X-ray Photoelectron Spectroscopy of High-\( k \) Dielectrics

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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

Monochromated X-Rays Al Kα

Energy Analyzer

Photoelectrons
XPS 30Å ALD Al$_2$O$_3$/H-Si
X-ray Photoemission of Si Surfaces

Si 2p
5 Angstrom SiO$_2$/Si
15 degree collection angle
How much interfacial SiO$_2$?

![Graph showing Si 2p peak for 5 Angstrom SiO$_2$/Si with a 15 degree collection angle.](image1)

![Graph showing ALD Al$_2$O$_3$/Si.](image2)
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:

$$Q = \alpha S - C/2$$

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

$$S = \sum_j \sum_i n_{j,i} - m_{j,i} - n_{j,i} \log \left( \frac{n_{j,i}}{m_{j,i}} \right)$$
Hafnium Silicate reconstructed using maximum entropy algorithm
Al₂O₃ Thickness as a function of SiOₓNy underlayer: the role of induction
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)
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• Angle resolved photoemission
  – Maximum entropy algorithm
  – Implementation to ALD, nitrided \((\text{HfO}_2)_x(\text{SiO}_2)_{1-x}\)
  – Limitations to AR-XPS, max entropy

• Future work and conclusions
Monochromated X- Rays

Slab 1
Slab 2
Slab 3

\[ \theta \]

Substrate

Photoelectrons

(Species 1, Species 2, ..., Species n)
Input
Intensity $I(x)$ for n elements

Initial Depth Profile

Optimize Species $r$ within slab $j$

Done with all species?

Done with all slabs?

Yes

Recalculate Functional for the iteration $k$

Convergence Attained?

Yes

Output concentration as a function of Depth

No

Yes
\[ S = \sum_j \sum_i n_{j,i} - m_{j,i} - n_{j,i} \log \left( \frac{n_{j,i}}{m_{j,i}} \right) \]
Initial Estimate of Profile (PHI Version of Program)
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
\[ C = \chi^2 = \sum_k \left( \frac{I_k^{\text{calc}} - I_k^{\text{obs}}}{\sigma_k^2} \right)^2 \]
Comparison between simulated and measured integrated concentration (PHI program)
Variables

• Role of functional, $\alpha$
• 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, $\delta$-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

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