



# **ANALYTICAL AND MICROSTRUCTURAL MICROSCOPY APPROACHES FOR MATERIALS CHARACTERIZATION**

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# General Outline

- Why (electron) microscopy?
- History of and introduction to TEM
  - Conventional imaging
  - Scanning TEM and high-angle imaging
  - Sample preparation
  - Analytical strategies (EELS)
- Data analysis methods and real-world examples:
  - SiC wide bandgap MOSFETS
  - Solid oxide fuel cell cathodes

# Why Microscopy?

Seeing is believing!



8x Optical



JWST



First TEM (Ruska and Knoll)

# Why Electron Microscopy?

Dramatic resolution improvement  
compared to visible light (or x-rays)...

Rayleigh Criterion:

$$\delta \text{ (resolution)} \approx 0.61\lambda \text{ (wavelength)}$$

	Wavelength	Best Resolution
Visible Light	380 nm to 750 nm	$\approx 200 \text{ nm}^*$
X-rays	0.01 nm to 10 nm	$\approx 20 \text{ nm}$
Electrons	0.002 nm to 0.004 nm	<b>0.055 nm</b>



# BASICS OF TRANSMISSION ELECTRON MICROSCOPY

# Brief history of TEM

- **1897/1924** – Thompson discovers electrons/De Broglie wave duality
- **1931** – First research TEM (Ruska and Knoll)
- **1943** – Electron energy loss spectroscopy (Hillier)
- **1956** – First HRTEM lattice image (Menter)
- **1964** – FEG Electron source (Crewe)
- **1970** – First demonstrated STEM (Crewe)
- **1986** – Digital CCD for TEM (Mochel)
- **2004** – Commercial aberration-corrected TEMs available

# Brief introduction to TEM

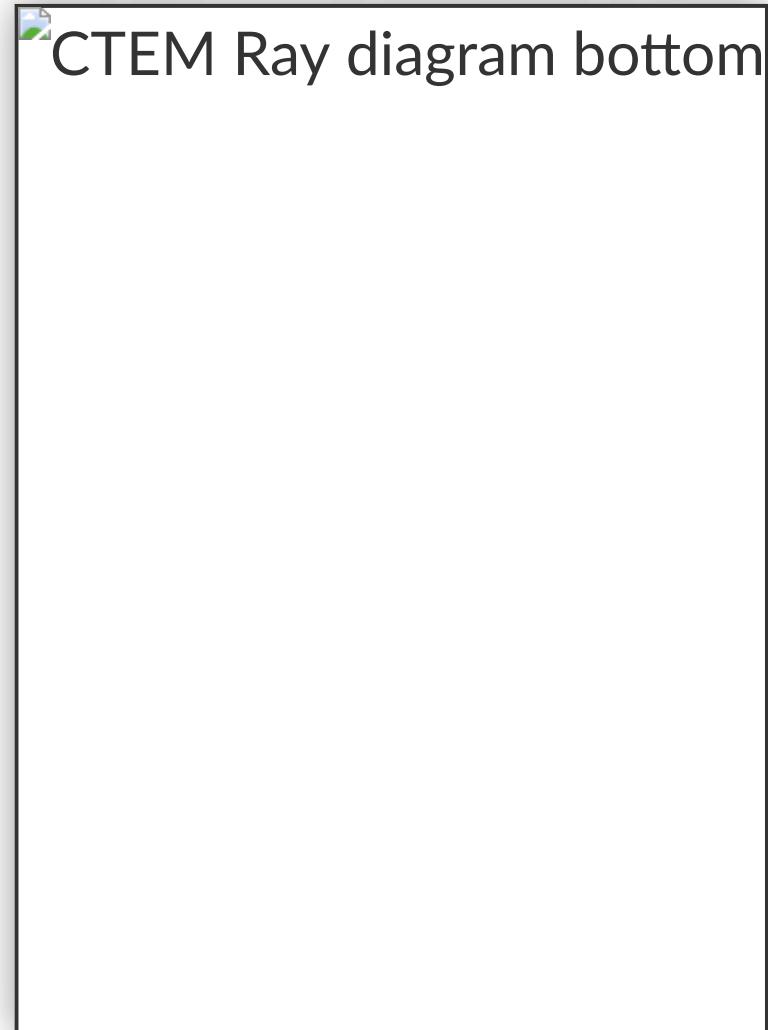
- Fundamentally similar to transmitted light microscopy
- Electrons rather than photons
  - Better resolution
  - Electromagnetic lenses, rather than glass lenses
- Easily combined with analytical techniques
  - EELS, EDS, CL, etc.
  - Enables chemical analysis together with structural information

# Brief introduction to TEM



# "Conventional" TEM

- Specimen illuminated with "parallel" beam of electrons
- Scattering of incident beam by specimen → contrast
- Diffraction and mass-thickness
- Phase contrast
- Image intensity proportional to projected potential (approx.)



# Scanning TEM

- Specimen illuminated with converged beam of electrons
- Record point signal as beam scans sample
- Different detectors for different angles

 STEM detection angles

# Scanning TEM

- Image with transmitted, diffracted, or scattered electrons
  - Bright field (BF) - *transmitted e<sup>-</sup>*
  - Annular dark field (ADF) - *Bragg diffracted e<sup>-</sup>*
  - High angle annular dark field (HAADF) - *Rutherford scattered e<sup>-</sup>*



# HAADF-STEM

Can change angle of HAADF collection by adjusting camera length ( $L$ ) settings. Shorter  $L$  increases collection angles ( $\beta$ ).  
A schematic diagram illustrating the HAADF collection angle. It shows a central vertical axis labeled "HAADF collection". Two diagonal lines extend from the top and bottom ends of this axis to form an angle at the top, which is labeled  $\beta$ .

# HAADF-STEM Example



Pennycuok STEM

Imaging Sb-implanted Si with different TEM modalities.

In HAADF-STEM, intensity  $I \propto Z^2$

# Potential TEM pitfalls

- Loss of depth information in projection
- Mixing of electron wavefunction phase/amplitude
- Diffraction/focus effects (particularly at edges)
- Delocalization of electron probe
- Beam damage (and other dynamic effects)



Beam damage

# FIB/SEM sample prep



TEM sample prep



# BASICS OF ELECTRON ENERGY LOSS SPECTROSCOPY

# Brief introduction to TEM



# Fundamental process

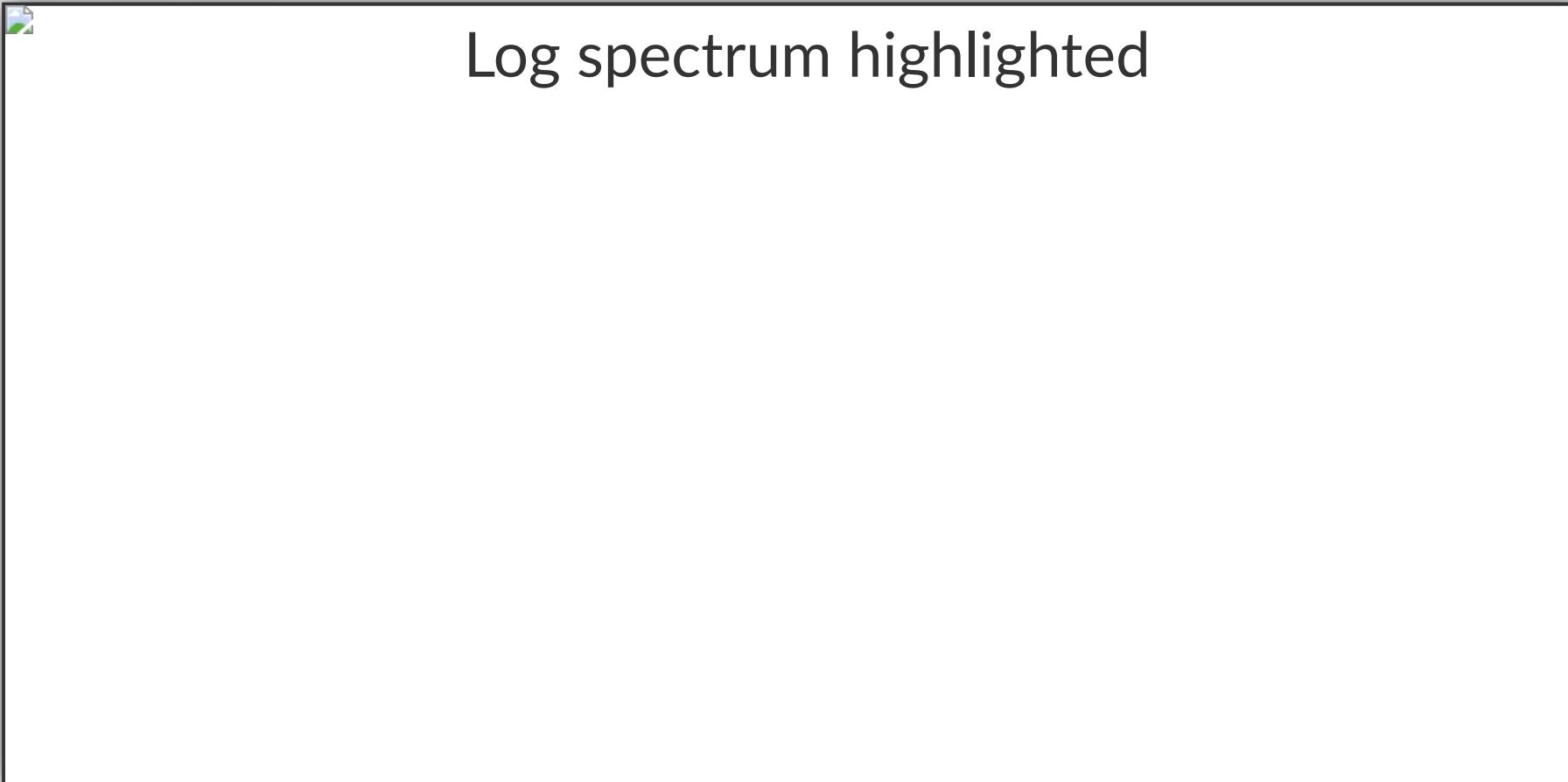
- Incoming electron interacts with electron cloud
  - Many interactions; most used is core excitation
  - Creates characteristic x-ray
  - Electron loses energy (inelastic scattering)



# EELS Instrumentation

EELS schematic

# Example EELS spectra



# Low-loss EEL spectra



## Linear spectrum

- Primary feature is zero-loss peak (ZLP)
  - Vast majority of electrons have no interaction
  - Can be used to measure energy resolution
  - Very intense, not enough dynamic range to capture entire spectrum at once

# Low-loss EEL spectra



## Linear spectrum

- Next most intense is plasmon peak
  - Collective excitation of electron gas by beam
  - Position of peak dependent on electron density
    - $E_p = 28.82 \text{ eV} \sqrt{\frac{z\rho}{A}}$  (Drude model; see Egerton 2010)
  - Can be used for fingerprinting with known standards

# Core-loss EEL spectra



- **Provide information about tightly-bound electrons**
  - Compositional information in edges (not peaks)
  - Power-law fitting background subtraction
  - ELNES provides information about electronic structure
  - Core-loss edges continue beyond 2,000 eV

# EELS core-loss edges

- Excitations of core-level electrons into empty states
- X-ray notation used instead of atomic
  - $1s \rightarrow K$
  - $2s \rightarrow L_1$
  - $2p(\frac{1}{2}, \frac{3}{2}) \rightarrow L_{2,3}$
  - Etc.



# EELS composition quantification



EELS quantification

# EELS composition quantification

- Integrated intensities of edge give areal density

- $N \approx \frac{I_c(\beta, \Delta)}{I_l(\beta, \Delta)} \sigma_c(\beta, \Delta)$

- Taking ratio of two elements makes low-loss and thickness info irrelevant:

- $\frac{N^A}{N^B} = \frac{I_c^A(\beta, \Delta)}{I_c^B(\beta, \Delta)} \frac{\sigma_c^B(\beta, \Delta)}{\sigma_c^A(\beta, \Delta)}$



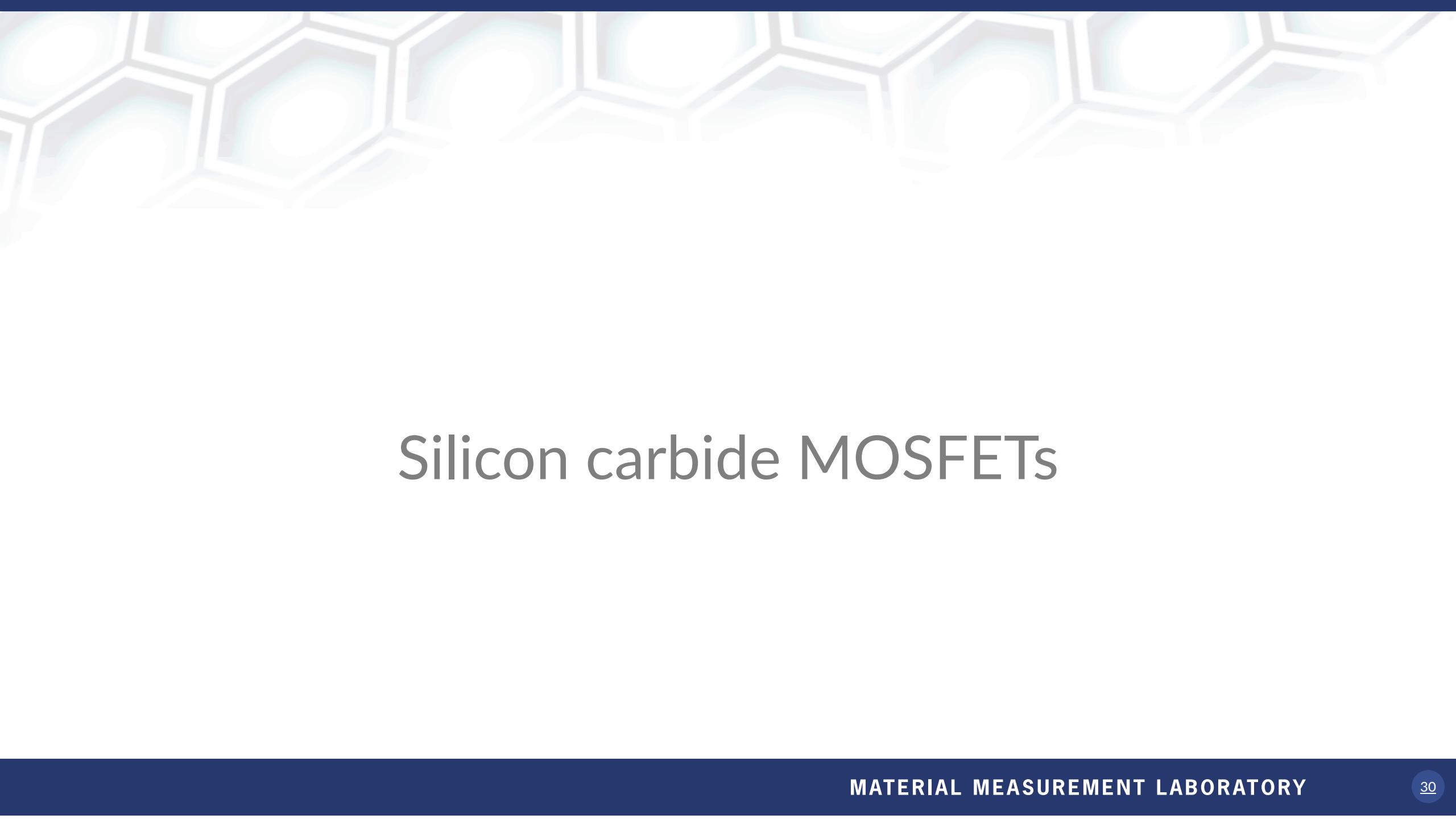
EELS quantification

# Spectrum imaging

Three-dimensional spectrum imaging figure  
Gatan spectrum imaging data collection process



# SOME REAL-WORLD EXAMPLES



# Silicon carbide MOSFETs

# SiC Semiconductors

- Wide bandgap (3.26 eV) material, good for power electronics
  - High mobility
  - High critical field
  - High thermal conductivity
- (Almost) drop in replacement for silicon
  - Native SiO<sub>2</sub>
  - Lighter and more efficient than Si in high power

# SiC promise



# SiC structure



SiC has over 250 polymorphs;  
We are interested in 4H for electrical devices

# Issues facing SiC

- High wafer cost
  - Orders of magnitude higher than Si
- Low device mobility ( $\mu_e$ )
  - Interface traps within  $E_g$  of 4H-SiC limit mobility to about 1% of bulk value



# Issues facing SiC

- **High wafer cost**
  - Orders of magnitude higher than Si
- **Low device mobility ( $\mu_e$ )**
  - Interface traps within  $E_g$  of 4H-SiC limit mobility to about 1% of bulk value
- **Limited device reliability**
  - Threshold ("on") voltage shifts with bias and temperature stress



SiC Trap density

# How to improve $\mu_e$ ?



- **NO annealing incorporates N at interface; with dramatic improvement in device mobility**
  - Passivation of some mobility-limiting defects

# How to improve $\mu_e$ ?

- Change substrate orientation
  - Relevant for trench MOSFET designs
- Dramatic improvement in mobility on a-face
  - Origins not totally clear
  - Different surface termination on a-face



a-face improvement

# Opportunities for TEM

- **Structure and chemical states at the interface are unclear**
  - Nitrogen is there, but how is it incorporated?
  - Are there distinct chemical states (a "transition layer")?
- **Effects of processing conditions and device orientation**
  - Does NO-annealing work differently on different surfaces?
  - How do different passivation strategies compare?



# Effect of NO-anneal time on interfacial width

# Investigating transition layer

- NO annealing improves mobility, but no significant change in structure visible in HRTEM



Si-miscut HRTEM

# Interfacial characterization



HAADF-STEM Si- $L_{2,3}$  edge at interface

# Core-level shifts

- Between semiconductor and insulator, band diagram shifts
  - Bandgap grows, core levels depressed
  - $\Delta E_t$  corresponds to observed EELS edge onset shift



# Interfacial characterization

- Change in onset energy of edge reflects change in bandgap (roughly)
  - Probes bonding configuration of silicon atoms
  - Measure onset energy as function of NO-annealing time
  - Width of transition region defined as  $w_{TL}$



Crystal structure

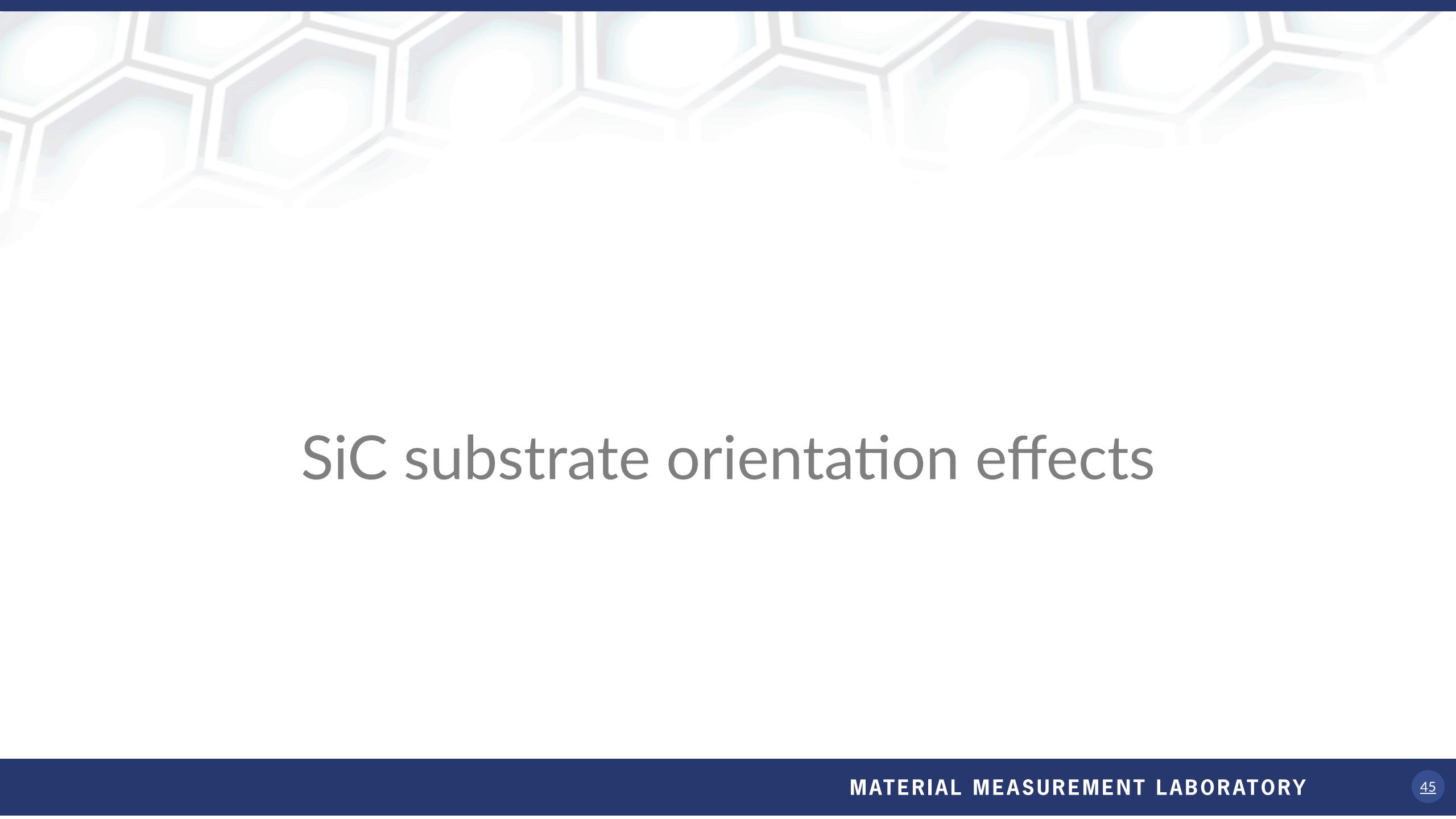
# NO time series results



$w_{TL}$  decreases with NO anneal  
time



$w_{TL}$  inversely related to  
 $\mu_e$



# SiC substrate orientation effects

# Samples investigated

- MOS devices in three substrate orientations:
  - Si-face with 4° miscut (commercial standard)
  - Si-face without miscut (poor epilayer growth)
  - a-face
- Processing conditions for each orientation:
  - Thermally oxidized
  - 2 hour post-oxidation anneal

 Crystal structure

# HRTEM results

- Like before, little structural evidence of interfacial states  
Miscut HRTEM

# EELS analysis

- Need to analyze content of signal at interface, not just its size (beyond  $w_{TL}$ )

# Hyperspectral decomposition

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

$$\begin{aligned}\text{Data} &= \text{Scores} \times \text{Loadings} \\ \mathbf{D}_{(x,y),E} &= \mathbf{S}_{(x,y),n} \times \mathbf{L}_{(E,n)}^T\end{aligned}$$

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

# Hyperspectral software tool

- HyperSpy: Open-source hyperspectral data analysis tool
  - Easy access to PCA, ICA, NMF, and signal modeling



# Hyperspectral software tool

- HyperSpy: Open-source hyperspectral data analysis tool
  - Can be used in Jupyter notebook for complete reproducibility

 **HyperSpy Notebook**

# Decomposing Si-L<sub>2,3</sub> signal

- No significant variation between orientations
  - a-face results shown here
- NO-anneal showed interfacial state in all samples
  - No such state in
  - Very similar to Si<sub>3</sub>N<sub>4</sub>

# Analysis of Si-L<sub>2,3</sub> signal



Effect of substrate  
orientation



Comparison to Si<sub>3</sub>N<sub>4</sub>  
literature

# Decomposing C-K signal

- Again, no significant variation between orientations
  - a-face results shown here
- NO-anneal showed interfacial state in all samples
  - No such state in oxidized samples
  - Very similar to the Si-L<sub>2,3</sub> results
- Interfacial state has pre-edge intensity
  - Indicative of  $sp^2$ -like bonding
  - Influence of nitrogen is apparent

# Analysis of C-K signal



Hu C-N EELS

# Decomposing O-K signal

- Only sample with interface is a-face NO

- Interface has edge onset 2 eV to 3 eV below  $\text{SiO}_2$

- Reduced bandgap
  - Increased dielectric constant
  - Enhanced mobility

- Only clue as to

MATERIAL MEASUREMENT LABORATORY  
the a-face

# Orientation effects summary

- Thermally oxidized samples do not exhibit distinct bonding configurations at interface
  - All NO-annealed samples did
- N from NO participates in bonding with Si and C, regardless of orientation
- Oxide effects only observed on the a-face
  - Potential origins of enhanced mobility
- Not shown: No differences between Si-face with and without miscut
  - Miscut of substrate does not influence chemical states; just roughness



# Next-generation processing

# Motivation

- "Next-generation" passivation techniques more poorly understood than NO process
- *Phosphorus and boron passivations are particularly promising*
  - Devices fabricated by S. Dhar's group at Auburn
  - One TEM study of P, none of B
  - How do they differ from NO-annealing?



Phosphorus passivation

# Phosphorus imaging results



HRTEM of P-annealed interface



HAADF-STEM of same interface

# Phosphorus EELS results

Bright spots in HAADF-<sup>STEM</sup> image correspond to P-rich clusters  
**Phosphorus EELS**

# Boron imaging results



HRTEM of B-annealed interface



HAADF-STEM of same interface

# Boron EELS results

Boron accumulates at interface but some distributed throughout oxide  
**Boron EELS**

# "Next-generation" summary

- Both P and B incorporate into oxide differently than NO
  - More oxide impact than nitridation
- Phosphorus distributes into nm-sized P-rich clusters
  - Impacts on polarization stability
  - Opportunities for gate oxide engineering
- Boron segregates to SiC/oxide interface
  - Like NO, but more boron remaining through BSG layer
  - B diffuses slightly into SiC



# Solid oxide fuel cell (SOFC) cathode materials

# Motivation

- Composite cathode SOFC materials degrade prematurely when exposed to certain atmospheres
  - H<sub>2</sub>O, CO<sub>2</sub>, Cr-vapor, etc.
- Analysis of degradation mechanisms is needed
  - LSM: (La<sub>0.8</sub>Sr<sub>0.2</sub>)<sub>0.95</sub>MnO<sub>3+δ</sub>
  - YSZ: (Y<sub>2</sub>O<sub>3</sub>)<sub>0.08</sub>(ZrO<sub>2</sub>)<sub>0.92</sub>
- EELS provides a powerful chemical state analysis tool for these perovskite materials

# H<sub>2</sub>O-aged LSM-YSZ EDS

- TEM-EDS analysis of YSZ grain boundaries in composite cathode
- Mn and La observed to migrate to YSZ boundaries
  - Distribution of cations suggests surface diffusion mechanism
- What is chemical state of these mobile cations?



LSM-YSZ EDS

# H<sub>2</sub>O-aged LSM-YSZ EELS

- Analysis of the Mn-L edges
- Again, evidence of Mn at YSZ grain boundaries
- Intensity ratio of L<sub>2</sub> and L<sub>3</sub> peaks reveals information about average Mn valence
  - In this case, Mn<sup>2.5+</sup>
    - S. Shih, et al. *J. Electrochem. Soc.* **158**, B1276 (2011).
  - Charge balance will contribute to  $V_O^{..}$  formation
    - M. Backhaus-Ricoult, *Solid State Ionics* **177**, 2195 (2006).



## LSM-YSZ EELS

# H<sub>2</sub>O-aged LSM-YSZ EELS

- Analysis of the O-K edge
- Triple phase boundary locations reveal a clear surface state
  - Lack of peaks in ELNES suggests O-deficient oxide
  - Evidence of high oxygen vacancy concentration in LSM
- High  $[V_O^\ddot]$  encourages oxygen incorporation at surfaces
  - Agrees with kinetic enhancements observed under humidification during EIS



LSM-YSZ EELS

# Degradation mechanism

- Degradation mode had been proposed, but not verified by TEM
  - J. Nielsen and M. Mogensen, *Solid State Ionics*, 189, 74 (2011)

# SOFC Summary

- EDS and EELS in the TEM can be used to analyze fuel cell materials
- Cation valence analysis enables insight into ionic state and defect distributions throughout the electrochemical system
- Evidence of cation migration and reduction of Mn at the LSM/YSZ interface
  - Impacts for short- and long-term kinetics of cell operation



# END MATTER

# Summary

- TEM is a powerful and versatile technique for materials analysis
  - Conventional, scanning, and high-angle imaging
  - Sample preparation using FIB/SEM
  - Analytical strategies (EELS)
- Data analysis methods:
  - Machine learning tools enable new avenues of inquiry
- Real-world examples:
  - Detailed analysis of SiC MOS interfacial states
  - Cation and vacancy analysis in SOFC cathodes

# More reading (1):



- *Transmission Electron Microscopy: A Textbook for Materials Science*, David Williams and Barry Carter (2009) - [link](#)
- *Electron Energy-Loss Spectroscopy in the Electron Microscope*, Ray Egerton (2011) - [link](#)
- *Introduction to Focused Ion Beams*, Lucille Giannuzzi (2005) - [link](#)

# More reading (2):



- *Scanning Transmission Electron Microscopy: Imaging and Analysis*,  
Stephen Pennycook (2010) - [link](#)
- *Transmission Electron Microscopy and Diffractometry of Materials*,  
Fultz and Howe (2013) - [link](#)
- Paul Voyles, "Informatics and data science in materials microscopy",  
*Current Opinion in Solid State and Materials Science* (2016) - [link](#)

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  - Aivars Lelis - ARL
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