X-ray Photoelectron Spectroscopy of High-*k* Dielectrics

Anoop Mathew, Korhan Demirkan, R. L. Opila

Materials Science and Engineering

The University of Delaware

Newark, DE 19711

Chang-Gong Wang and Glen Wilk

ASM America

Phoenix, AZ 85034

David G. Watson

Physical Electronics

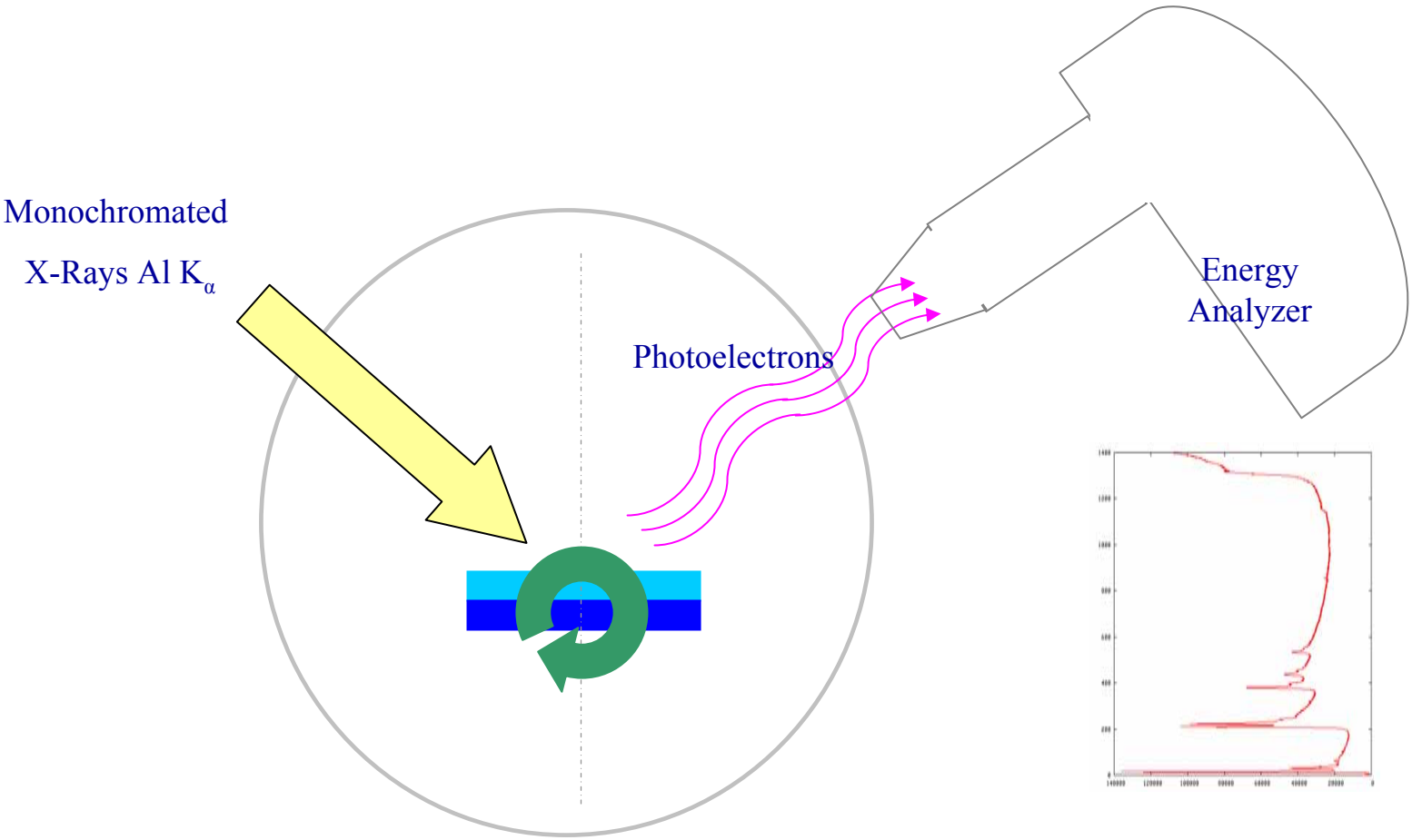
Chanhassen, MN 55317

opila@udel.edu

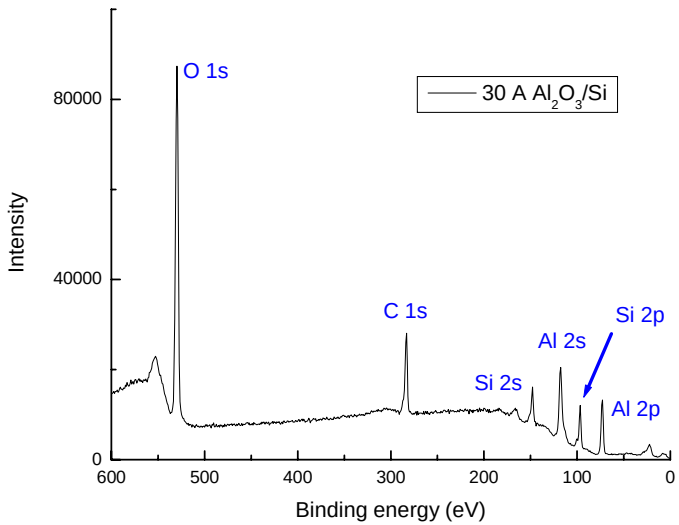
XPS of High-κ Dielectrics

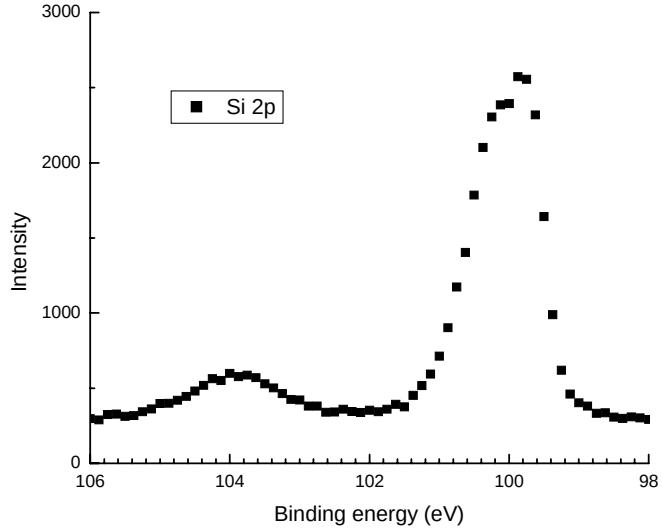
- Photoelectron spectroscopy
  - Composition
  - Chemical shift
  - Depth profile (maximum entropy)
  - Interfacial charge
- Angle resolved photoemission
  - Maximum entropy algorithm
  - Implementation to $(HfO_2)_x(SiO_2)_{1-x}$
  - Limitations to AR-XPS, max entropy
- Future work and conclusions

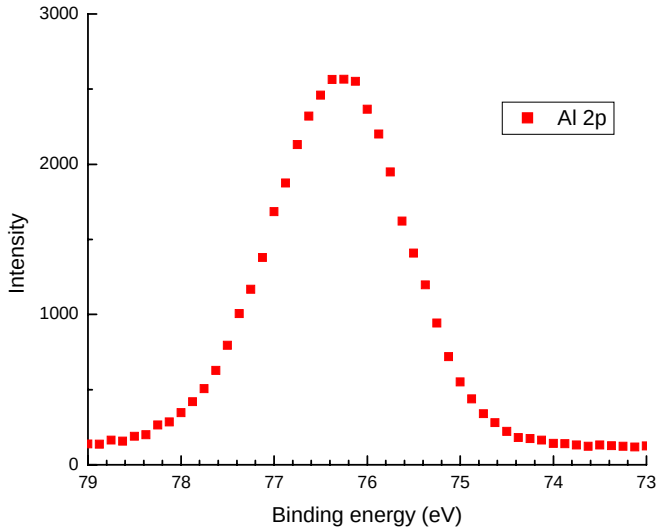
X-Ray Photoelectron Spectroscopy

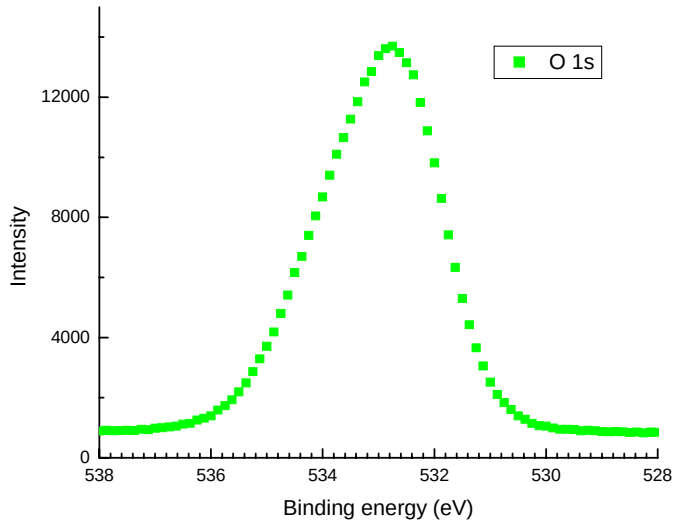


XPS 30Å ALD Al_2O_3/H-Si

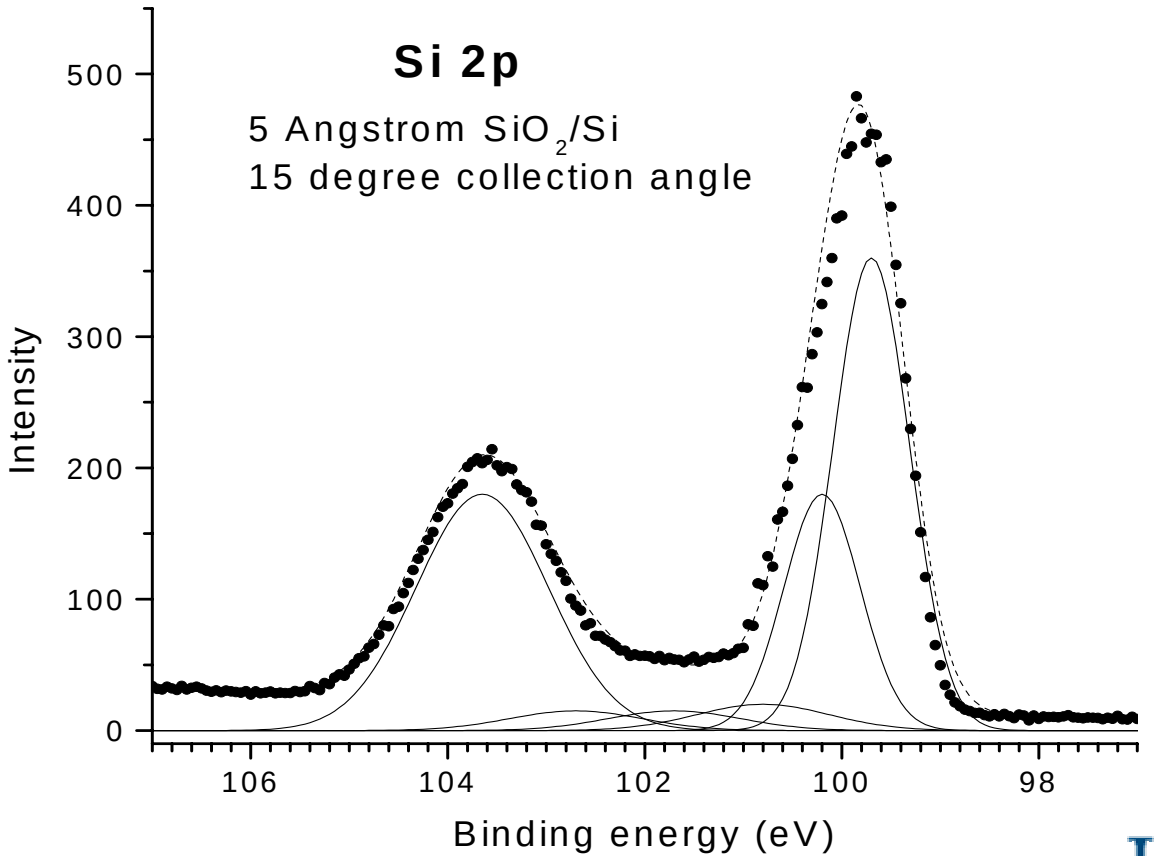






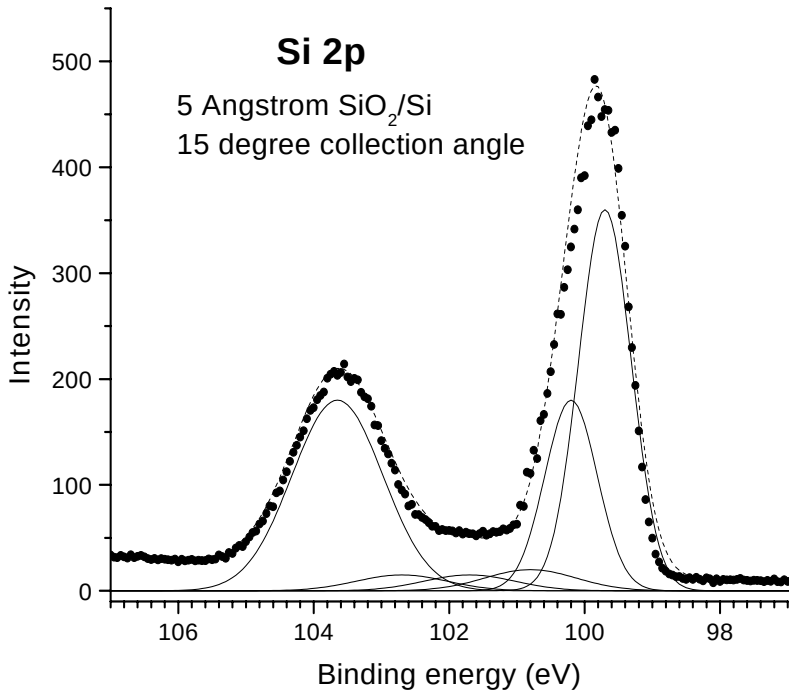


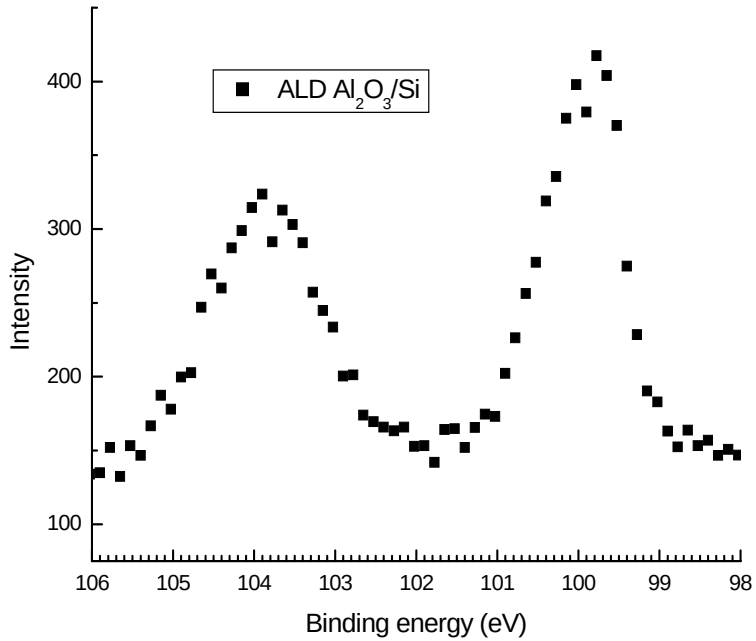
X-ray Photoemission of Si Surfaces



UNIVERSITY OF DELAWARE

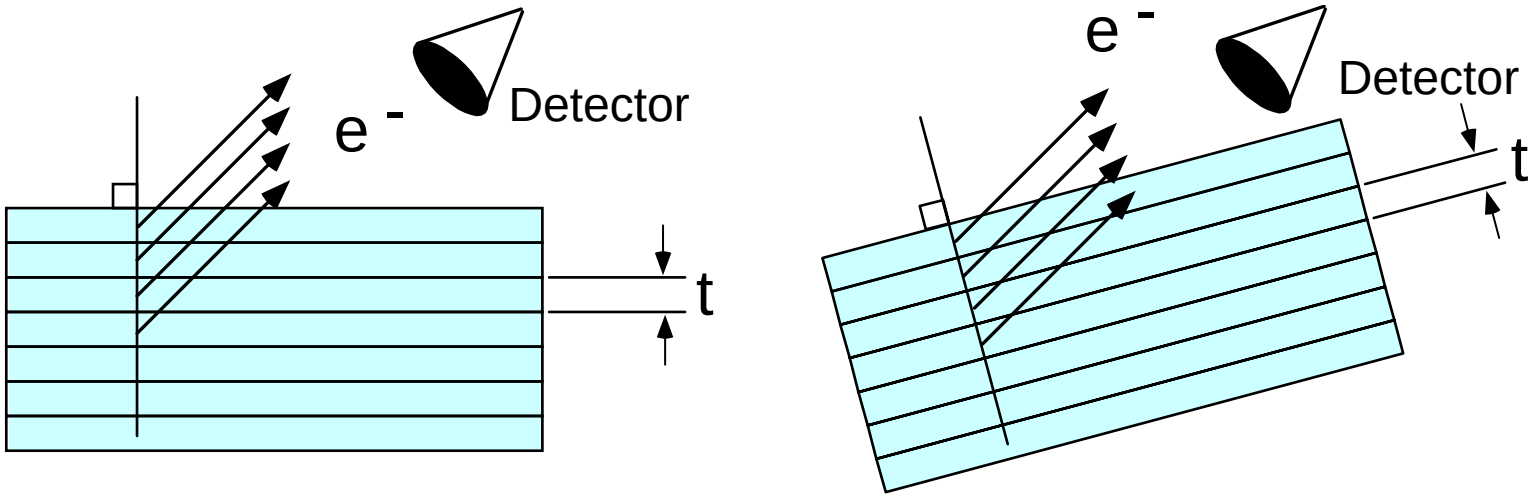
How much interfacial SiO_2?





DETERMINING THE COMPOSITION DISTRIBUTION:

Angle-resolved XPS and the Maximum Entropy Method



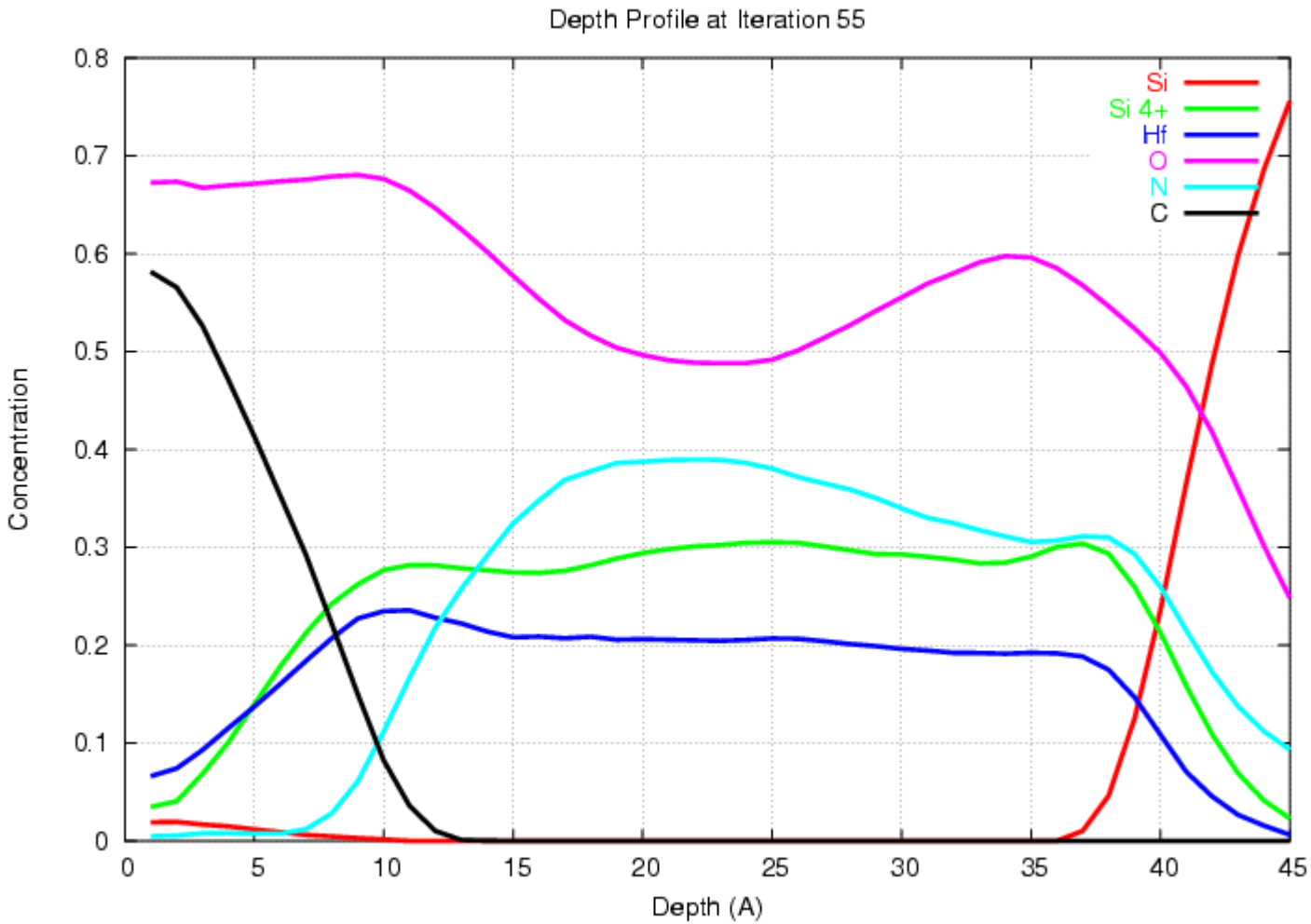
- The Maximum Entropy Method
  - Record photoemission spectra as a function of angle.
  - Using integrated intensities, maximize functional:

$$\mathbf{Q = \alpha S - C/2}$$

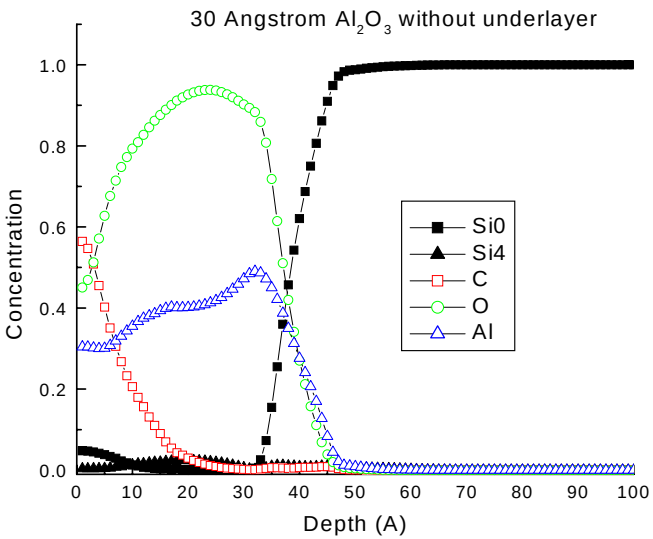
$$C = \chi^2 = \sum_k \frac{(I_k^{calc} - I_k^{obs})^2}{\sigma_k^2}$$

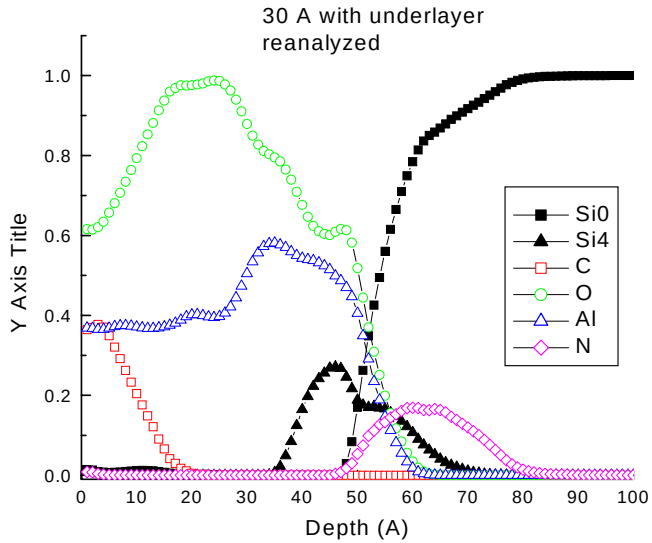
$$S = \sum_j \sum_i n_{j,i} - m_{j,i} - n_{j,i} \log\left(\frac{n_{j,i}}{m_{j,i}}\right)$$

Hafnium Silicate reconstructed using maximum entropy algorithm



Al_2O_3 Thickness as a function of SiO_xN_y underlayer: the role of induction



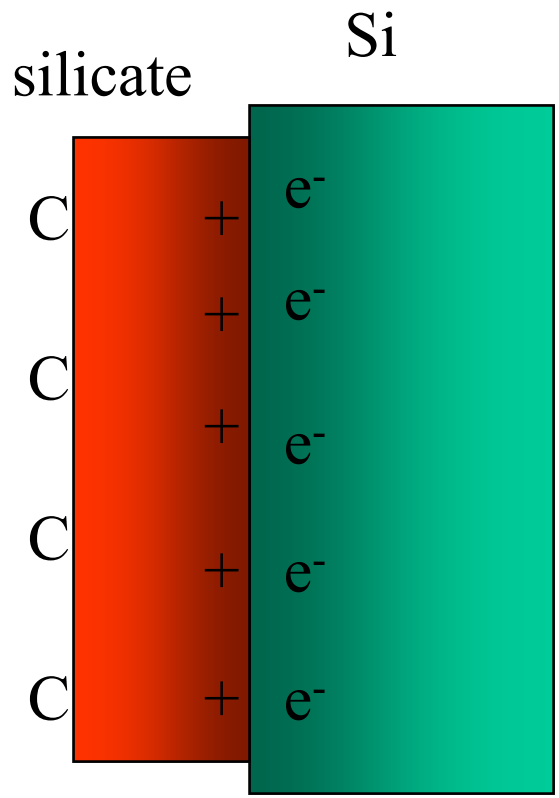


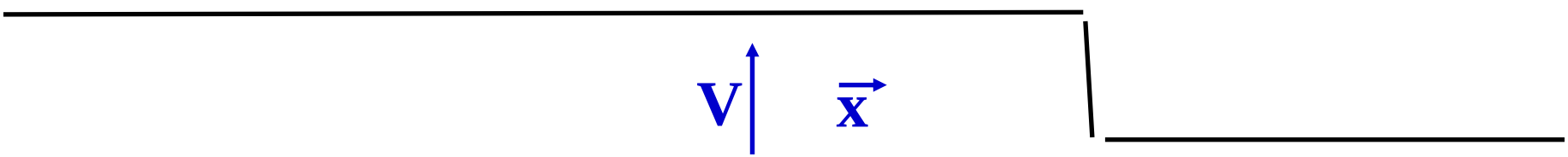
UNIVERSITY OF DELAWARE

Interface charge and photoelectron binding energies

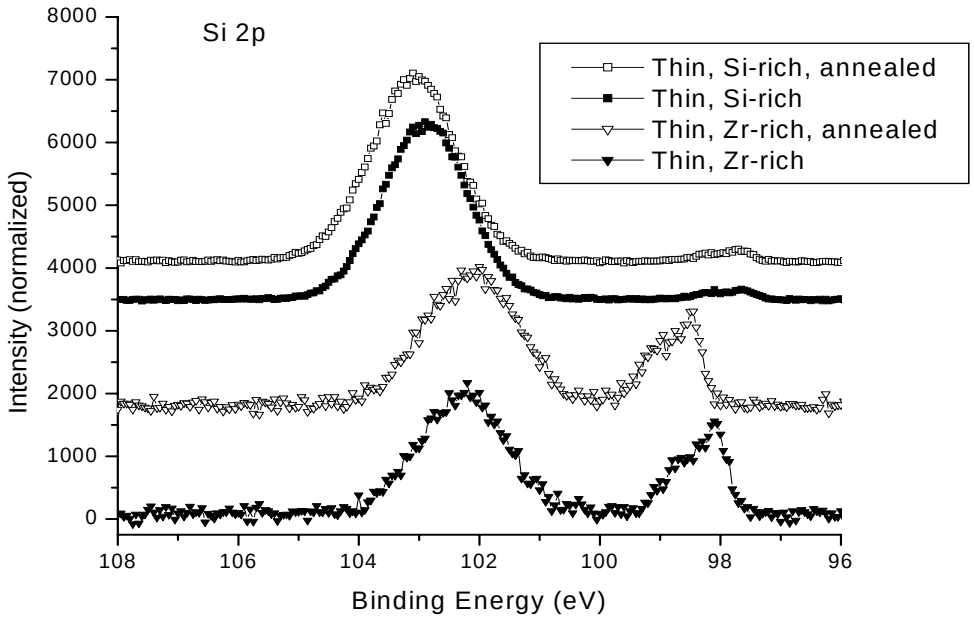
Silicate and adventitious carbon photoelectrons will be more energetic than silicon substrate, due to charge at interface.

Annealing in forming gas (H_2) decorates some dangling bonds, and reduces interface charge.





Interface charge and The effects of annealing

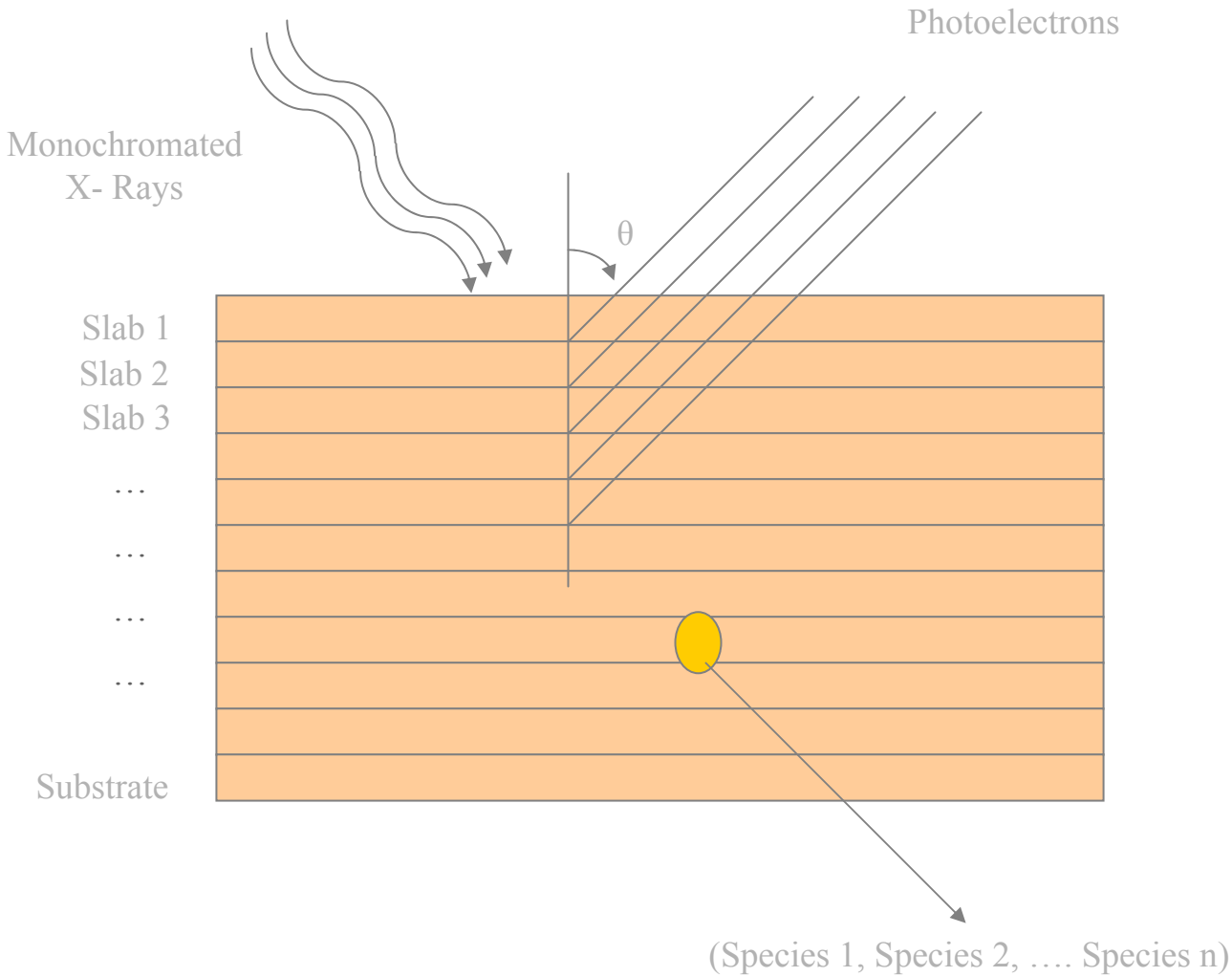


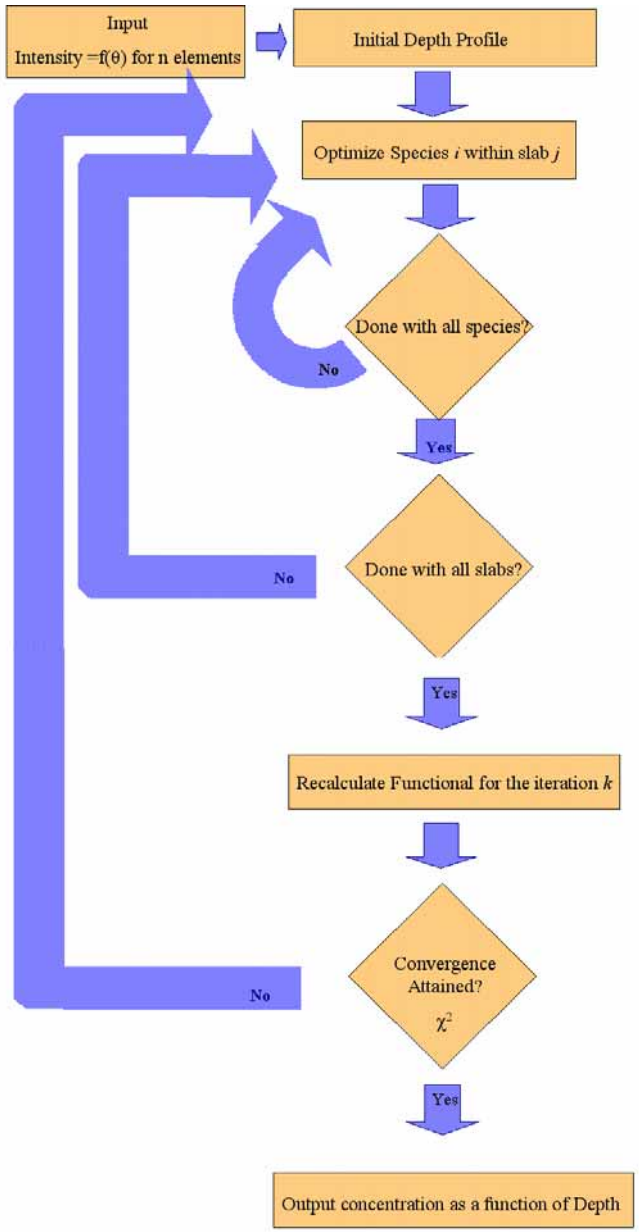
When referencing the outer oxide peak positions to C 1s at 285.0 eV the underlying Si^0 appears at binding energies < 99.6 eV.

(annealing for 30 minutes in forming gas at 400°C reduces apparent shift)

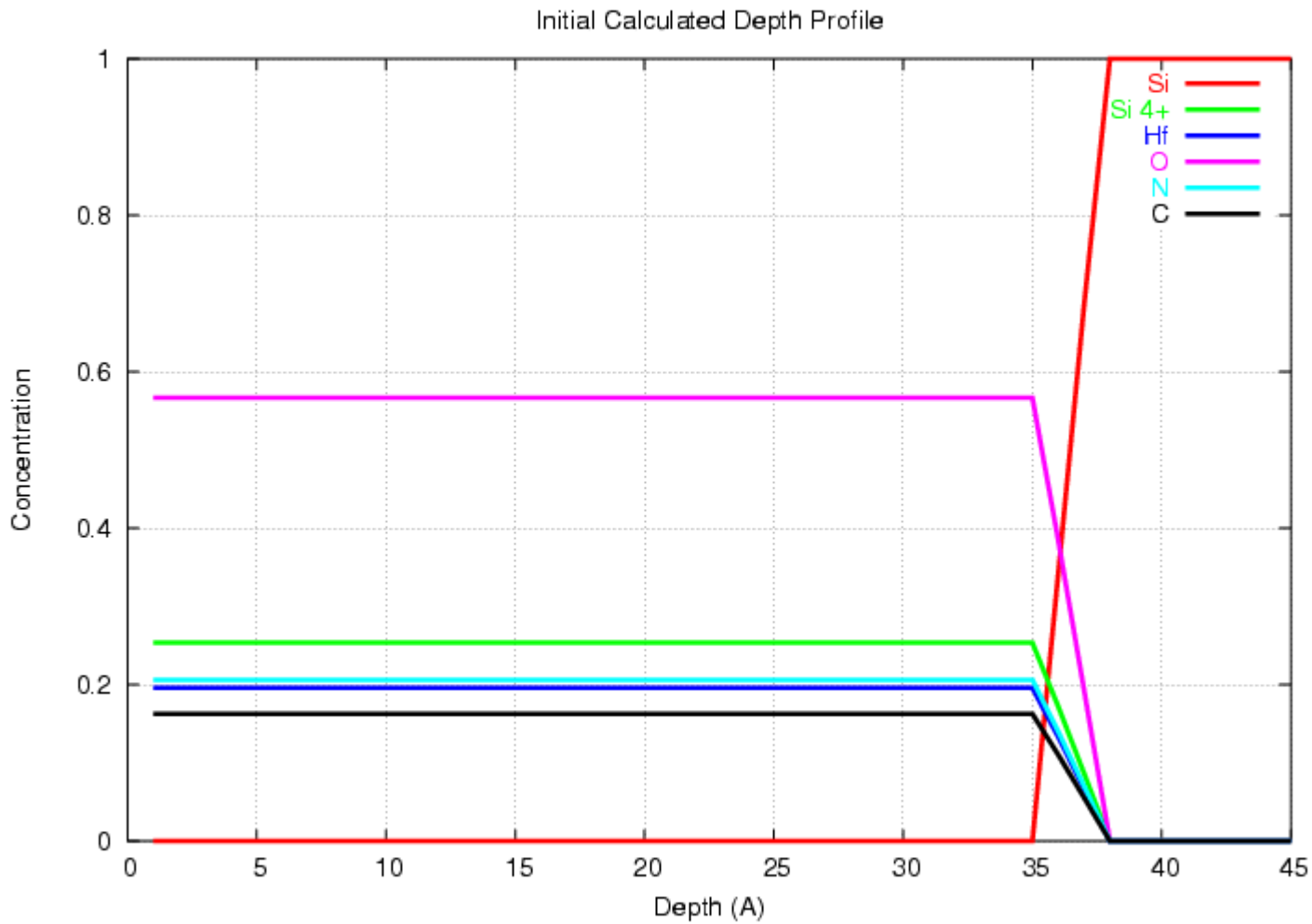
XPS of High-κ Dielectrics

- Photoelectron spectroscopy
  - Composition
  - Chemical shift
  - Depth profile (maximum entropy)
  - Interfacial charge
- Angle resolved photoemission
  - Maximum entropy algorithm
  - Implementation to ALD, nitrided $(HfO_2)_x(SiO_2)_{1-x}$
  - Limitations to AR-XPS, max entropy
- Future work and conclusions

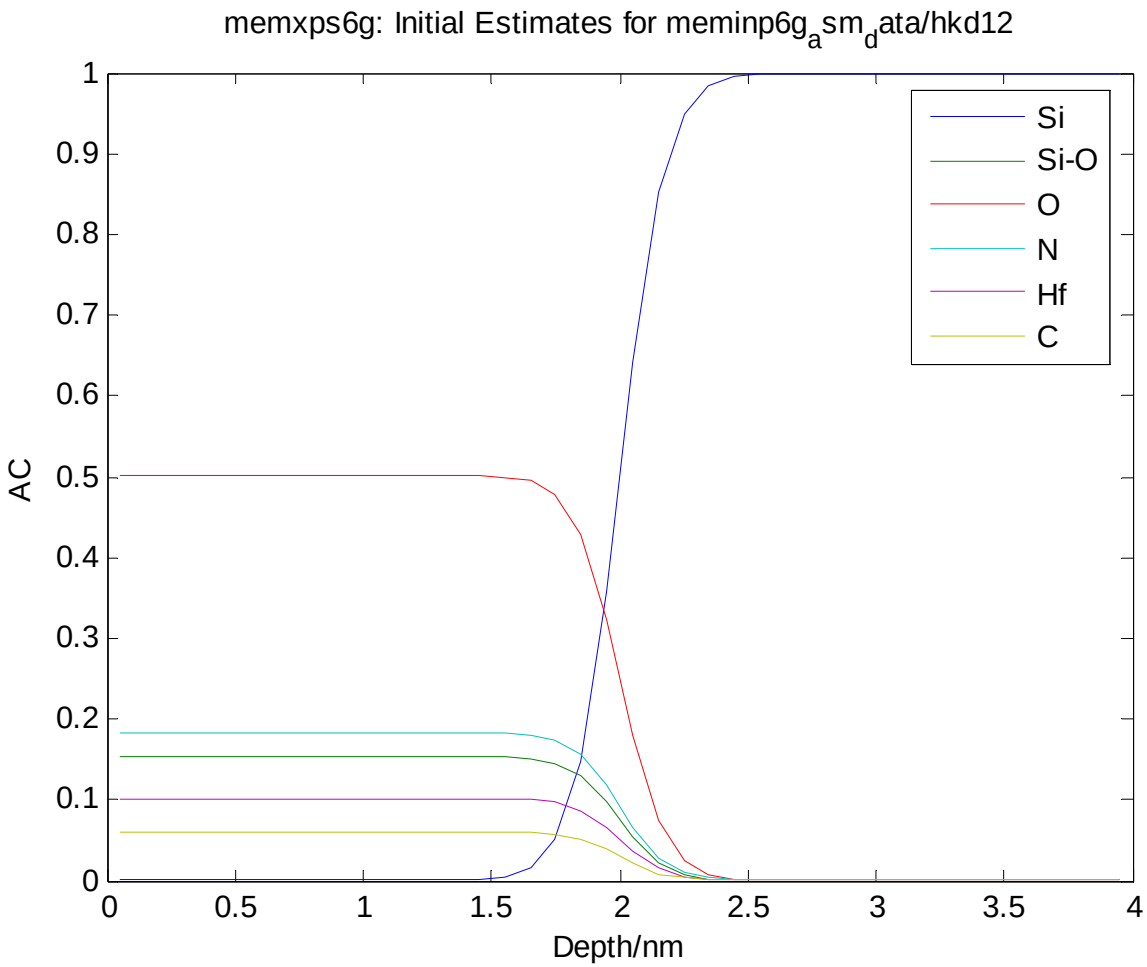

Photoelectrons
Monochromated
X- Rays
θ
Slab 1
Slab 2
Slab 3
…
…
…
…
Substrate
(Species 1, Species 2, …. Species n)



UNIVERSITY OF DELAWARE

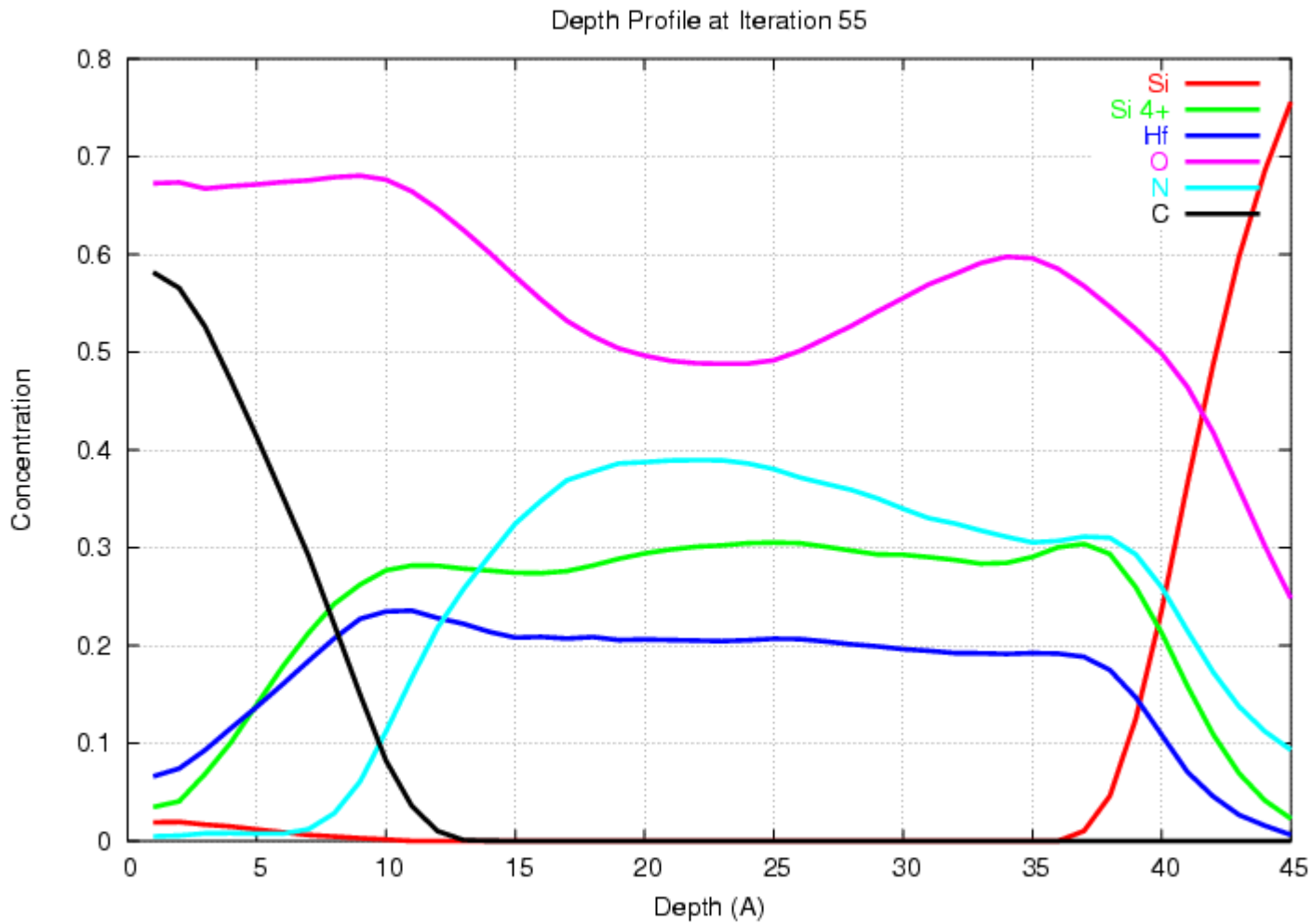


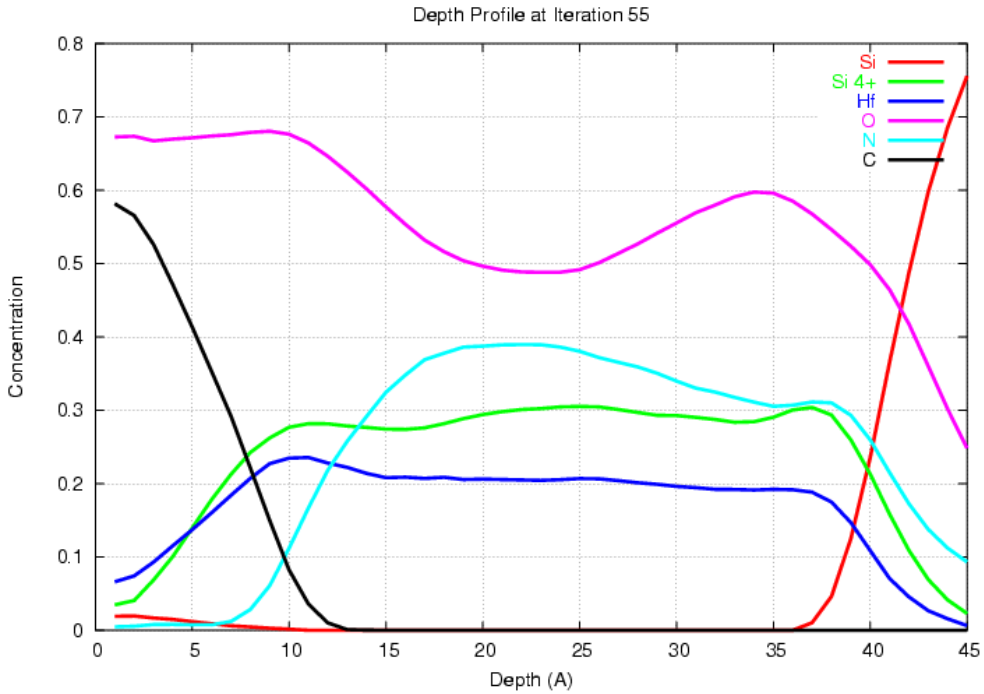
$$S = \sum_j \sum_i n_{j,i} - m_{j,i} - n_{j,i} \log\left(\frac{n_{j,i}}{m_{j,i}}\right)$$



Initial Estimate of Profile (PHI Version of Program)

UNIVERSITY OF DELAWARE


Depth Profile at Iteration 55
Concentration
Depth (A)
Si
Si 4+
Hf
O
N
C
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
5
10
15
20
25
30
35
40
45

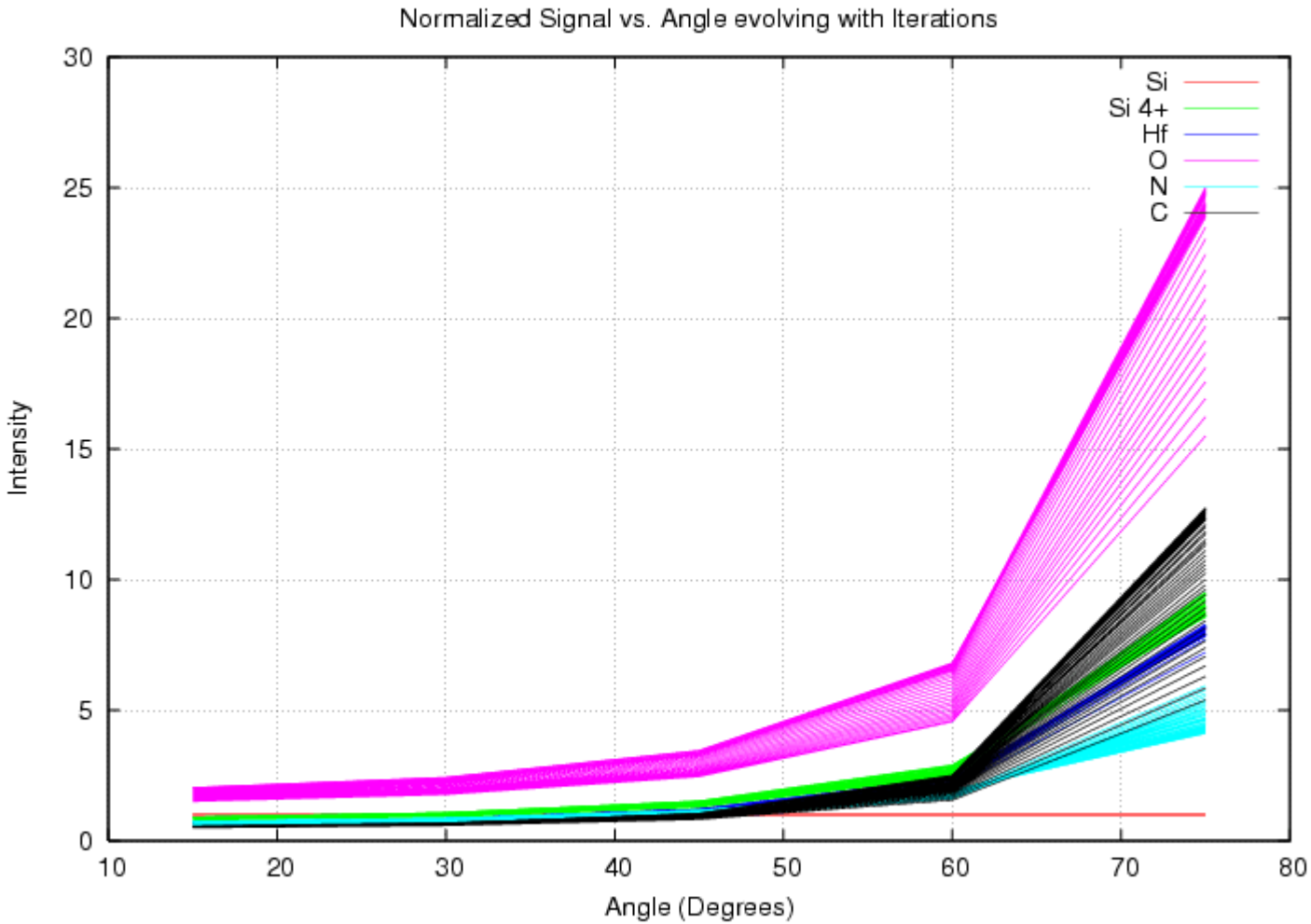


Observations:

1. Carbon restricted to outer surface.
2. Hf^{+4} and Si^{+4} concentrations are roughly constant
   - Interface is SiO_2?
3. N is deep within film (relative to O)
4. O is double humped
   - Surface is oxidized
   - Dielectric/Si interface is oxide?

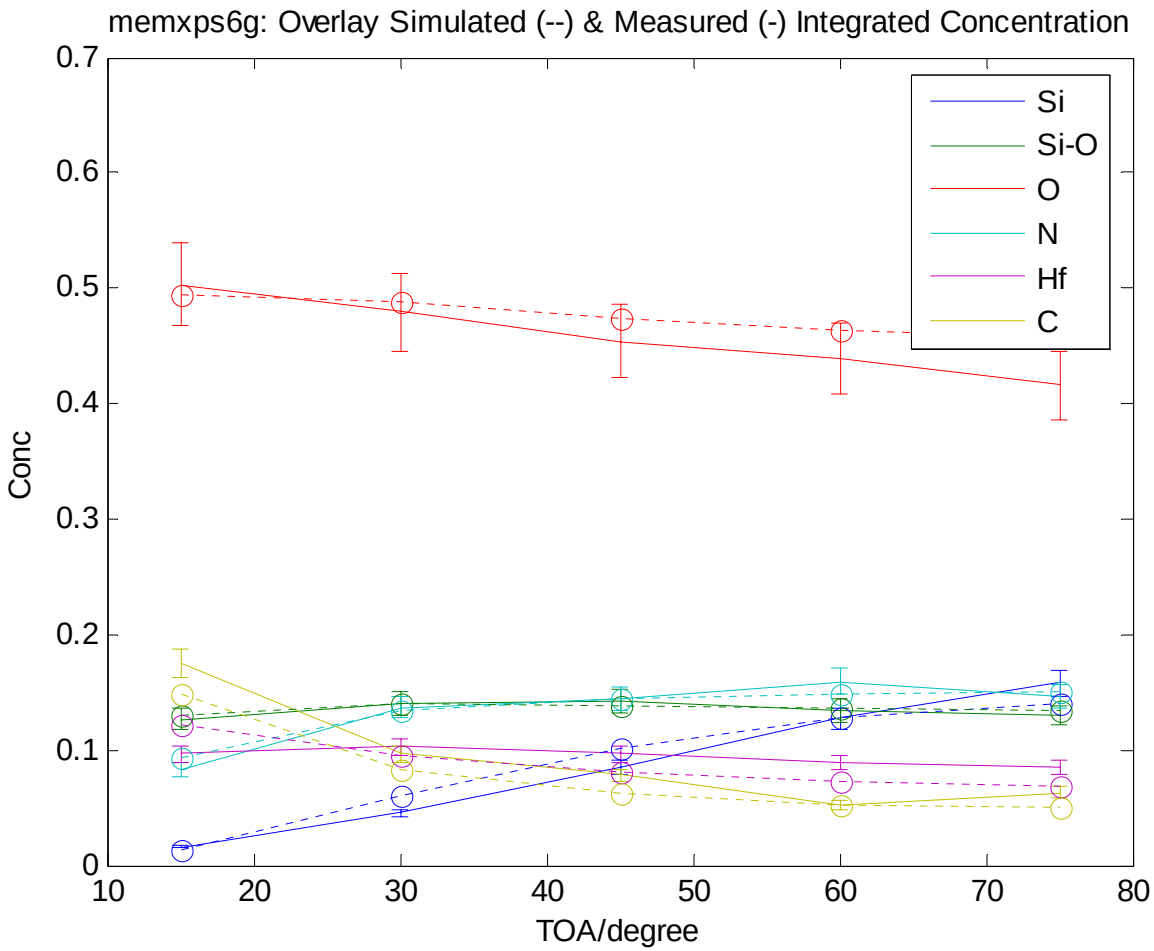
Limitations:

1. Broad interfaces
2. Concentrations depend upon sensitivity factors
3. Depths depend upon electron attenuation lengths



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

UNIVERSITY OF DELAWARE



Comparison between simulated and measured integrated concentration (PHI program)

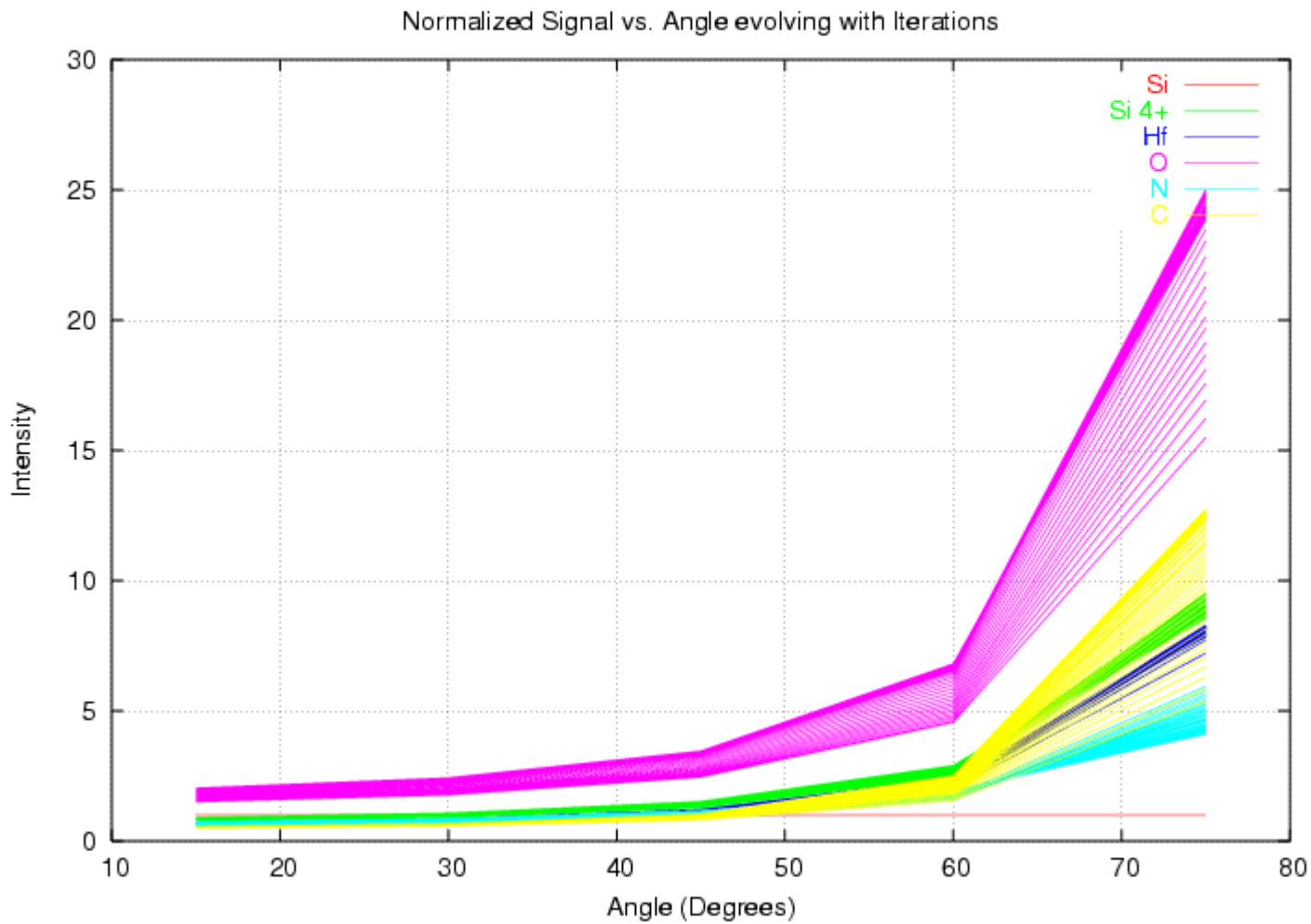
Variables

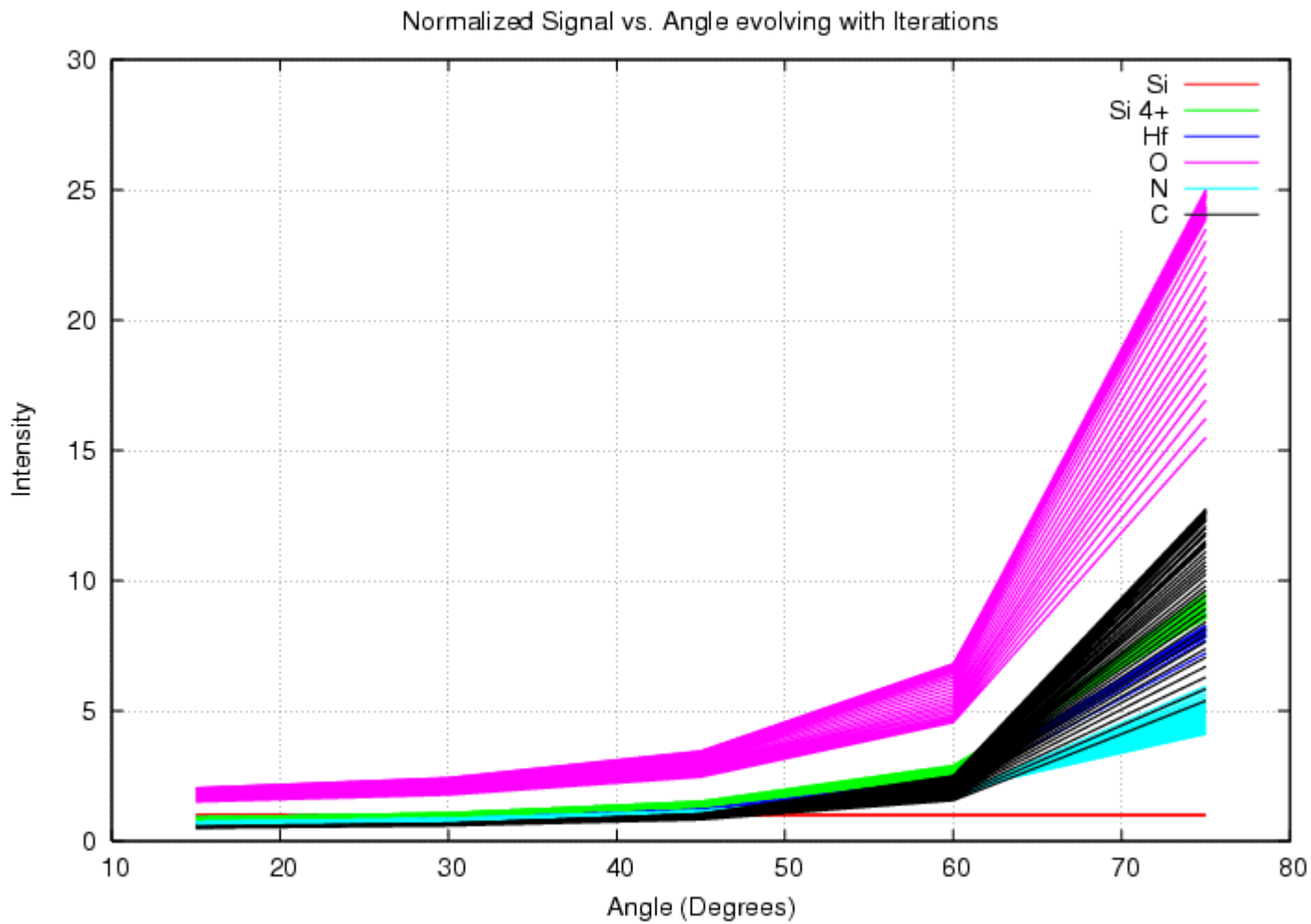
- Role of functional, α
- Better electron attenuation lengths
  - Kinetic energy effects
  - Matrix effects
- Better sensitivity factors
- Separate instrumentation and physical effects
  - Enhanced forward scattering at low collection angles.
- Pathological samples
  - Super lattices, δ-doping
- Depth dependence

Conclusions

- AR-XPS
  - Is a good qualitative tool
  - Can be used to compare families of specimens
  - Should be interpreted absolutely with caution
- ALD nitrided $(HfO_2)_x(SiO_2)_{1-x}$
  - Has oxide, silicon-rich interface with substrate
  - Has uniform N, Si, and Hf distribution in bulk of film
  - Outer surface is oxidized

Acknowledge Vincent Donnelly, Jane Chang, Joe Eng


Normalized Signal vs. Angle evolving with Iterations
Intensity
Angle (Degrees)
0
5
10
15
20
25
30
10
20
30
40
50
60
70
80
Si
Si 4+
Hf
O
N
C


Normalized Signal vs. Angle evolving with Iterations
Intensity
Angle (Degrees)
0
5
10
15
20
25
30
10
20
30
40
50
60
70
80
Si
Si 4+
Hf
O
N
C