CHARACTERIZATION OF THE OXIDE-SEMICONDUCTOR INTERFACE IN *4H*-SIC/SiO_2 STRUCTURES USING TEM AND XPS*

Joshua Taillon,[1] **Joe Ivanov**,[1] Karen Gaskell,[2] Gang Liu,[3] Leonard Feldman,[3] Sarit Dahr,[4] Tsvetanka Zheleva,[5] Aivars Lelis,[5] and **Lourdes Salamanca-Riba**[1]

10th Annual SiC MOS Program Review, College Park, MD
Thurs. August 13, 2015
Prince George's Room, 3:05PM

*Supported by ARL under contract no. W911NF-11-2-0044 and W911NF-07-2-0046 , as well as NSF Graduate Research Fellowship Grant DGE 1322106 (J. Taillon)

[1] Materials Science and Engineering, University of Maryland College Park
[2] Chemistry and Biochemistry, University of Maryland College Park
[3] Institute for Advanced Materials, Rutgers University
[4] Department of Physics, Auburn University
[5] U.S. Army Research Laboratory

THE DEPARTMENT *of* MATERIALS SCIENCE AND ENGINEERING

UNIVERSITY OF MARYLAND 18 56

Outline

- Motivation behind analytical microscopy of SiC microelectronics
  - Impacts of NO post-annealing
- TEM-EELS from a collection of SiC/SiO_2 interfaces
  - Previous findings related to the transition layer
  - HRTEM, hyperspectral imaging, machine learning techniques for signal deconvolution
  - Significant changes in interface character after NO-anneal
- Correlation with XPS results
  - What differences are observed with an NO-anneal?
- Conclusions: What's next?

Motivation and background

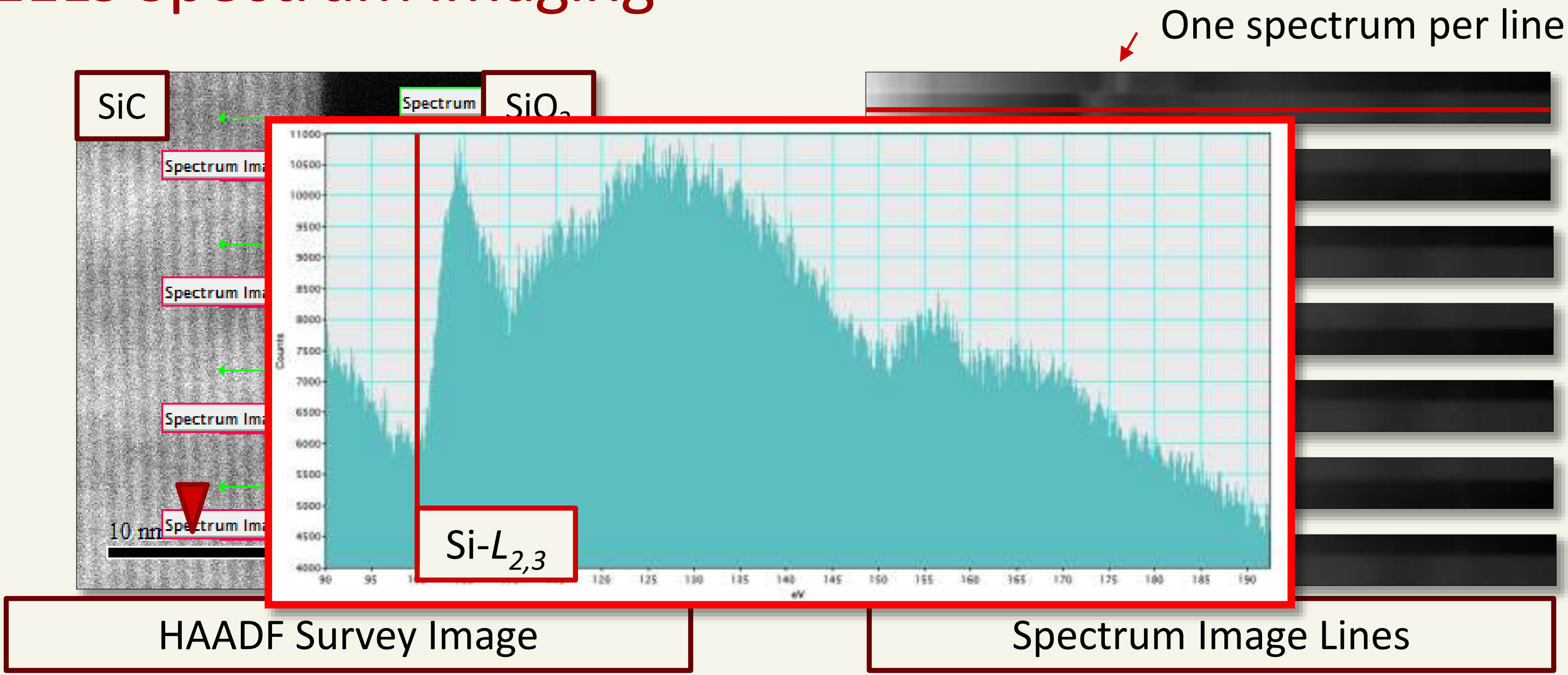
- SiC: Very promising for high temperature, high power, and high radiation environments
  - Limited by poor channel carrier mobility and reliability
  - Typical device μ_{FE}: 4H-SiC before NO anneal: $< 10\ \frac{\text{cm}^2}{\text{V}\cdot\text{s}}$; after NO anneal: ~ $45\ \frac{\text{cm}^2}{\text{V}\cdot\text{s}}$; bulk value: ~ $1{,}000\ \frac{\text{cm}^2}{\text{V}\cdot\text{s}}$
  - Electrically active defects at the SiC/SiO_2 interface inhibit devices during channel inversion
  - Other defects significantly affect the reliability and stability of devices over time

- What is the true nature of the interface, and how do our processing techniques really affect it?
  - EELS experiments suggest distinct transition region[1,2]
  - Other results (XPS, MEIS, etc.) suggest more abrupt transition [3 – 4]
  - What is NO post oxidation annealing really changing about the interface structurally and chemically?

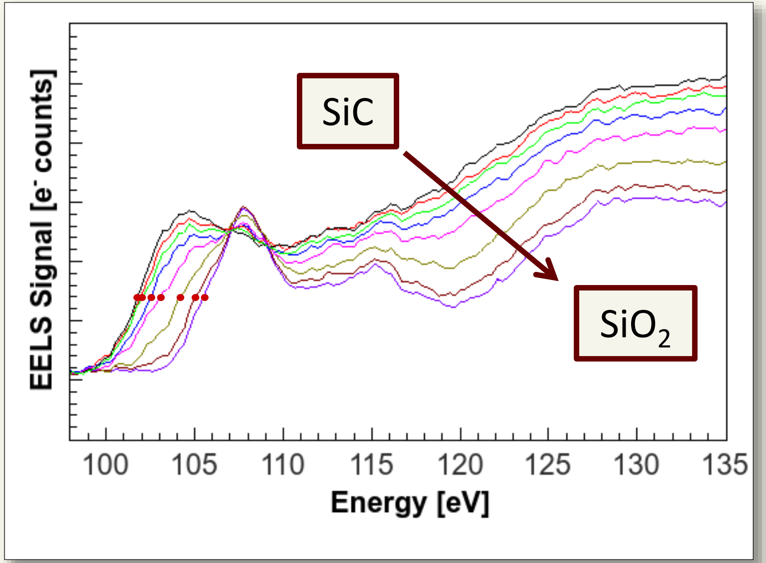
1 J. Taillon, L. Salamanca-Riba, *et al.*, J. Appl. Phys. 113, 044517 (2013).
2 Chang, K. C. *et al*. J. Appl. Phys. 97, 104920 (2005).
3 H. Watanabe, *et al.*, Appl. Phys. Lett., 99(2), 021907 (2011).
4 X. Zhu, *et al.*, Appl. Phys. Lett., 97(7), 071908 (2010).

TEM-EELS EXPERIMENTS

EELS Spectrum Imaging



Si-$L_{2,3}$ chemical shift

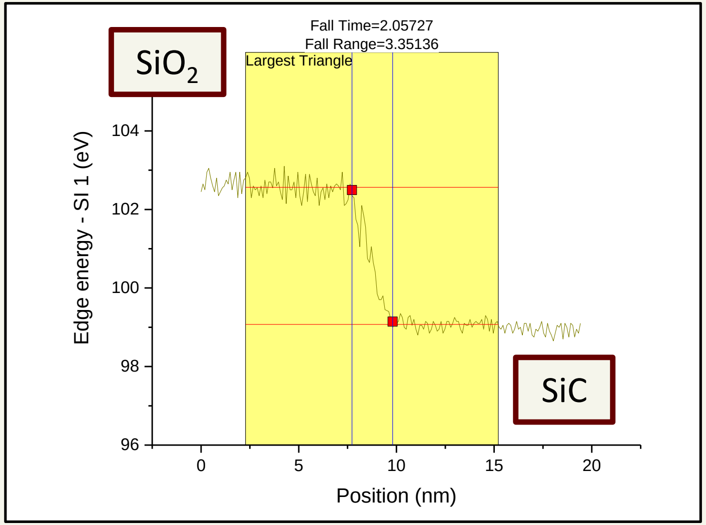


- EELS fine structure (ELNES) reflects local unoccupied density of states
  - Semiconductor → insulator
  - Edge onset → minimum energy needed to excite core shell e^-
  - Band gap widens, core levels depressed relative to E_F[1]
    - Charge transfer from Si → C/O
    - Onset shifts to higher energy

[1] D. Muller, Ultramicroscopy **78**, 163 (1999).

Si-$L_{2,3}$ chemical shift – measuring w_{TL}

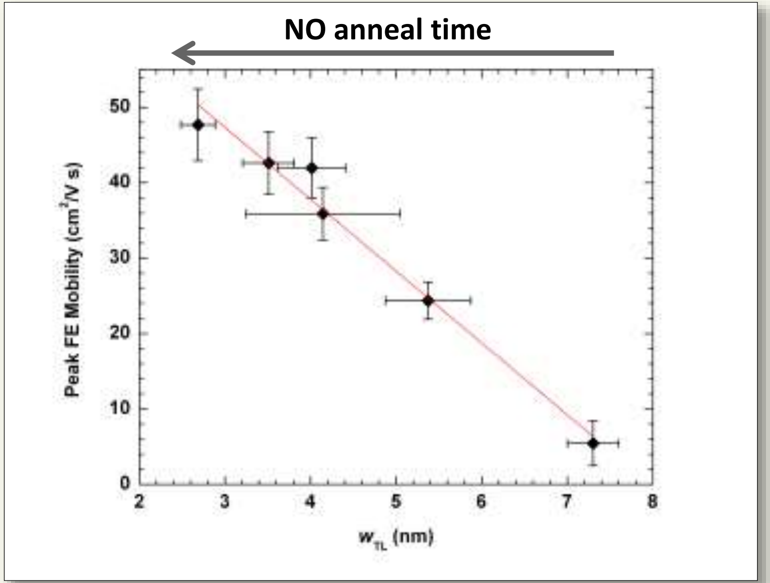
- Track inflection point of edge onset across interface[1]
- Gradual and monotonic shift
  - Si bonding changes gradually and uniformly across the interface
- Measured using rise/fall time calculations typical in signal processing



[1] D. Muller, P. Batson, and J. Silcox, Physical Review B **58**, 11970 (1998).

NO-anneal results (previous results)

- w_{TL} correlates inverse-linearly μ_{FE}
  - Also correlates with decreased trap density: John Rozen, *et al*. IEEE Trans. Elec. Dev. (2011).
- NO-anneal removes/passivates mobility-limiting defects
  - Compositionally and electronically
- **Conclusions:**
  - w_{TL} decreases with increasing NO anneal time
    - New chemical shift of Si-$L_{2,3}$ edge onset was most reliable method
    - No excess C on either side of interface



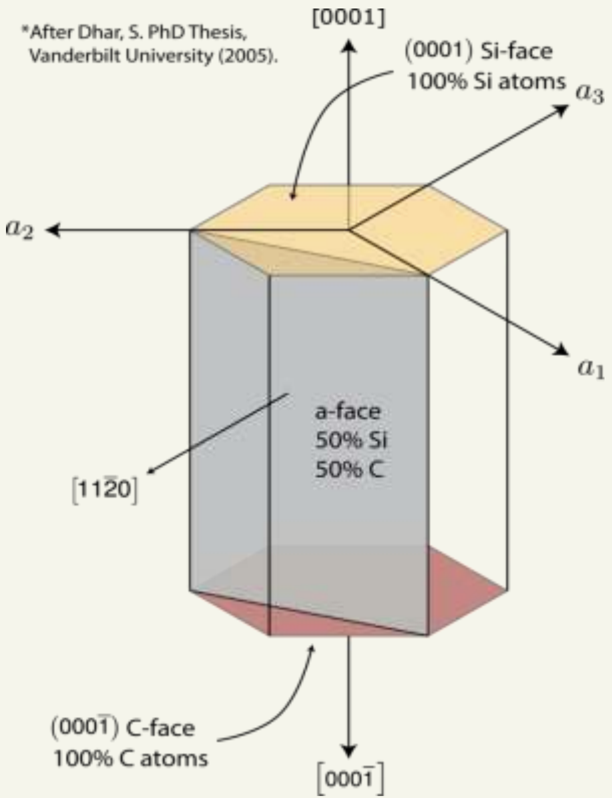
J. Taillon, L. Salamanca-Riba, *et al., J. Appl. Phys.* **113**, 044517 (2013).

Samples investigated – TEM/EELS

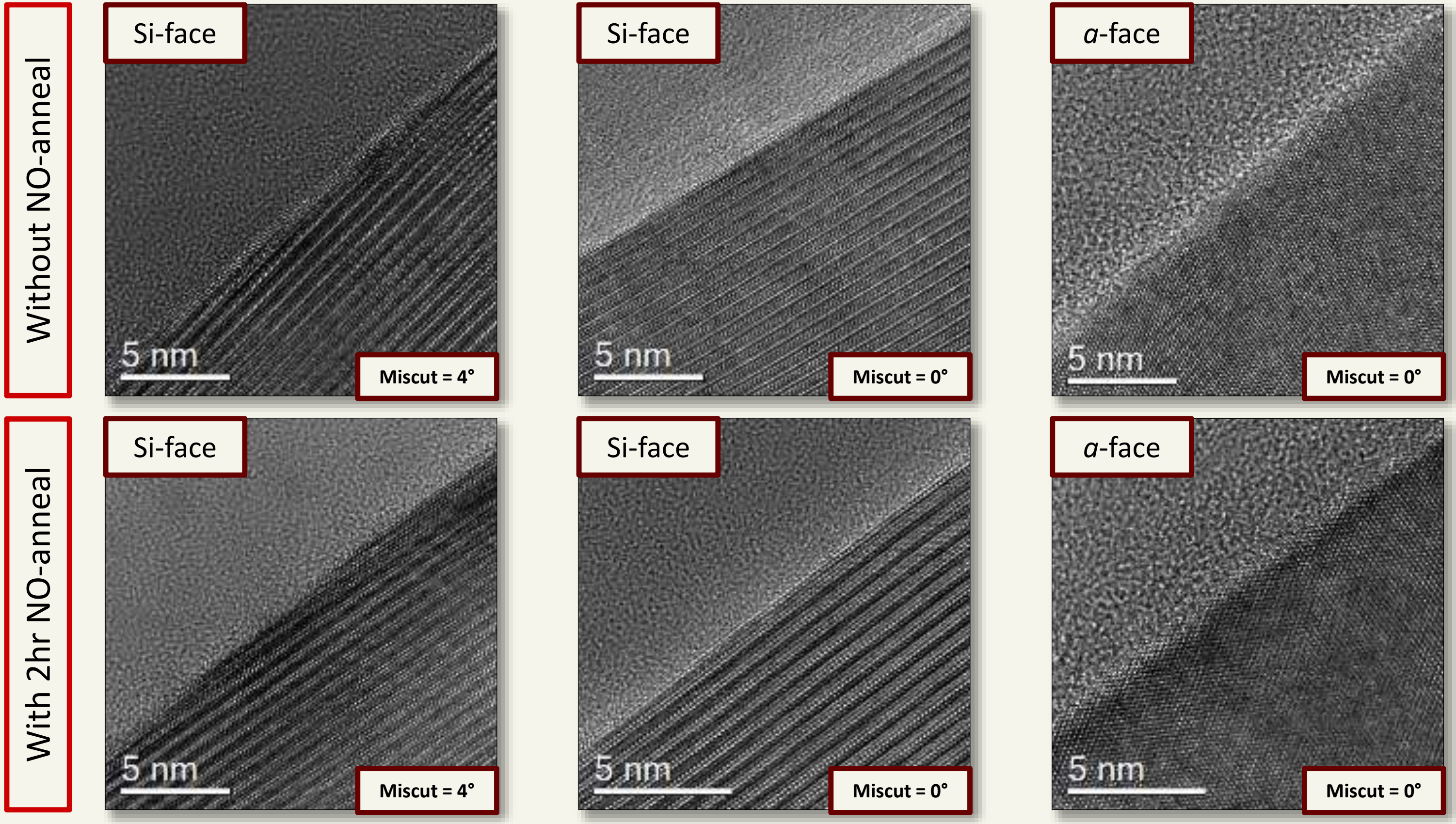
- 2 x 3 matrix aimed at comparing substrate orientation (and miscut) with processing conditions:
  - NO POA is for 2hr, all SiC substrates are n-type, SiO_2 ~60 nm thick

Sample Labels:	**Only oxidized**	**NO Post-annealed**
Si-face on-axis	Si-O_2-0	Si-N-0
Si-face miscut (4°)	Si-O_2-4	Si-N-4
a-face on-axis	a-O_2-0	a-N-0

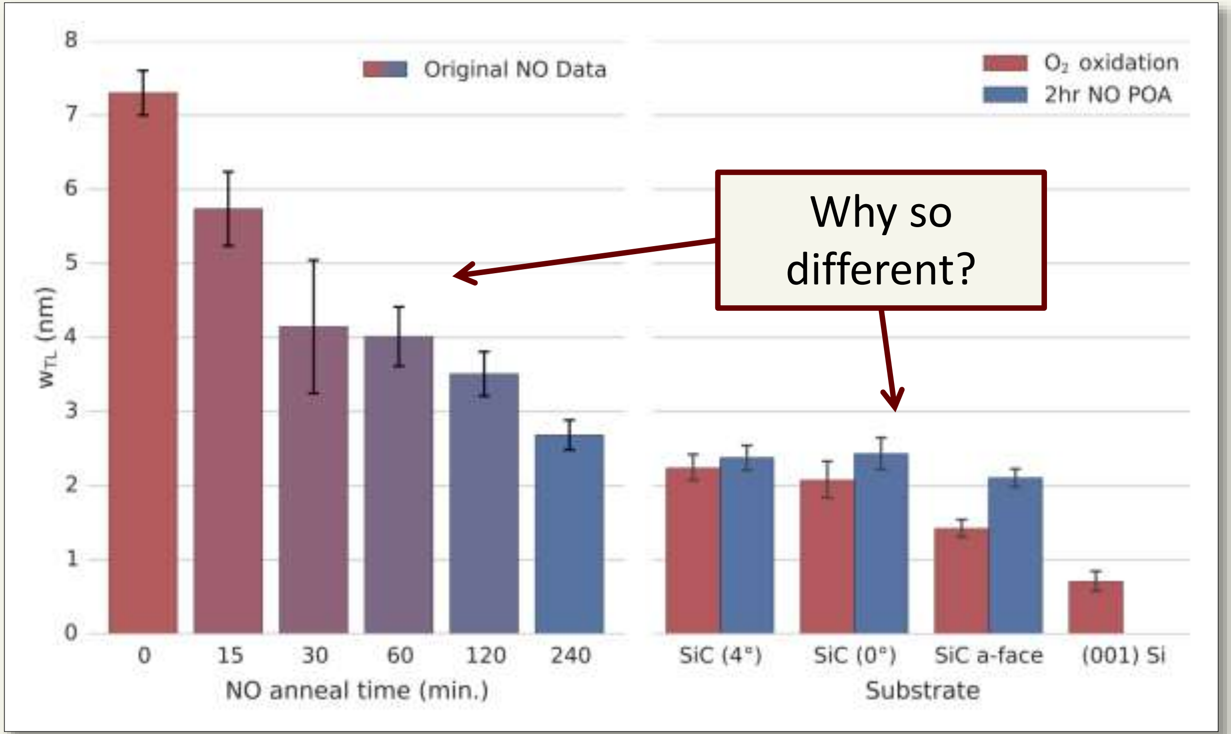
*After Dhar, S. PhD Thesis, Vanderbilt University (2005).



HRTEM of Si-face and *a*-face with and without NO annealing



w_{TL} measurements



- Results from STEM EELS transition layer measurements show that w_{TL} values are similar
- w_{TL} in NO-annealed samples for these devices are actually slightly larger than the non-annealed
- a-face interfaces are the smallest, which does correspond with their higher mobilities (in NO)
  - 40 cm^2/V s for Si-face
  - 85 cm^2/V s for a-face

NEW ANALYSIS TECHNIQUE

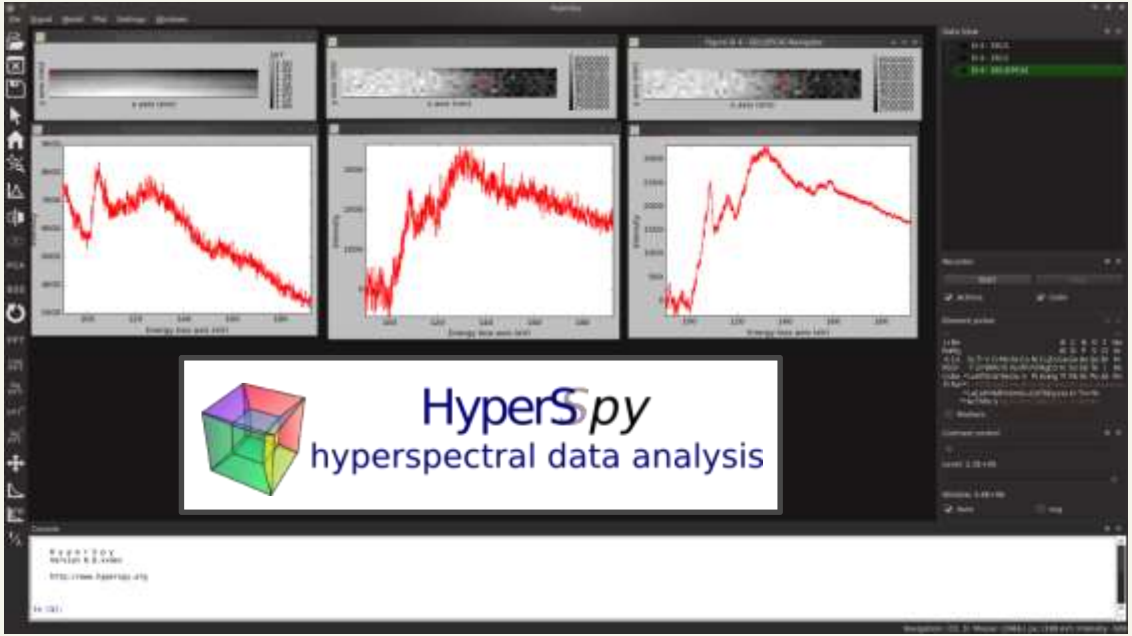
Hyperspectral signal decomposition – machine learning

- Si-$L_{2,3}$
- Low-loss EELS
- Phosphosilicate glass samples

HyperSpy for analytical microscopy

http://hyperspy.org

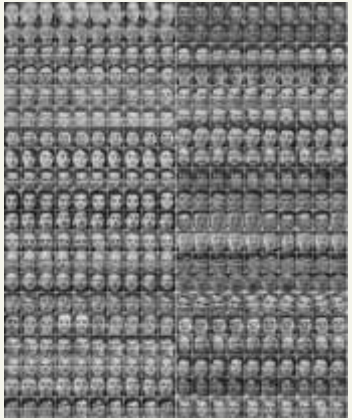
DOI 10.5281/zenodo.16850



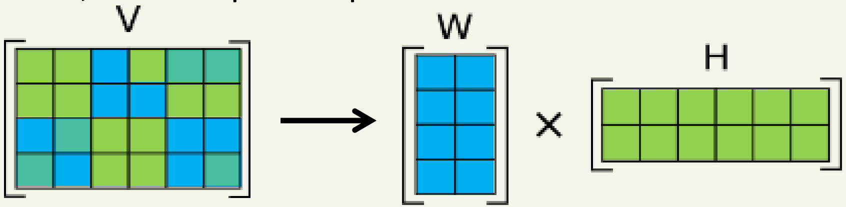
- **Open source** hyperspectral analysis package for Python
  - GUI and/or web notebook (traceability!)
- Data-agnostic, but…
  - Specialized routines for EDS and EELS
- Easy access to PCA, ICA, and signal modeling

Decomposition analysis

- Machine learning for hyperspectral decomposition
  - How to tease out convoluted and complex signals
  - Use redundancy of information in spatial dimensions to learn more about differences in the signal dimension(s)
  - Used in EEG, audio processing, fMRI, etc.



- Non-negative matrix factorization and Blind source separation
  - Finding simpler descriptive basis vectors of overall data; one component per "source"



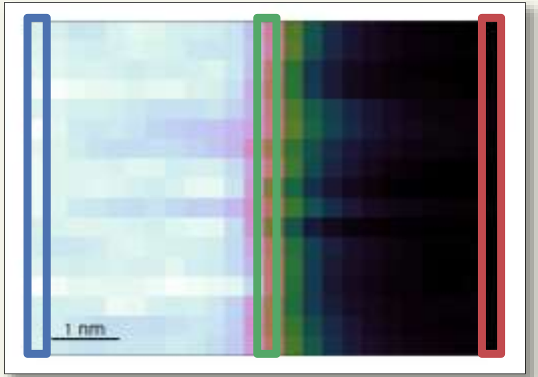
Adapted from: https://upload.wikimedia.org/wikipedia/commons/f/f9/NMF.png

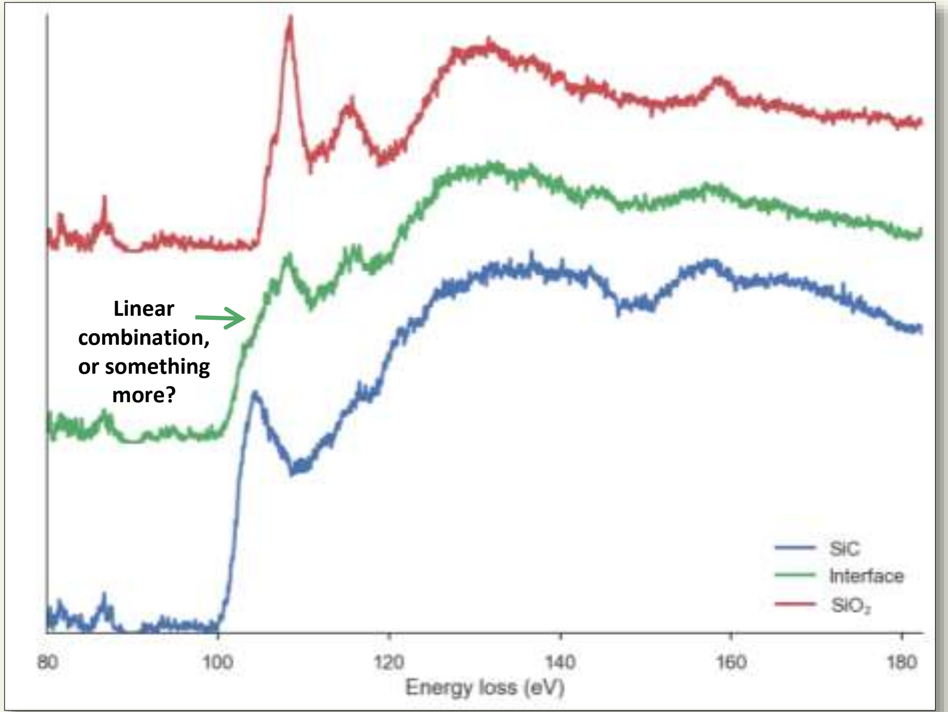
Example applied to Olivetti faces

What features are found most often in the training set?

Decomposition of Si-$L_{2,3}$

Interface components at NO-annealed interfaces

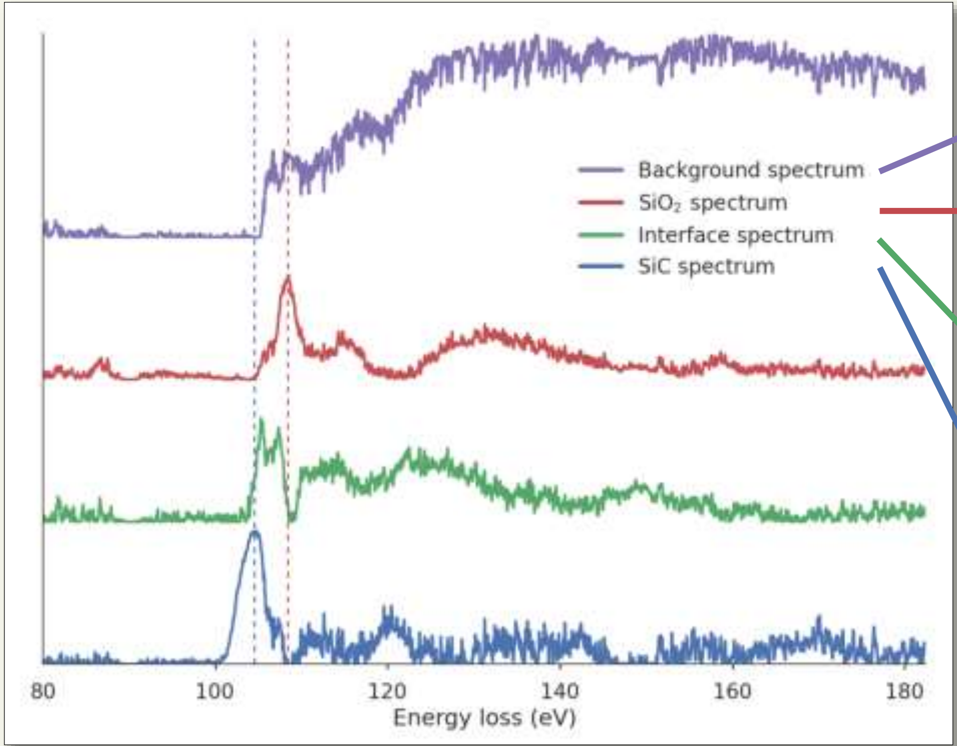


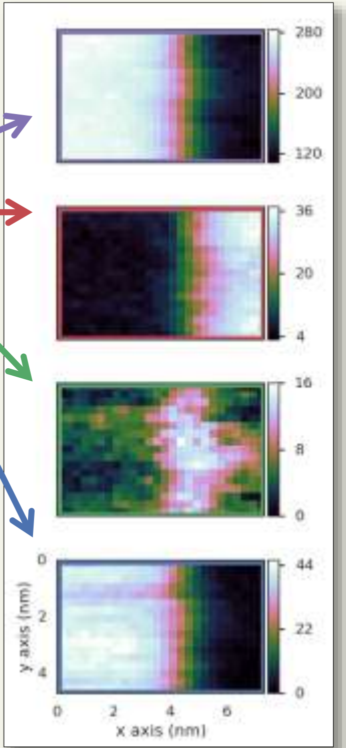


- Simple sum improves S/N, but cannot detect faint or overlapping signals

Interface components at NO-annealed interfaces

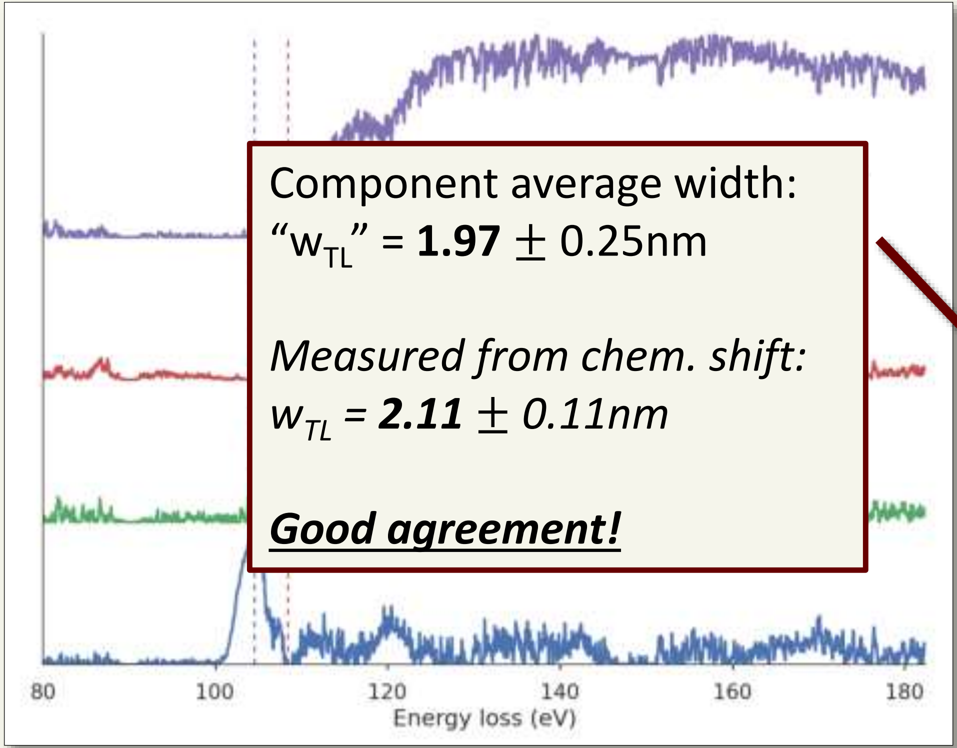
- Signal decomposition (NMF) is much more powerful
  - Significant detection of unique orthogonal component at interface
- New component that is distinct from SiO_2 and SiC was observed
  - Non-linear combination of signals!





Interface components at NO-annealed interfaces

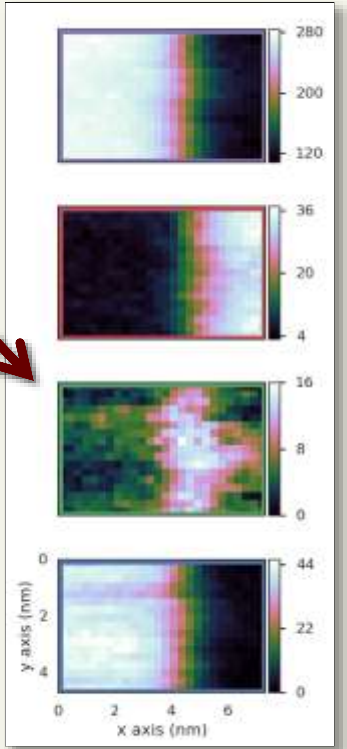
- Signal decomposition (NMF) is much more powerful
  - Significant detection of unique orthogonal component at interface
- New component that is distinct from SiO_2 and SiC was observed
  - Non-linear combination of signals!

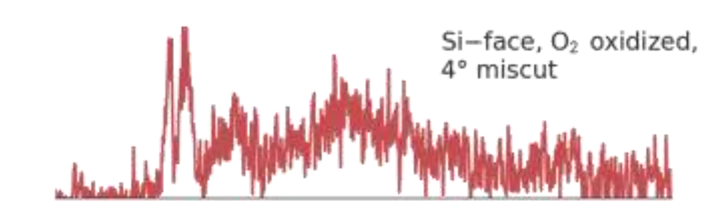
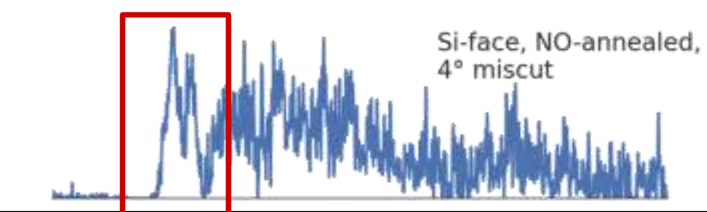
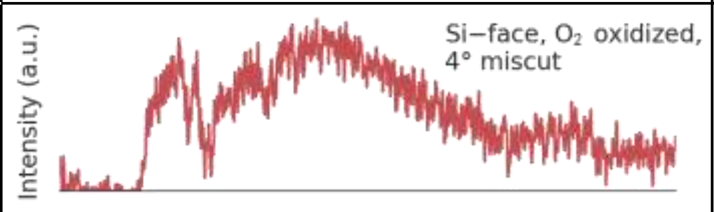
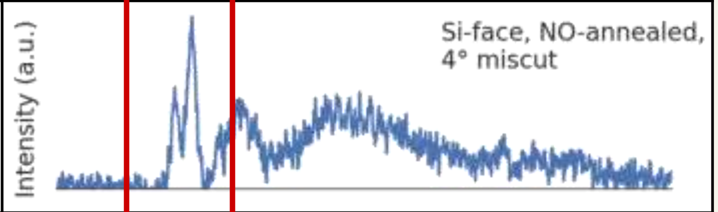
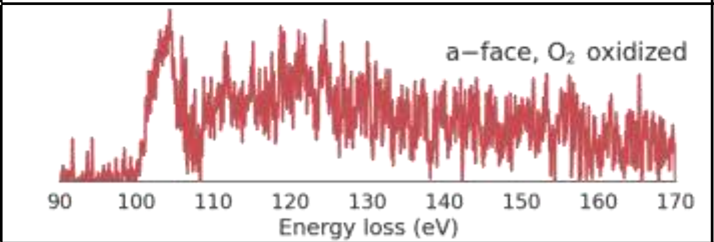
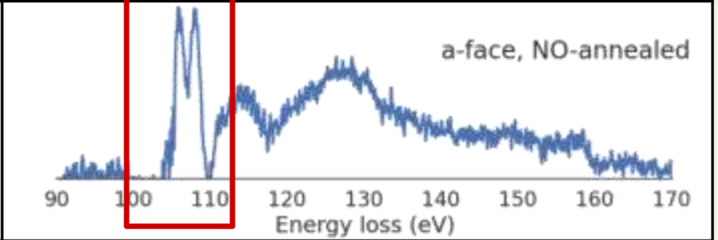


Component average width:
"w_{TL}" = **1.97** ± 0.25nm

Measured from chem. shift:
*w_{TL} = **2.11** ± 0.11nm*

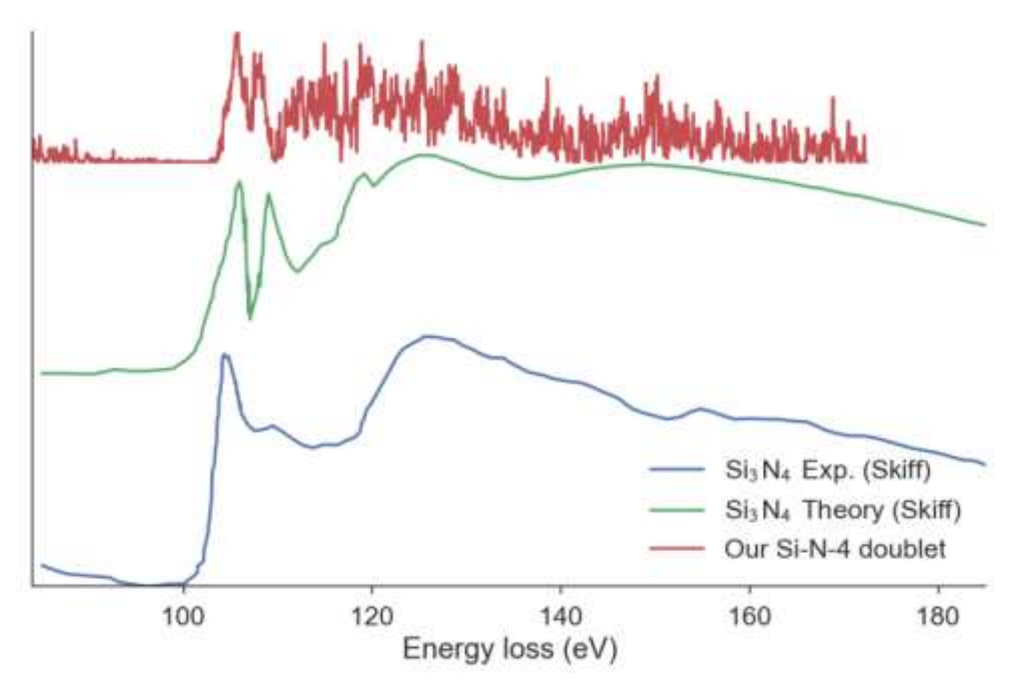
<u>Good agreement!</u>



Face / Treatment	O_2 oxidation	O_2 oxidation + NO POA
Si-face 4° miscut (Si-X-4)		
Si-face no miscut (Si-X-0)		
a-face no miscut (a-X-0)		

What does it mean?

- Si_3N_4 theory and experiment (Skiff et al.)
  - Calculated ΔE between doublet peaks 3.4 eV compared to our 2.08 eV
- Not SiO_2 or SiC
  - Those were also identified, and peak positions do not match
- Effect of N-bonding
  - Si-C-N-O bonding configurations?
  - Likely that this is evidence of N-bonding at interface
  - DFT modeling will reveal further details

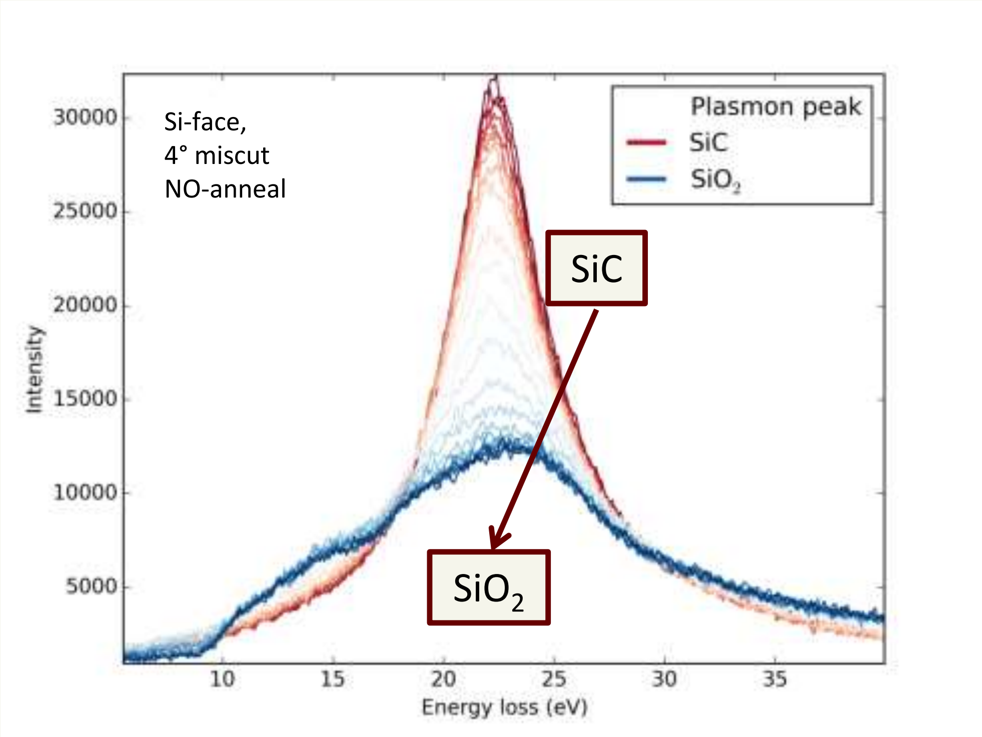


Skiff, W. M., *et al.*, *J. Appl. Phys.* **62,** 2439–2449 (1987).

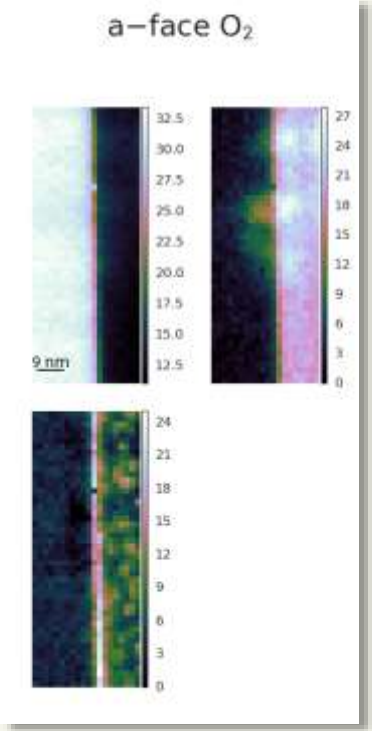
Decomposition of Low-loss EELS signal

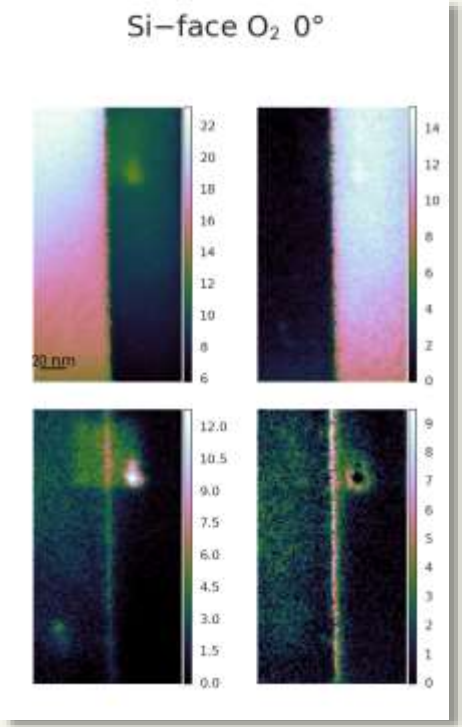
Low-loss EELS

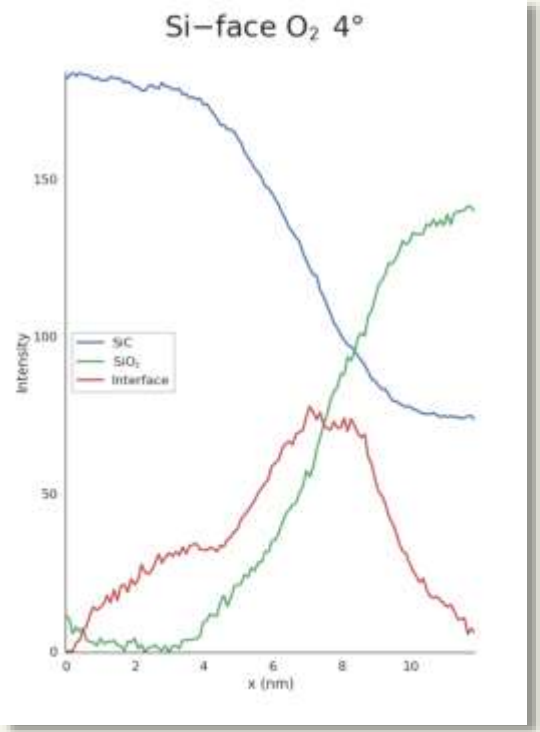
- Reveals information originating from inelastic scattering by outer shell electrons
  - Plasmon interactions
    - (Collective oscillations of electrons within the sample: bulk, surface, interface, etc.)
  - Energy related to valence e^- density
  - Width is indicative of the damping effect of single electron transitions
  - Information about dielectric response
  - Can be used for spectral "fingerprinting"



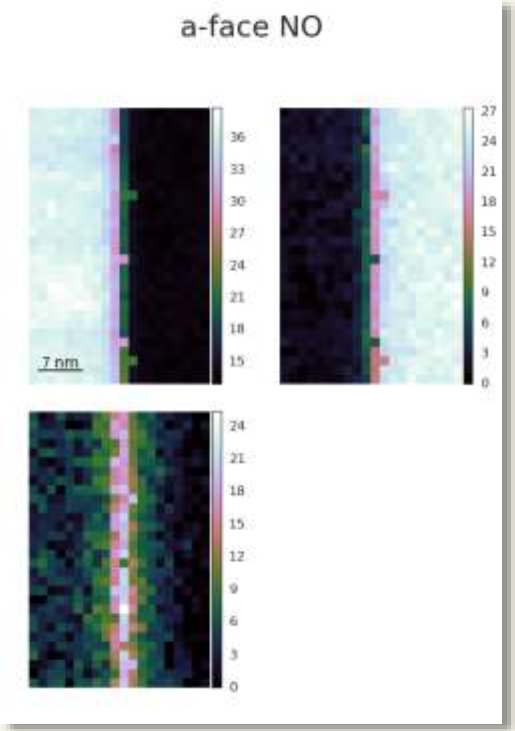
O_2 oxidation – decomposition loadings

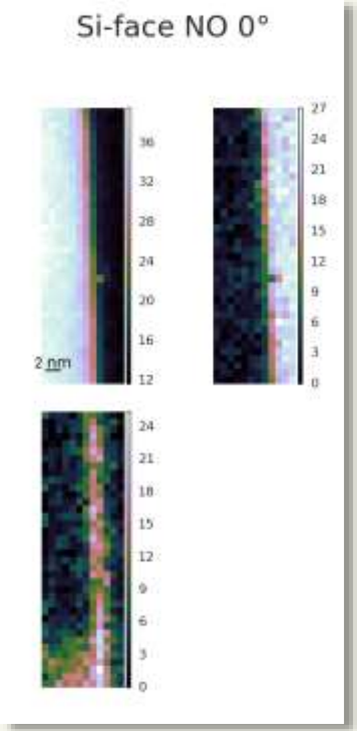


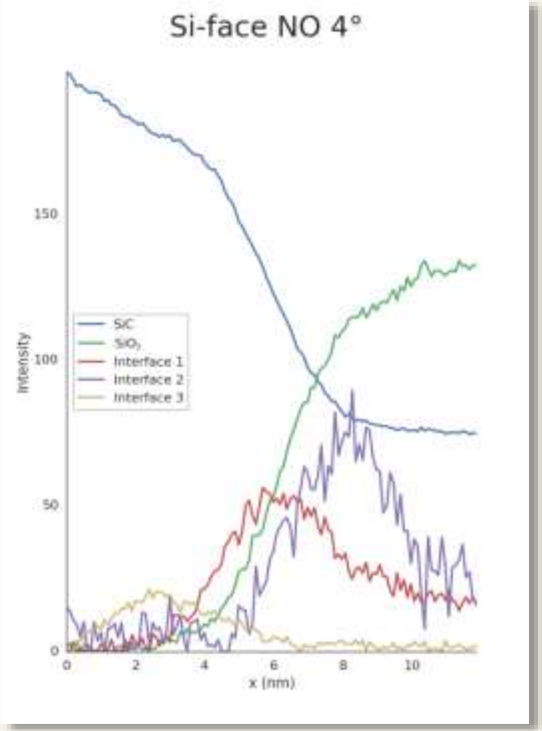




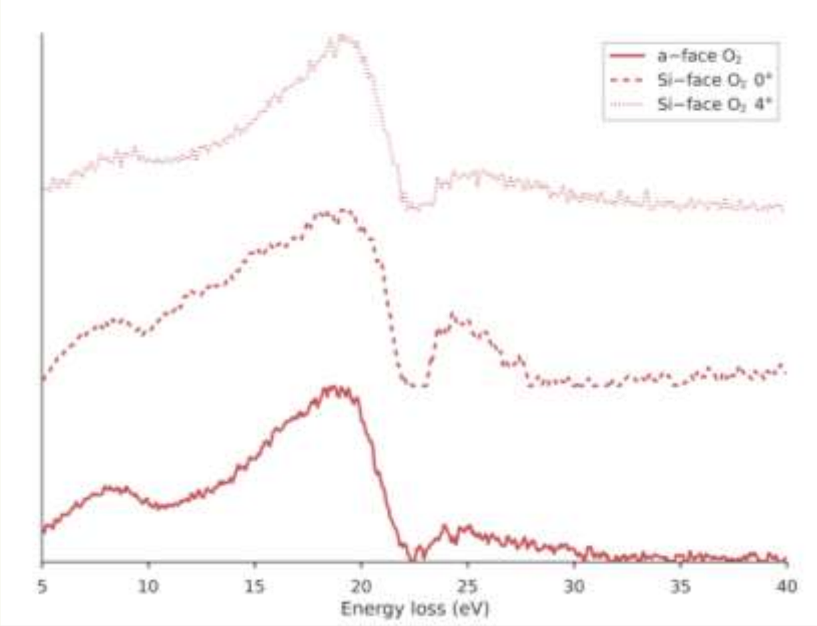
NO post-anneal – decomposition loadings



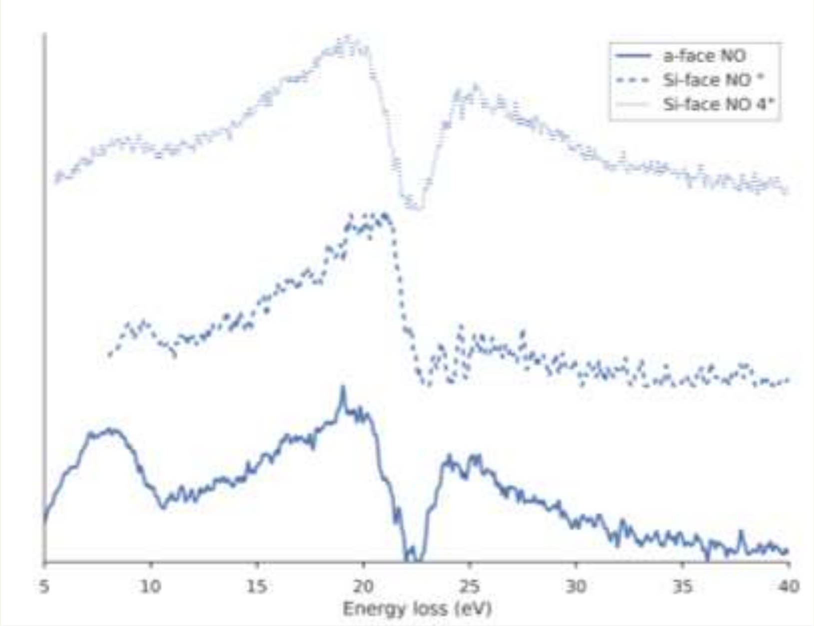




Low-loss Interface component - comparison



O_2 oxidation

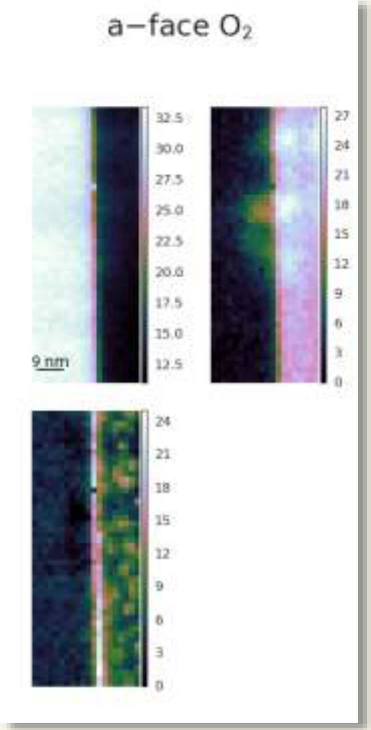


NO post-anneal (2hr)

Low-loss decomposition results

- **Results:**
  - Interface components observed for all samples investigated
  - Specific component shapes appear very similar
    - Limited NO impact in this range of spectrum
  - Finite transition layer regardless of interface/treatment

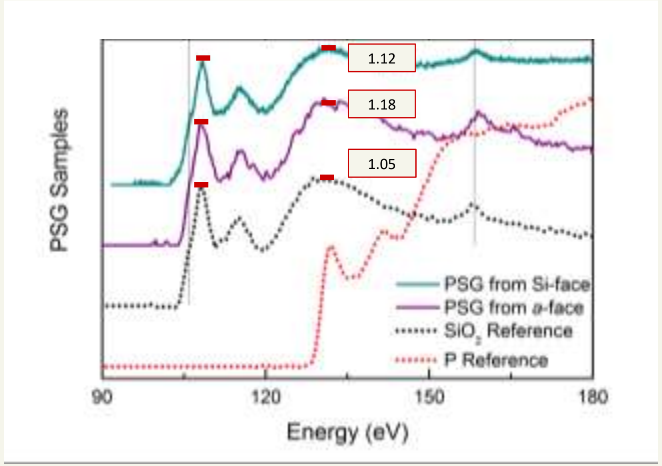
- "w_{TL}" from low-loss component ≈ 2.2nm



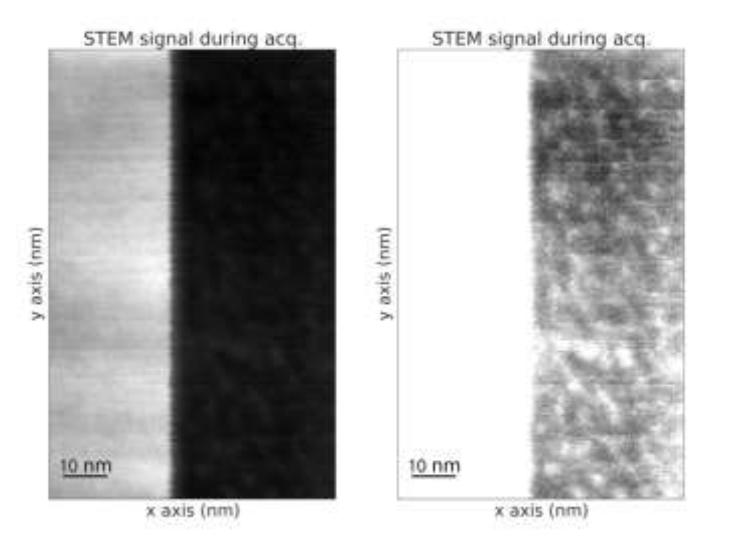
Decomposition of Phosphosilicate glass (PSG)

Phosphorus PSG process – decomposition analysis

- 2013 results:
  - Si-face and a-face PSG
  - w_{TL} on same order as NO-anneal
  - Difficult to see P on top of Si signal:



a-face PSG sample (STEM data):



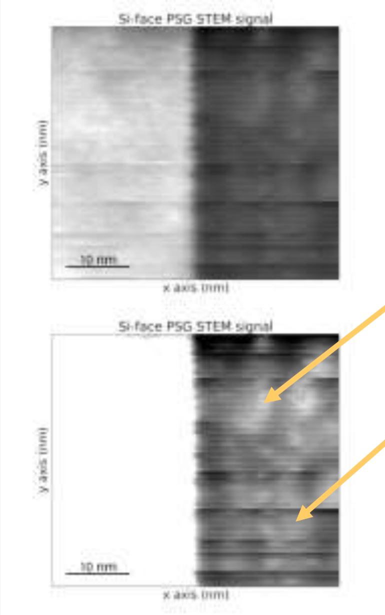
as acquired | enhanced contrast

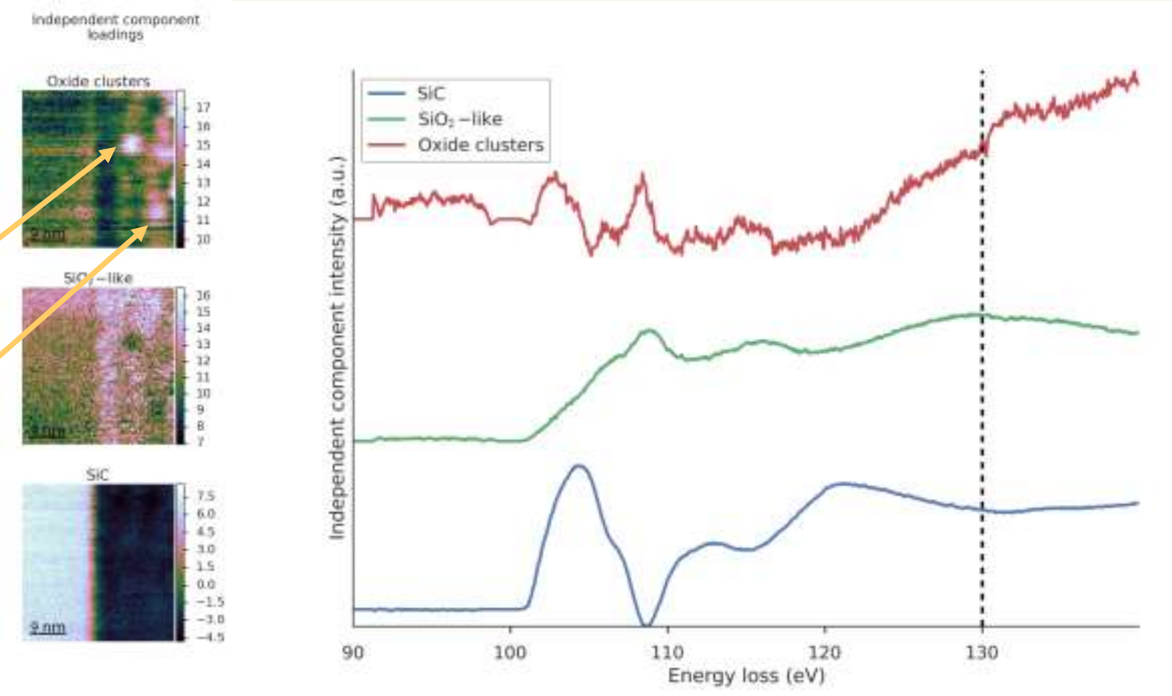
Initially thought contamination…

…but maybe there's more.

PSG decomposition results

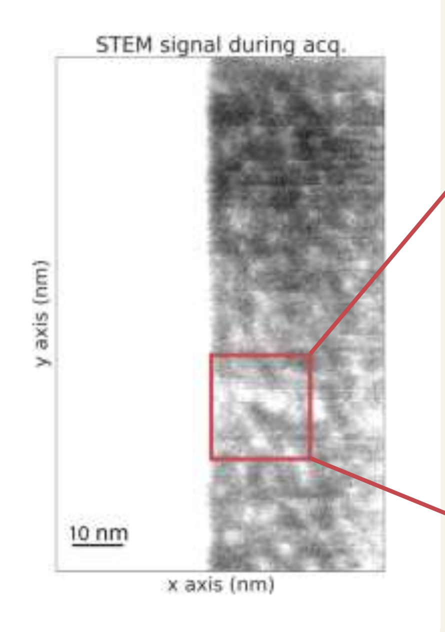
Si-face PSG STEM and EELS:

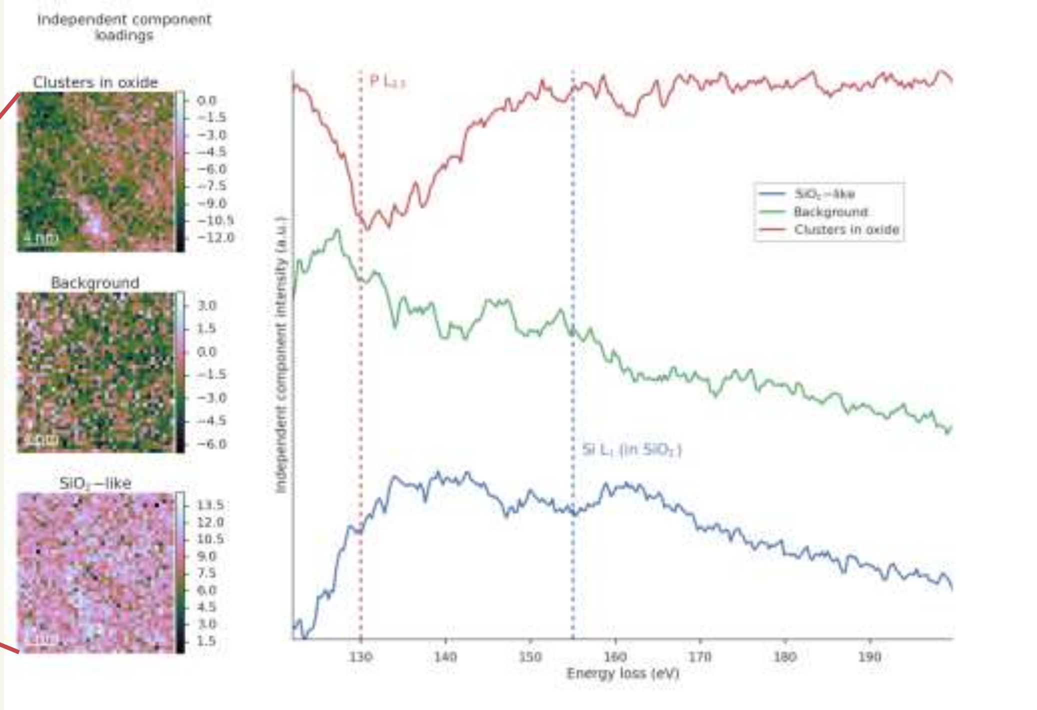




PSG decomposition results

a-face PSG STEM and EELS:

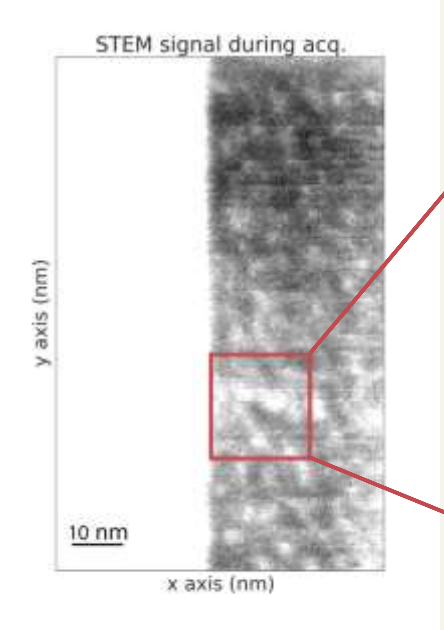


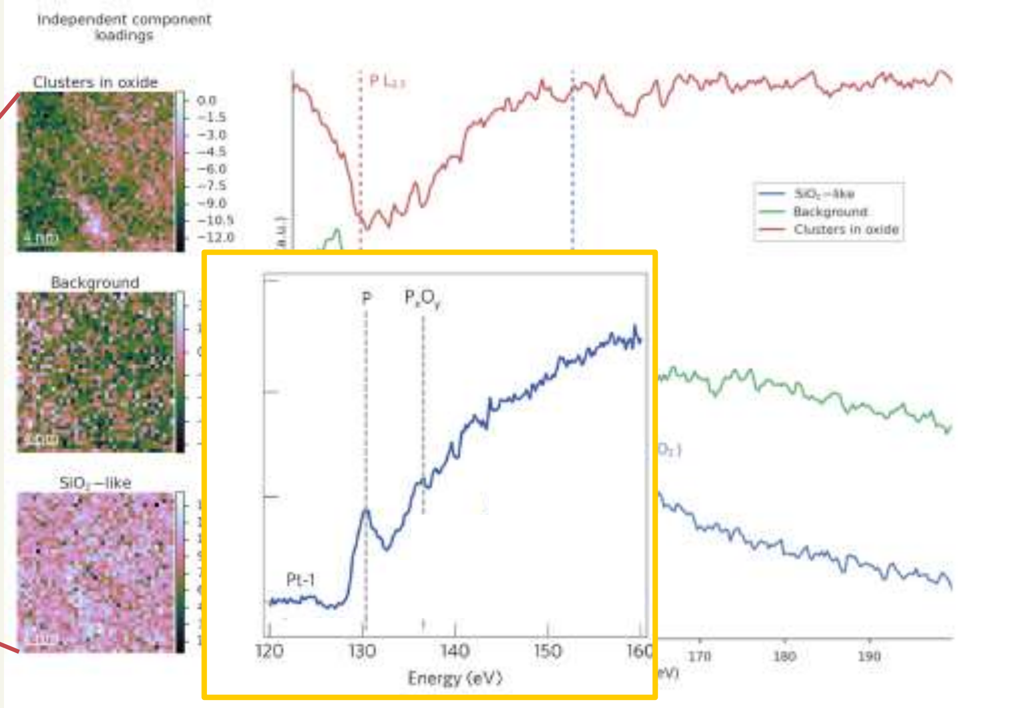


PSG decomposition results

Favron *et al.*, Nature *Materials*, **14**, 826–832 (2015)

a-face PSG STEM and EELS:

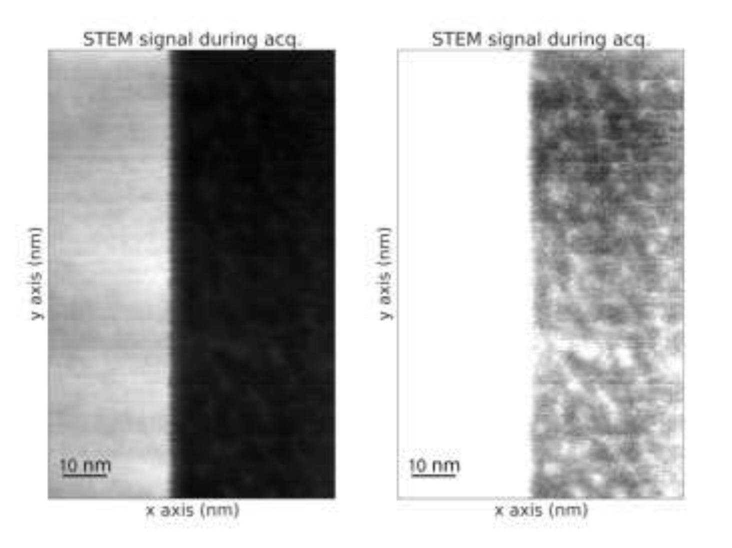




PSG decomposition results

- **Results:**
  - "Clusters" observed in STEM imaging are not contamination or sample preparation artifacts, as initially thought
  - P is not evenly distributed throughout the PSG
  - Rather, appears to be P inclusions within SiO_2
  - Are newer PSG samples similar?
    - Further analysis of PSG process (see Sarit's talk)

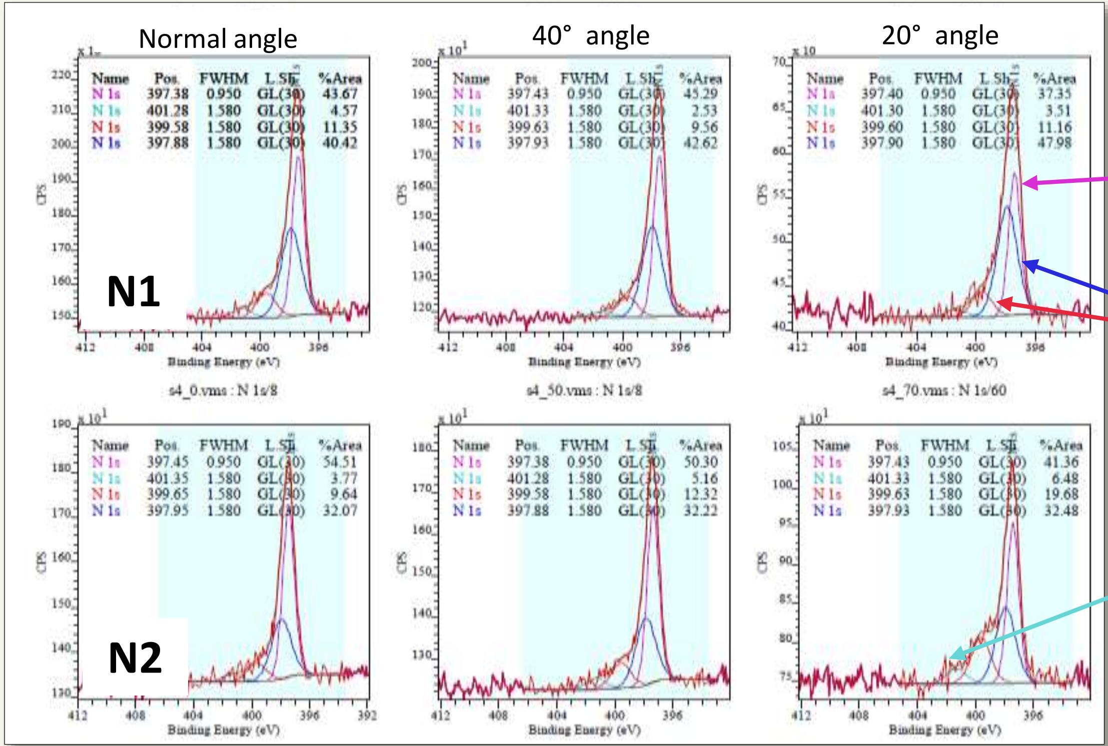
a-face PSG sample (STEM data):



as acquired enhanced contrast

XPS DEPTH PROFILING

XPS N 1*s*



- 4 components found in constrained fit:
  - Primary peak is consistent with silicon nitride-like bonding
  - Other peaks likely to be successively more oxygen bonding and/or carbon bonding
  - Additional component at higher energy compared to previous results[1]

[1]Y. Xu, L. C. Feldman, *et al.*, J. Appl. Phys., 115(3), 033502 (2014).

XPS N 1*s*

Completely etched

2 – 4 nm oxide layers

Elemental composition (peak area integration)				
Measurement	C 1s %	N 1s %	O 1s %	Si 2p %
N1 - normal	40.95	1.67	9.56	47.82
N1 – 40°	41.43	2.66	16.44	39.47
N1 – 20°	41.20	2.73	20.59	35.49
N2 – normal	29.92	1.01	21.80	47.28
N2 – 40°	33.59	1.37	29.46	35.58
N2 – 20°	36.28	1.45	33.57	28.70

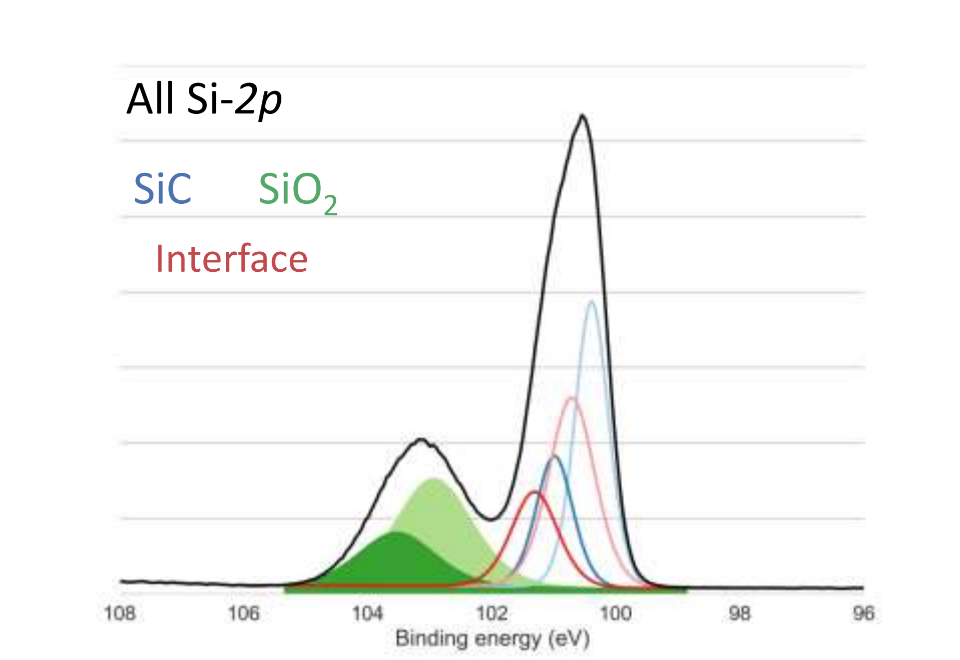
- N content decreases when thick oxide is present, and is still present after all original oxide is etched off
- N is localized in SiC near interface (in agreement with recent findings from Rutgers[1])

- Results are consistent with TL observed by EELS
  - Further corroboration of N-bonding hypothesis of what is being observed at the interface

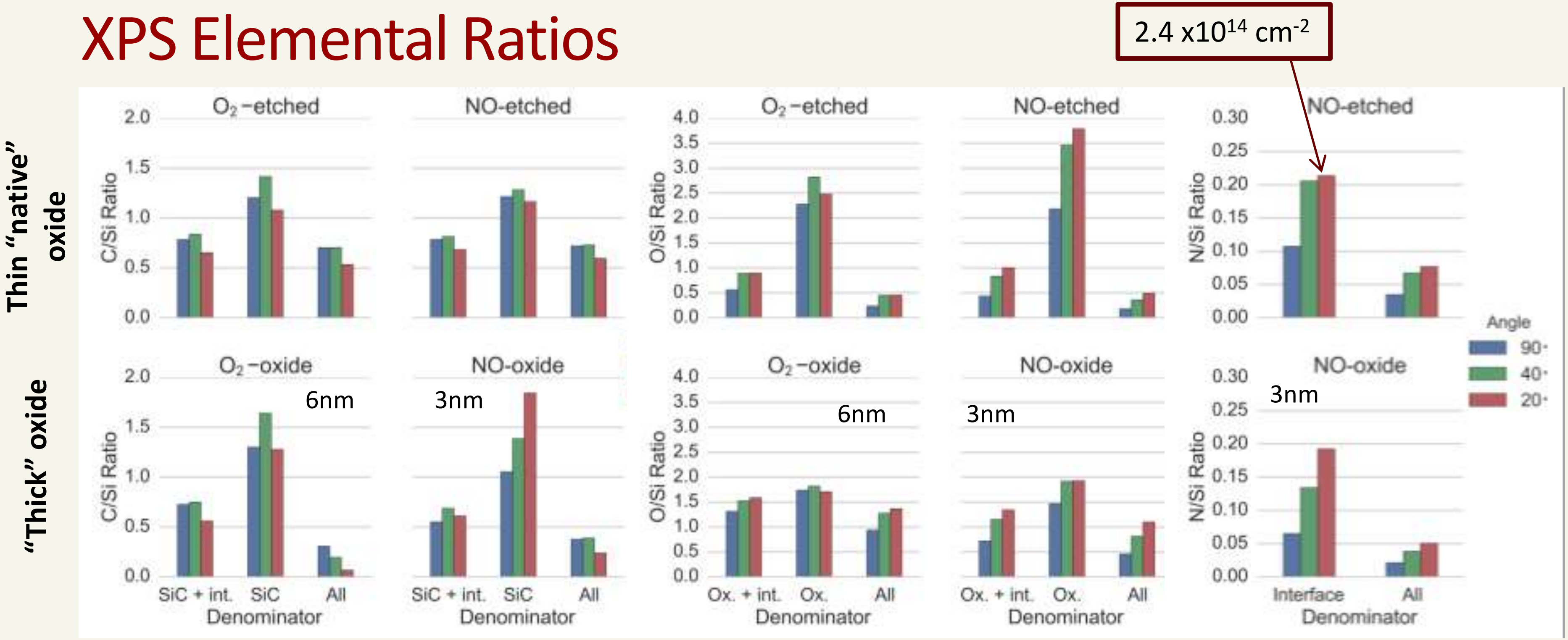
[1]Y. Xu, L. C. Feldman, *et al.*, J. Appl. Phys., 115(3), 033502 (2014).

XPS Elemental Ratios

- Looking at absolute elemental ratios is not always accurate/ideal
  - Hydrocarbon contamination
  - Normalizing by appropriate signal
- Example:
  - Si 2p quantification



XPS Elemental Ratios



Best normalization by Si in SiC

O ratio ≈ 1.5… lower than expected

N as expected

With proper normalization, XPS reveals approximately expected stoichiometry

Summary

- The shift of the Si-$L_{2,3}$ edge is a good indicator of the width of the transition region in 4H SiC/SiO_2.
  - Newer devices do not follow previously observed trend
  - Measuring interface width does not reveal what is happening inside
- Decomposition of Si-$L_{2,3}$ EELS edge reveals a chemically/electrically distinct interface state
  - Likely significant impacts on mobility and performance
  - Spatial distribution matches measurements of w_{TL}
- Decomposition of low-loss EELS shows same-sized interface component
  - Not dependent on NO anneal
- XPS indicates Si_3N_4-like N bonding at the interface, with N incorporated primarily at interface
- PSG passivation does not cause a uniform PSG dielectric (clusters of P within oxide)

Future work

- Further analysis of EELS signals (O-*K* and C-*K* edges) at the interface
- Theoretical modeling of DOS for explanation
- Exploration of lattice strain in different substrate orientations (CBED, Geo. Phase Analysis)

Acknowledgements

- ARL Contracts W911NF-11-2-0044 and W911NF-07-2-0046.
- NSF Graduate Research Fellowship Grant DGE 1322106
- AIMLab at UMD – supported by NSF

HyperSpy
hyperspectral data analysis
DOI 10.5281/zenodo.16850

HyperSpy developers:

- Francisco de la Peña
- Pierre Burdet
- Tomas Ostasevicius
- Vidar Tonaas Fauske
- And many others…

THANK YOU

Questions/comments/discussion?