Advanced Analytical Microscopy at the Nanoscale:

Applications in Wide Bandgap and Solid Oxide Fuel Cell Materials

Joshua Taillon

Dissertation Examination

Examination committee:

Professor Lourdes Salamanca-Riba – *Chair*
Associate Professor John Cumings
Professor Neil Goldsman – *Dean's Representative*
Professor Eric Wachsman
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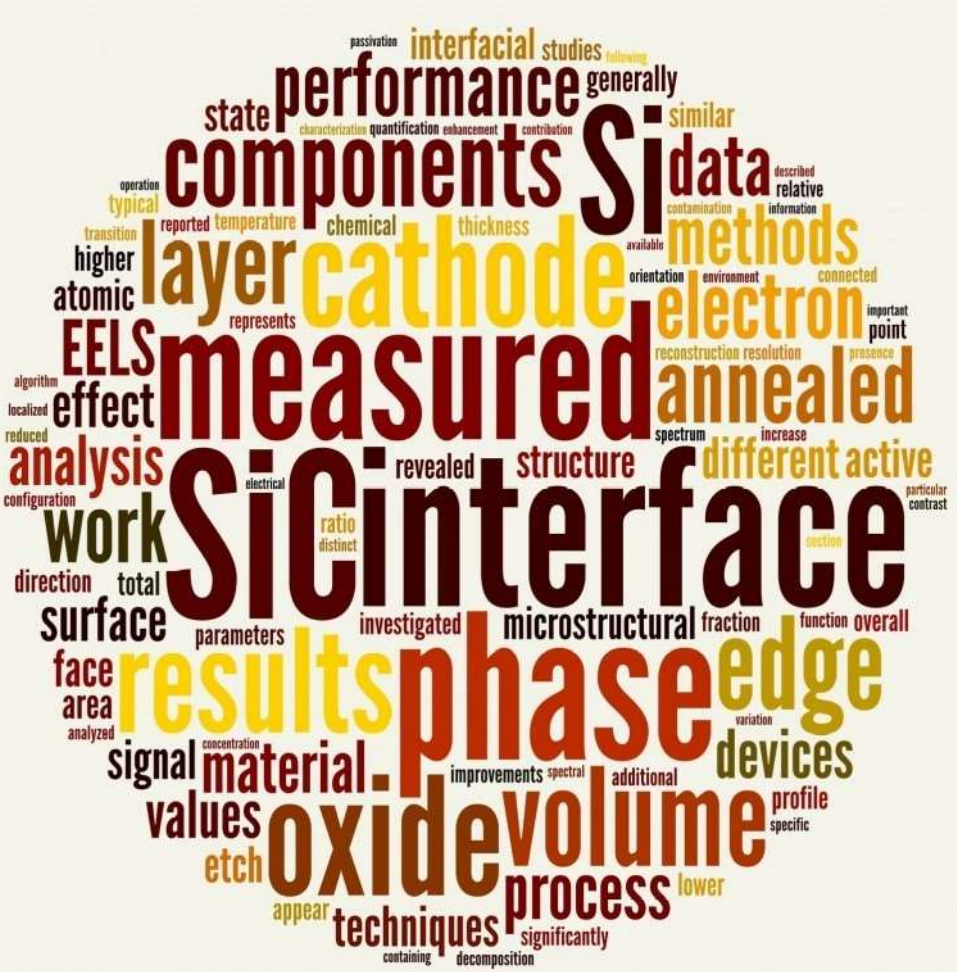
Friday July 8th, 2016
College Park, MD
AV Williams
Room 1146

Outline

- Overall introduction
- SiC MOSFET characterization
  - Transition layer measurements
  - XPS interface analysis
  - Effects of crystallographic orientation
- Solid oxide fuel cell reconstructions
  - Intro & Methodology developments
  - LSM-YSZ cathode degradation
  - LSCF-GDC cathode degradation
- Conclusions and Future work



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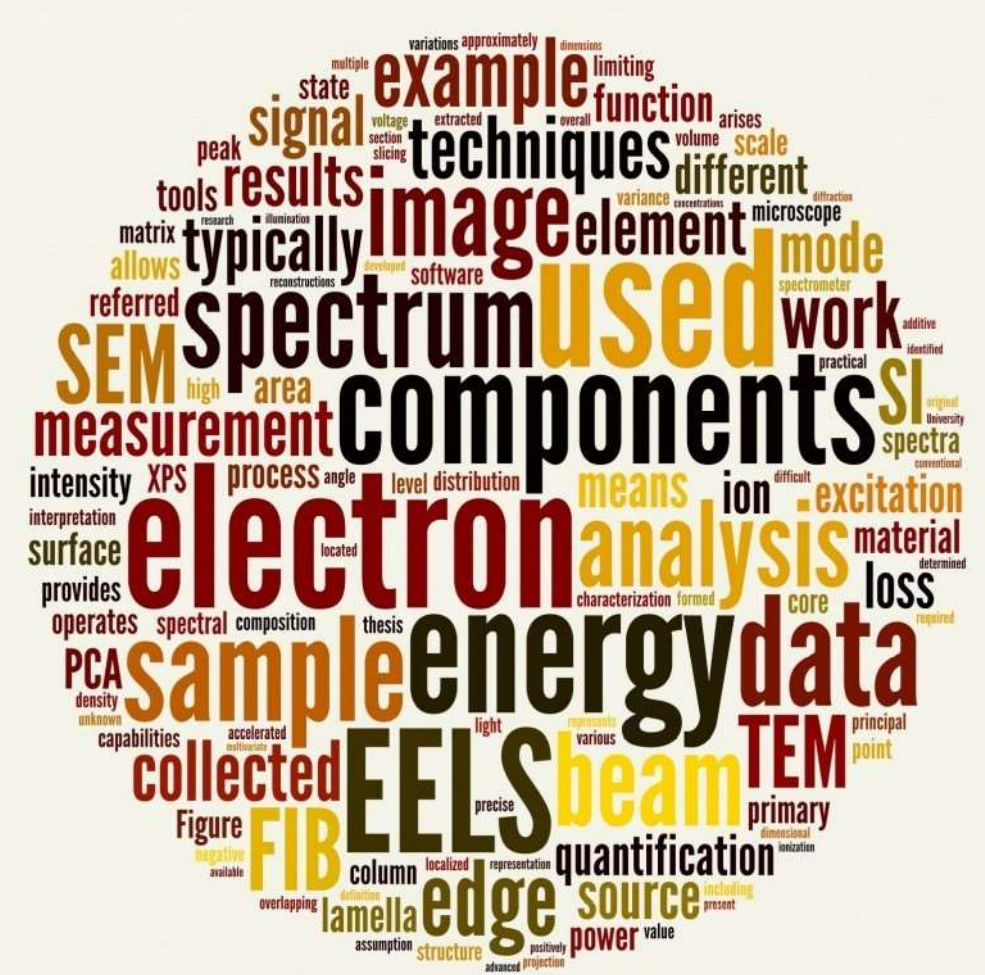


Why Microscopy?

Seeing is believing!

GeoSafari 8x optical

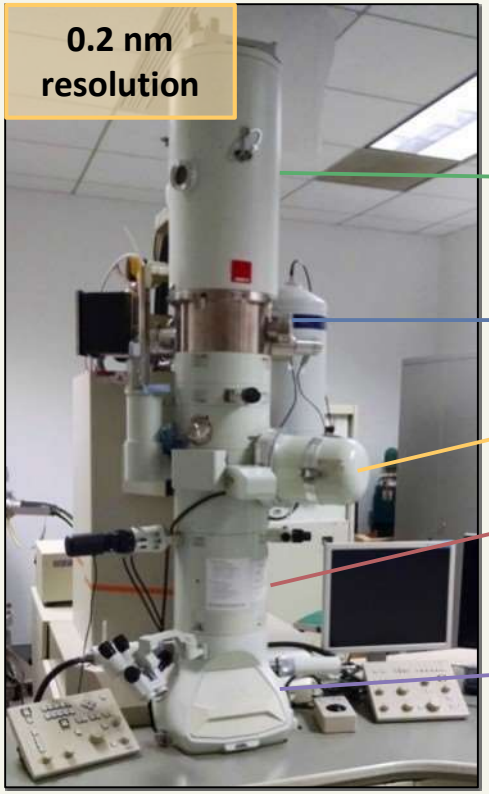
JWST Infrared telescope

First TEM (Ruska and Knoll)

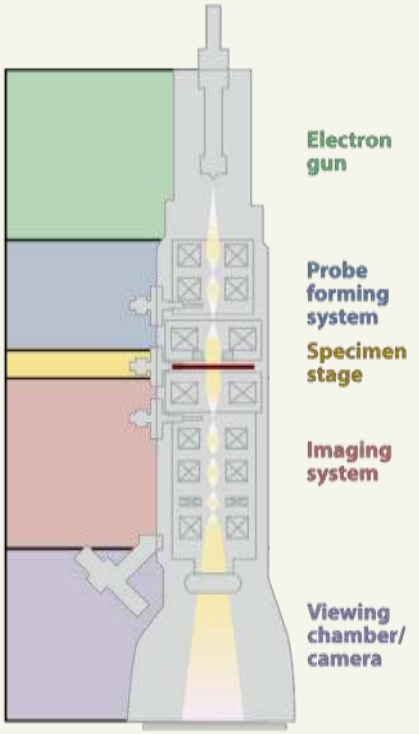
(Very) Brief introduction to TEM

- **Fundamentally similar to transmitted light microscopy**
- **Electrons rather than photons**
  - Better resolution!
  - Electromagnetic lenses, rather than glass lenses
- **Easily combined with analytical techniques (EDS, EELS, etc.)**
  - Enables chemical analysis together with structural information

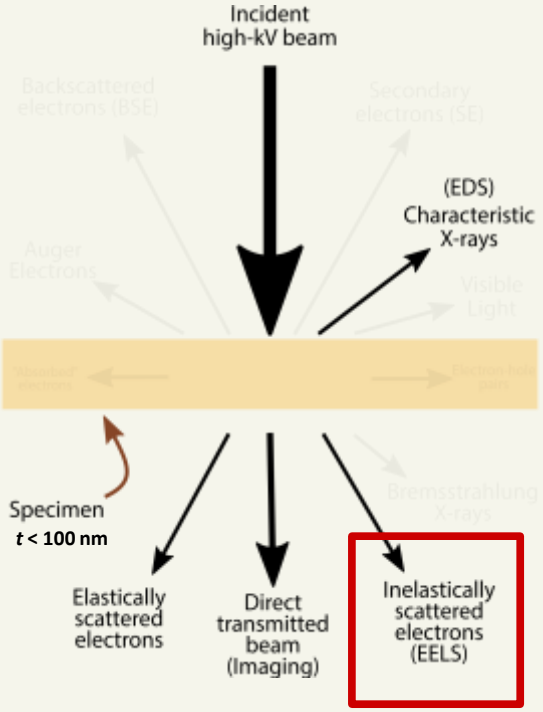
(Very) Brief introduction to TEM



JEOL *JEM-2100F*



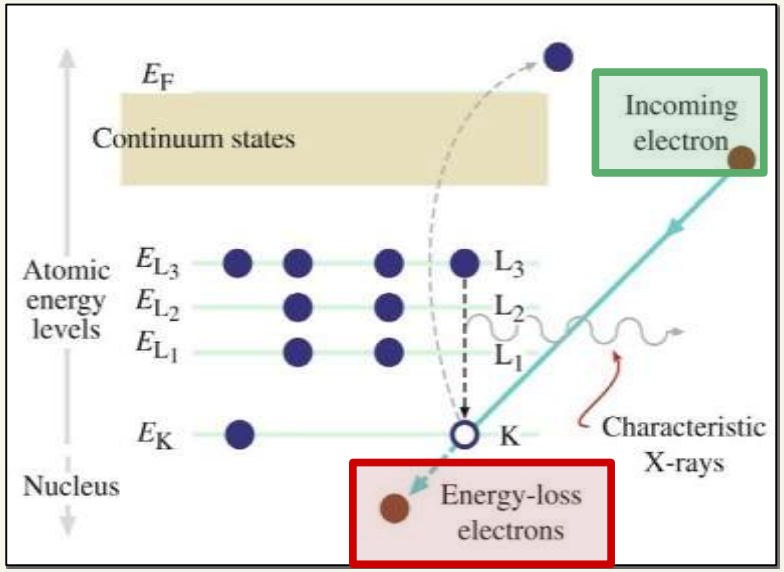
TEM Schematic



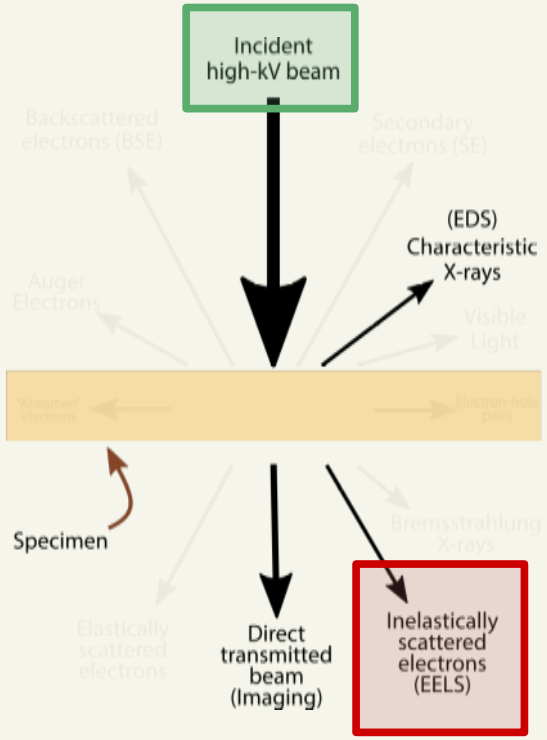
Electron-sample interactions
(adapted from Williams and Carter, 2009)

(Very) Brief introduction to TEM-EELS

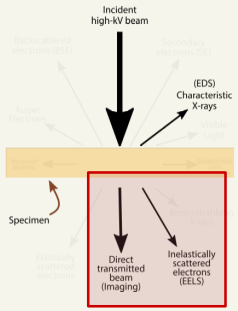
Electron
Energy
Loss
Spectroscopy



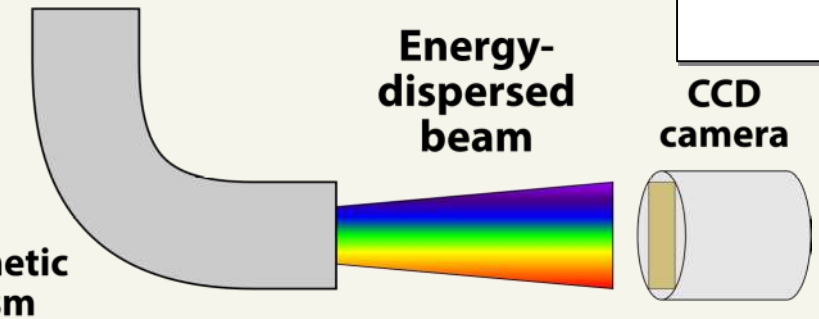
EELS energy band schematic
(*Williams and Carter, 2009*)

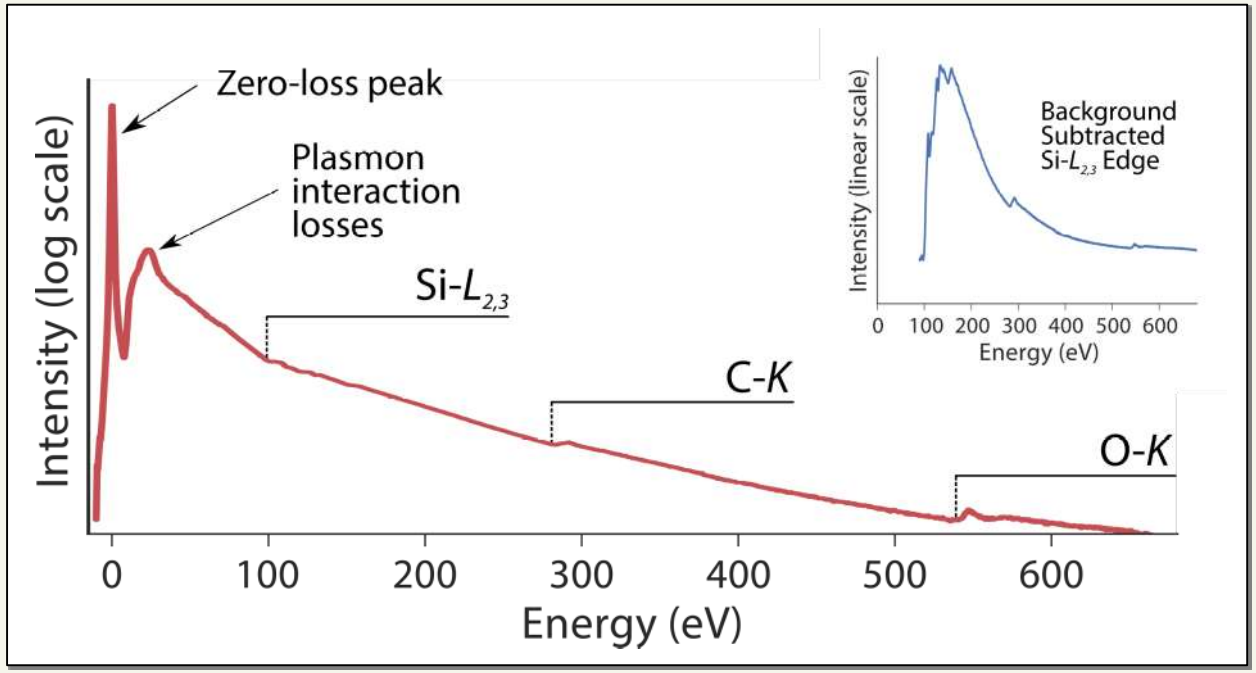


(Very) Brief introduction to TEM-EELS



Transmitted beam (all energies)

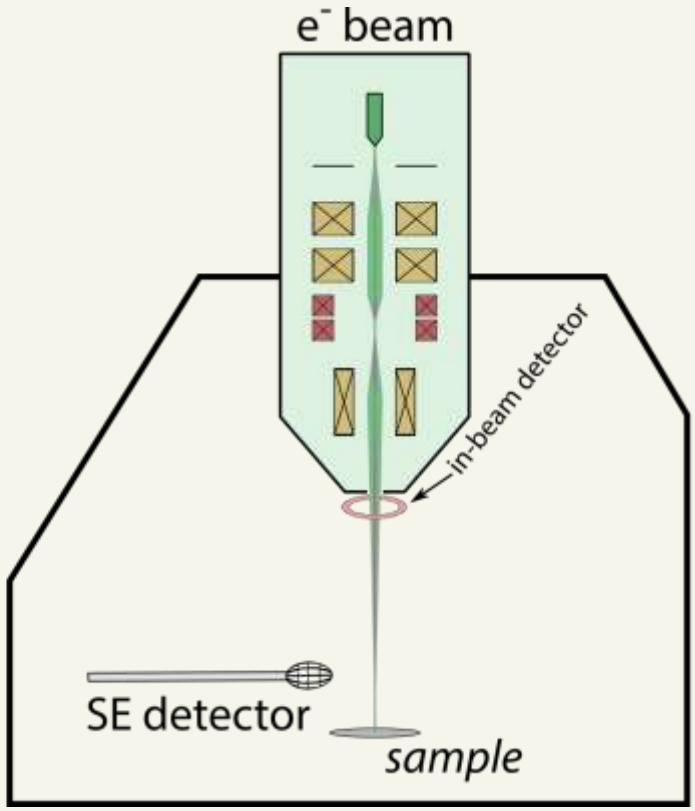




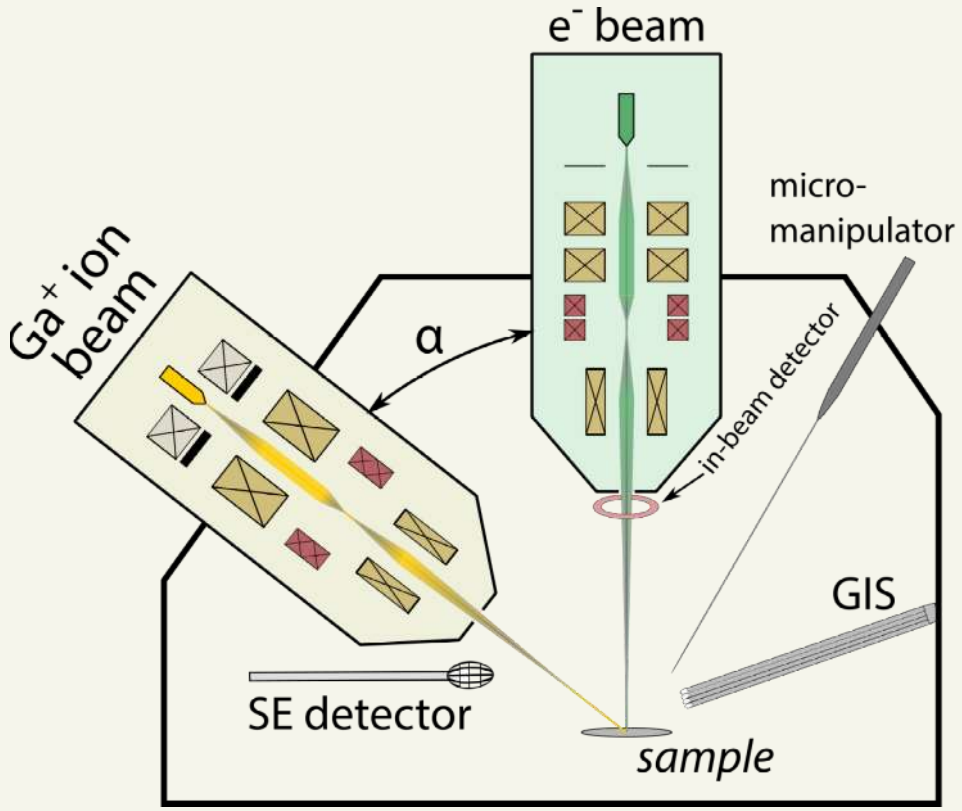
(Very) Brief introduction to Focused Ion Beams (FIB)

- **Scan a finely focused beam of ions across a sample**
  - Very similar to SEM technique
- **Heavy ions rather than electrons**
  - Worse resolution, but more interactions
  - Electrostatic lenses, rather than electromagnetic
- **Combined with SEM, enables almost unparalleled analytical capabilities**

(Very) Brief introduction to FIB/SEM

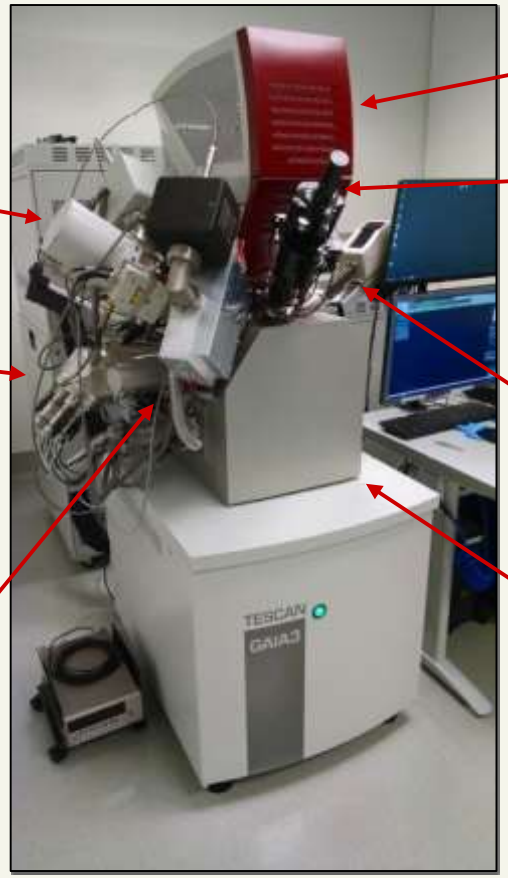


Typical SEM configuration

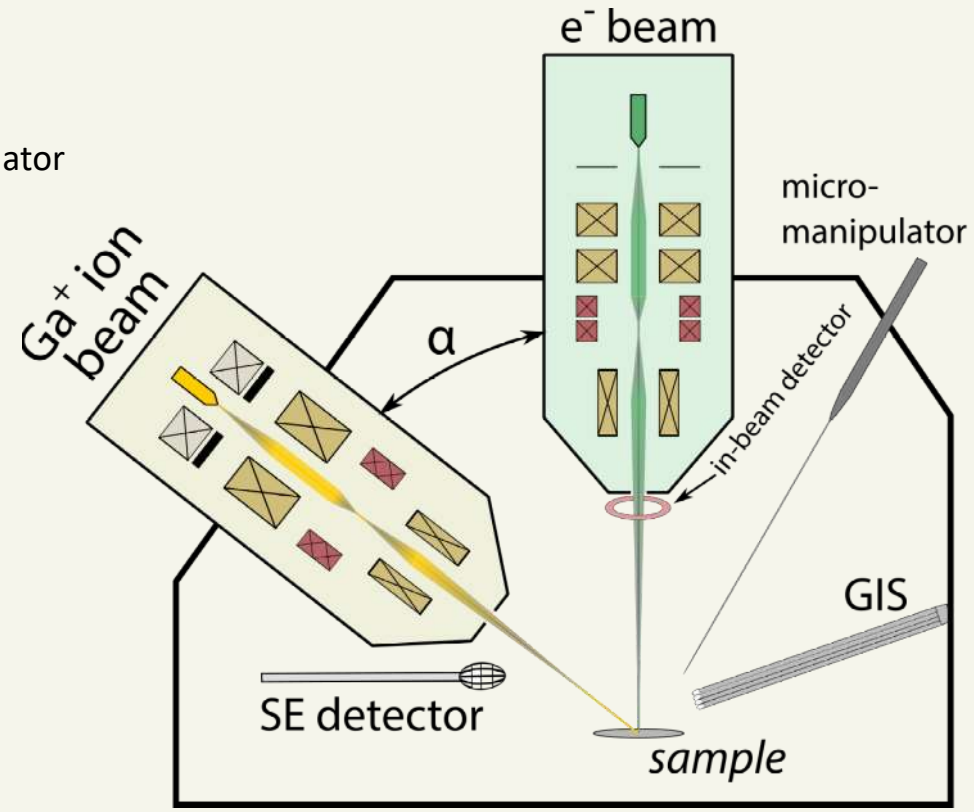


Dual-beam FIB/SEM configuration

(Very) Brief introduction to FIB/SEM



Tescan *Gaia* FIB at UMD

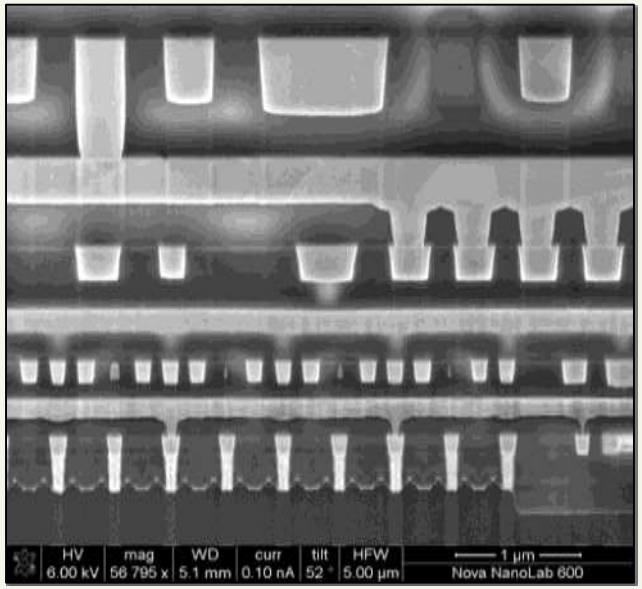


Dual-beam FIB/SEM configuration

Unique capabilities of FIB/SEM

In situ cross sections

65nm IC cross section



FEI Company (2016)

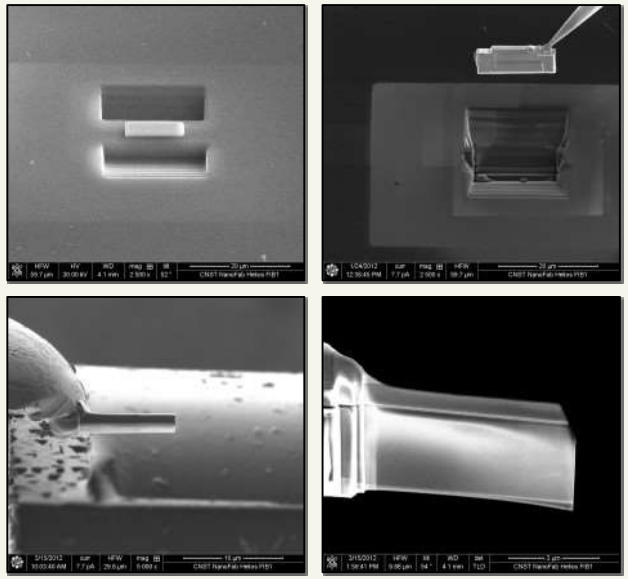
Material deposition

"Nano-trek"

T. Hoshino *et al.*, *EIPBN* (2003)

TEM Sample Prep

***In situ* liftout technique**



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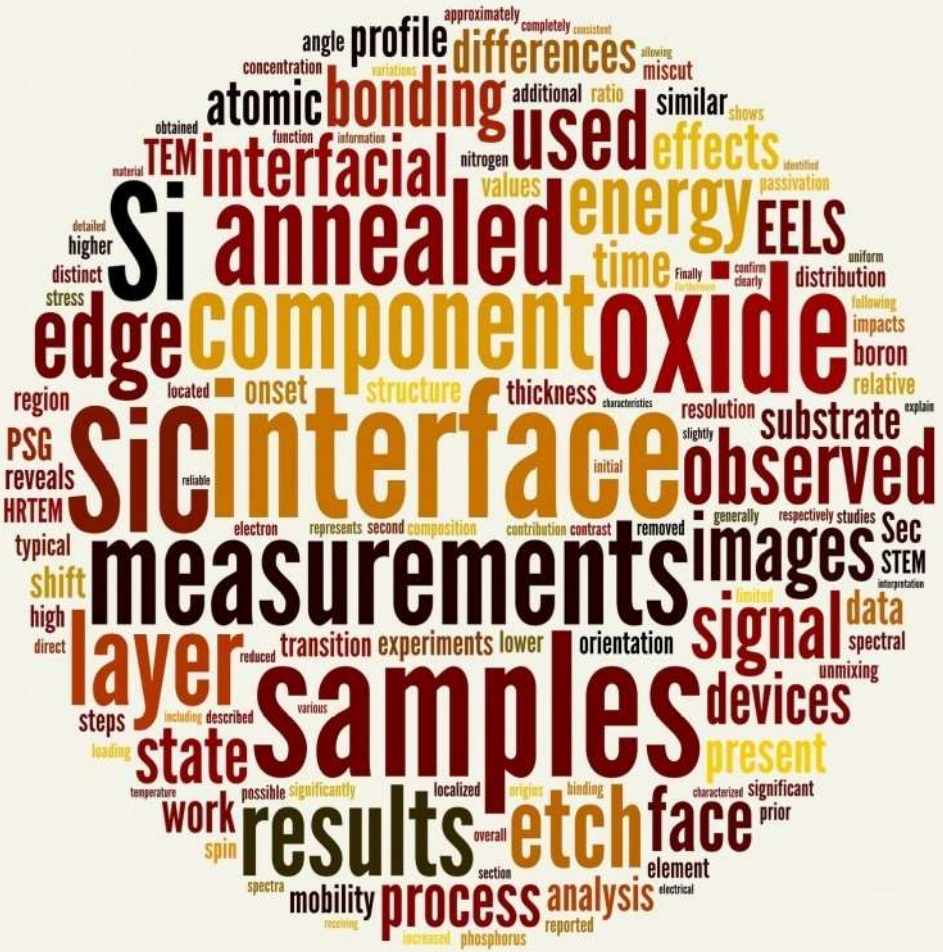

Introduction to wide bandgap (WBG) materials

- **What is a WBG?**
  - Electronic materials beyond silicon
  - Semiconductor with $E_g > 3$ eV
  - Example properties:

	4H-SiC	GaN	Silicon
E_g (eV)	**3.26**	**3.39**	1.12
μ_e ($cm^2/V\ s$)	900	**1600**	1400
Critical field (MV/cm)	**3 – 5**	**5**	0.3
Thermal cond. (W/cm K)	**3.7**	1.3	1.3

- **Why WBG materials?**
  - Good mobilities
  - High critical fields
  - High thermal conductivity
  - Useful where silicon is limited

← Fast switching

← Can block high voltage

← Efficient heat removal

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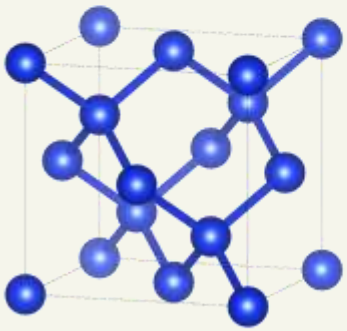
Why silicon carbide (SiC)?

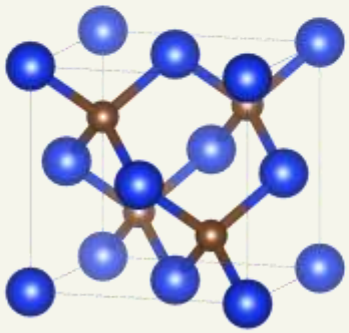
- **Native oxide**
  - SiO_2 grows natively
  - Easily integrates with existing processes
- **Lighter, more efficient than Si in high power applications**

SiC structure(s)

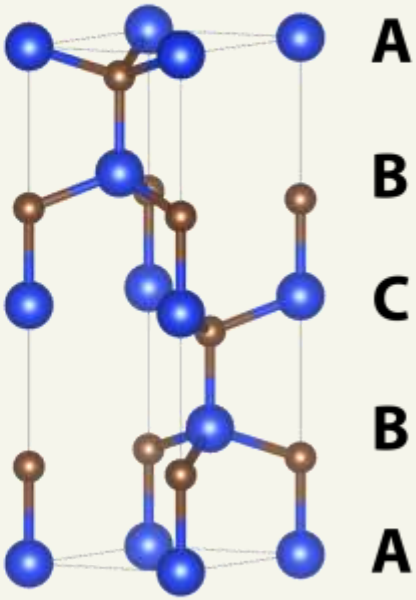
- **SiC has over 250 polymorphs**
  - Determined by stacking sequence
  - 4H is the most relevant for electrical devices



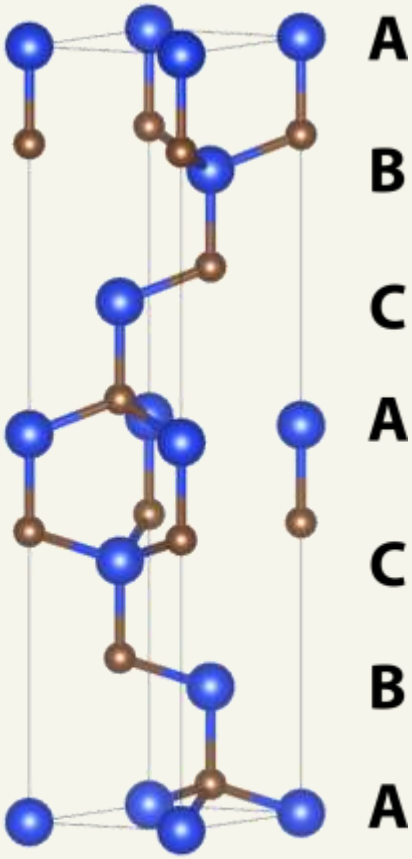
Silicon



3C-SiC



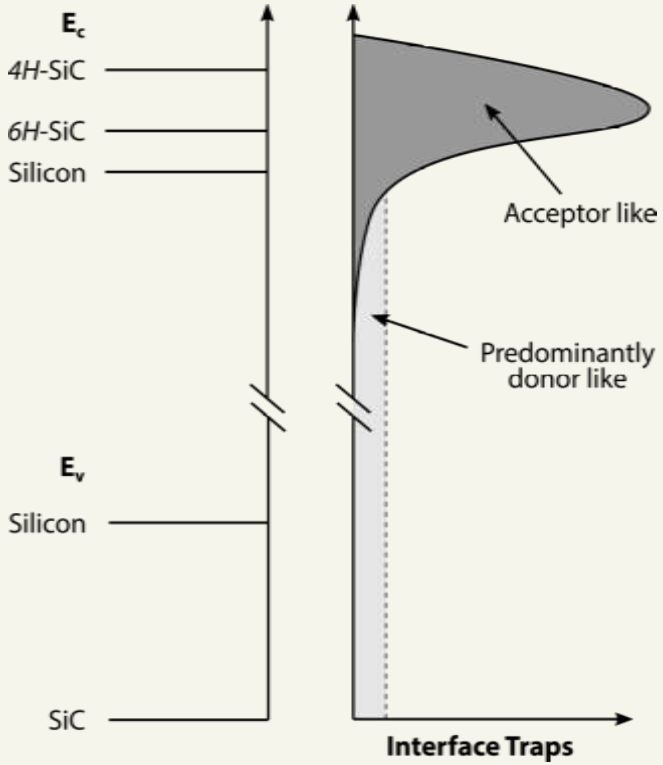
4H-SiC



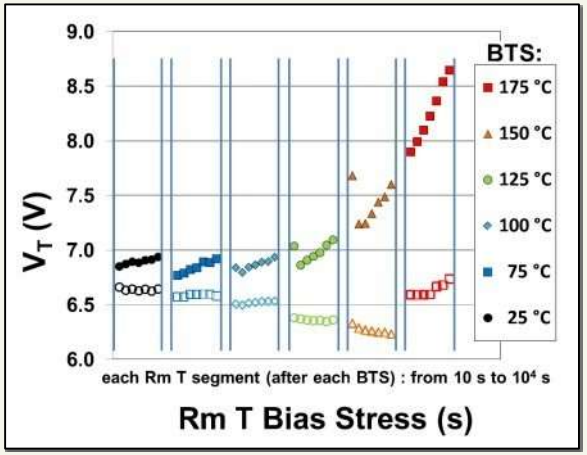
6H-SiC

Why *not* silicon carbide (now)?

- **High cost**
  - 3” wafer $2,000 (compared to $60 for Si)
- **Low device mobility**
  - Interface traps limit μ_e in inversion layer
  - Device μ_e 1% of bulk value
- **Limited device reliability**
  - Threshold (“on”) voltage shifts with bias and temperature stress



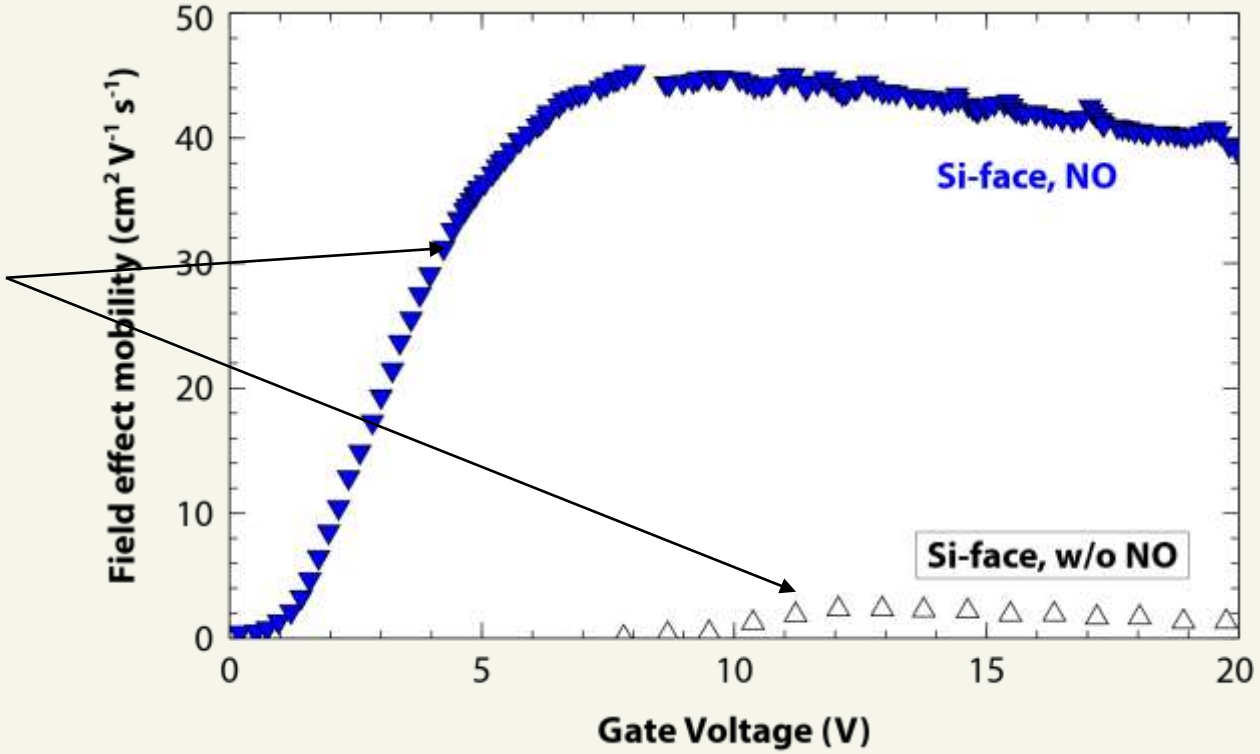
Interface trap density vs. energy
(*Adapted from Schörner, 1999*)



V_{th} shift after bias stressing
(*Lelis, 2015*)

What can be done?

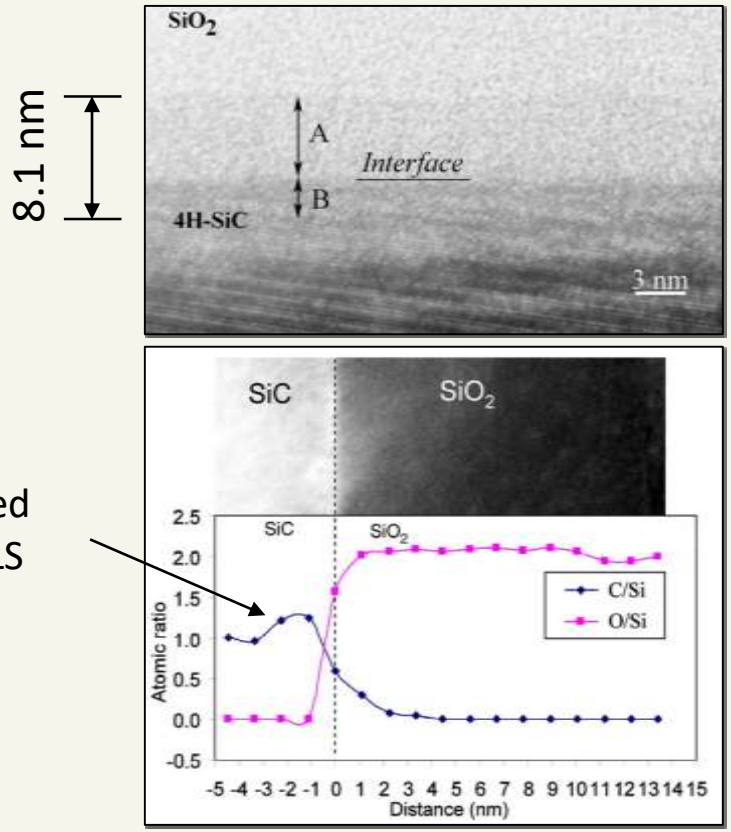
- **NO post-oxidation anneal**
  - Developed in the late 1990s at Auburn, Vanderbilt, and Rutgers Universities
- **Significantly higher mobilities**
  - Order of magnitude improvement
  - Has enabled commercialization of SiC components (*Wolfspeed*, *Rohm*, *etc.*)
- **How does it work?**
  - Incorporation of N close to SiC/SiO_2 interface
  - Passivation of mobility-limiting defects
  - N also introduces hole traps causing negative bias-temperature instability (reliability concern)



SiC MOSFET μ_e before/after NO-annealing
(*Dhar, 2006*)

What is happening at the interface? (prior research)

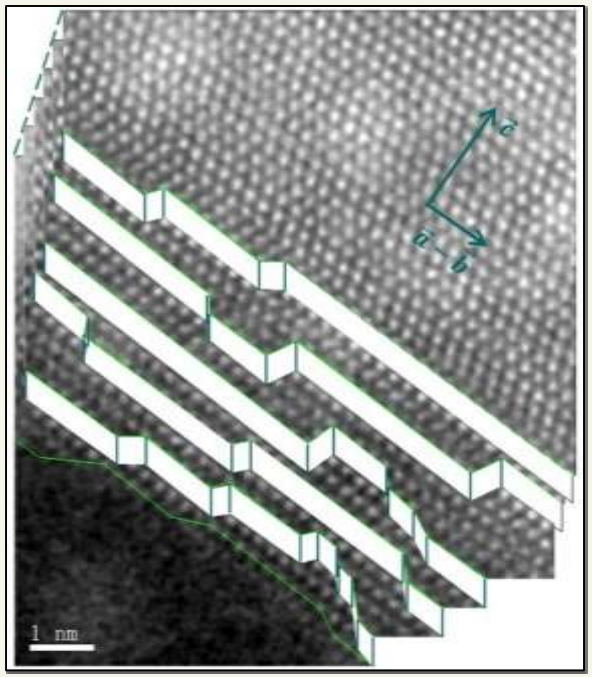
HRTEM & EELS



Excess carbon measured with EELS

Transition layers at SiC/SiO_2 interface
(*Zheleva, 2008*)

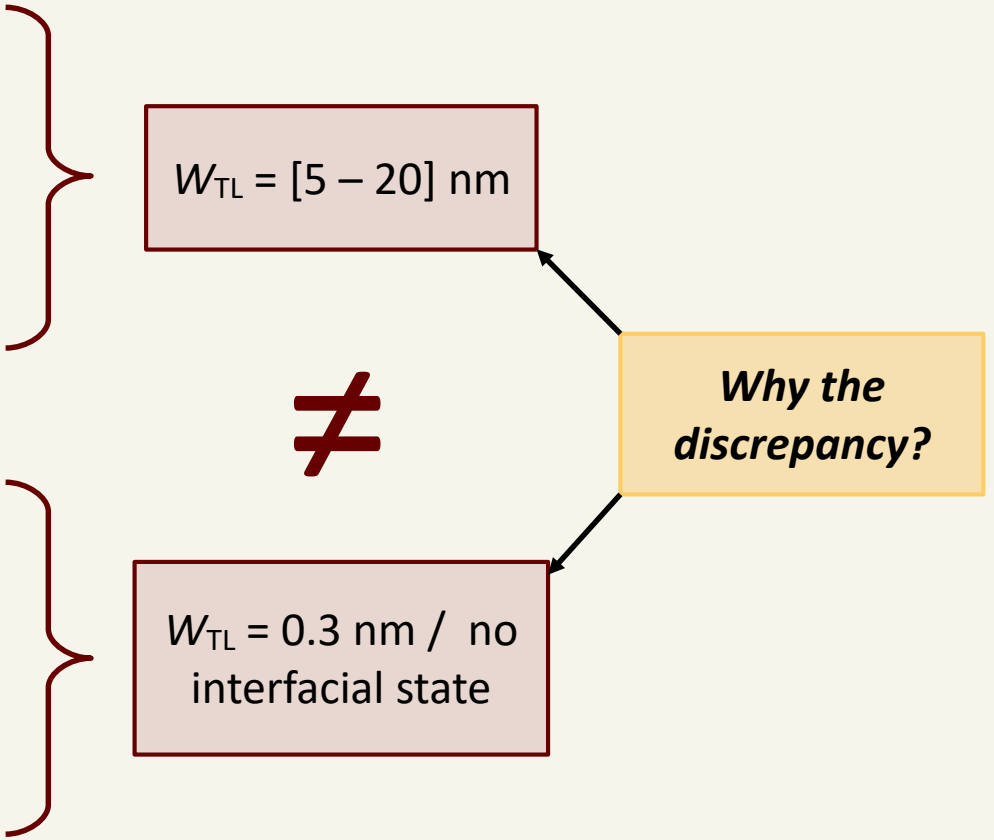
HR-STEM & EELS



No "transition layer", just roughness of about 2 nm
No excess carbon measured by EELS
(*Liu, 2014*)

Problem!

- **EELS evidence of enhanced C concentration in SiC at interface**
  - T. Zheleva, *et al*. Appl. Phys. Lett. **93**, 022108 (2008).
- **Transition layer narrows with NO post-anneal**
  - T. Biggerstaff, *et al*. Appl. Phys. Lett. **95**, 032108 (2009).
- **Angle resolved XPS of interfacial state**
  - L. I. Johansson, *et al.*, Surf. Sci. **529**, 515–526 (2003).
- **HR-STEM focal reconstruction of structure**
  - Measured a few monolayers of roughness and attributed the transition region solely to structural effects
  - P. Liu, *et al*. J. Vac. Sci. Technol. A, **32**, 060603 (2014).



Goals of this Research

- **Investigate the *4H*-SiC/SiO_2 interface and resolve its structure**
  - Discrete transition layers, or no? Size of the layers? Bonding states at the interface?
  - Aim to contribute definitive evidence of the interfacial structure
- **Corroborate EELS and XPS measurements**
  - Measurements by the two techniques give very different results, but the methods have never been combined in one report from the same research group
- **Analyze the effects of substrate orientation and roughness**
  - What is the origin of the drastically improved mobility on the *a*-face?
  - Does roughness at the interface affect the interfacial chemical states?

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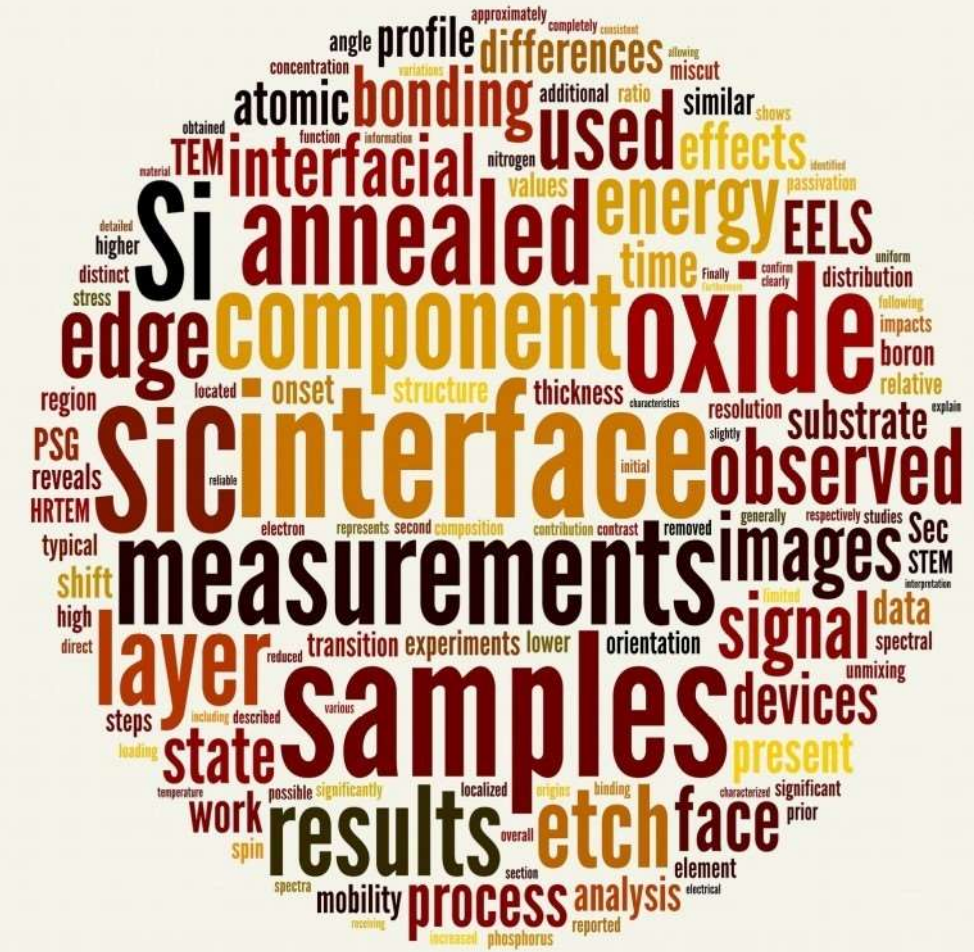
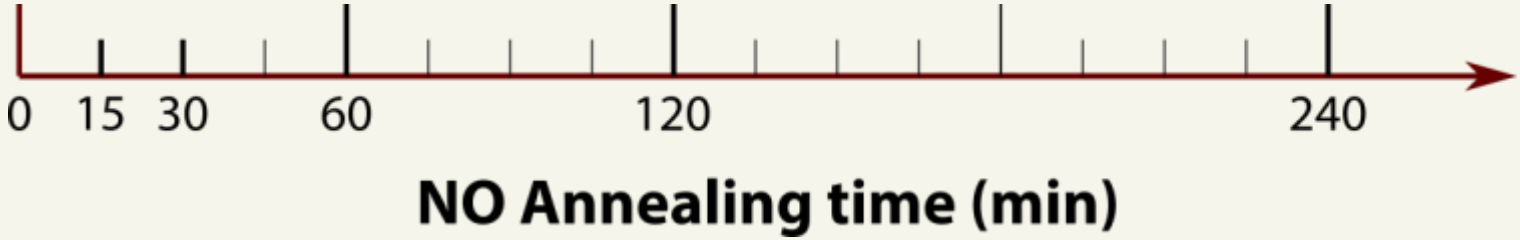


Experimental design

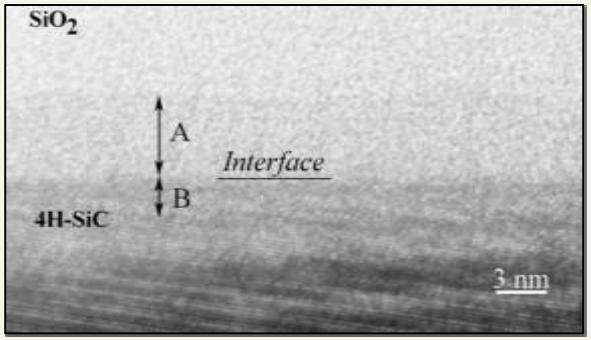
- **Six (6) SiC/SiO_2 MOSFET devices**
  - (0001) 4° miscut Si-face wafer substrate
  - NO post-oxidation anneal (0 – 240 minutes)
    - μ increases with NO-anneal time
  - FIB/SEM extraction of TEM lamellae from gate region

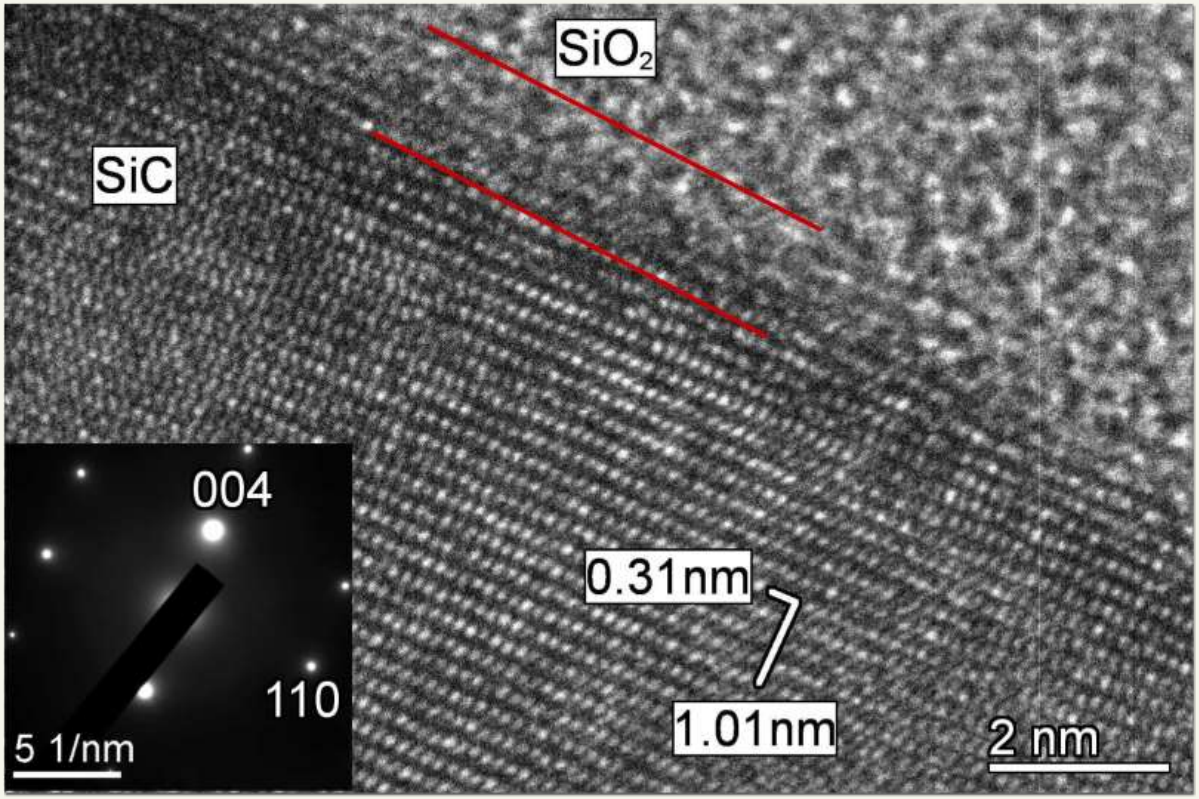


HRTEM of the SiC/SiO_2 interface

- **Structurally, no large distinct transition layers**

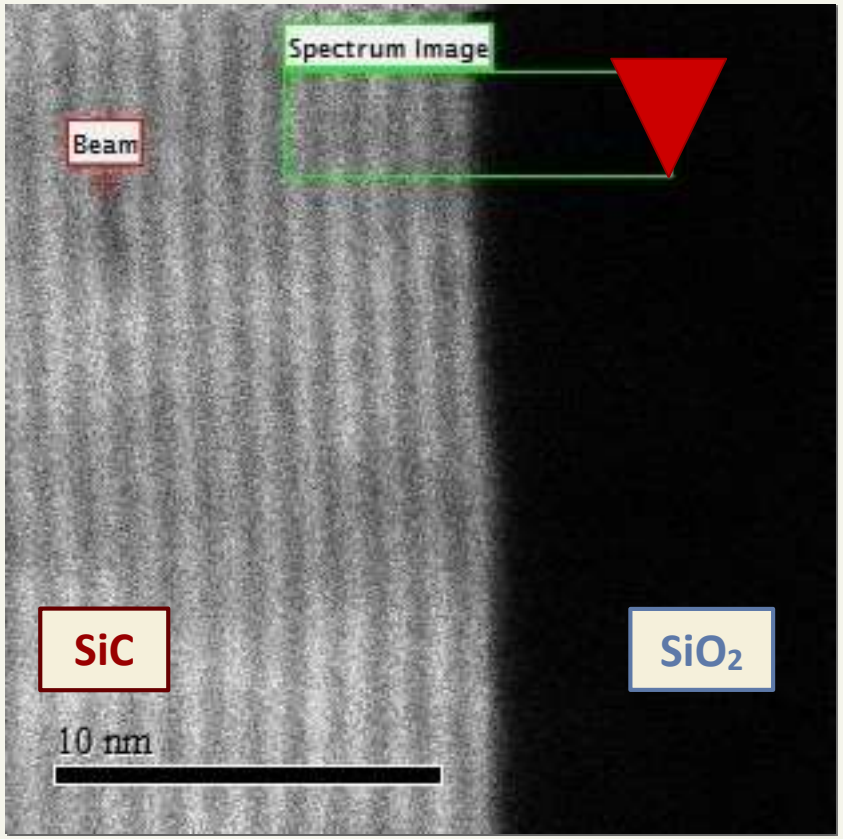
- **Compare to Zheleva *et al.*:**





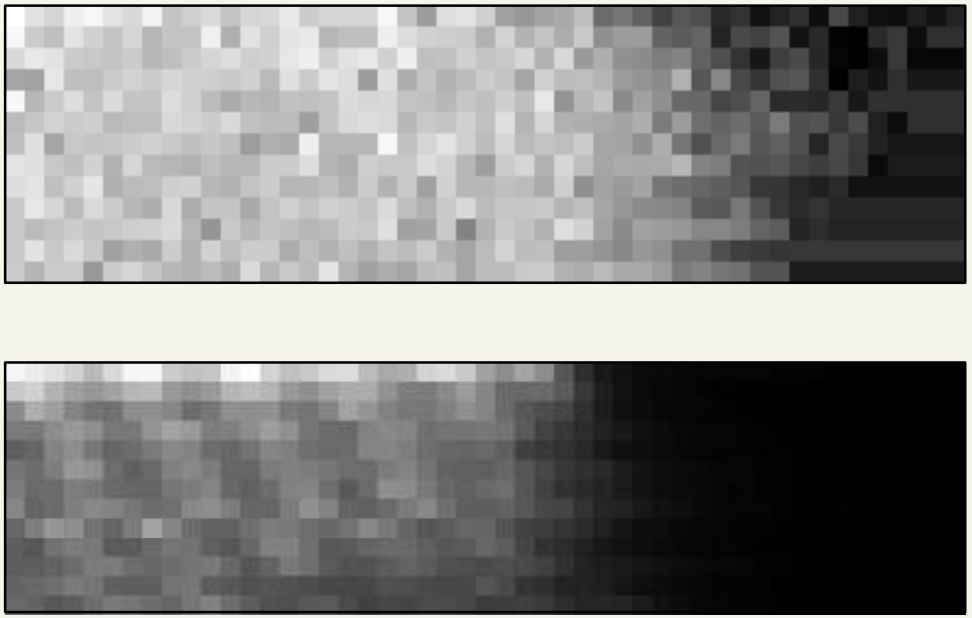
4H-SiC/SiO_2 interface from 60 minute NO-annealed MOSFET device

EELS Spectrum Imaging



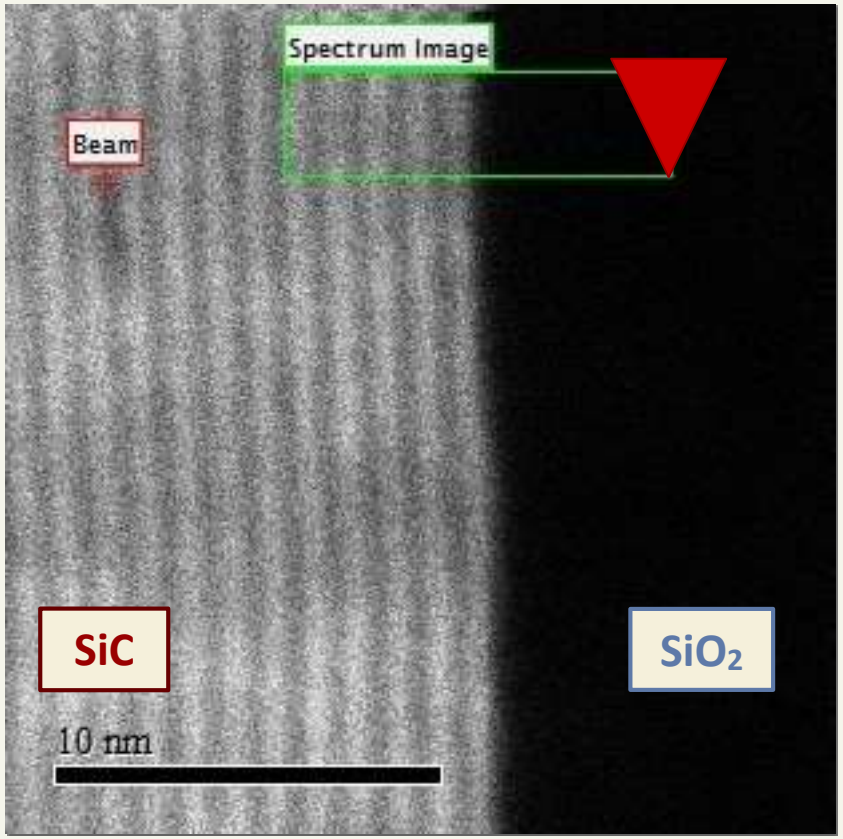
STEM survey image at interface

EELS spectrum collected at each point



STEM signal measured at each point

EELS Spectrum Imaging



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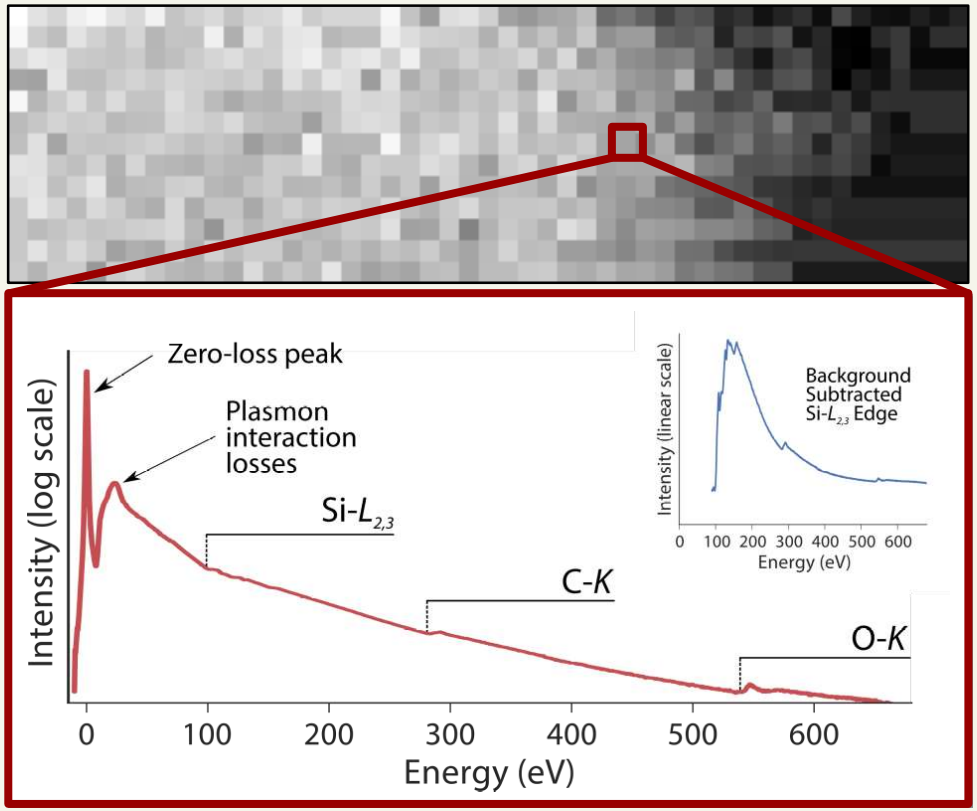
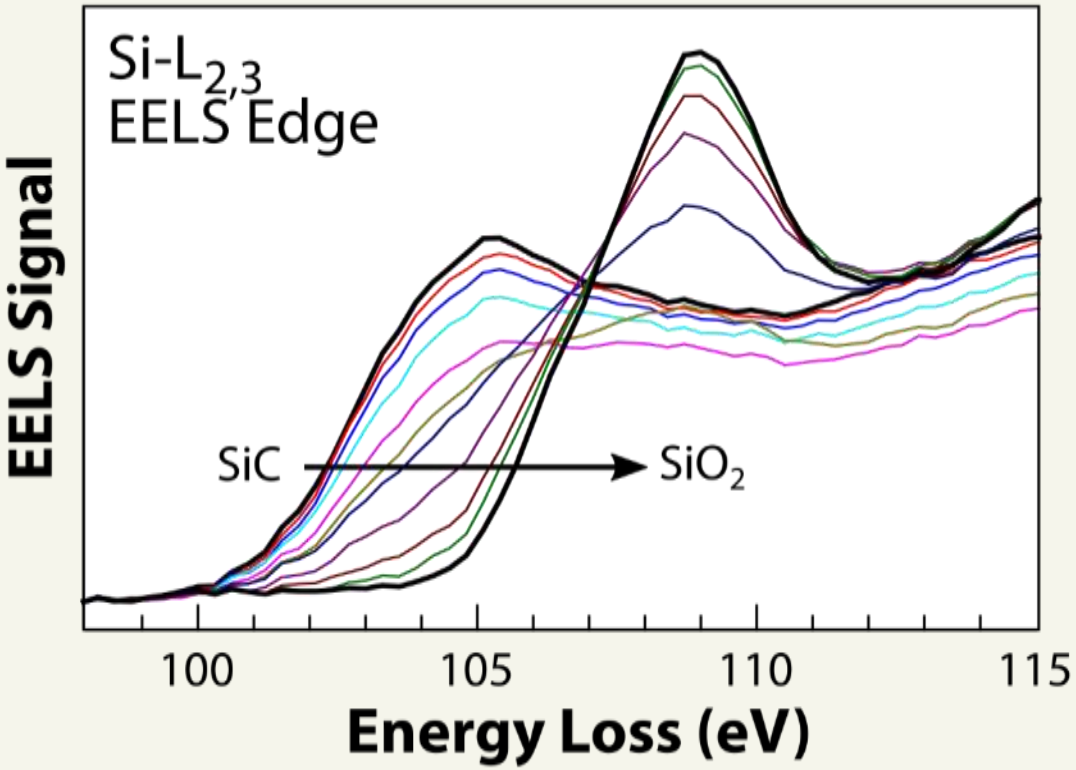
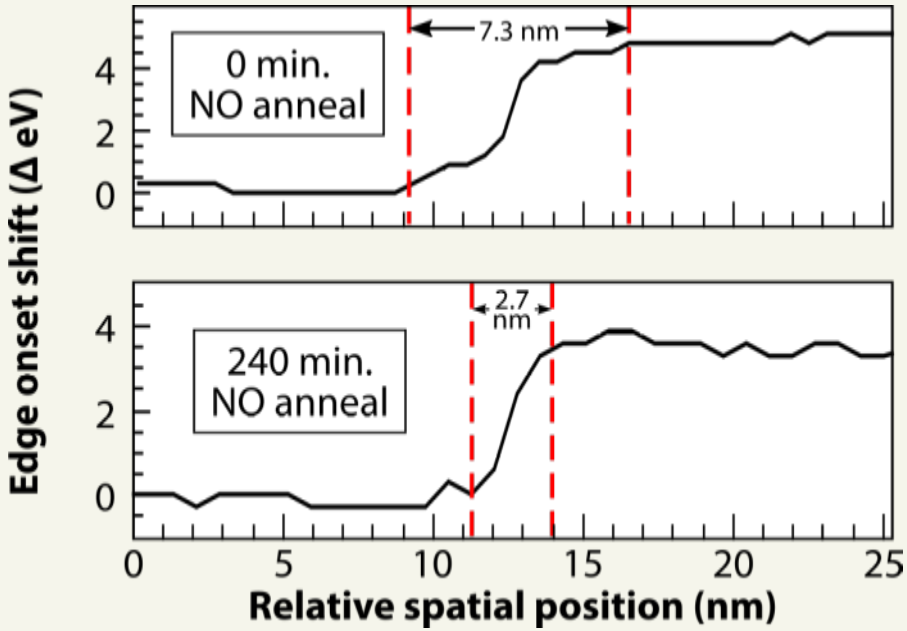


Chemical shift of Si-$L_{2,3}$

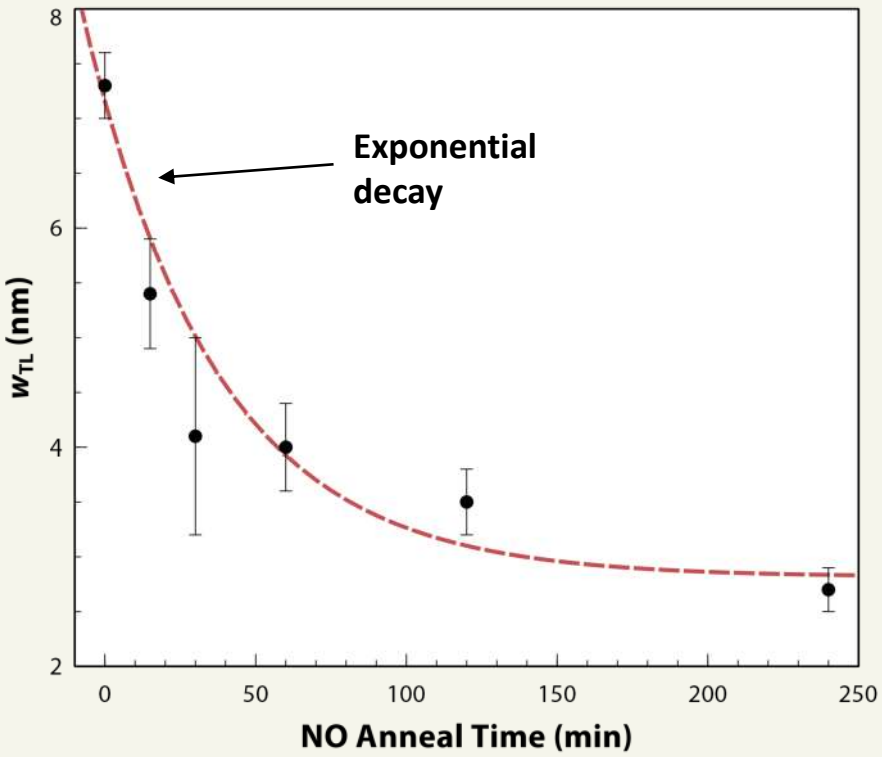


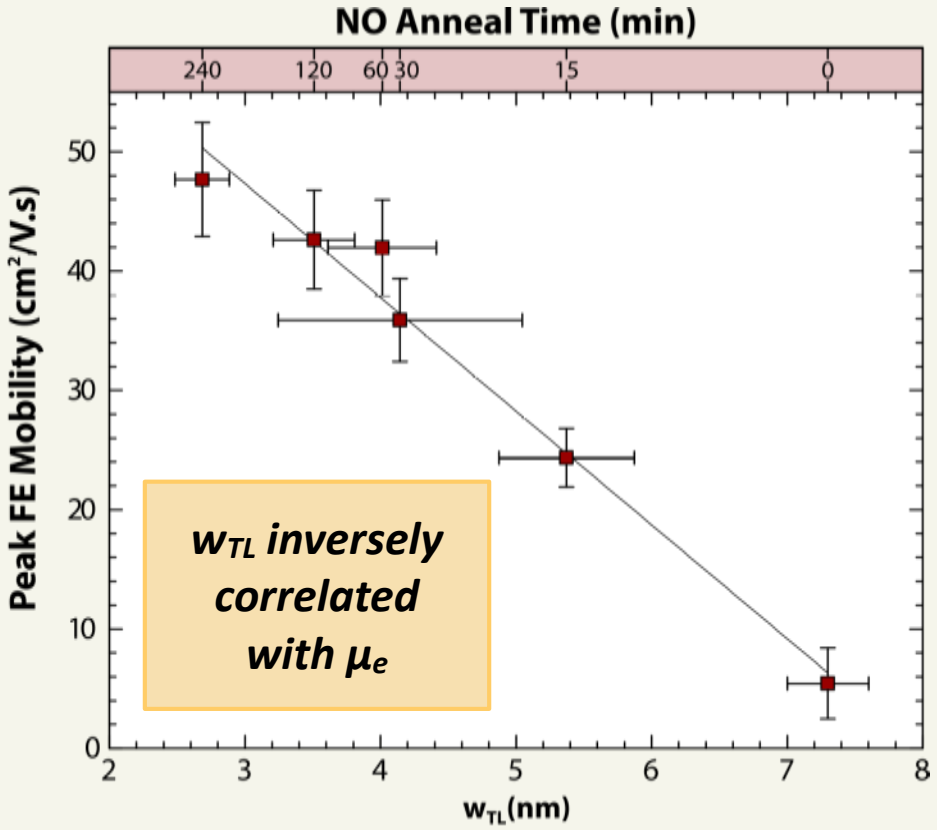
- **Onset energy of edge reflects the bandgap**
  - Probes bonding configuration of silicon atoms
  - Measure onset energy across interface



w_{TL} results (Chemical shift method)

w_{TL} decreases with NO anneal time





NO Annealing summary

- **Little structural evidence (HRTEM) for distinct TL**
  - HRTEM suggests only 1 nm or so, but chemical evidence contradicts this
- **No excess carbon at any of the interfaces**
  - In agreement with a number of recent works, and contradicting older (before 2008) studies
- **w_{TL} decreases with NO anneal time, N-coverage, and mobility**
  - Si-$L_{2,3}$ chemical shift method developed as most reliable metric of w_{TL}
- **NO-anneal chemically "sharpens" interfacial area**

Results published in J. Applied Physics:
J. Taillon, L. Salamanca-Riba, *et al.*, J. Appl. Phys. **113**, 044517 (2013)

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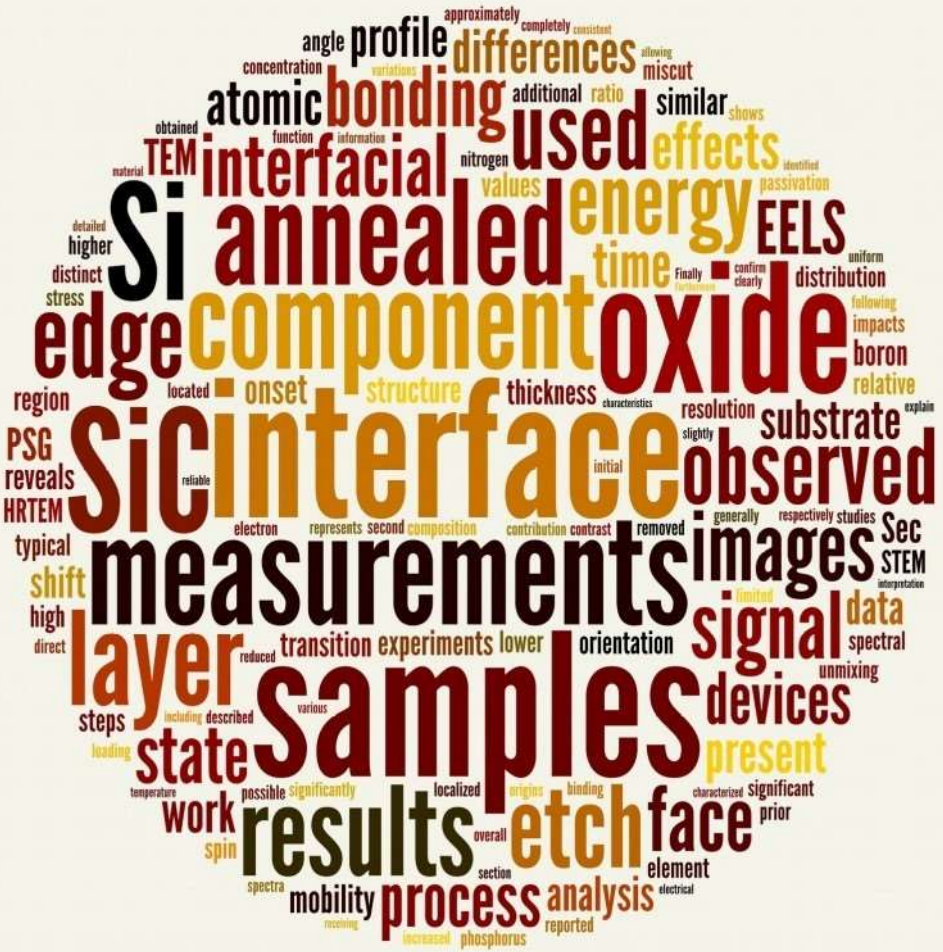


Motivation for XPS experiments

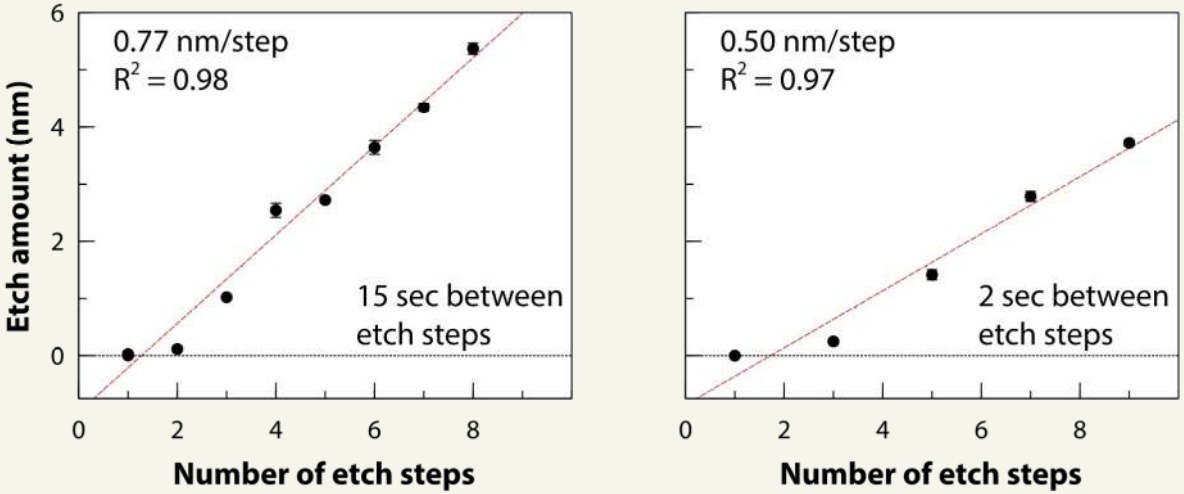
- **Previous experiment only showed changes in size of TL**
  - No specific information about what is changing chemically
- **General disagreement in literature between EELS and surface techniques**
  - First study to directly compare the two methods
- **Prior SiC XPS works have not maintained fidelity of interface**
  - Etch all the way to substrate
  - Measure interface during growth
  - Sputter profile – physically alters interface

Experimental design

- **Four SiC/SiO_2 MOSFET devices**
  - (0001) 4° miscut Si-face wafer substrate
  - 55 nm gate oxides
  - 2 samples only oxidized
  - 2 with 2hr NO post-anneal

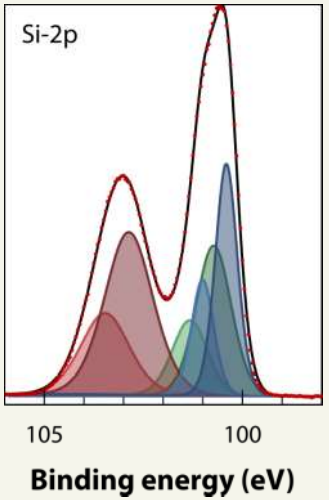
Spin-etch technique

- **Adopted from Si/SiO_2 literature**
  - F. J. Grunthaner, P. J. Grunthaner, *et al.*, *J. Vac. Sci. Technol.*, **16**, 1443 (1979)
- **Drip HF etchant onto spinning substrate**
  - Careful introduction of etchant allows fine control of etch rate
  - No additional contamination/damage to interface
- **Demonstrated sub-nm uniform etch control:**

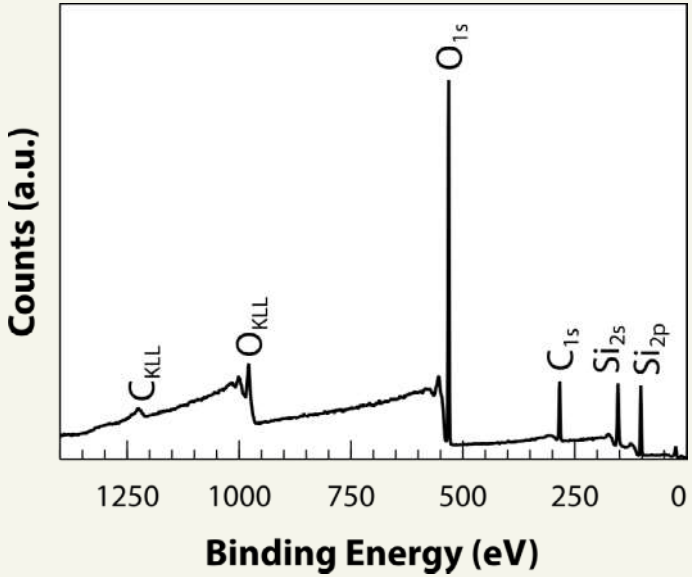


Brief XPS Review

- **X-ray Photoelectron Spectroscopy**
- **Utilizes photoelectric effect to measure binding energy of electrons within 5 – 10 nm of sample surface**
  - X-rays in → electrons out
  - Spectrum of binding energies
- **Can measure:**
  - Atomic composition
  - Chemical states at the surface
  - Species and orbital-specific information
  - Depth information with angle-resolved measurements



High resolution scan
- *Chemical information*
- *Component deconvolution*



Elemental survey scan
- *Overall composition*
- *Auger and core peaks*

w_{TL} from angle resolved XPS

- **Thickness of thin films can be measured by comparing signal intensities at different angles**
  - "Attenuation model" (Johansson, 2003)
  - Integrate interface intensity and compare to SiC-substrate intensity

Integrated intensities

Atomic conc. of silicon

Interface thickness

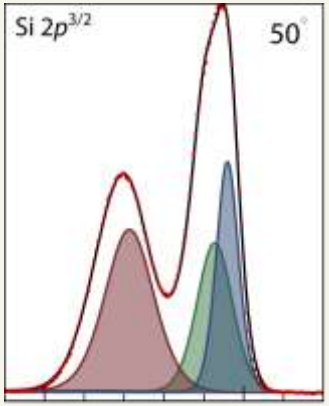
$$\frac{I_{\mathrm{int}}}{I_{\mathrm{SiC}}} = \frac{c_{\mathrm{int}}}{c_{\mathrm{SiC}}}\left(e^{\frac{d_{\mathrm{int}}}{\lambda \cos\theta}} - 1\right)$$

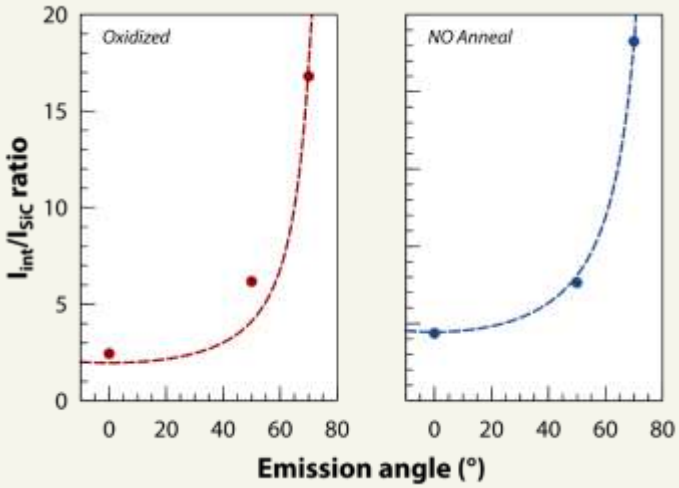
Attenuation length of e^-

Measurement angle

- **Results:**

	$w_{\mathrm{interface}}$
Oxidized	2.9 nm
NO Anneal	1.6 nm

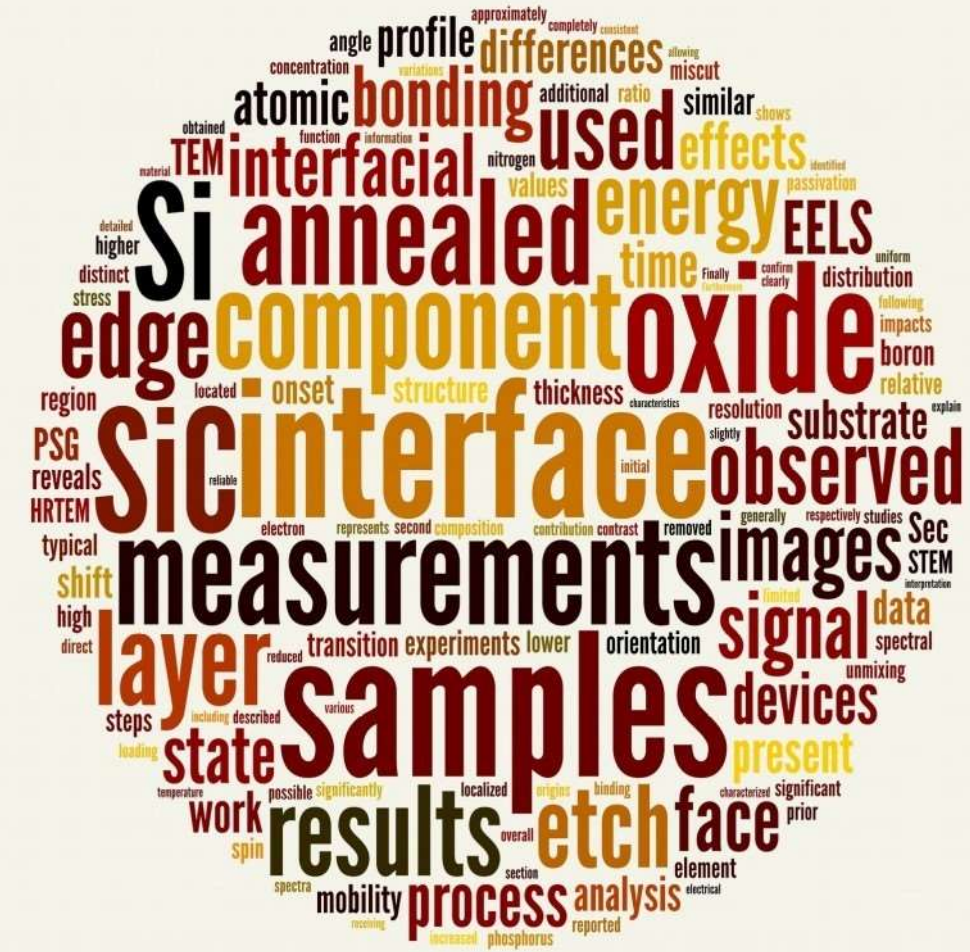




- **Spatial distribution of interfacial signal changes with NO anneal**
- **Similar w_{TL} to those measured by EELS**

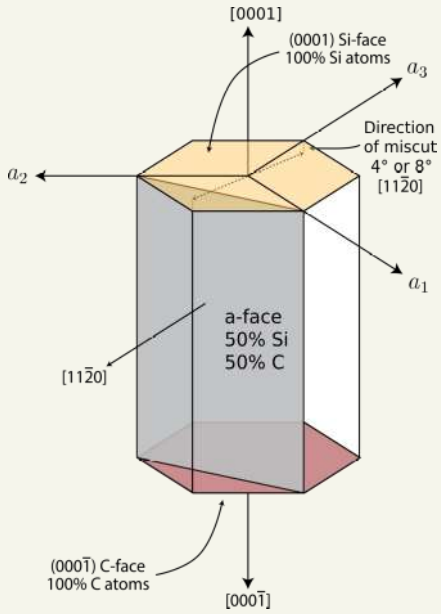
Outline

- Overall introduction
- **SiC MOSFET characterization**
  - Transition layer measurements
  - XPS interface analysis
  - **Effects of crystallographic orientation**
- Solid oxide fuel cell reconstructions
  - Intro & Methodology developments
  - LSM-YSZ cathode degradation
  - LSCF-GDC cathode degradation
- Conclusions and Future work

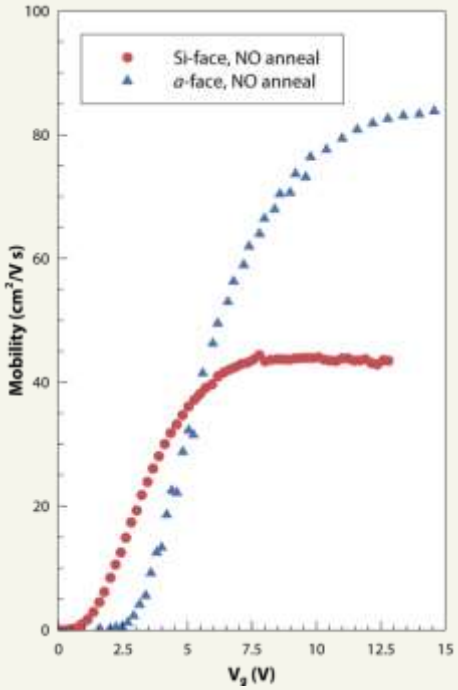


Motivation for orientation experiments

- **Origins for mobility enhancement on *a*-face are poorly understood**
- **Roughness from miscut angle is known to reduce mobility**
  - Does it have a substantial effect on the interface chemistry as well?
- **Does NO anneal operate in a different manner for the *a*-face compared to the Si-face?**



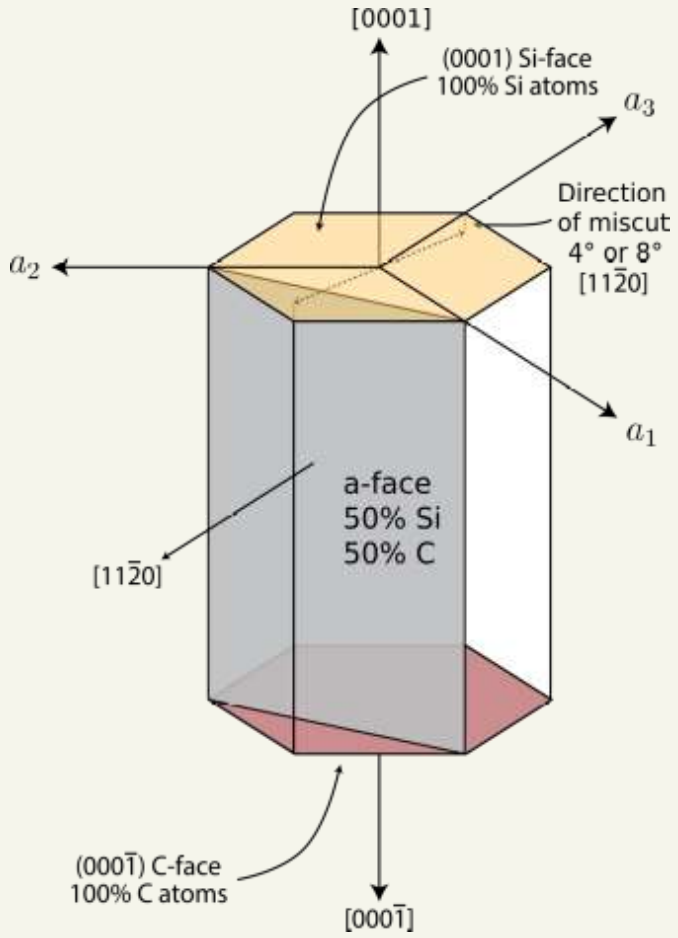
SiC crystal face orientations
(Adapted from Dhar, 2005)



Mobility of *a*-face vs. Si-face
(Liu, 2013)

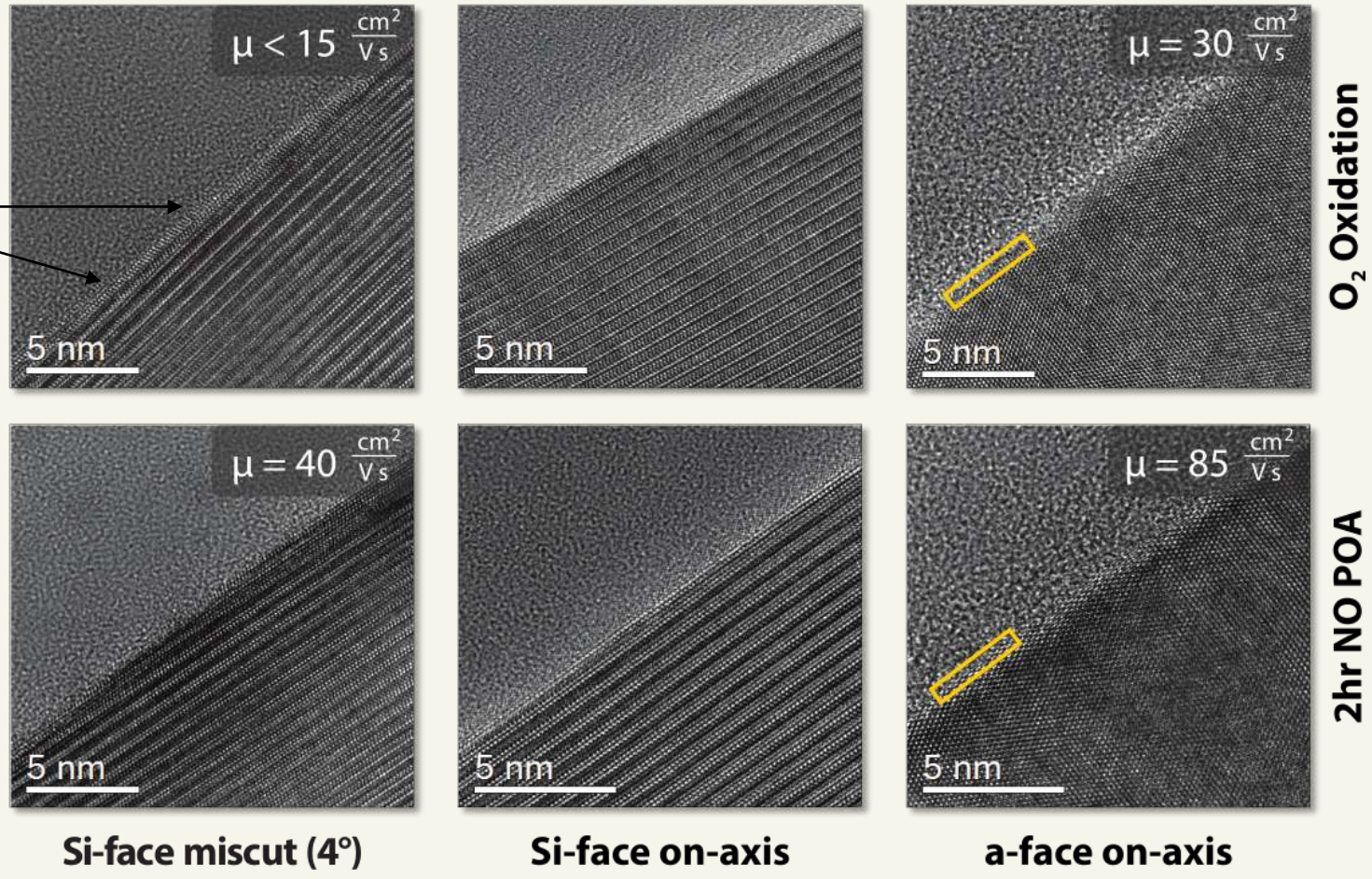
Experimental design

- **Six SiC/SiO_2 MOSFET devices**
  - 2 (0001) 4° miscut Si-face devices
  - 2 (0001) on-axis Si-face devices
  - 2 (1120) *a*-face devices
  - ≈ 60 nm gate oxides
  - For each orientation, 1 sample just oxidized; 1 with 2hr NO post-anneal

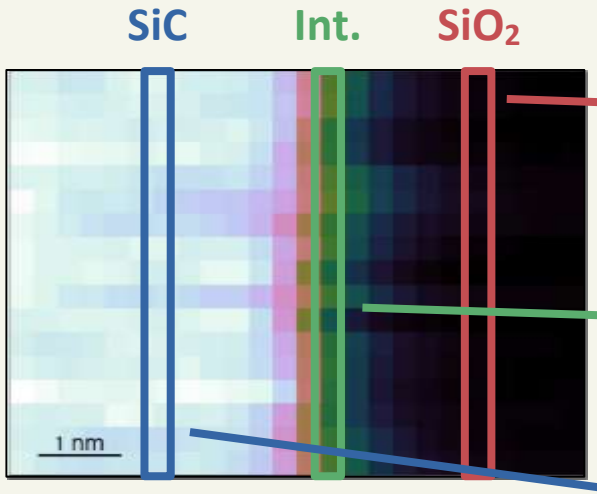


HRTEM of different orientations

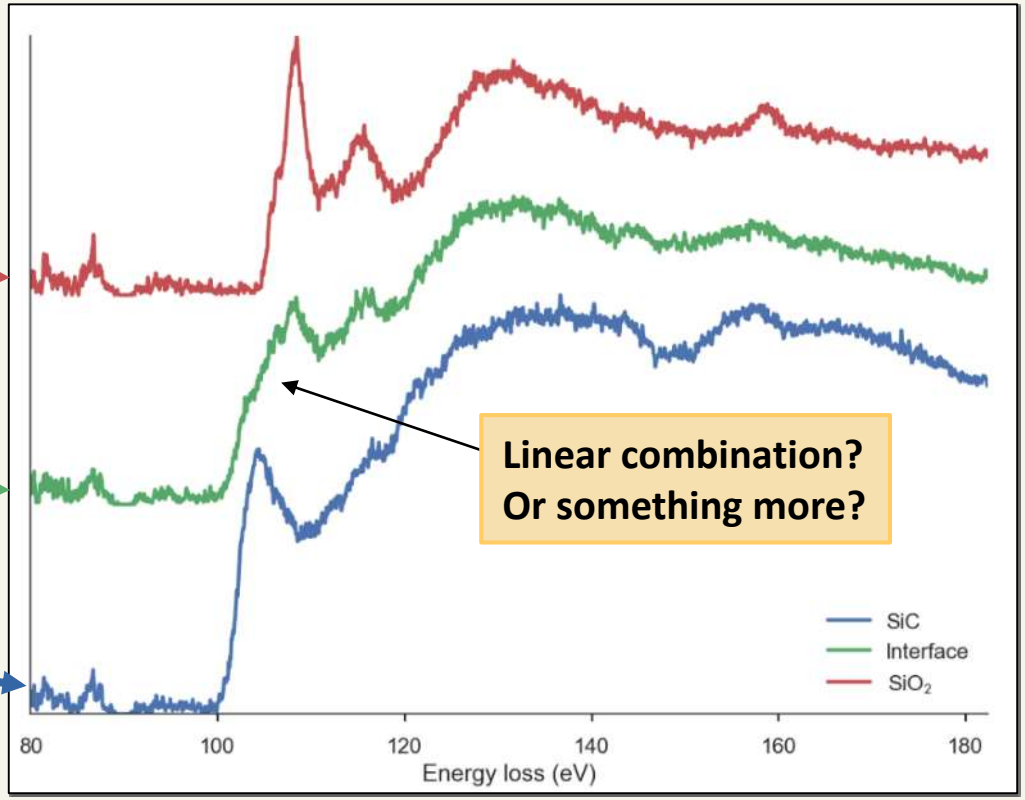
- Miscut steps evident
- Few steps in on-axis samples
- No clear structural transition region (like previous results)



What is at the interface?



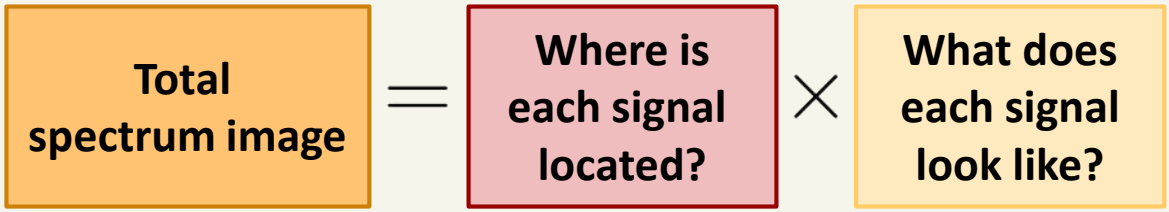
EELS Spectrum Image



Si-$L_{2,3}$ ELNES signal

Hyperspectral decomposition (or unmixing)

- Technique to recover multiple unknown signals from a spectrum image
- Consider a spectrum image as a matrix, and use matrix decomposition:



Hyperspectral decomposition (or unmixing)

- **Technique to recover multiple unknown signals from a spectrum image**
- **Consider a spectrum image as a matrix, and use matrix decomposition:**

$$\mathbf{D}_{(x,y),E} = \mathbf{S}_{(x,y),n} \times \mathbf{L}^{\mathrm{T}}_{(E,n)}$$

Original spectrum image

Position

Energy

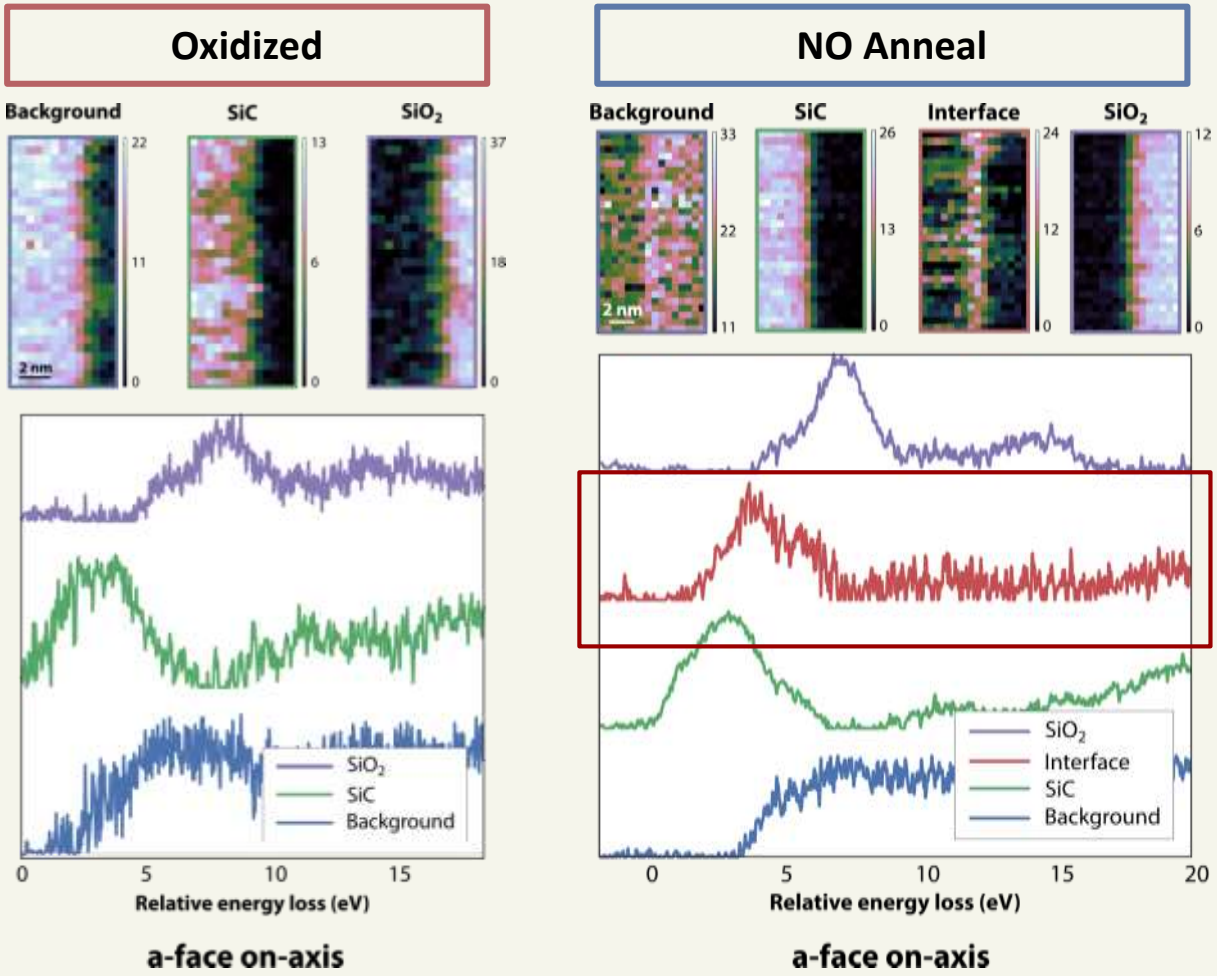
Score "maps"

Component number

Loading spectra (eigenvalues)

- **Any number of decomposition strategies can be used**
  - Non-negative Matrix Factorization (NMF) is very suitable for EELS data
  - Unbiased; unsupervised; only assumption is positivity of data

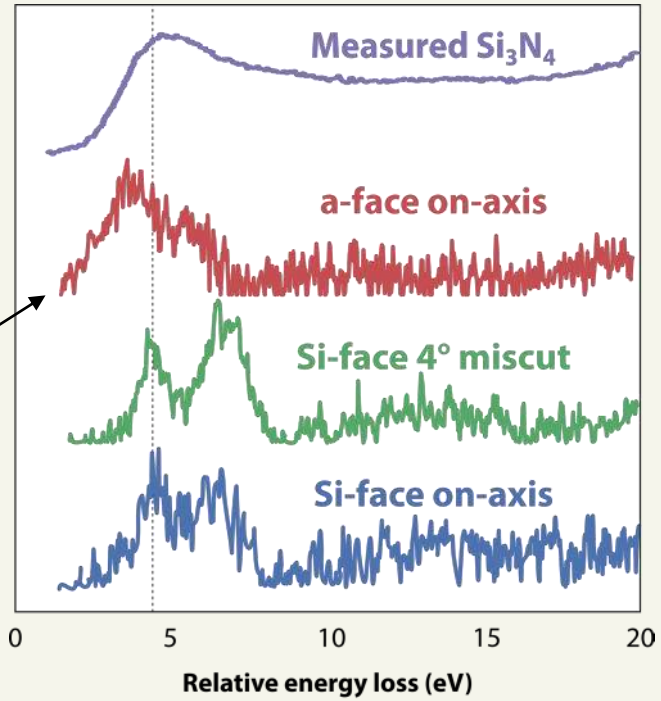
Unmixing of Si-$L_{2,3}$ EELS signal



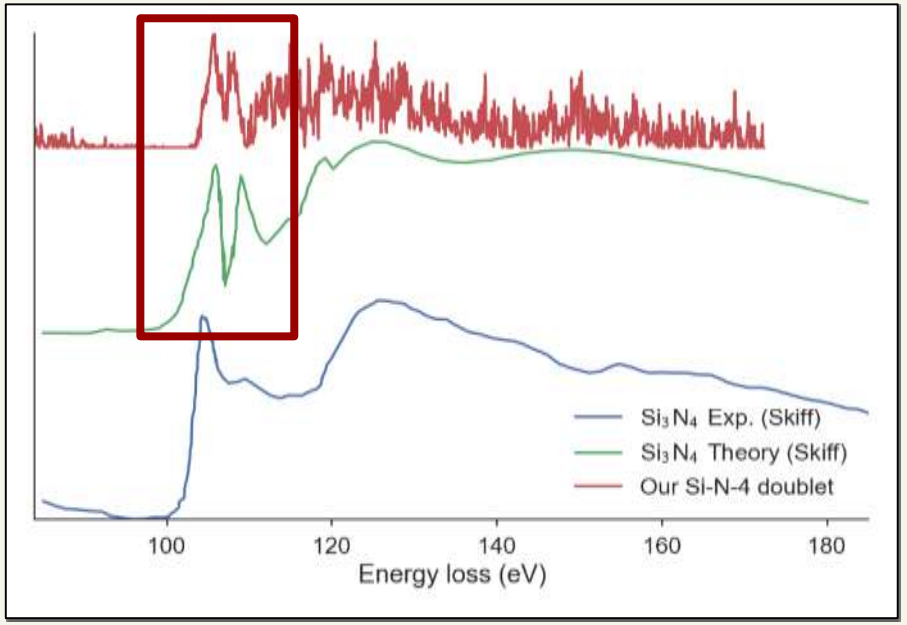
- **No significant variation between different orientations**
  - *a*-face results shown
- **NO anneal gives rise to interfacial state in all samples**
  - No such state in samples only oxidized

Si-$L_{2,3}$ Interface – Evidence of N bonding

Reduced edge onset for *α*-face



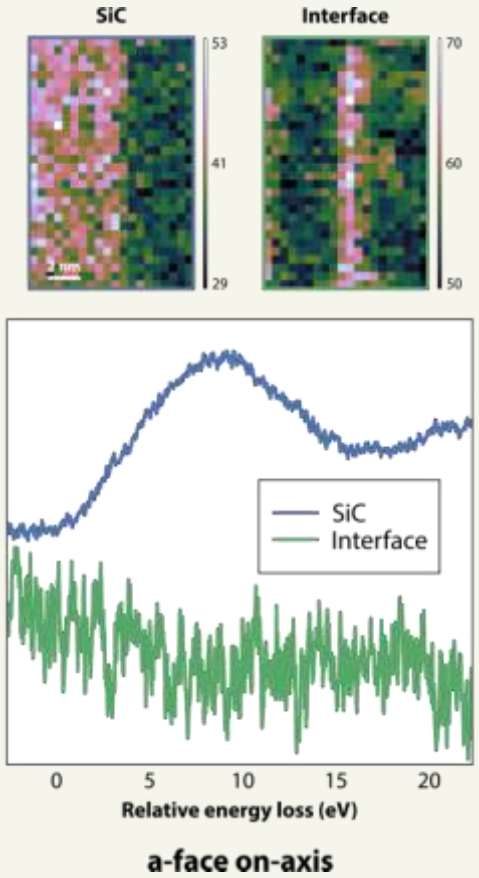
Comparison of interface components to measured Si_3N_4



Comparison to Si_3N_4 literature
(Skiff, 1987)

Unmixing of C-*K* EELS signal

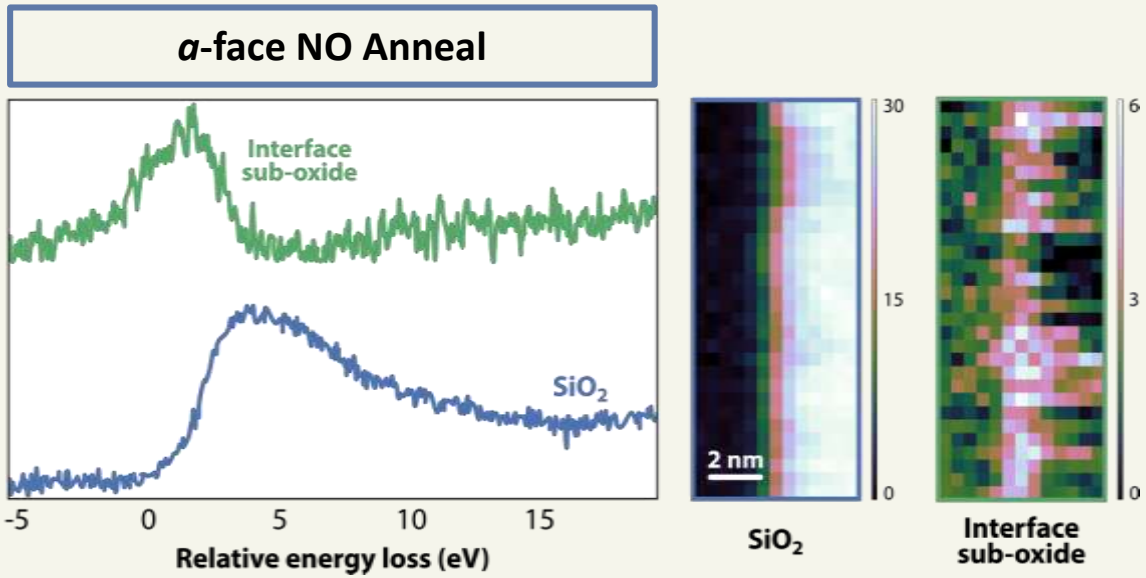
NO Anneal



- **NO anneal gives rise to interfacial state in all samples**
  - No such state in samples only oxidized
- **Pre-edge intensity indicative of sp^2 bonding, rather than sp^3**
  - Often observed in C-N configurations
- **Strong presence of N in carbon bonds**

Interfacial nitrogen's effects observed in Si and C signals, in all samples

Unmixing of O-*K* EELS signal



- **Only sample with interfacial component was *a*-face with NO anneal**
- **Interface has edge onset 2-3 eV lower than SiO_2**
  - Reduced bandgap
  - Increased dielectric constant
  - Enhanced mobility
- **Likely part of the drastically enhanced mobility on the *a*-face**
  - Silicon/carbon oxynitride configuration

Crystallographic orientation summary

- **Confirmation of Si_3N_4-like bonding, measured at Si-$L_{2,3}$ edge**
  - Further agreement between EELS and XPS results
  - Miscut/roughness alone does not appear to alter chemical states
- **Carbon bonds have sp^2 character in NO annealed devices (C-*K* edge)**
  - Signals the N bonds to both Si and C
- **Distinct oxygen interfacial signal only in NO annealed *a*-face device**
  - *a*-face enables additional bonding configurations that affect the oxide signal
  - Nanometer scale region of reduced bandgap likely origin of enhanced mobility in such orientations

Review of SiC experiments

- **w_{TL} measurement in NO-anneled SiC/SiO_2 devices**
  - Smaller transition layer width correlated with improved device mobility
- **Angle resolved XPS exploration of interfacial states**
  - w_{TL} measured by XPS corroborates EELS measurements
- **Substrate orientation investigation**
  - Miscut of Si-face does not appreciably alter chemical states (just adds roughness)
  - NO anneal creates distinct interfacial bonding state for Si and C in all samples
  - NO anneal only creates interfacial state for O in the *a*-face sample, proposed as the origin of enhanced mobility

Outline

- Overall introduction
- SiC MOSFET characterization
  - Transition layer measurements
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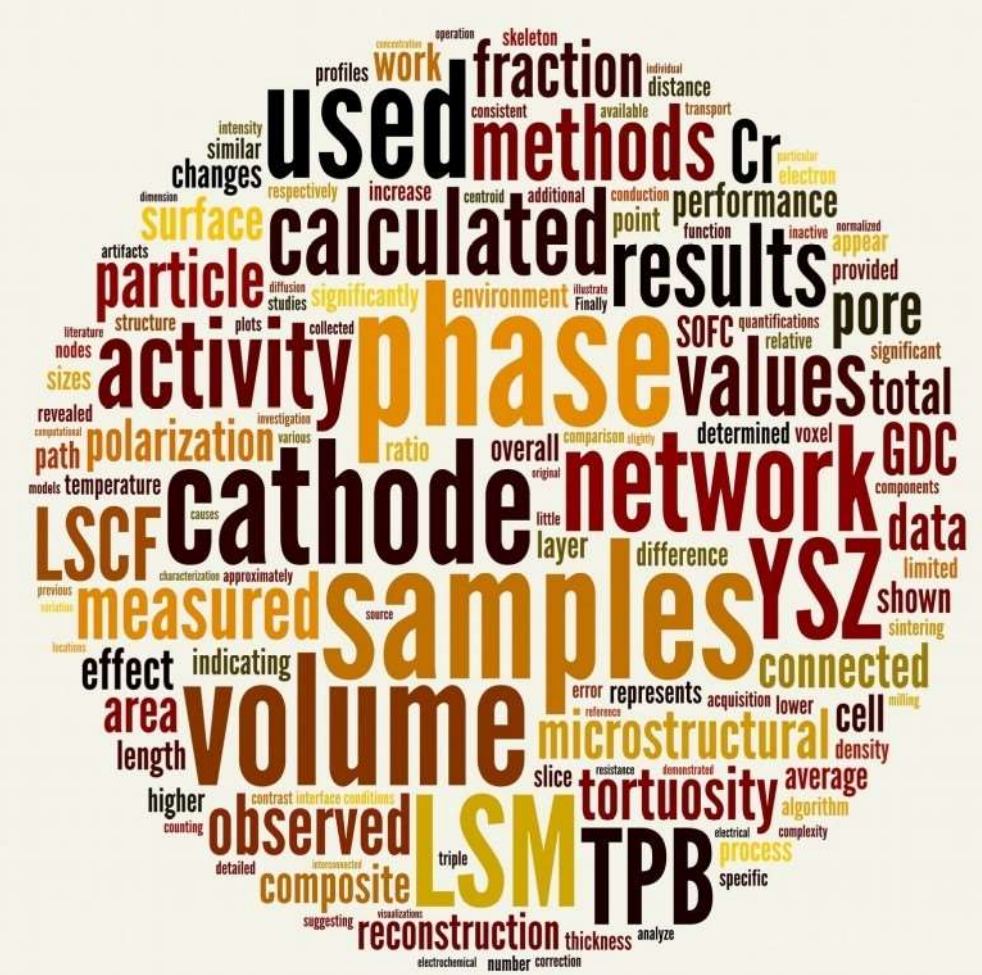
- **Solid oxide fuel cell reconstructions**
  - **Intro & Methodology developments**
  - **LSM-YSZ cathode degradation**
  - **LSCF-GDC cathode degradation**
- Conclusions and Future work



Introduction to solid oxide fuel cells (SOFCs)

- **SOFCs provide clean, energy efficient energy conversion**
  - Flexible fuels, low emissions, up to 90% efficient (in combined heat & power applications)

- **Operational basics:**
  - Oxidation of fuel(s) at the anode:

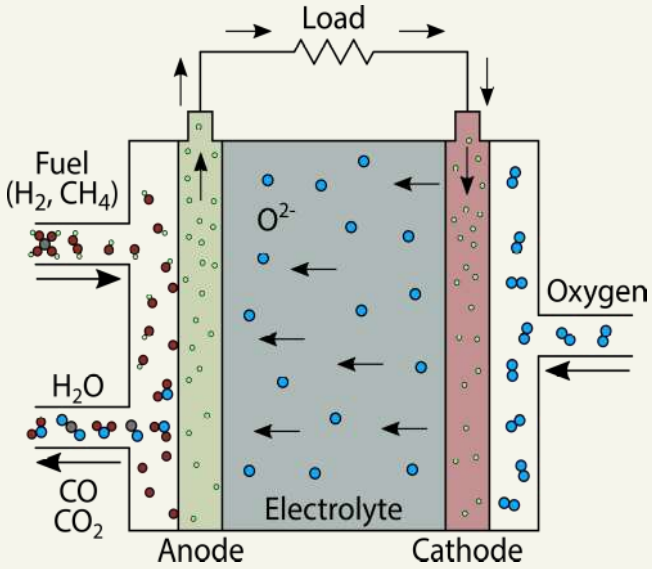
$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$
$$CO + O^{2-} \rightarrow CO_2 + 2e^-$$
$$CH_4 + 4O^{2-} \rightarrow 2H_2O + CO_2 + 8e^-$$

  - Reduction of air (O_2) at the cathode:

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$$

"Bloom Box"

Redox "Cube"

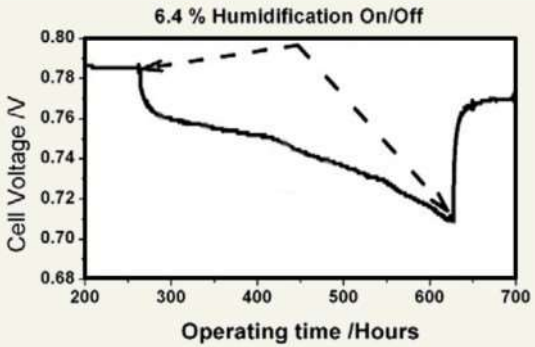


Challenges facing SOFCs

- **Widespread commercialization has still not been achieved**
  - High temperature / operation costs
  - Overall system costs high
  - **Performance degradation (limited durability)**

Cathode degradation is biggest problem

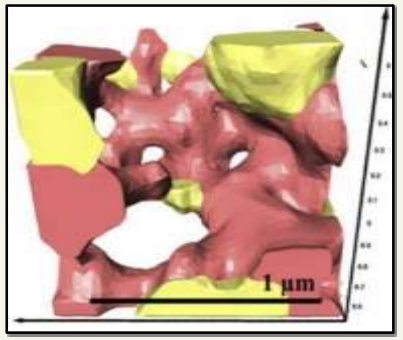
- **Cathode polarization losses due to degradation**
  - Longer term effects such as coarsening, secondary phase formation, etc. reduce performance
  - H_2O, CO_2, and Cr vapor can accelerate performance losses (Nielsen, 2011)
  - Adverse effects on polarization, conductivities, and activation (Adler, 2004)

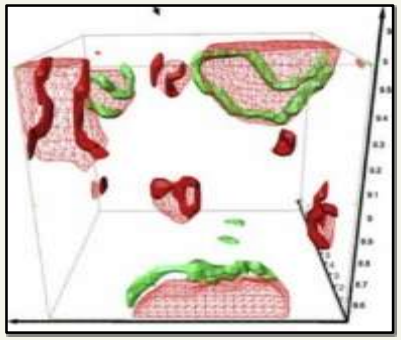


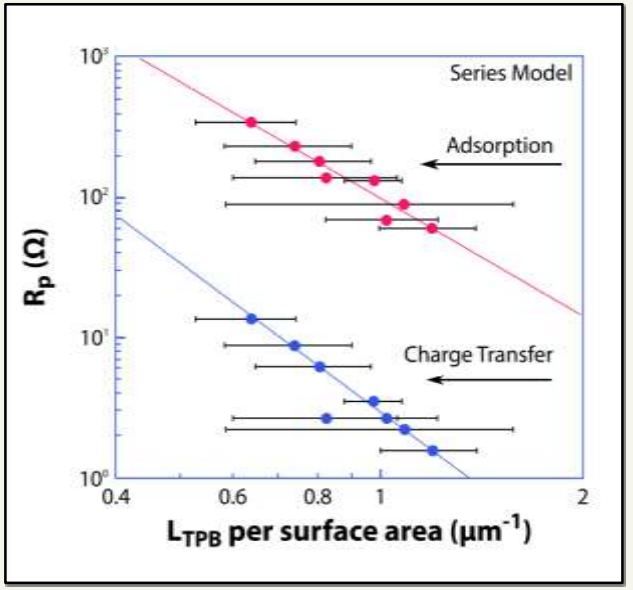
Origins of performance degradation

- **Within the cathode, both kinetics and microstructure control ultimate performance**
  - Generally:
    - Kinetics → transient effects
    - Microstructure → permanent effects

- **Microstructure can be studied (and quantified) with FIB/SEM**
  - FIB-nanotomography:
    - TPB quantification and activity – J. R. Wilson, *et al.*, Nat. Mater. **5**, 541 (2006).
    - Correlation to cell performance – J. R. Smith, *et al.*, Solid State Ionics **180**, 90 (2009).







SOFC cathode materials

- **Two types of SOFC devices systems with composite cathode layers**
  - Composite cathode: both electrolyte (ion conducting) and cathode (electron conducting) materials are mixed and sintered together to form a composite structure

1) LSM:

- $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3+\delta}$
- Perovskite structure
- Pure electronic conductor
- High temperature applications
- Well matched with YSZ electrolyte: $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$

2) LSCF:

- $(La_{0.6}Sr_{0.4})_{0.95}(Co_{0.2}Fe_{0.8})O_{3-\delta}$
- Perovskite structure
- Mixed ionic electronic conductor
- Intermediate temperature applications
- Well matched with GDC
- electrolyte: $(Gd_2O_3)_{0.2}(CeO_2)_{0.8}$

Goals of this Research

- **Investigate SOFC cathode microstructures using FIB-*nt***
  - Quantify various microstructural parameters (phase fractions, connectivity, TPB networks, etc.)
- **Quantify changes in high temp. LSM-YSZ cathodes upon aging in humid environment**
  - Analyze changes induced by aging conditions, and compare to electrochemical performance
- **Quantify changes in intermediate temp. LSCF-GDC cathodes upon aging in H_2O, CO_2, and Cr vapor**
  - Again, examine any changes induced by aging conditions, and compare to performance data
- **Develop open, repeatable, and documented FIB-*nt* analysis methods**
  - Every research group uses its own methods, hindering comparison of results, since specifics of implementations are rarely available; open development of methods is greatly needed

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- Overall introduction
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  - Transition layer measurements
  - XPS interface analysis
  - Effects of crystallographic orientation
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  - LSM-YSZ cathode degradation
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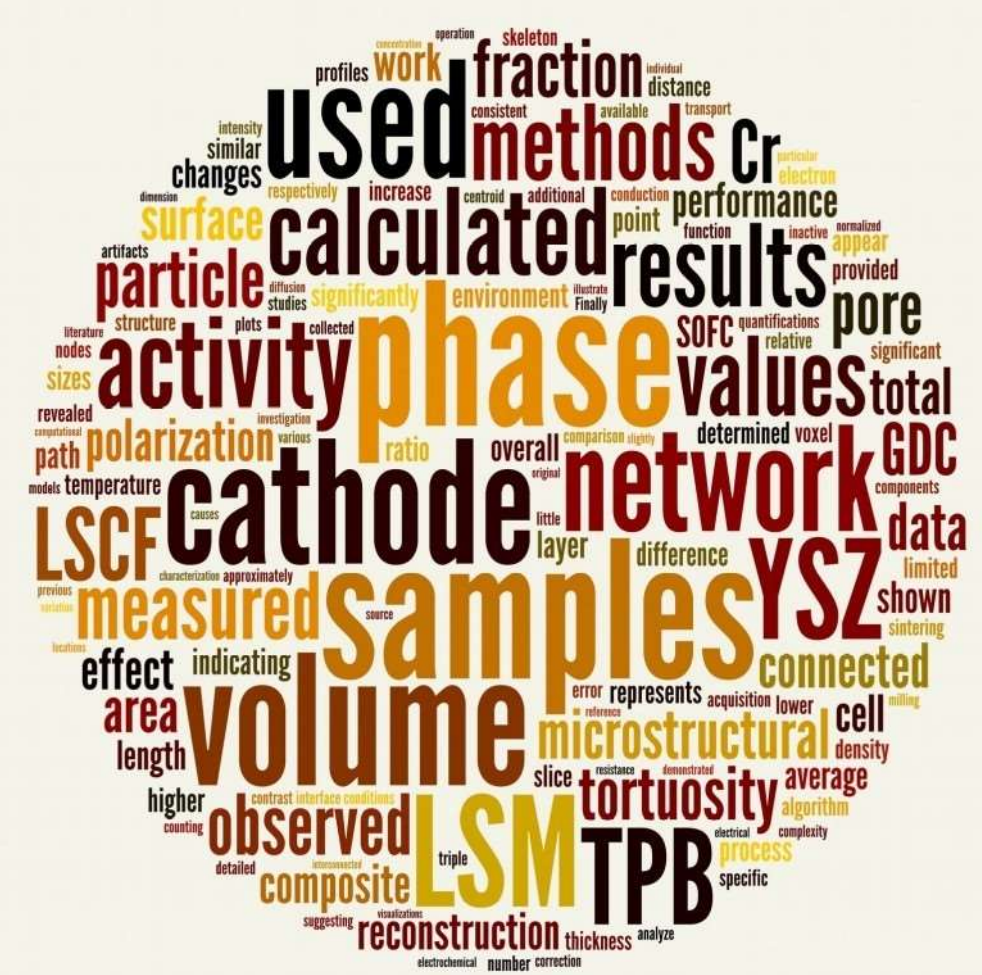
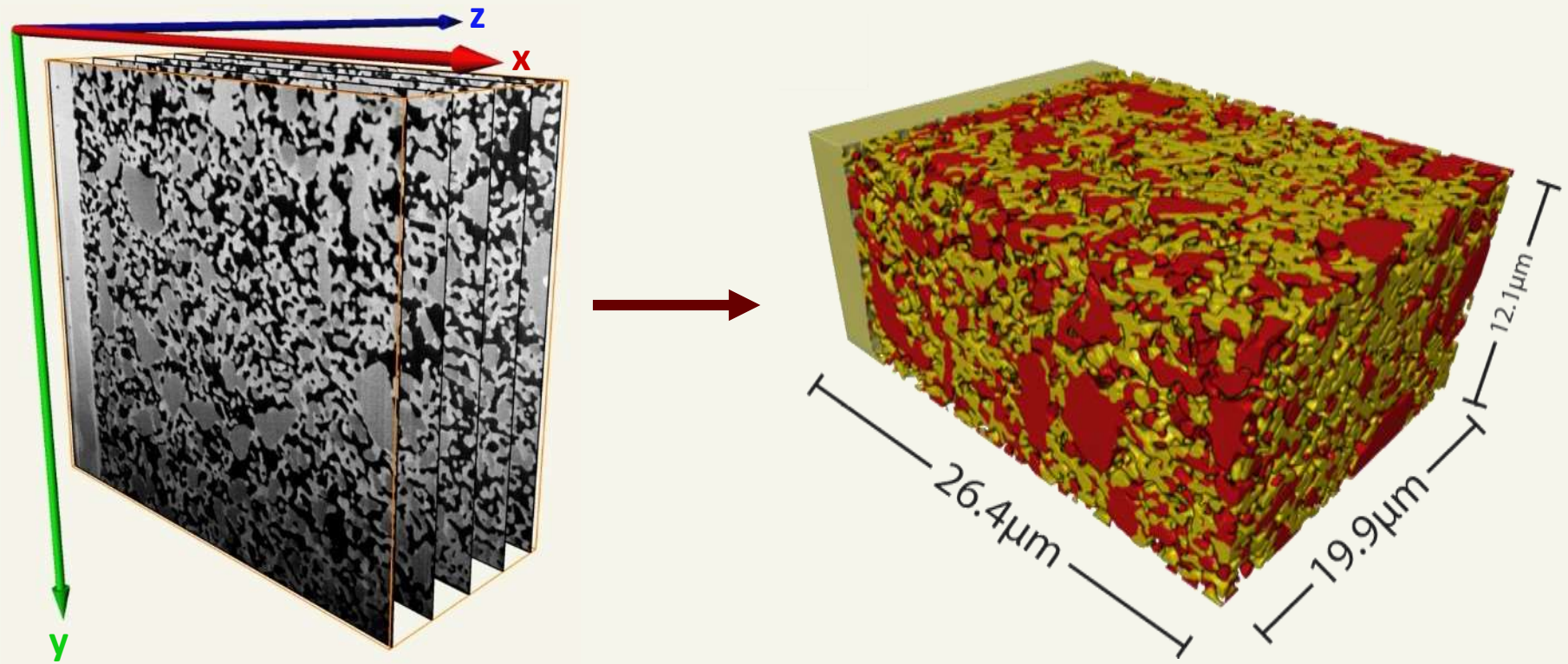


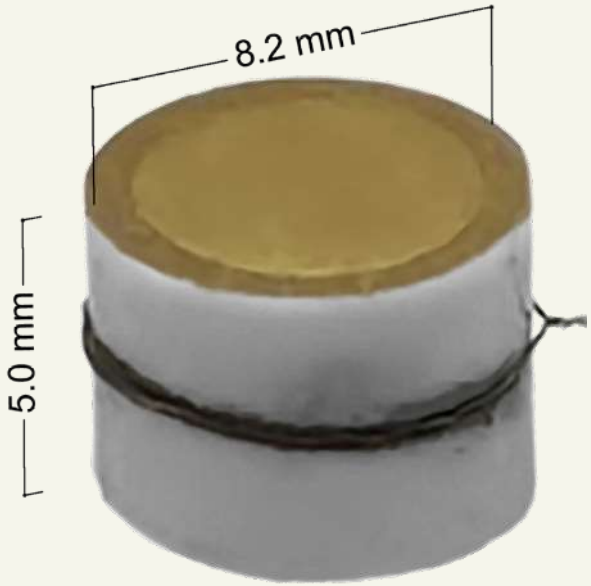
Introduction to FIB-nanotomography

- **Serial process of cutting and imaging – 2D slices to 3D volume**

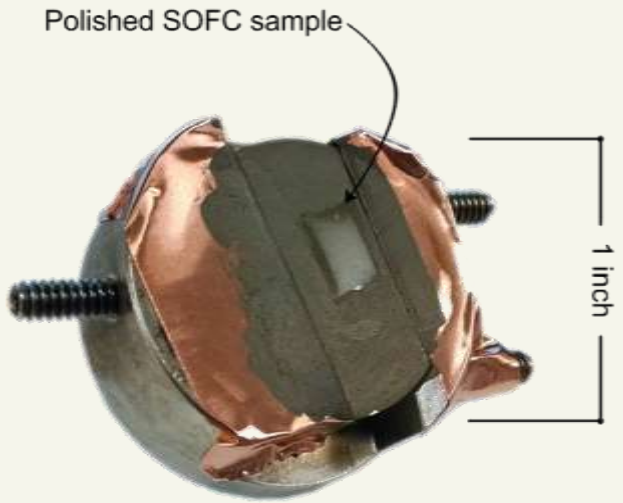


Experimental and sample preparation

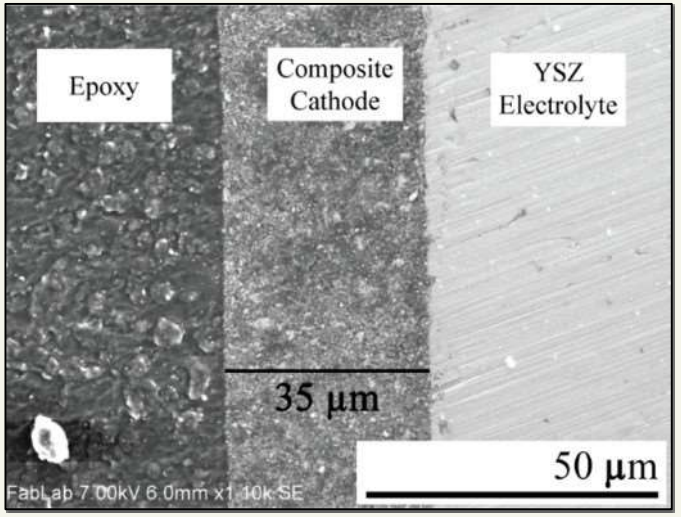
Symmetric cathode fuel cells for EIS testing



Preparation for FIB/SEM investigation

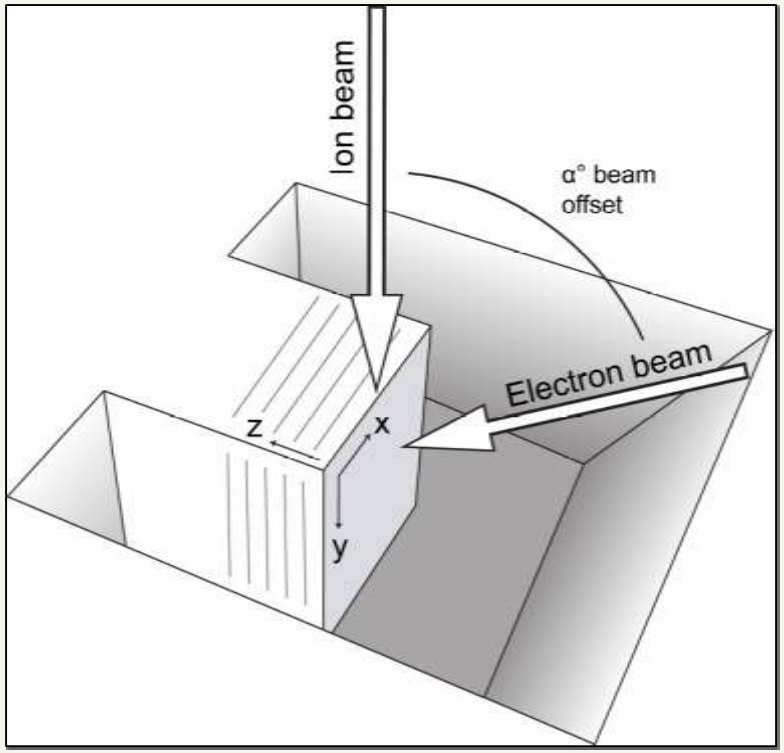


Cross section analysis

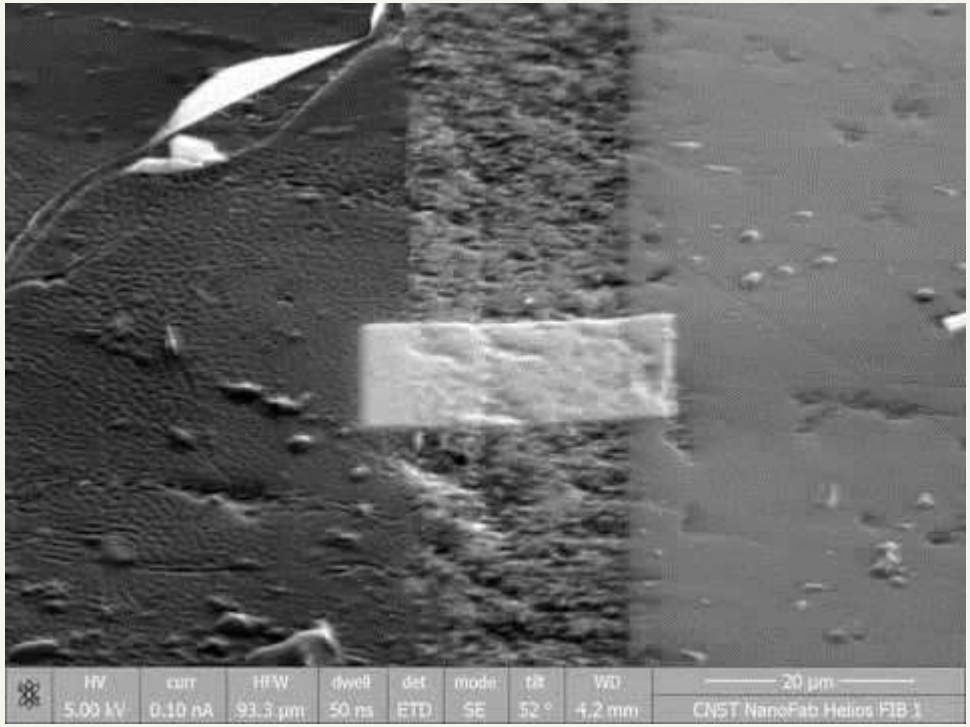


Experimental and sample preparation

Schematic of FIB-nt process

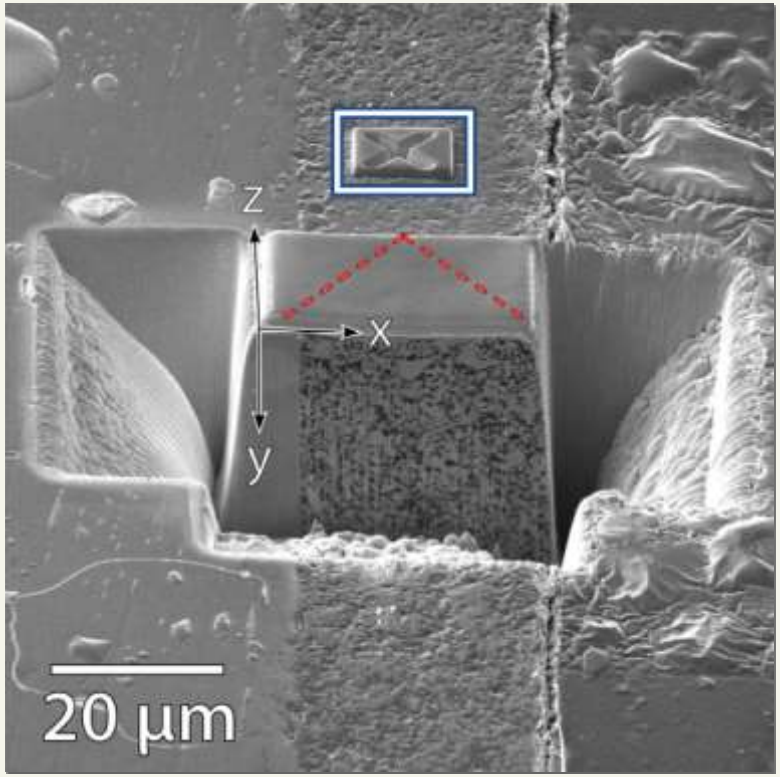


Sample site preparation

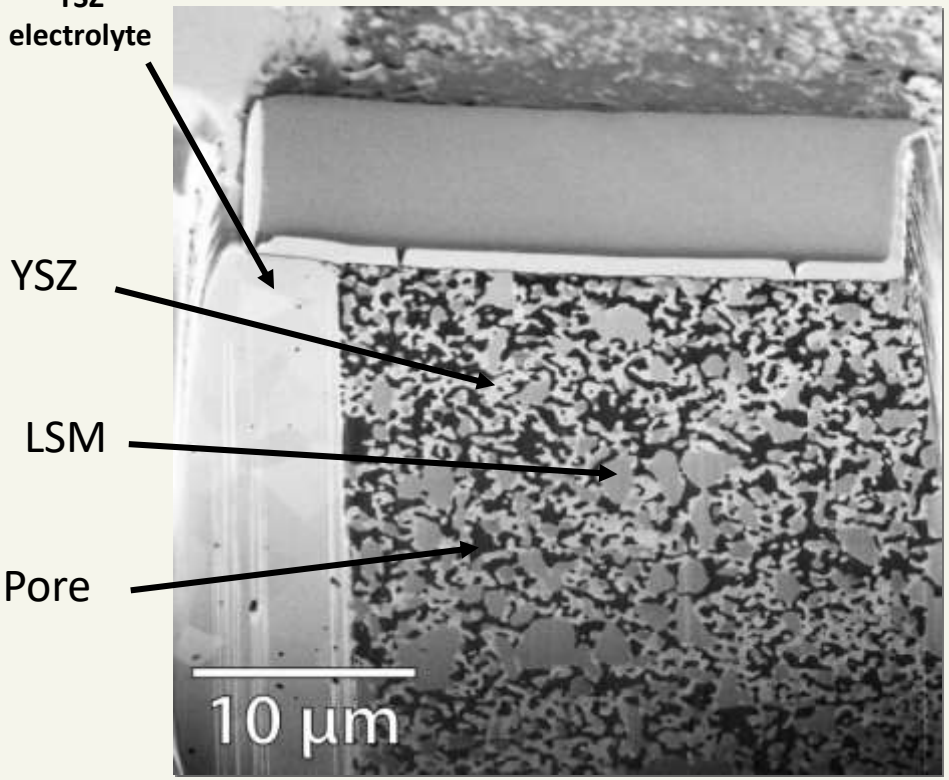


Experimental and sample preparation

Finished site preparation

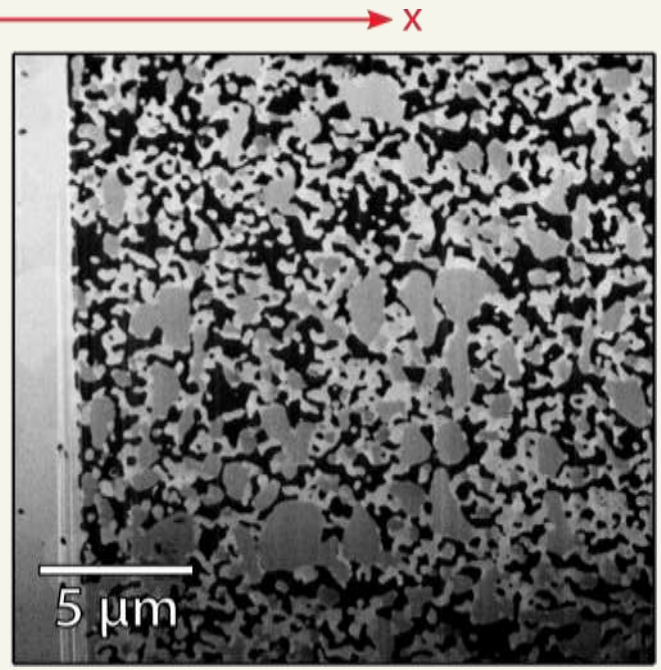


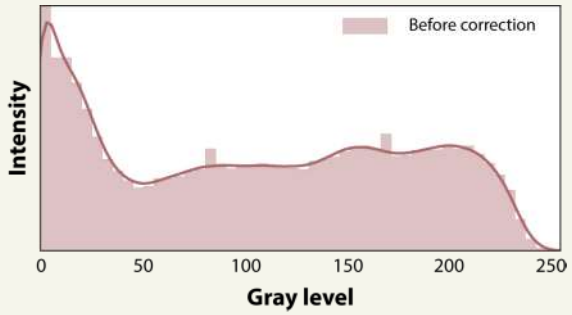
Example raw collected slice



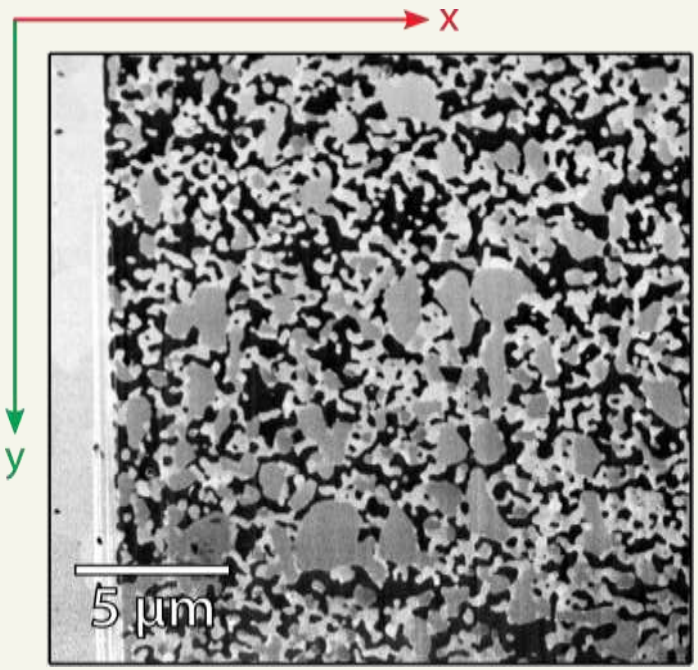
Novel Gradient correction algorithm

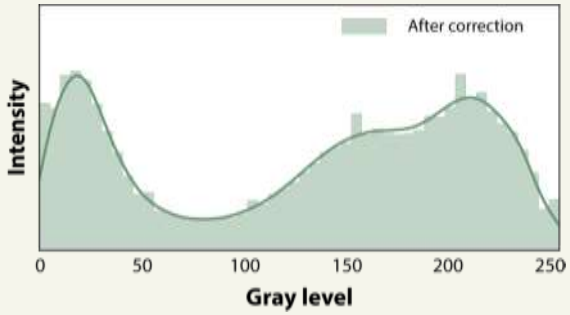
Original image





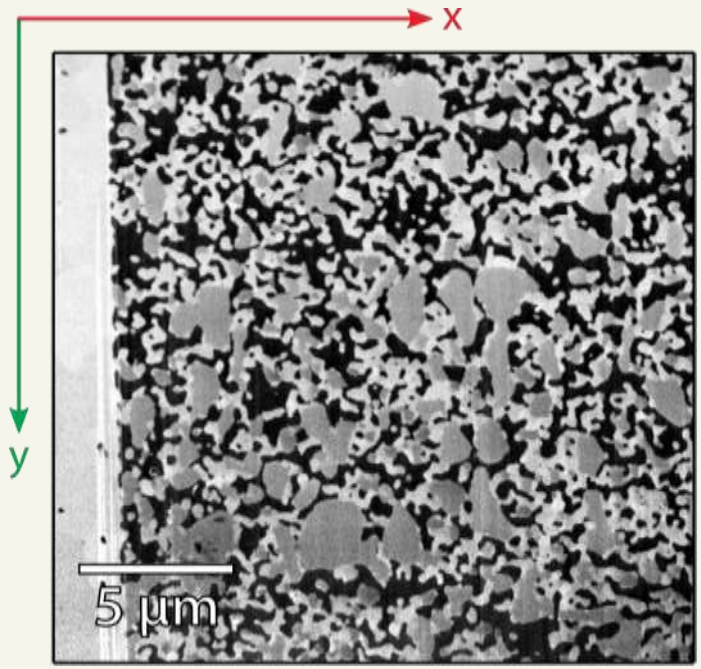
Normalized image

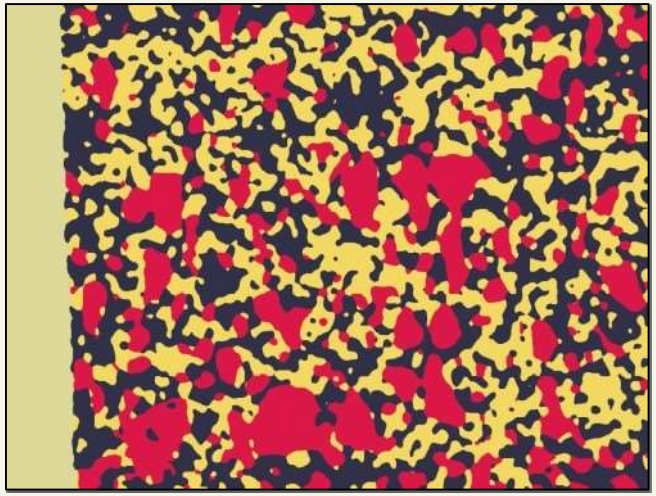




Grayscale to 3D volume

- **Watershed segmentation method**





Normalized image

Segmented data

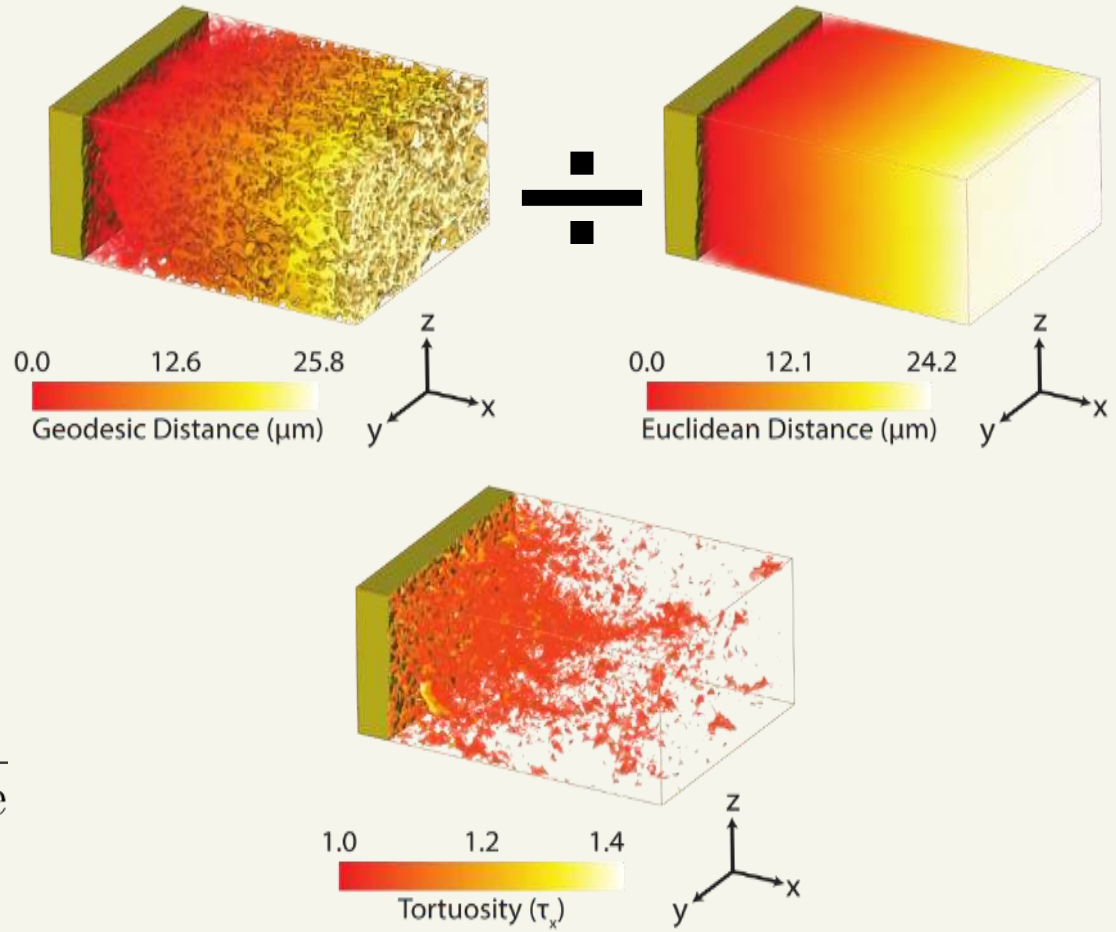
Calculation of tortuosity (τ)

- **Measures added resistance to diffusion introduced by microstructure**
- **Phase fraction (η) and tortuosity (τ) determine effective diffusivity:**
  (Kim, 1999)

$$D_{\text{eff}} = \frac{\eta}{\tau} D$$

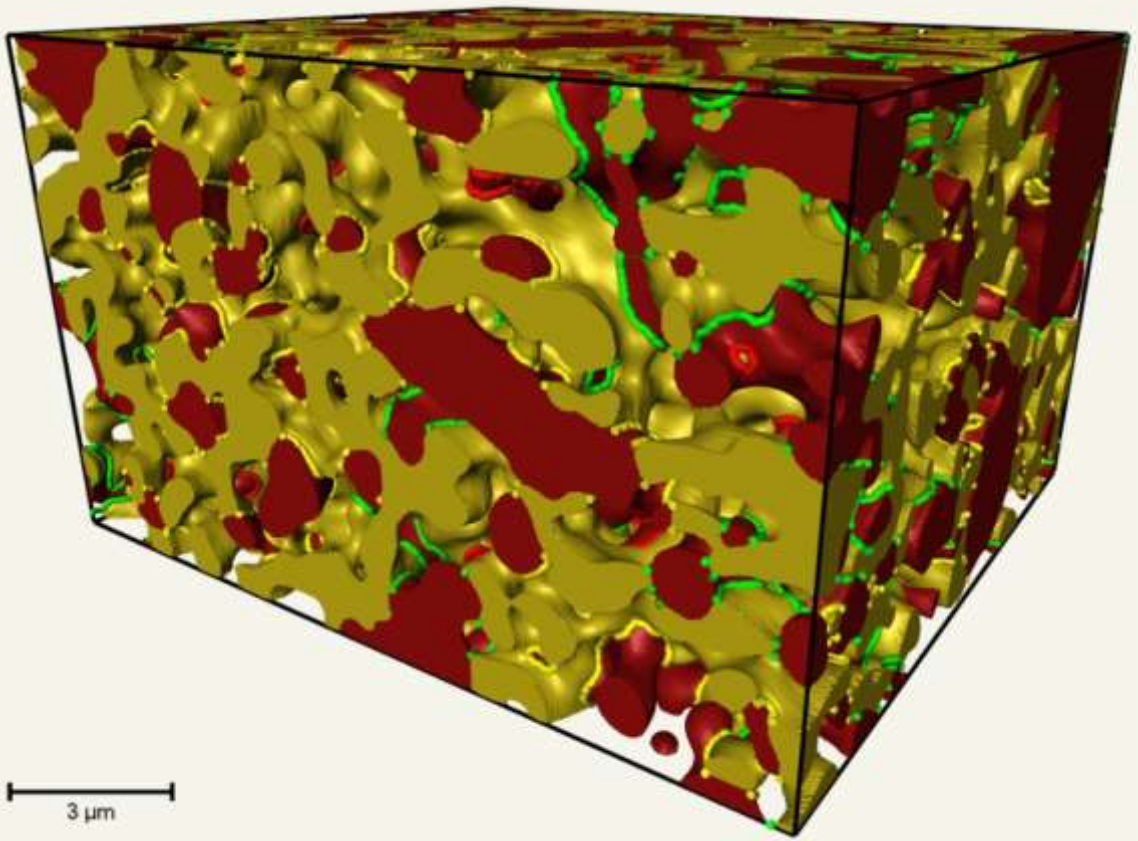
- **This work uses geometric tortuosity:**
  (Gommes, 2009)

$$\tau = \lim_{L_G, L_E \to \infty} \frac{\text{Geodesic distance}}{\text{Euclidean distance}}$$

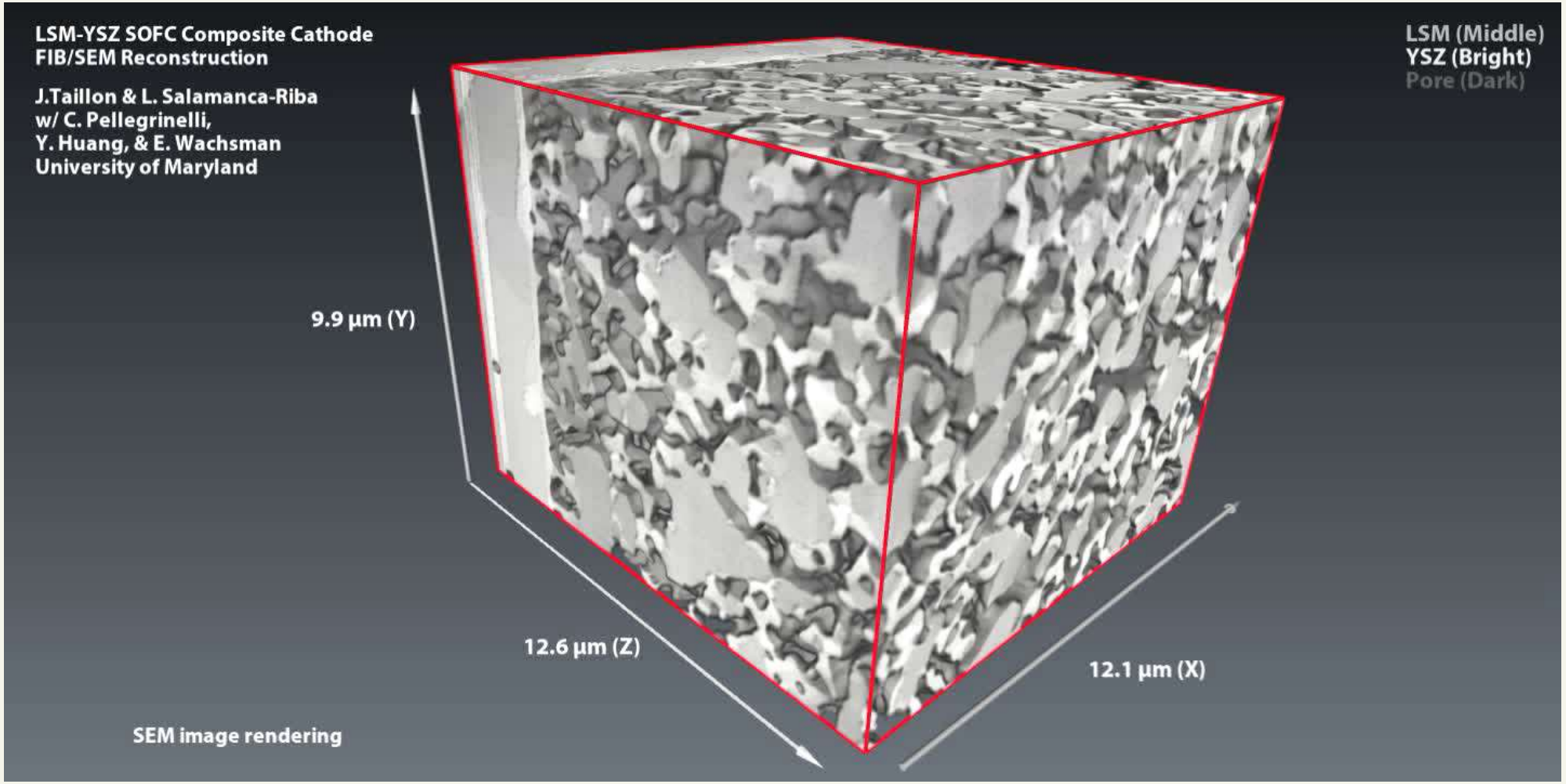


TPB network calculation

- **Oxygen reduction can only occur at or near TPB points**
- **Implemented a smoothed edge-counting method**
  - Significantly more accurate than methods used in present literature
- **Developed in collaboration with Scientific Applications and Visualization Group (NIST)**
- **Analyze expected activity of TPB points by their connectivity**



Visualization of LSM-YSZ reconstruction



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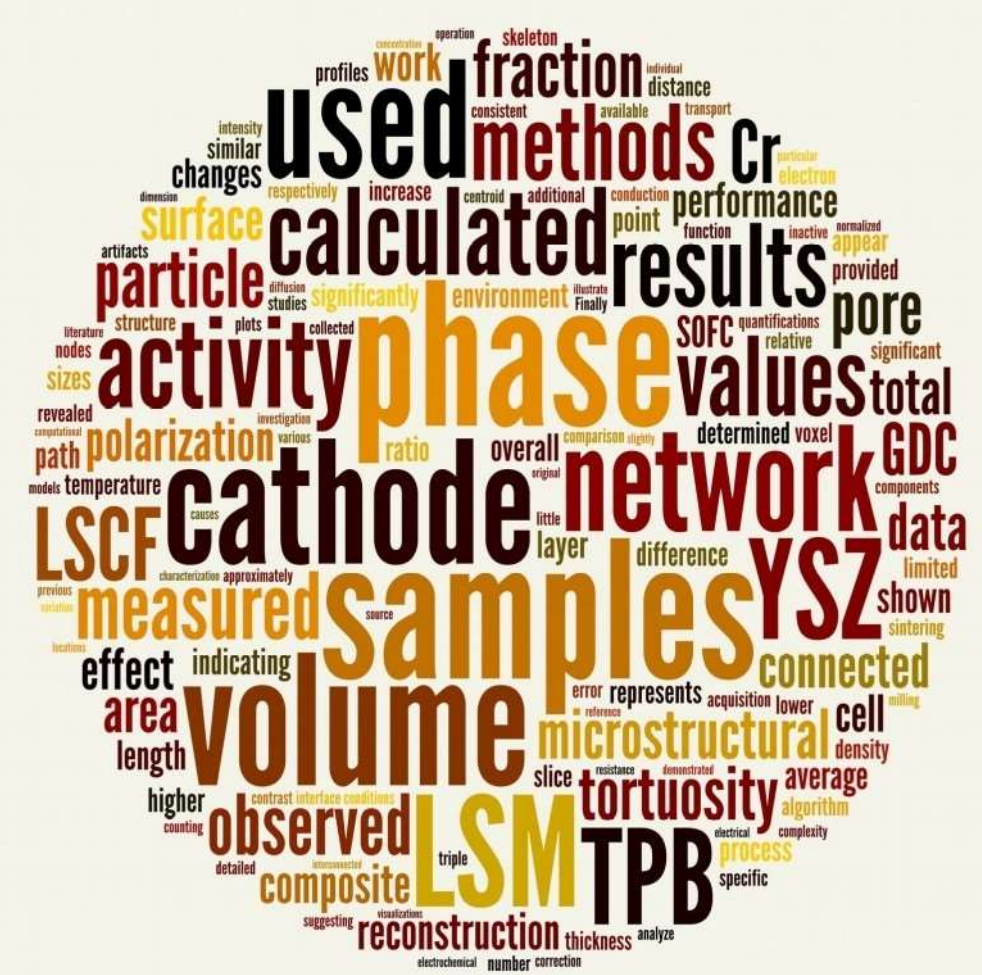
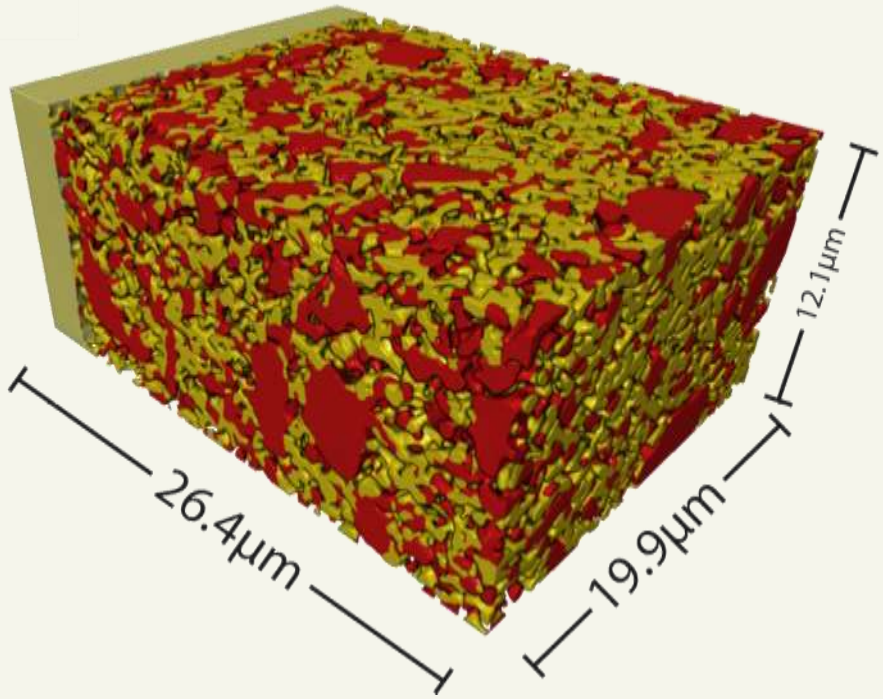
  - LSCF-GDC cathode degradation
- Conclusions and Future work



LSM-YSZ aging conditions

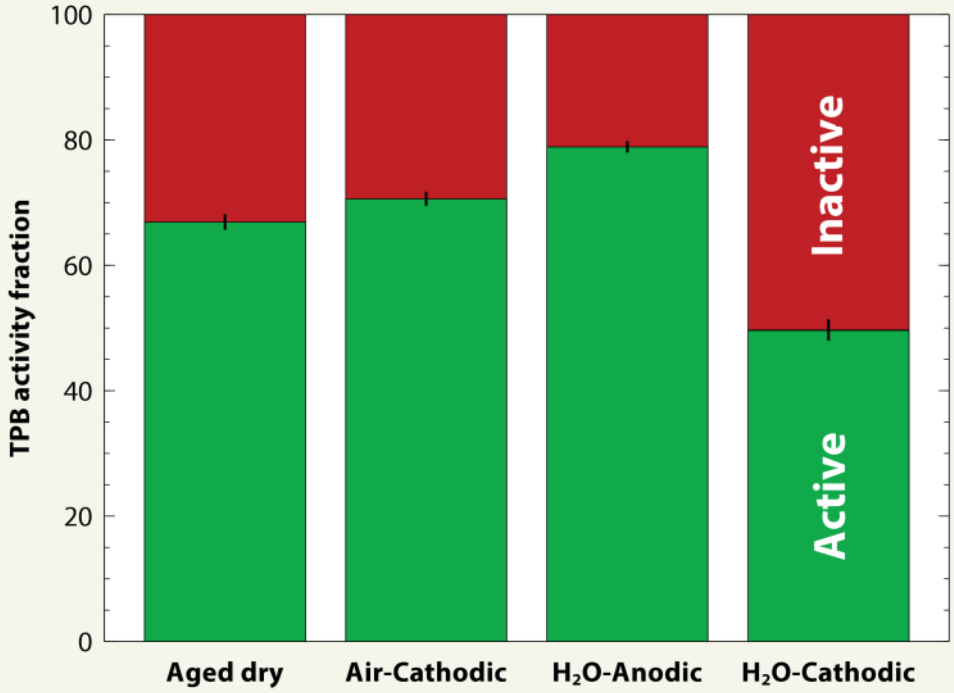
- **Four composite cathodes aged in varying conditions:**
  - Air
  - Air – cathodic polarization
  - 3% H_2O – anodic polarization
  - 3% H_2O – cathodic polarization
- **Aged for 500 h at 800°C (-0.7V potential)**
- **FIB/SEM analysis performed post-aging**
  - Total volumes reconstructed range from 2000 – 6400 μm^3



H_2O-Cathodic Reconstruction

LSM-YSZ microstructural results

- **Quantified:**
  - Phase volume information
  - Phase distribution
  - Connectivity
  - Tortuosity
  - Triple phase boundary information



Fewer active TPBs in H_2O-Cathodic

LSM-YSZ microstructural result summary

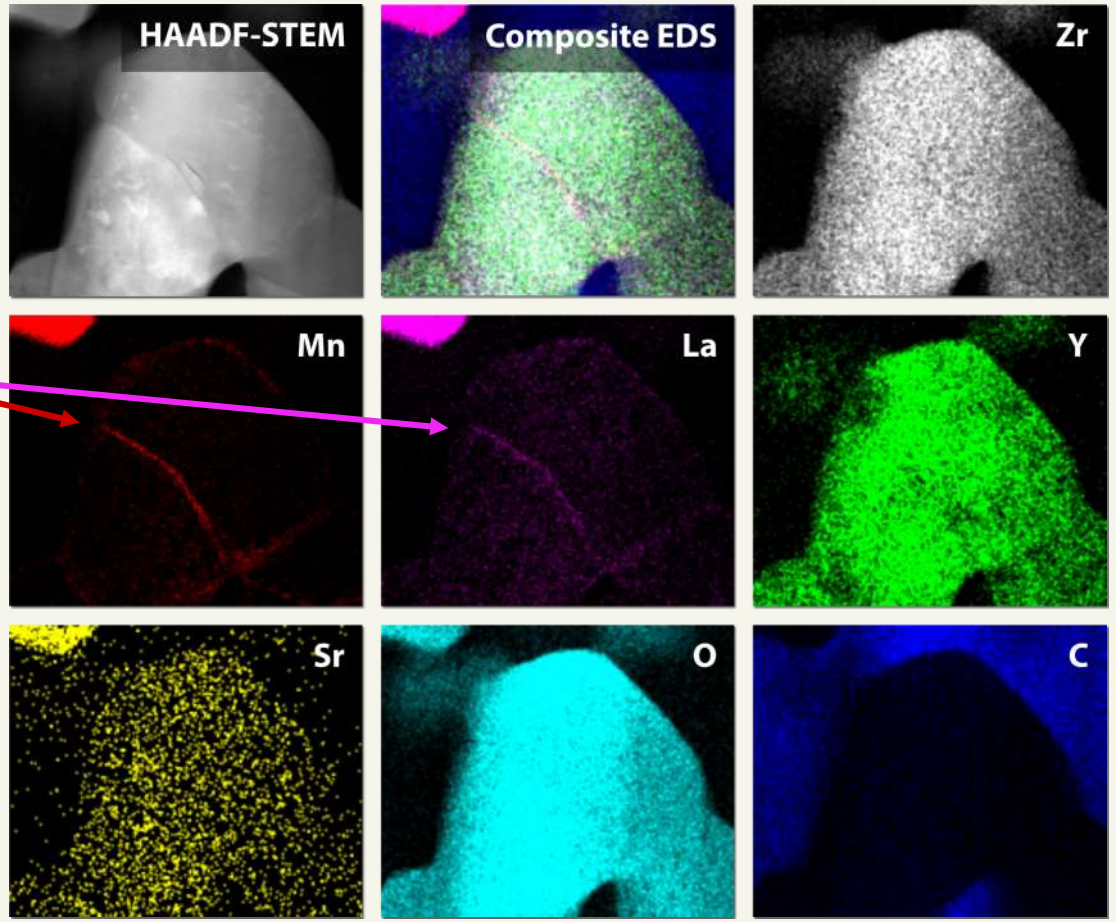
- **Generally, only H_2O-Cathodic sample any significant alterations to microstructure**
  - Larger YSZ particles, least connected LSM, and lowest fraction of active TPBs
- **Otherwise, little to no changes in microstructure**
  - Phase fractions, phase distributions, tortuosity, and connectivity relatively unchanged by polarization and H_2O (using the conditions in this study)
- **To stimulate degradation of microstructure, more extreme conditions needed**
  - Longer aging times, varied temperatures, higher H_2O concentrations, etc.

Relationship to electrochemical performance

- **Electrochemical impedance spectroscopy (EIS) data collected by collaborators in the Wachsman Lab**
  - Both constant aging and condition cycling tests performed
- **Generally, observed changes in performance were reversible**
  - Suggests kinetic effects, rather than microstructural ones
  - Reversible changes cannot be measured by FIB/SEM
- **H_2O-Cathodic experienced *enhanced* performance during humidification**
  - Effect was reversible, however
  - TEM chemical analysis reveals some clues as to origin of improvement

H_2O-aged LSM-YSZ TEM-EDS analysis

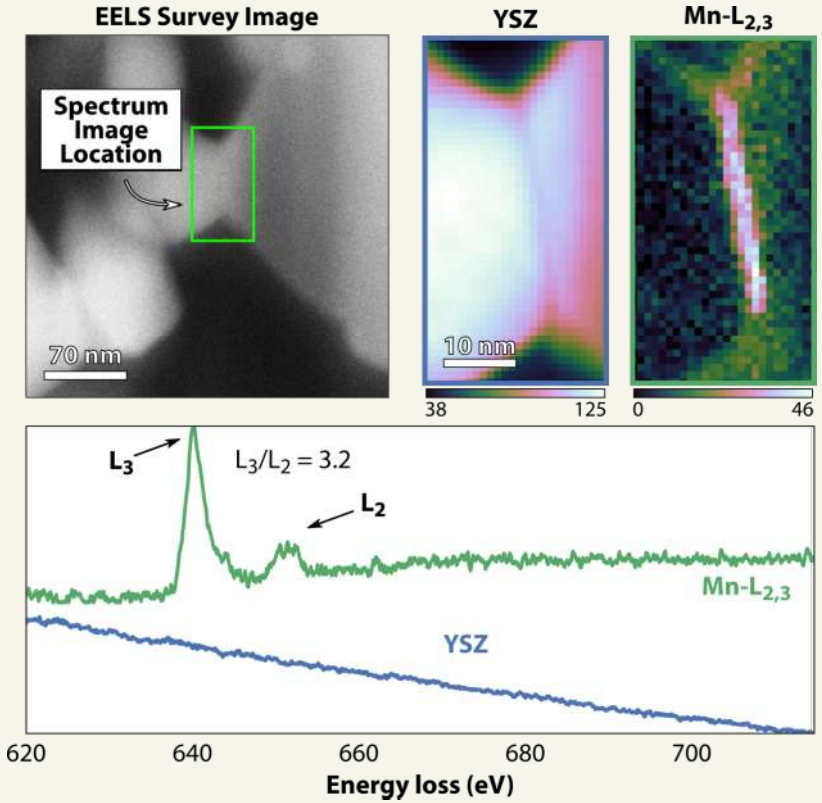
- TEM-EDS analysis of YSZ grain boundaries
- Mn and La cations observed to migrate to YSZ boundaries and surfaces
- These species are volatile during aging, and distribution suggest surface diffusion
- No evidence of significant secondary phase formation



Data courtesy of FEI Company

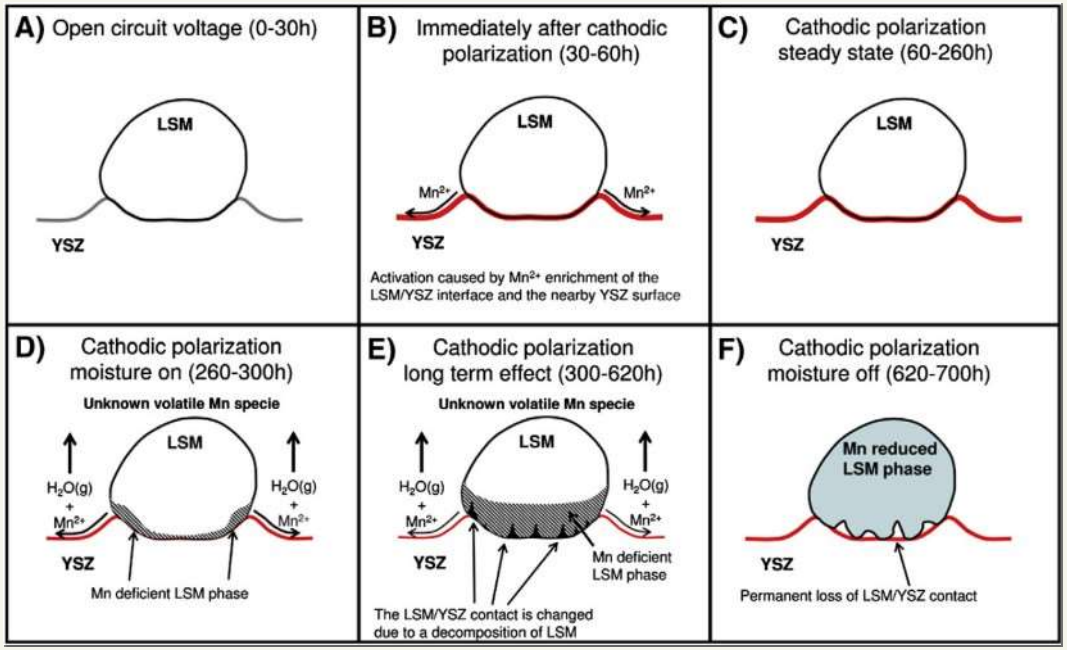
H_2O-aged LSM-YSZ TEM-EELS analysis

- **Mn-$L_{2,3}$ EELS edge reveals information about Mn atoms**
- **Like EDS, EELS reveals high concentration of Mn at YSZ grain boundaries/surfaces**
  - Observed regardless of applied polarization bias in humid samples
- **L_3/L_2 ratio indicates average valence of $Mn^{2.5+}$**
  (Backhaus-Ricoult, 2006 & Shih, 2011)
  - Also will contribute to $V_O^{\bullet\bullet}$ formation

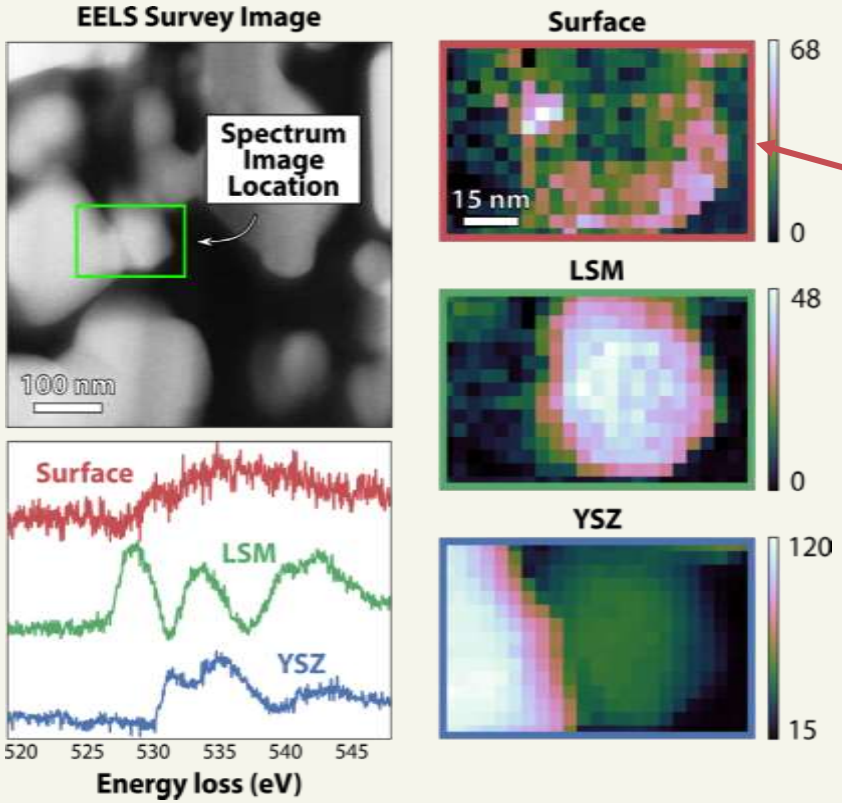


H_2O-aged LSM-YSZ TEM-EELS analysis

- **First experimental evidence of Nielsen's proposed LSM-YSZ/H_2O degradation mechanism**
  (Nielsen & Mogensen, 2011)
  - Proposed formation of volatile Mn^{2+} species under humidification, but no experimental evidence
  - Enhances performance in the short-term, but leads to long term loss of LSM-YSZ interface



H_2O-aged LSM-YSZ TEM-EELS analysis



- **O-*K* EELS edge from triple phase boundary region**
- **Clear surface state, with spectrum representative of O-deficient oxide**
  - Evidence of a high oxygen vacancy concentration in LSM
- **High $V_O^{\bullet\bullet}$ encourages oxygen incorporation at surfaces**
  - Likely a source of kinetic enhancements observed with humidification during EIS

LSM-YSZ degradation summary

- **Overall, few changes in microstructure at conditions tested**
  - H_2O-Cathodic evidenced some changes, but not enough to degrade performance compared with kinetic enhancement effects
- **Significant migration of La and Mn in humid samples**
  - Regardless of applied polarization bias, La and Mn were observed at grain boundaries using both EDS and EELS, also creating an abundance of $V_O^{\bullet\bullet}$
- **$Mn^{\approx 2+}$ measured by EELS, confirming Nielsen mechanism**
  - Indicates that observed humidity enhancement is likely a temporary effect, and continued aging would induce degradation of the TPB boundaries

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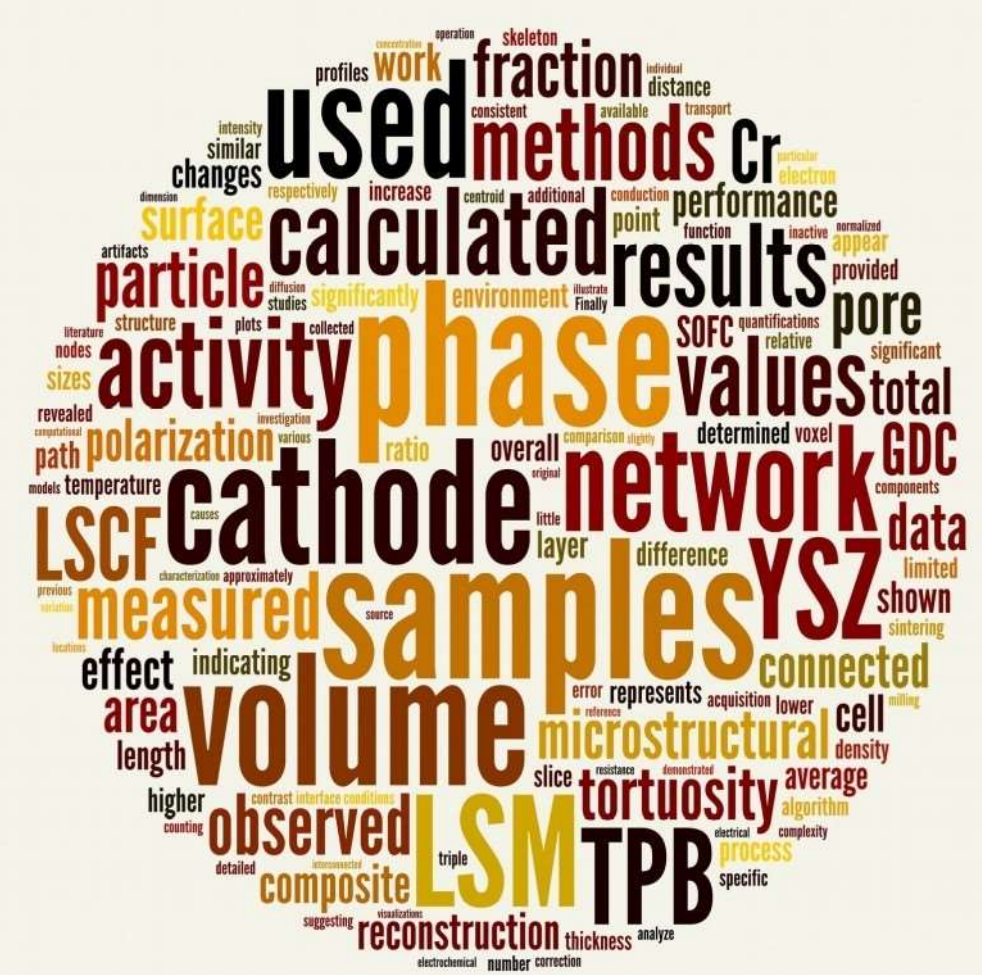
  - **LSCF-GDC cathode degradation**
- Conclusions and Future work

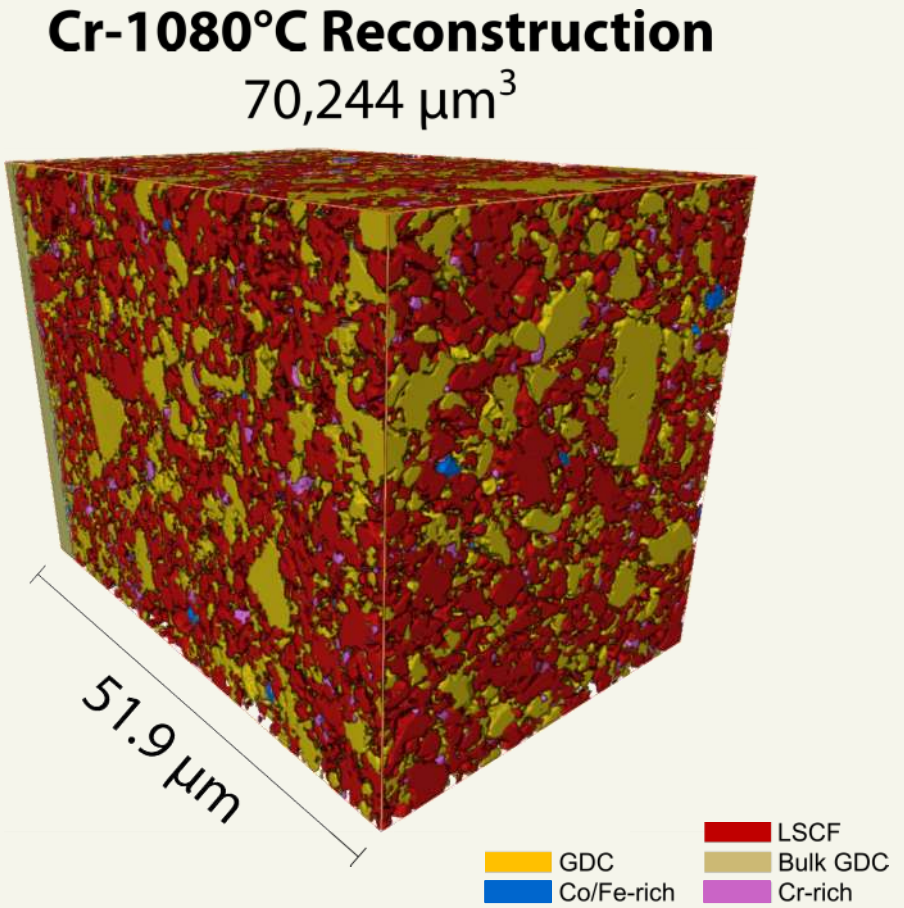


LSCF-GDC aging conditions

- **Seven composite cathodes aged in varying conditions:**
  - Air – cathodic polarization
  - 3% H_2O – no applied bias
  - 3% H_2O – cathodic polarization
  - 5% CO_2 – no applied bias
  - 5% CO_2 – cathodic polarization
  - Cr-vapor – sintered at 950 °C
  - Cr-vapor – sintered at 1080 °C

- **Aged for 500 h (200 h for Cr samples) at 750°C**

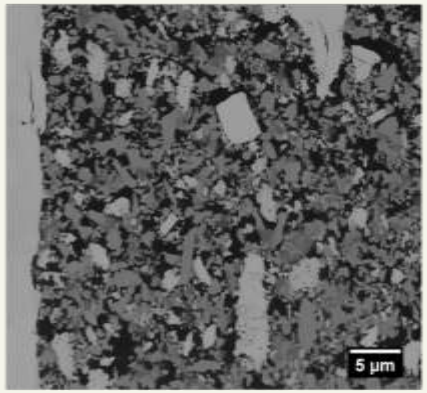
- **FIB/SEM analysis performed post-aging**
  - Total volumes reconstructed range from 16,000 – 70,000 µm^3
  - Order of magnitude larger than existing literature



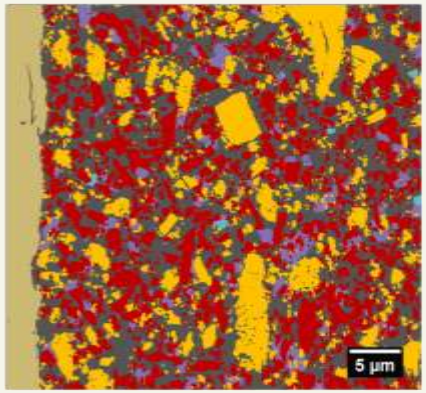
LSCF-GDC Chromium impacts

- **Sintering temperature drastically affects Cr-phase formation**

950 °C



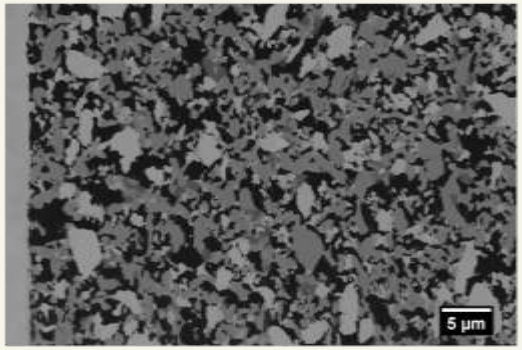
Collected images

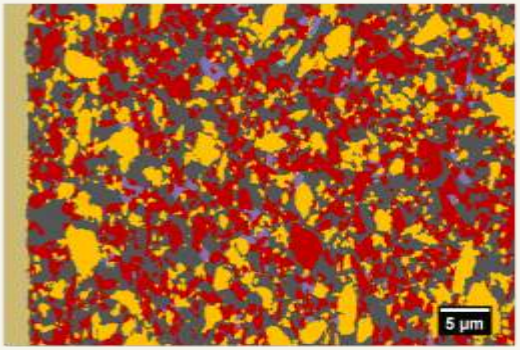


Segmented data

6.4% Cr phase (by volume)

1080 °C

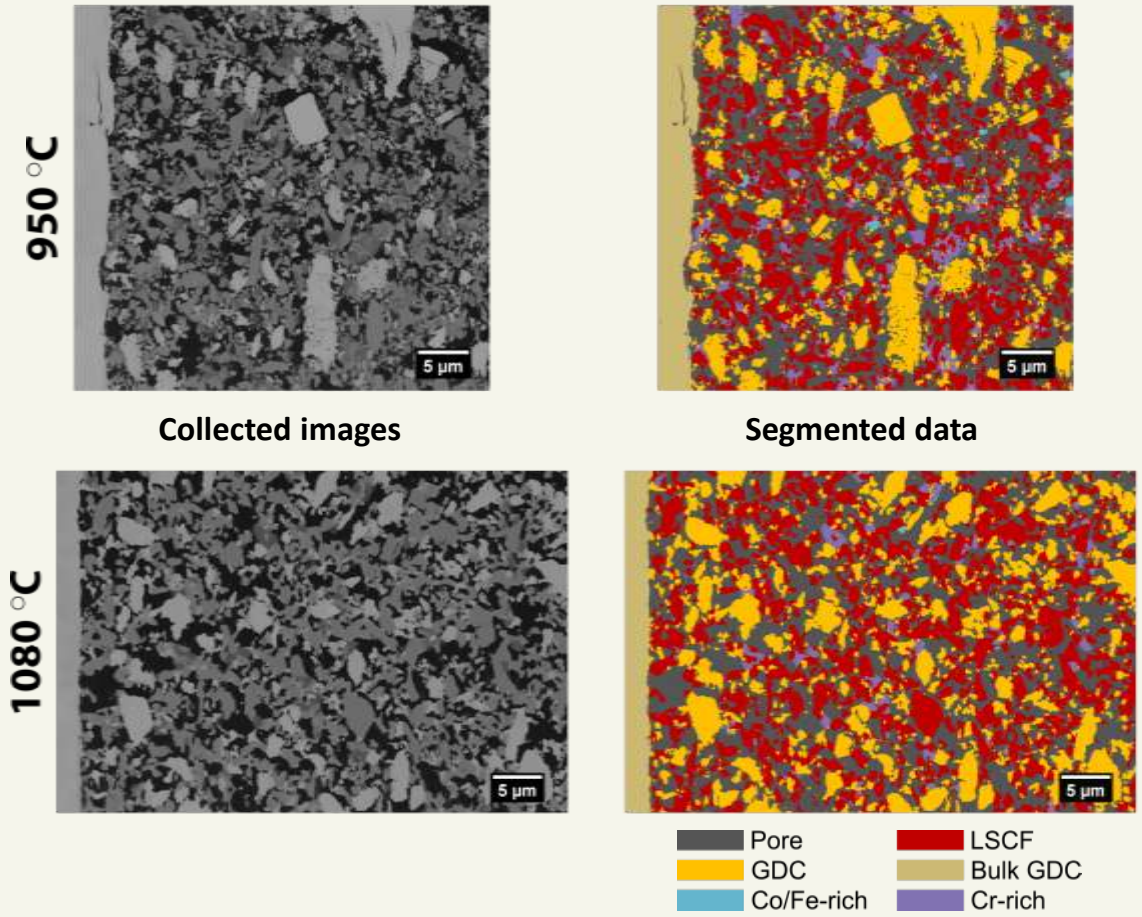


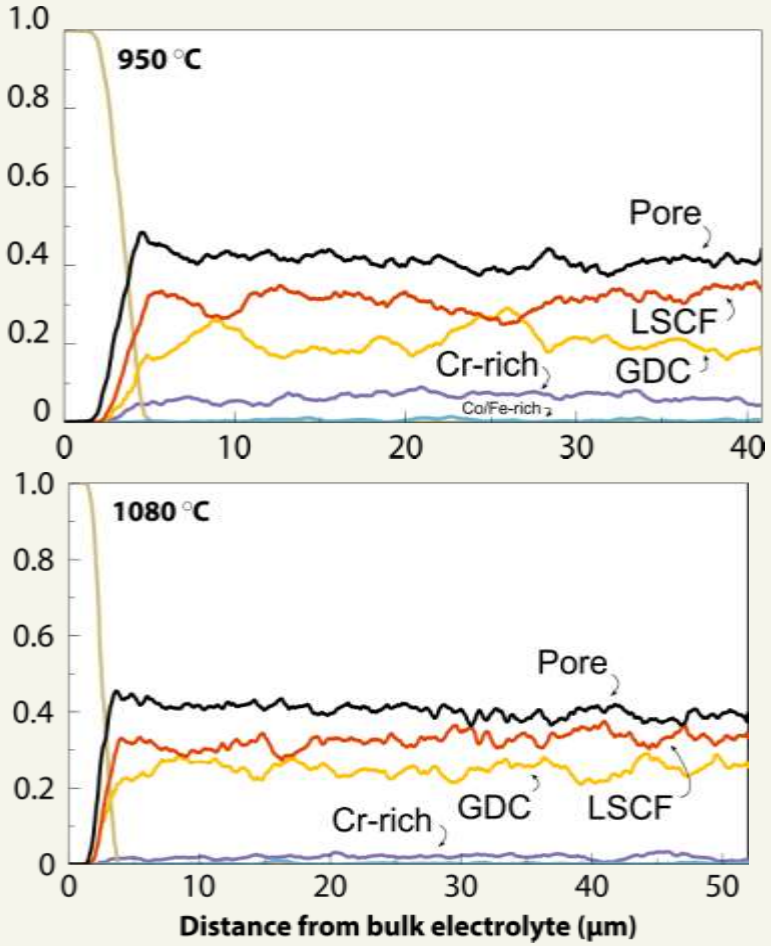


1.9% Cr phase (by volume)

LSCF-GDC Chromium impacts

- **Sintering temperature drastically affects Cr-phase formation**





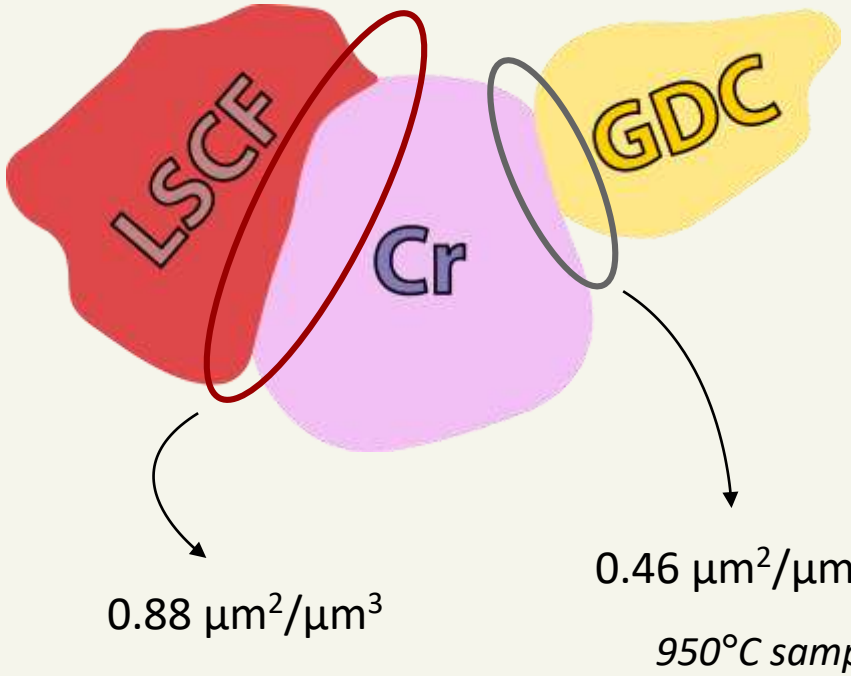
LSCF-GDC Chromium impacts

Results indicate a gaseous Cr reaction mechanism at particle surfaces

- **Lower sintering temperature = lower pore sizes → greater S.A.**

	Average pore size
950°C	712 nm
1080°C	891 nm

- **Cr-phases have double the contact area with LSCF vs. GDC**



Relationship to electrochemical performance

- **Chromium poisoning:**
  - Irreversible increases in Ohmic and Polarization resistances
  - 6x greater losses for 950 °C than 1080 °C
  - Correlates to greater Cr-phase content in lower temperature sample

- **H_2O exposure**
  - Like LSM-YSZ, slight enhancement; most changes in performance reversible
  - Irreversible increase in Ohmic resistance attributed to electrolyte sintering
    - Correlates with increased GDC particle sizes in H_2O samples

- **CO_2 exposure**
  - Compared to H_2O, similar (but smaller) changes that were mostly irreversible
  - May correlate with decrease in active TPB fraction, but not conclusive
  - On/off nature of tests complicates analysis of results

Review of SOFC experiments

- **Developed novel algorithms and methodology to improve FIB-*nt* quantification**
  - Software made available in public repository for use by the scientific community
- **FIB-*nt* and TEM-EDS/EELS analysis of LSM-YSZ composite cathode degradation**
  - Little significant degradation observed in microstructure for conditions tested
  - Mobile Mn and La cations observed under humidification; agreement with Nielsen model of degradation
- **FIB-*nt* analysis of LSCF-GDC in H_2O, CO_2, and Cr vapor**
  - Again, few significant changes in H_2O, slightly more in CO_2
  - Cr poisoning causes substantial change in phase content; Cr-phase formation correlated with drop in electrochemical performance

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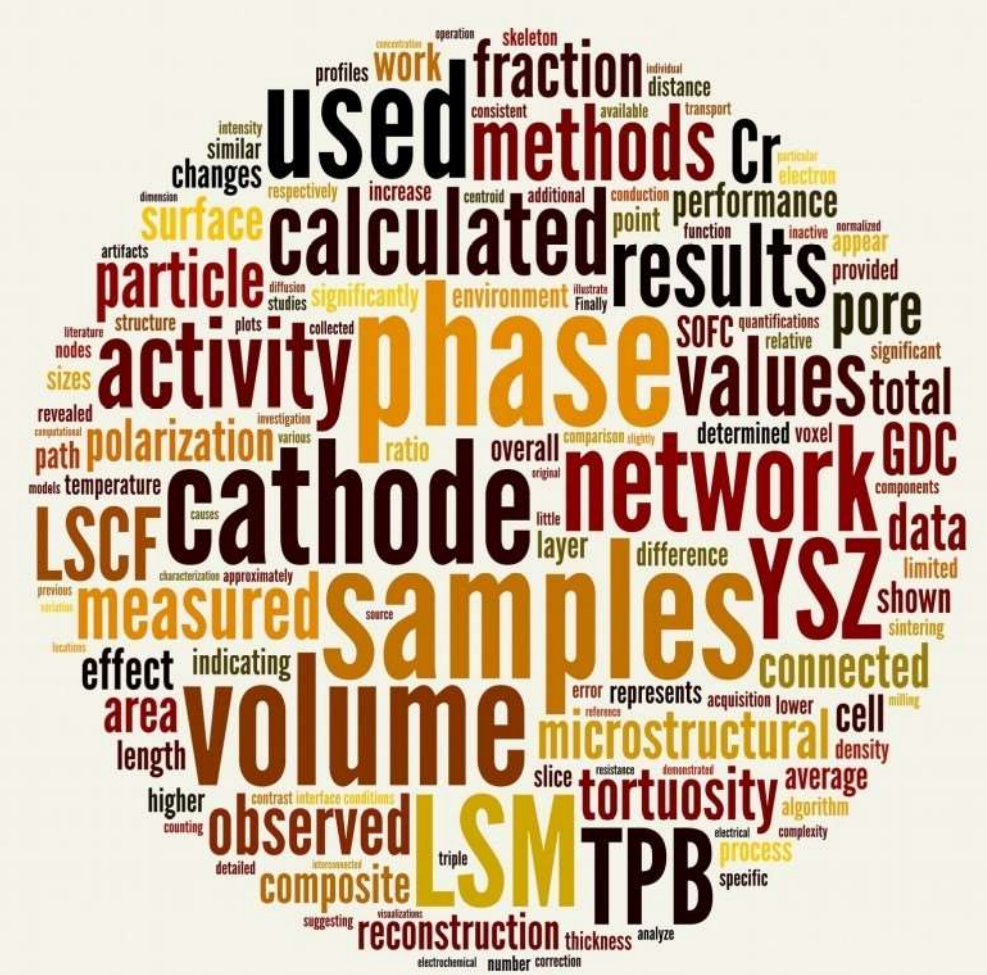

Remaining questions for SiC

- **Continued investigation of boron and phosphorus annealed oxides**
  - Results presented here are just the very surface
  - Can these oxides be tailored to improve performance, and how do the oxide characteristics change?

- **Analysis of substrate strain at the interface**
  - Could have significant effects on performance of devices, but little is known
  - Do the various processing conditions change the strain substantially?
  - How does *a*-face compare to Si-face?

Remaining questions for SOFC degradation

- **Similar analysis as presented here, but with systematic degradation**
  - This work provides clues as to degradation pathways, but without clear evidence of degradation, correlations to microstructure are difficult
  - Comparison of different aging times, changing concentration of contaminant, etc.

- **Further analysis of Cr degradation products**
  - Literature typically assumes only $SrCrO_4$
  - More complicated secondary phases were observed in initial TEM-EELS studies of the Cr-aged samples
  - Can provide a more detailed picture of *how* Cr reduces performance kinetically, as well as in microstructure

Interesting future methodology questions

- **Applicability and development of EELS spectral unmixing methods**
  - Important to develop a physical framework for understanding component results
  - NMF works well, but Bayesian Linear Unmixing (BLU) is a promising alternative (with little existing research)

- **FIB-nanotomography enhancements:**
  - Application of machine learning algorithms to image segmentation
  - More focused acquisition of only area of interest (speed up of data collection)
  - Compressive sensing acquisition of data (again, to increase speed)

Products of thesis research

Refereed manuscripts (published, submitted, and in preparation):

1. J. Taillon, J. Yang, C. Ahyi, J. Rozen, J. Williams, L. Feldman, T. Zheleva, A. Lelis, and L. Salamanca-Riba, "Systematic structural and chemical characterization of the transition layer at the interface of NO-annealed 4H-SiC/SiO2 metal-oxide-semiconductor field-effect transistors", *Journal of Applied Physics*, vol. 113, no. 4, p. 044 517, 2013.
2. J. Taillon, J. Hagedorn, C. Pellegrinelli, Y. Huang, E. Wachsman, L. Salamanca-Riba, "Improving microstructural quantification in FIB/SEM nanotomography", To be submitted to *Ultramicroscopy,* 2016.
3. J. Taillon, K. Gaskell, and L. Salamanca-Riba, "Refinement of a spin-etch technique for precise depth profiling of oxide films," *In preparation*.
4. J. Taillon, K. Gaskell, G. Liu, L. Feldman, S. Dhar, T. Zheleva, A. Lelis, and L. Salamanca-Riba, "TEM-EELS detection of unique interfacial states at NO-annealed 4H-SiC/SiO2 interfaces," *In preparation*.
5. J. Taillon, S. Dhar, T. Zheleva, A. Lelis, and L. Salamanca-Riba, "Nanoscale characterization of gate oxides in phosphorus and boron passivated 4H-SiC MOSFETs," *In preparation*.
6. D. Gostovic, J. Taillon, J. Smith, N. Vito, K. O'Hara, K. Jones, and E. Wachsman, "Comprehensive quantification of porous LSCF cathode microstructure and electrochemical impedance," Submitted to *Journal of the Electrochemical Society*, 2016.
7. C. Xiong, C. Pellegrinelli, J. Taillon, Y. Huan, L. Salamanca-Riba, and E. Wachsman, "Long-term Cr poisoning effect on LSCF-GDC composite cathodes sintered at different temperatures," Accepted to *Journal of the Electrochemical Society*, 2016.

Products of thesis research

Proceedings publications:

1. J. Taillon, C. Pellegrinelli, Y. Huang, E. Wachsman, and L. Salamanca-Riba, "Three dimensional microstructural characterization of cathode degradation in SOFCs using focused ion beam and SEM," *ECS Transactions*, **61**, 1, 109, 2014.
2. C. Pellegrinelli, Y. Huang, J. Taillon, L. Salamanca-Riba, and E. Wachsman, "A study of SOFC cathode degradation in H2O environments," *ECS Transactions*, **64**, 2, 17, 2014.
3. J. Taillon, K. Gaskell, G. Liu, L. Feldman, S. Dhar, T. Zheleva, A. Lelis, and L. Salamanca-Riba, "Characterization of the oxide-semiconductor interface in 4H-SiCSiO2 structures using TEM and XPS," *Microscopy and Microanalysis*, **21**, S3, 1537, 2015.
4. J. Taillon, C. Pellegrinelli, Y. Huang, E. Wachsman, and L. Salamanca-Riba, "Three dimensional microstructural characterization of cathode degradation in SOFCs using FIB/SEM and TEM," *Microscopy and Microanalysis*, **21**, S3, 2161, 2015.

Presentations:

1. Approximately 20 contributed/invited presentations from 2012 – 2016 at *Materials Research Society* meetings, *American Physical Society* meetings, *Microscopy & Microanalysis*, as well as a number of smaller research seminars and symposia.

"Extracurricular Activities"

- **Evaluation, analysis, and recommendations for UMD FIB/SEM acquisition**
  - Resulted in purchase of two Tescan FIB/SEM systems in the AIMLab
- **Public release of software tools developed in this research:**
  - Available in public repository:

https://bitbucket.org/jat255/jat255-python-modules

  - Active contributor to HyperSpy:

https://github.com/hyperspy/hyperspy

"Extracurricular Activities"

- **Frequent collaboration and characterization assistance with members of the Maryland community:**
  - C. Preston, D. Song, J. Taillon, J. Cumings, L. Hu, "Boron-Doped Few-Walled Carbon Nanotubes: Novel Synthesis and Properties", Submitted to *Nanotechnology* (2016).
  - H. Bai, J. Taillon, L. Salamanca-Riba, "Anisotropically Shaped CdS_xSe_{1-x} Pseudobinary Semiconductor Nanocrystals", Submitted to *Chemistry of Materials* (2016).
  - C. Gong, M. Dias, G. Wessler, J. Taillon, L. Salamanca-Riba, and M. Leite, "Fully Alloyed Noble Metal Nanoparticles via Physical Deposition for Plasmonics", Submitted to *Advanced Optical Materials* (2016).

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Backscatter electron image of PSG on SiC, after 2 minutes of patterning with the Gaia FIB (20pA current). Image contrast arises from the mass difference caused by Ga implantation into the sample

Facilities/Assistance

UNIVERSITY OF MARYLAND

MARYLAND NANOCENTER AIMLAB
ADVANCED IMAGING & MICROSCOPY LABORATORY

NIST

CNST Center for Nanoscale Science & Technology

Josh Schumacher

Scientific Applications & Visualization Group

John Hagedorn

Acknowledgments

Committee

Lourdes Salamanca-Riba
Eric Wachsman
Tsvetanka Zheleva
Neil Goldsman
John Cumings

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SiC Collaborators

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Leonard Feldman
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SOFC/SECA Collaborators

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Yilin Huang

Dan Gostovic
Nick Vito