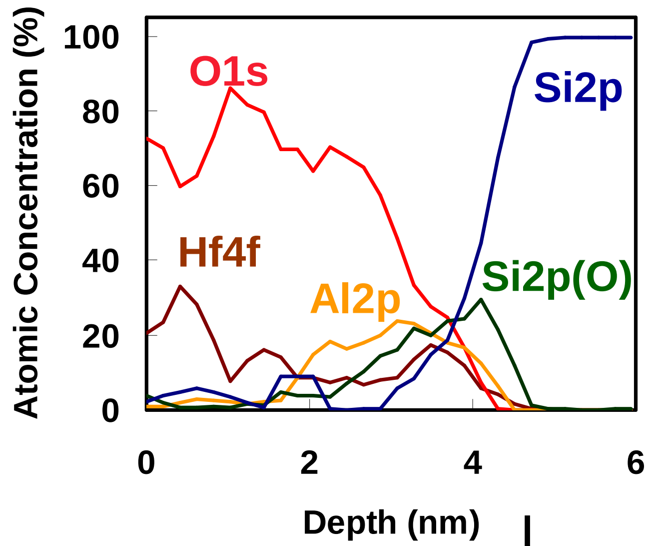
- 30-point profiles generated
- Profiles generated from angular range <62°
- Average 5 cycles of
  - 20,000 generations
  - Powell optimisation

Depth Profile Generation

Sample

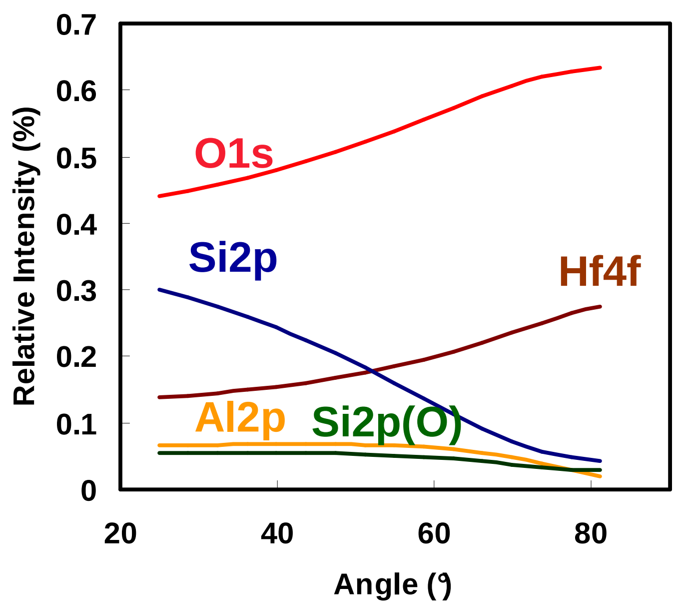


Generate Random Profile



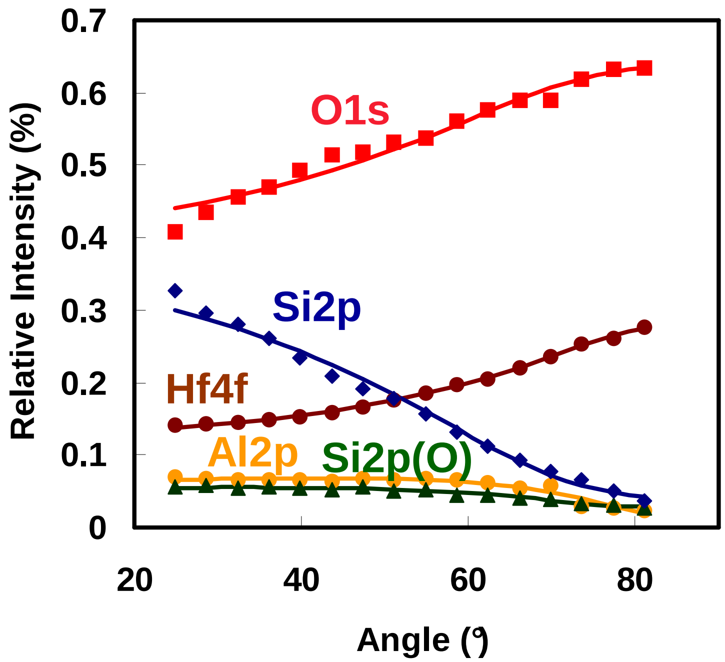
Calculate Expected ARXPS Data (Beer Lambert Law)

$T_j(\theta) = \exp(-t/\lambda\cos\theta)$



Depth Profile Generation (2)

Determine error between observed and calculated data:



$$\chi^2 = \sum_k \frac{\left(I_k^{calc} - I_k^{obs}\right)^2}{\sigma_k^2}$$

- Calculate the entropy associated with a particular profile (the probability of finding the sample in that particular state)

$$S = \sum_j \sum_i c_{j,i} - c_{j,i}^0 - c_{j,i} \log\left(\frac{c_{j,i}}{c_{j,i}^0}\right)$$

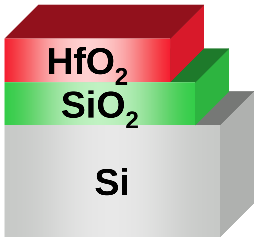
- $c_{j,i}$ is the concentration of element i in layer j

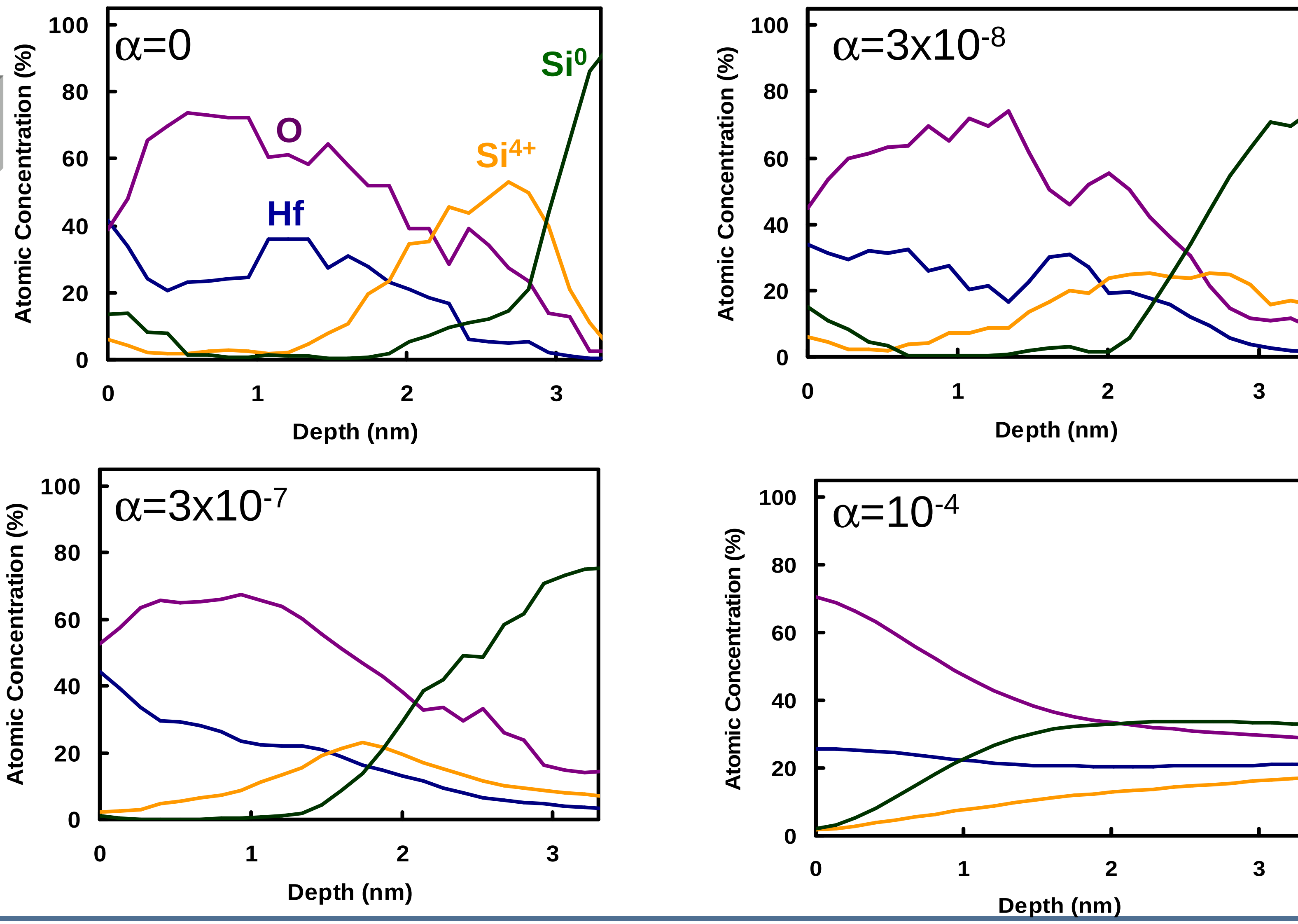
- Maximise the joint probability function

$$Q = \alpha S - 0.5\chi^2$$

- Repeat process to obtain most likely profile

Effect of Alpha on Generated, Unconstrained Profile

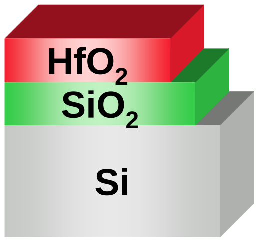


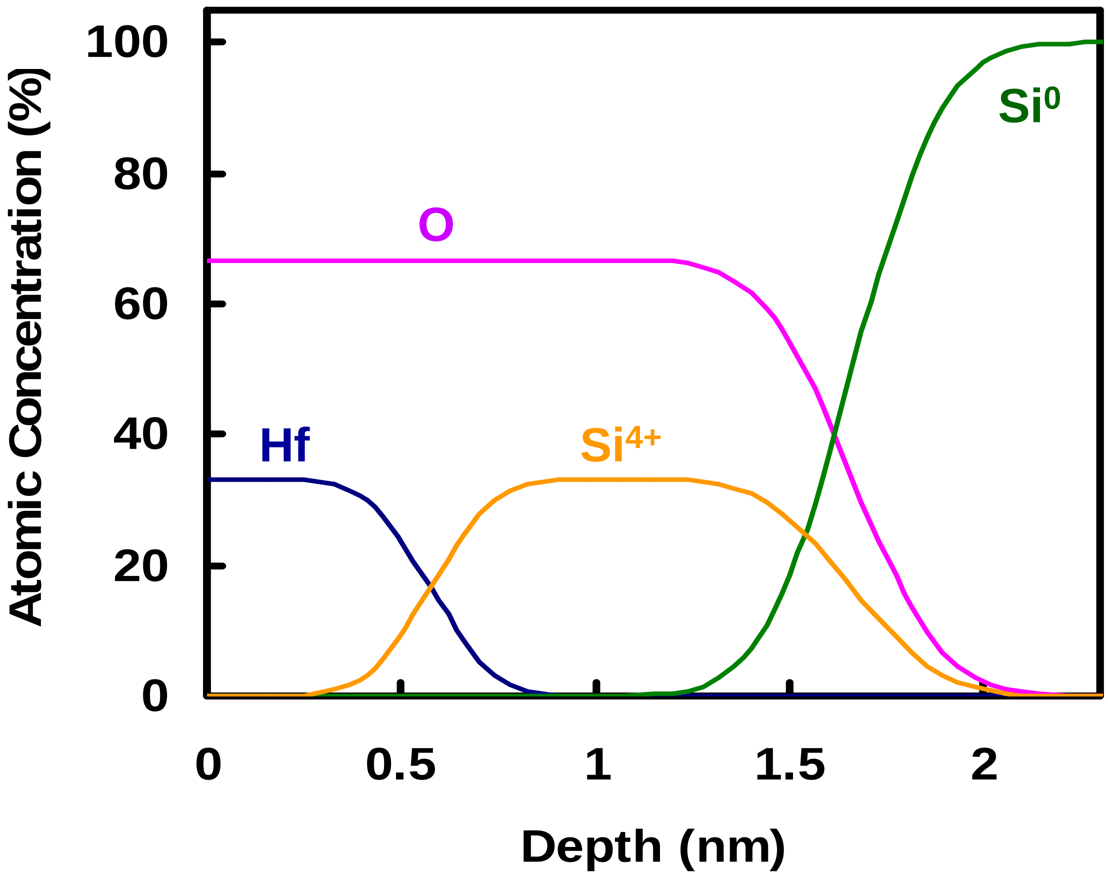


Add Constraints and Automate

- Need to apply constraints to prevent chemically unreasonable solutions (analogy to spectrum peak fitting)
  - We know the composition of the substrate
  - Assume mixtures of stoichiometric components ("Fit Units")
    - Examples
      - HfO_2 and SiO_2
      - $SiO_xN_y = (SiO_2)_a + (Si_3N_4)_b$
  - Non-stoichiometric components / "Free" oxygen
- Examine data to obtain the optimum value for 'α' (automated)
- Choose most appropriate angular range (automated)
  - Depends upon layer thickness

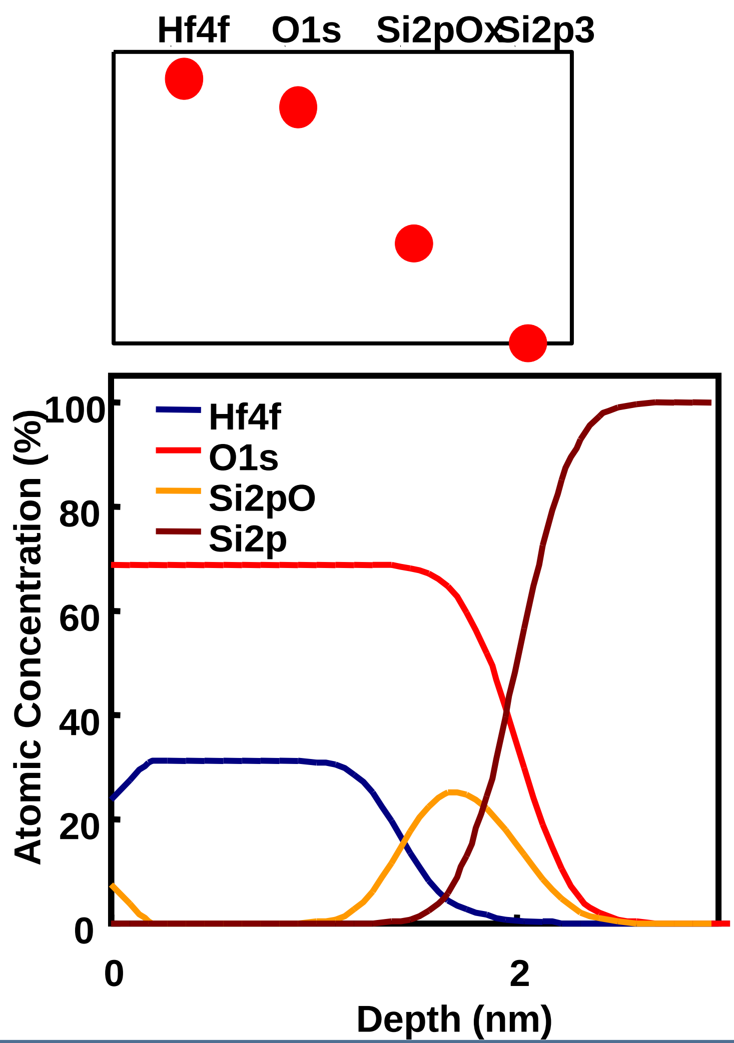
Use Fit Units



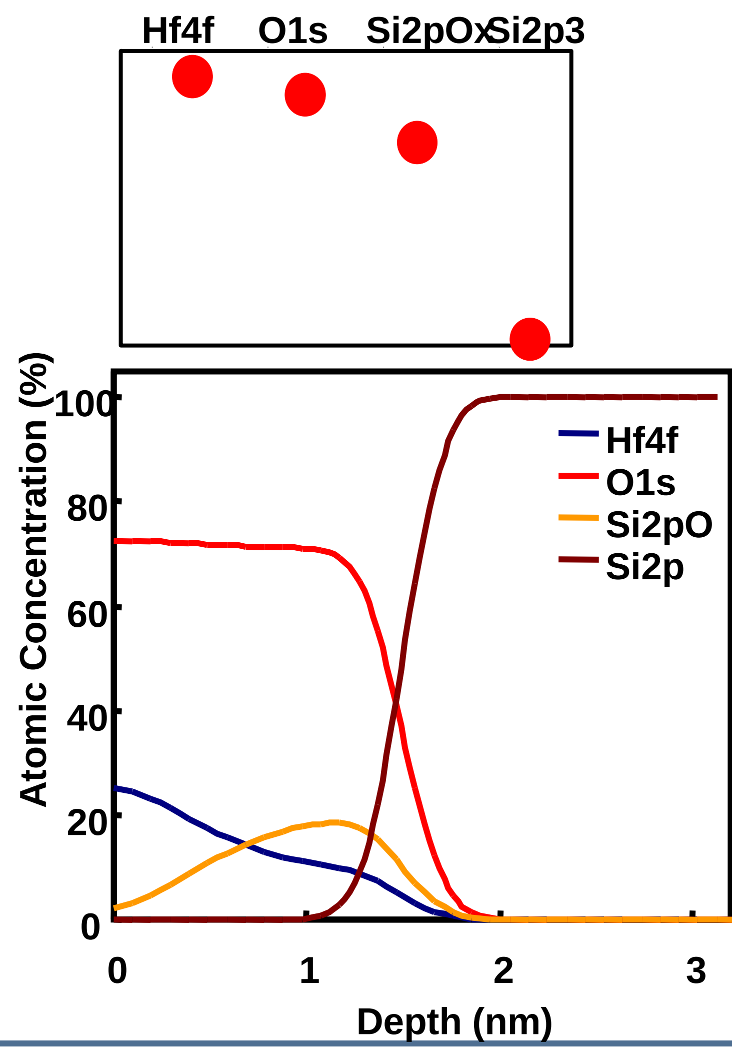


Effect of Interlayer on 30 Cycle ALD Layer

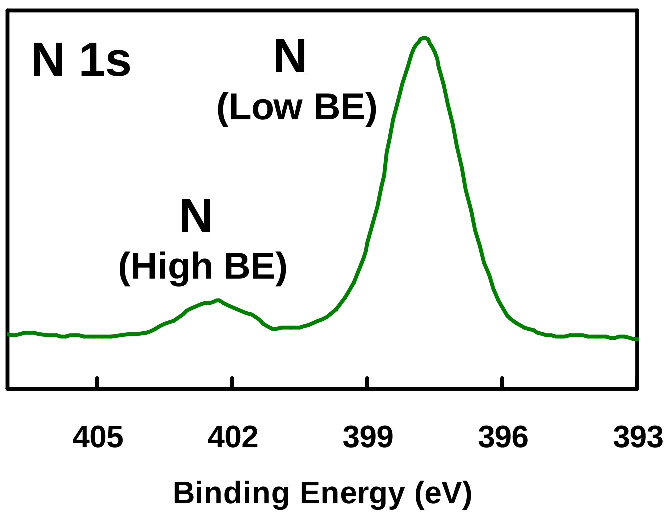
- Grown on thin SiO_2 layer

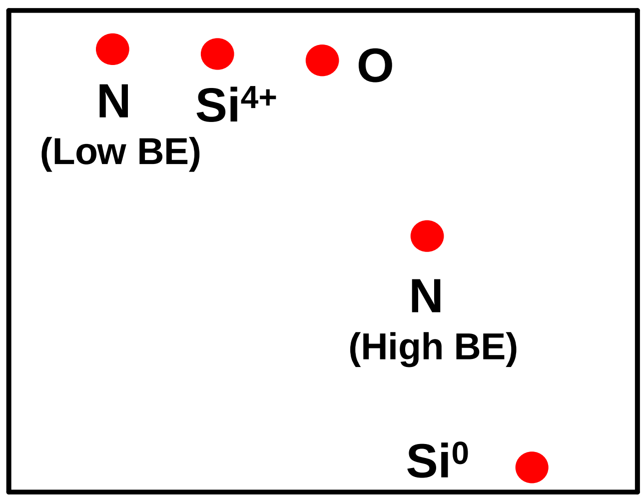


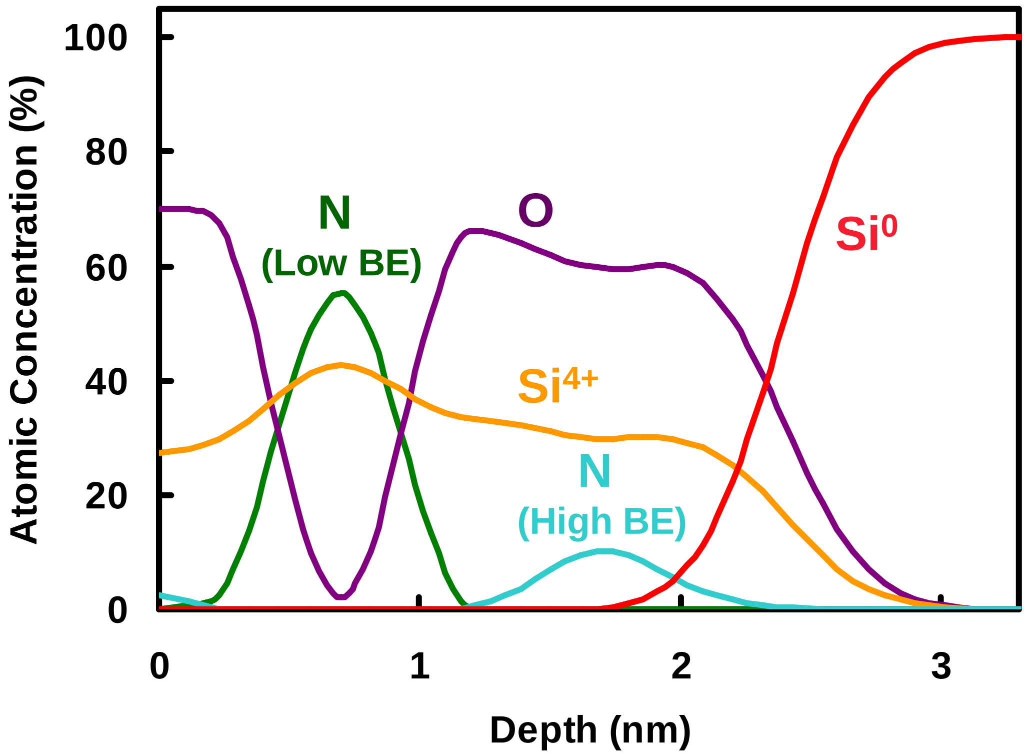
- Grown on HF last surface



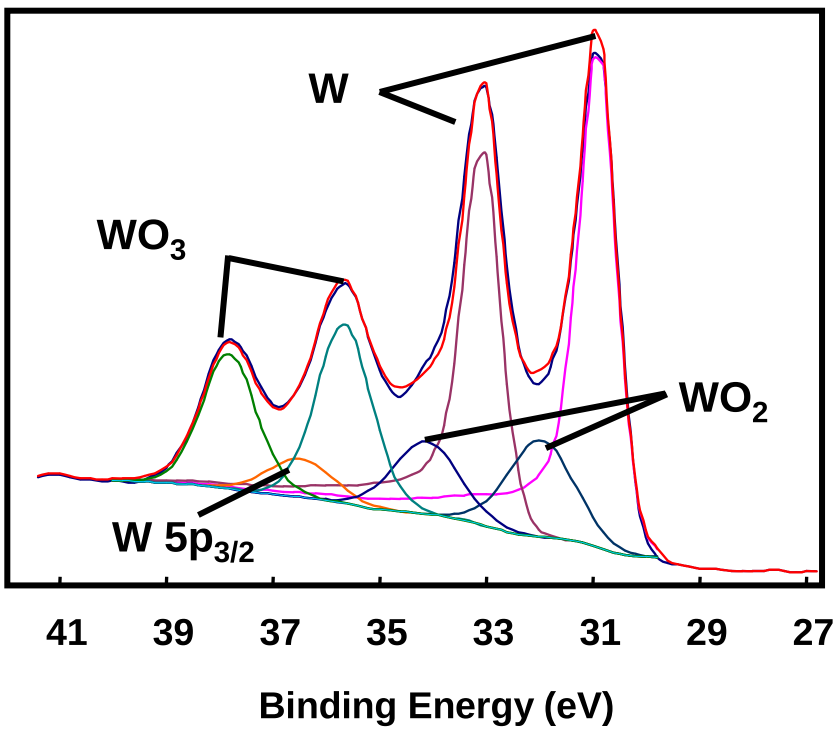
SiON Chemical State Profile



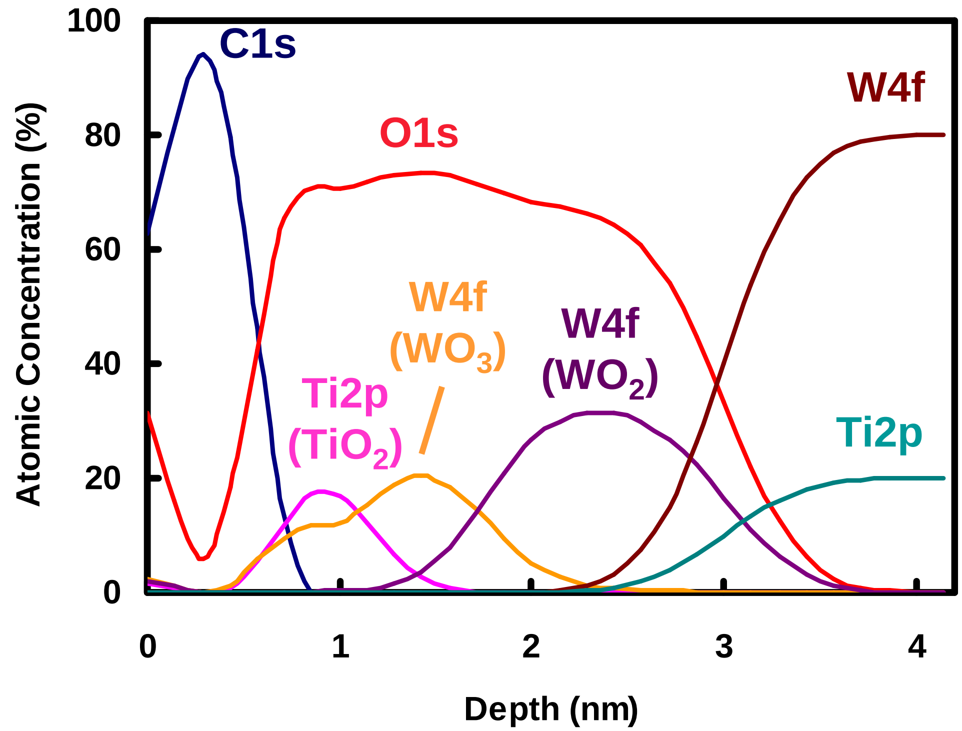




Ti/W Alloy



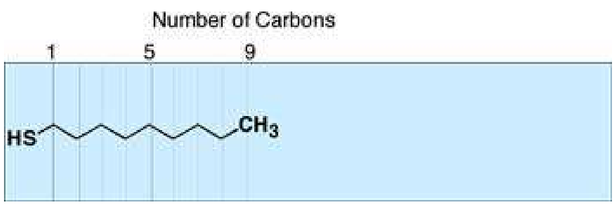
W
WO$_3$
WO$_2$
W 5p$_{3/2}$
41
39
37
35
33
31
29
27
Binding Energy (eV)

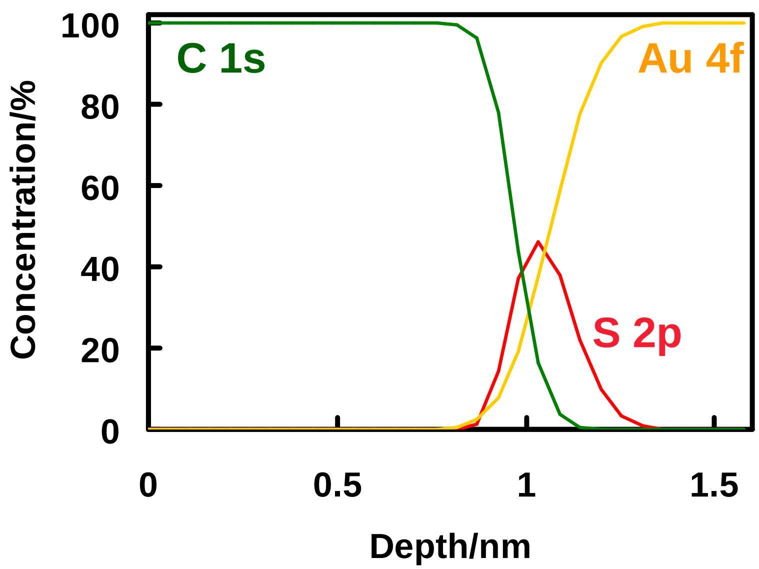


100
80
60
40
20
0
Atomic Concentration (%)
C1s
O1s
W4f
W4f (WO$_3$)
W4f (WO$_2$)
Ti2p (TiO$_2$)
Ti2p
0
1
2
3
4
Depth (nm)

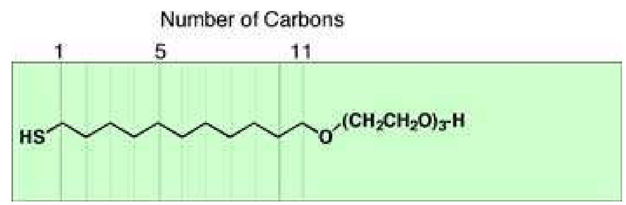
Profiles from SAMs

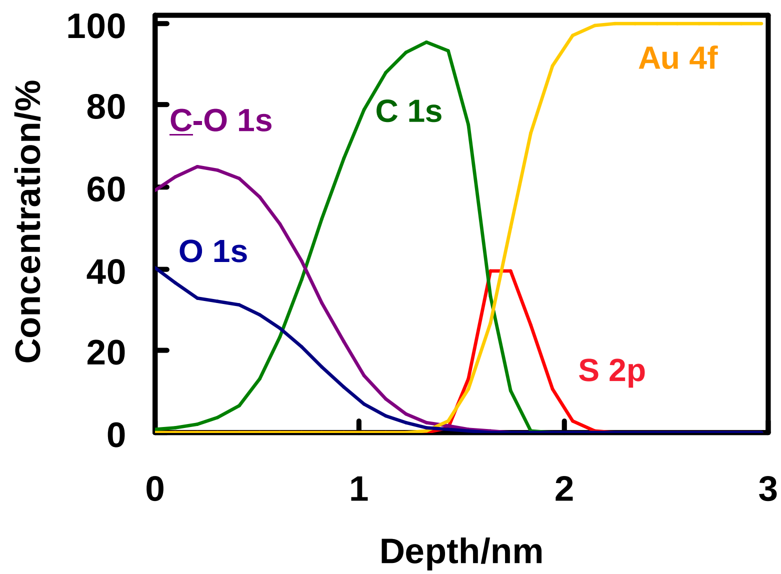
Nonanethiol





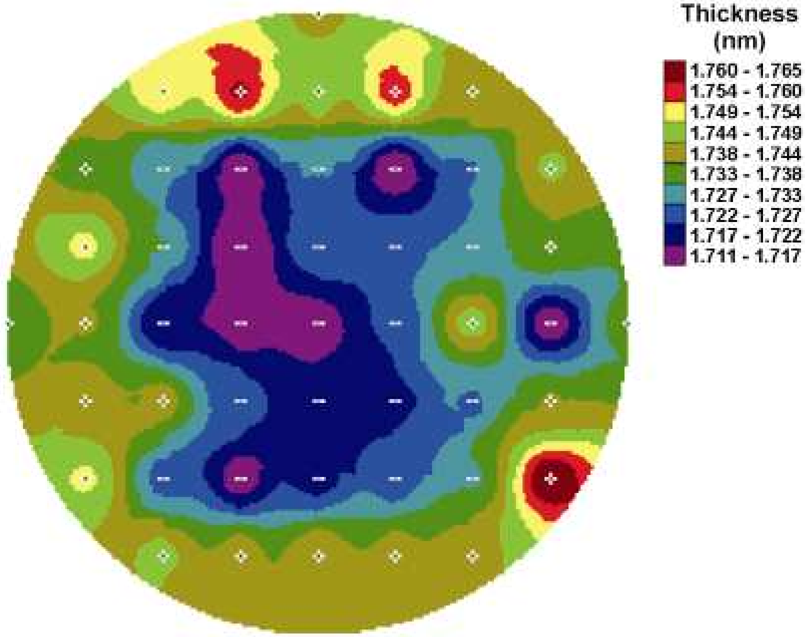
1-Mercapto-11-undecyl-tri(ethylene glycol)



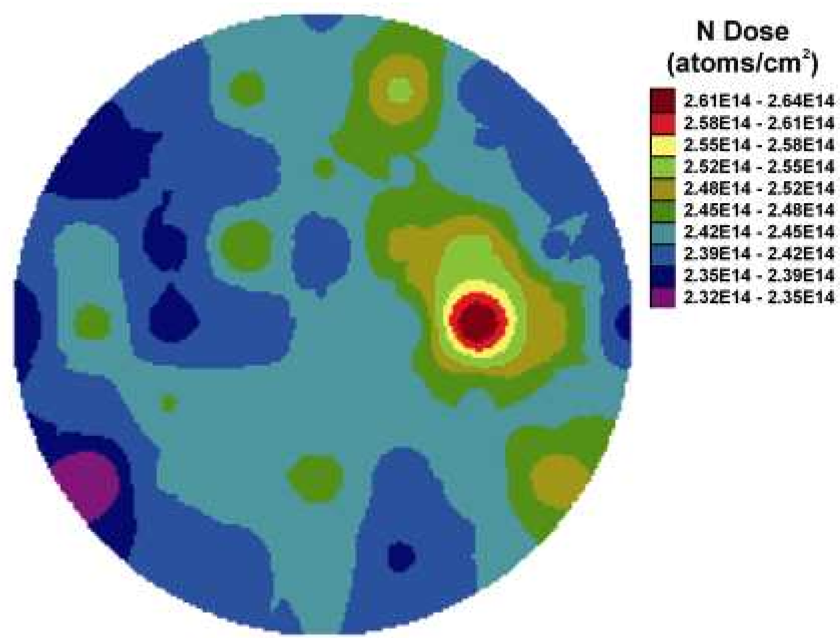


Nitrogen Dose and Thickness

- 300 mm wafer
- Single measurement
- 49-point maps



Thickness



Dose

Conclusions

- Angle Resolved XPS is a powerful tool for the characterisation of ultra-thin films
  - Layer ordering
  - Multiple layer thickness determination
  - Depth profiles
- Parallel ARXPS extends the capabilities of the technique
  - Small features
  - Large samples
  - Mapping
  - *Larger number of angles*

Acknowledgements

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