ANALYTICAL AND MICROSTRUCTURAL MICROSCOPY APPROACHES FOR MATERIALS CHARACTERIZATION

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U.S. Department of Commerce

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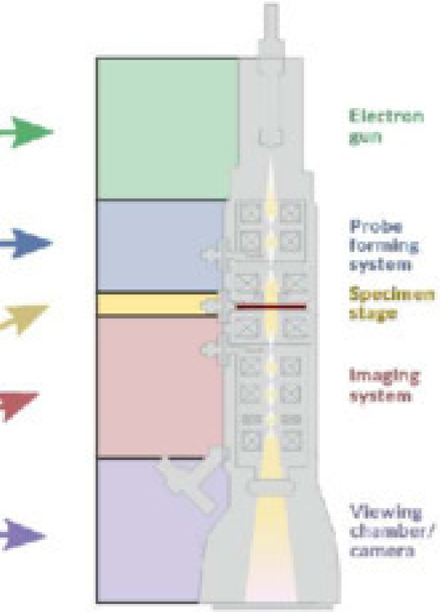
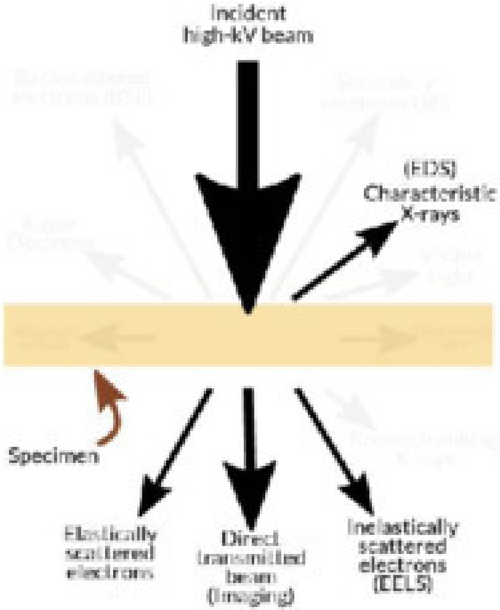
Brief introduction to TEM

JEOL JEM-2100F

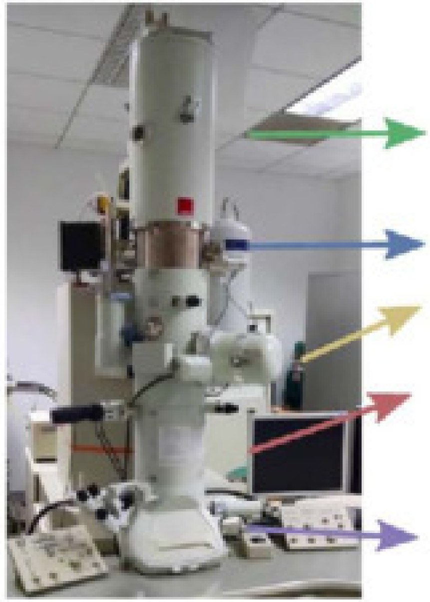


TEM Schematic

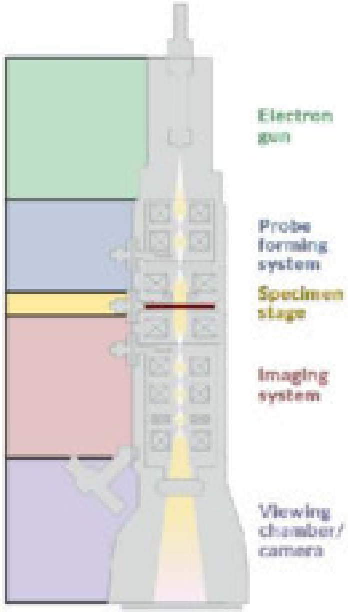


Electron-sample interactions
(adapted from Williams and Carter, 2009)

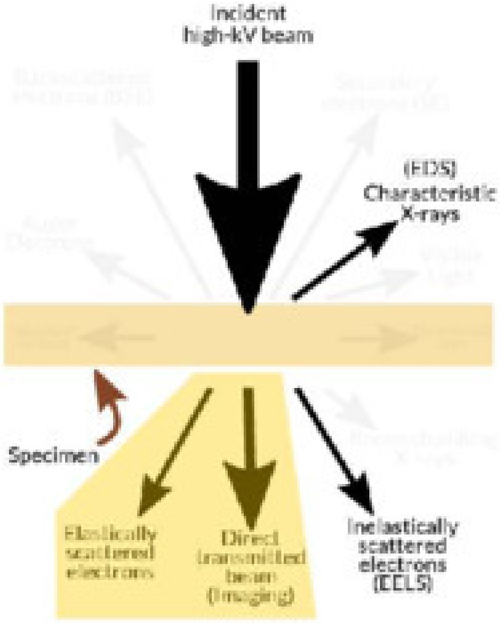
Brief introduction to TEM



JEOL JEM-2100F



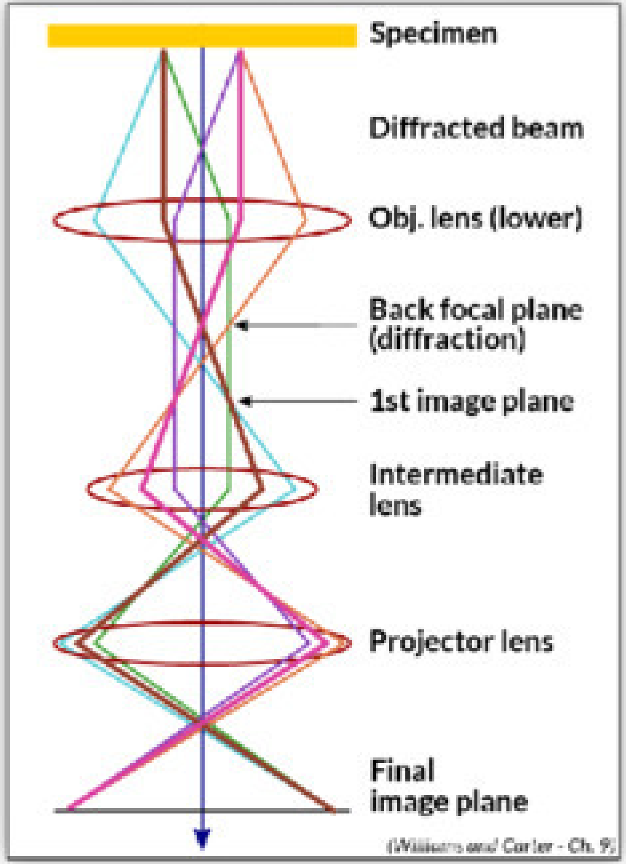
TEM Schematic



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

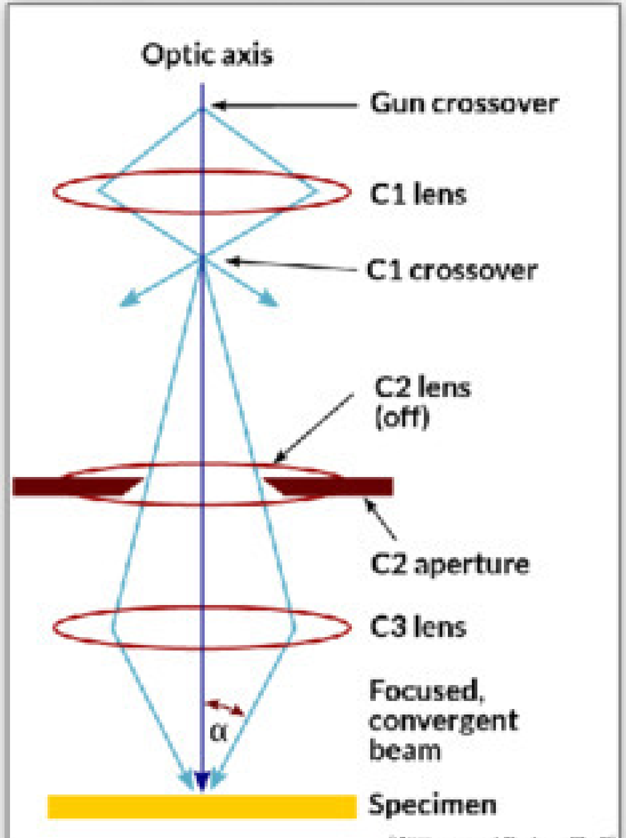
"Conventional" TEM

- 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

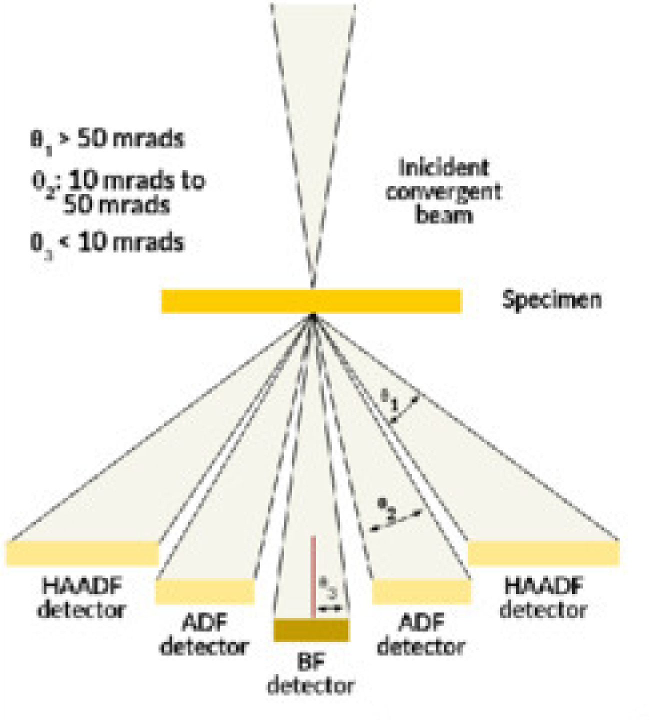
- Specimen illuminated with converged beam of electrons
- Record point signal as beam scans sample



(Williams and Carter - Ch. 9)

Scanning TEM

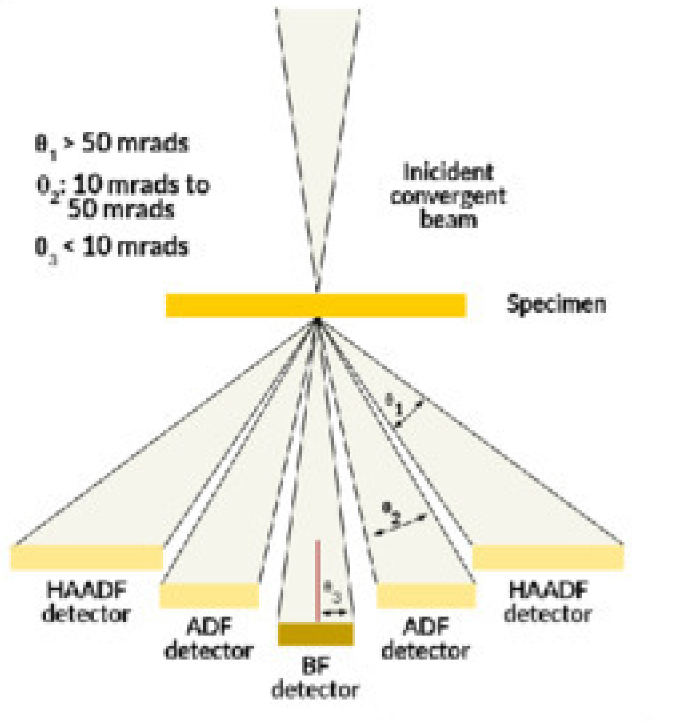
- Specimen illuminated with converged beam of electrons
- Record point signal as beam scans sample
- Different detectors for different angles



(Williams and Carter - Ch. 22)

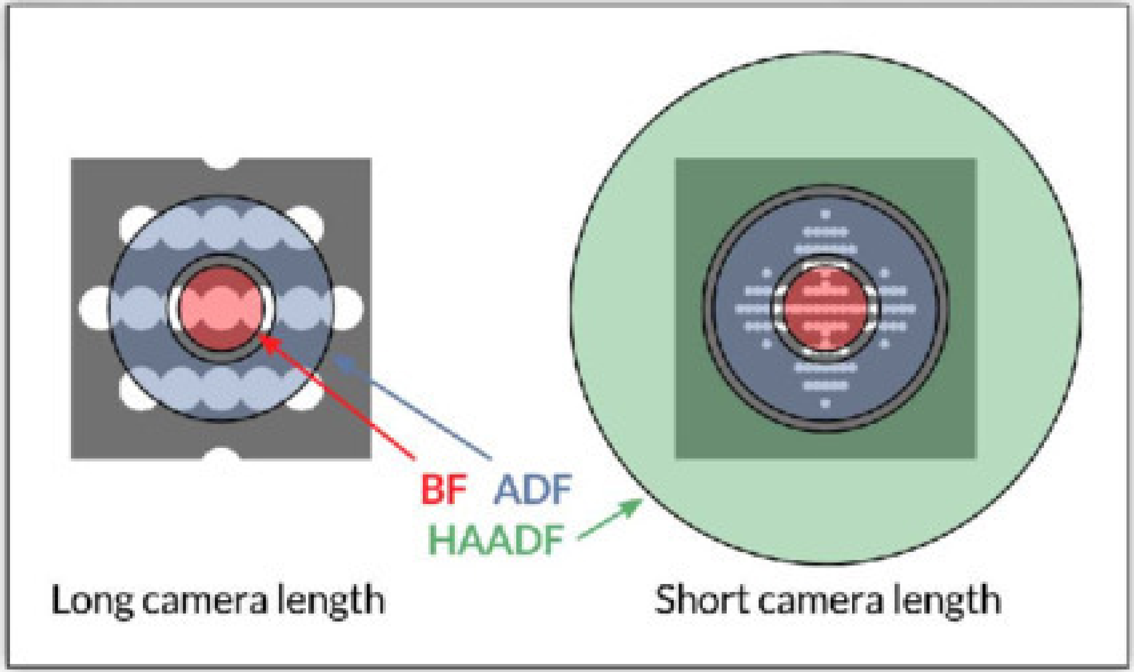
Scanning TEM

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



(Williams and Carter - Ch. 22)

HAADF-STEM



Can change angle of HAADF collection by adjusting camera length (L) settings. Shorter L increases collection angles (β).

HAADF-STEM Example

Conventional TEM:

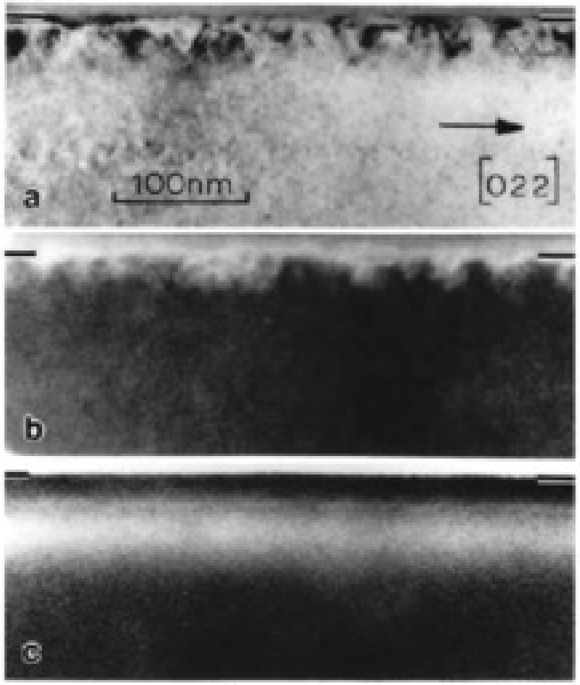
Phase-contrast image showing defects near surface from implantation

ADF-STEM:

STEM image also dominated by diffraction contrast (but greatly reduced phase information)

HAADF-STEM image:

Z-contrast image showing Sb elemental profile away from the implantation surface



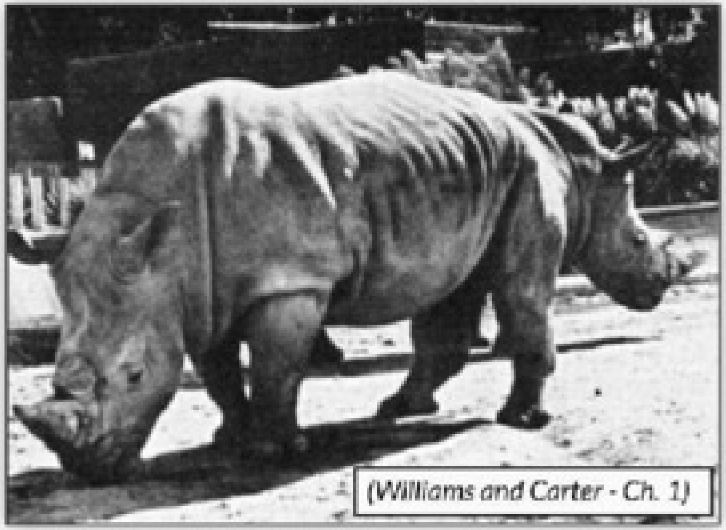
Pennycook and Narayan (1984)

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)



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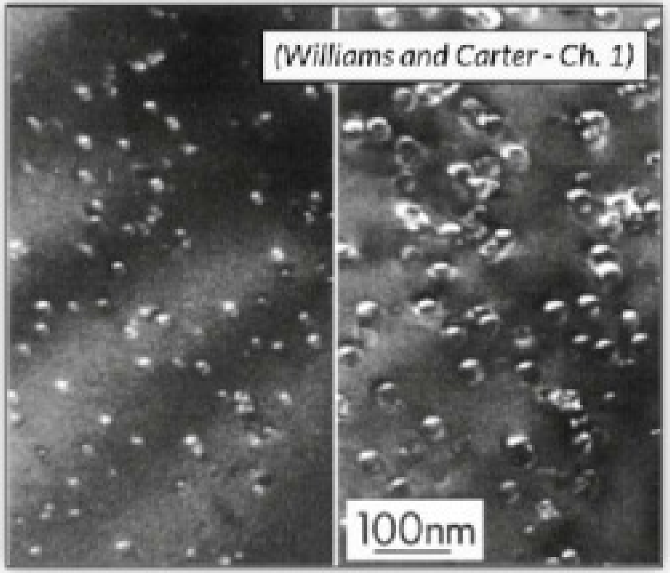
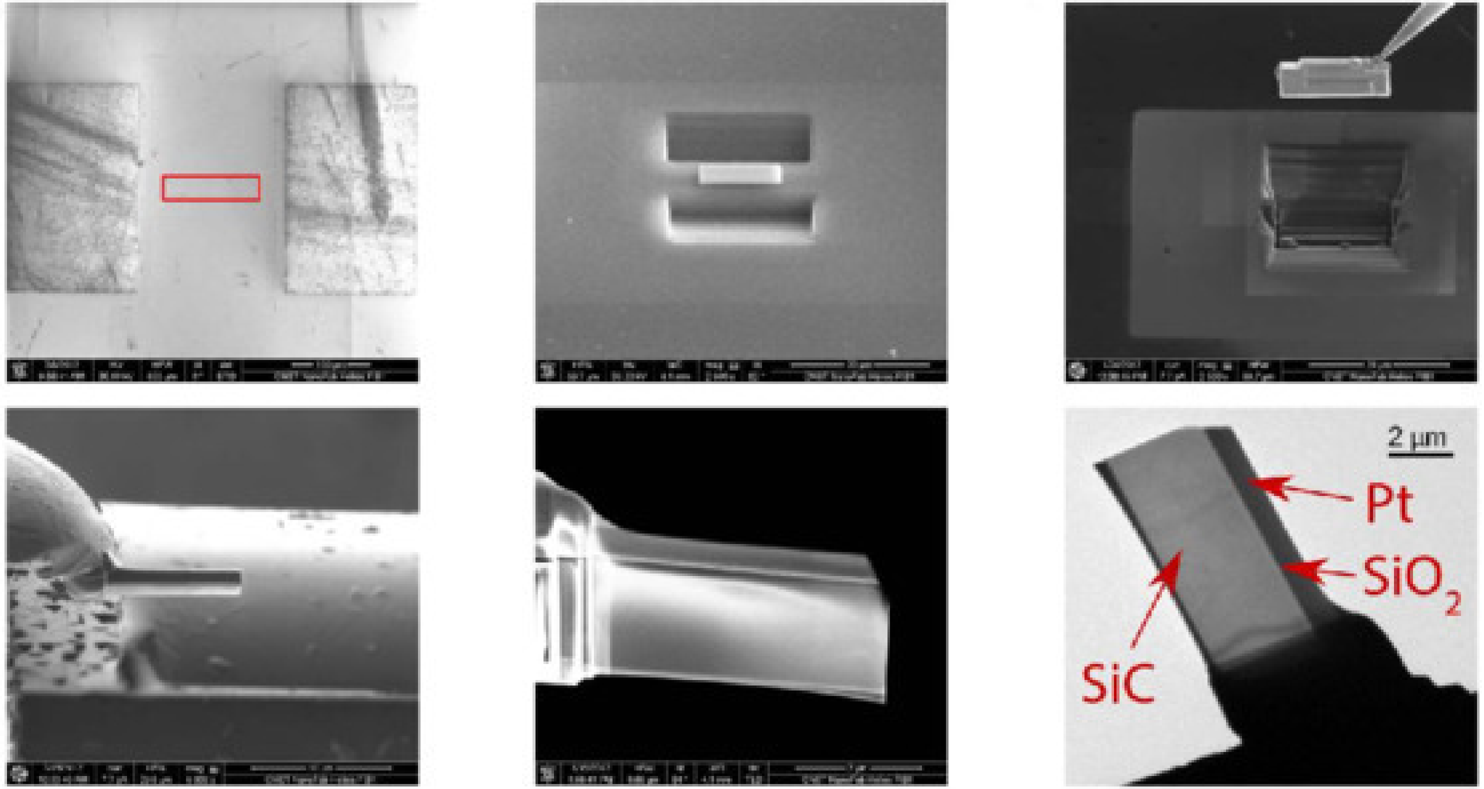


General Outline

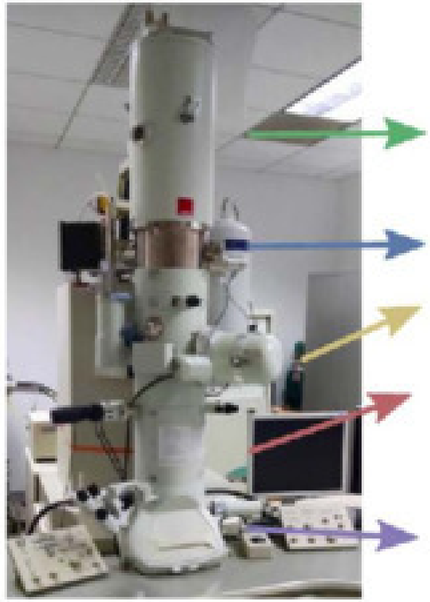
- **Why (electron) microscopy?**
- **History of and introduction to TEM**
  - Conventional imaging
  - Scanning TEM and high-angle imaging
  - Sample preparation
  - Analytical strategies (EELS)
- **Data analysis methods and real-world examples:**
  - SiC wide bandgap MOSFETS
  - Solid oxide fuel cell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

FIB/SEM sample prep

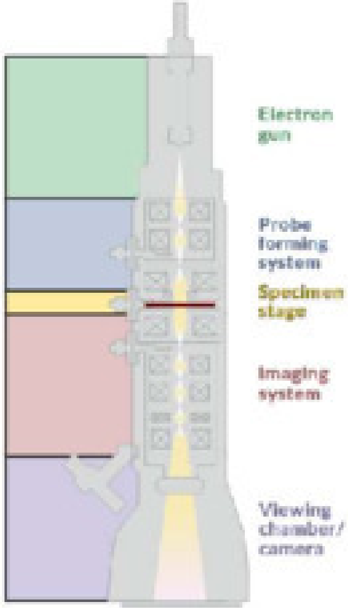


Basics of Electron Energy Loss Spectroscopy

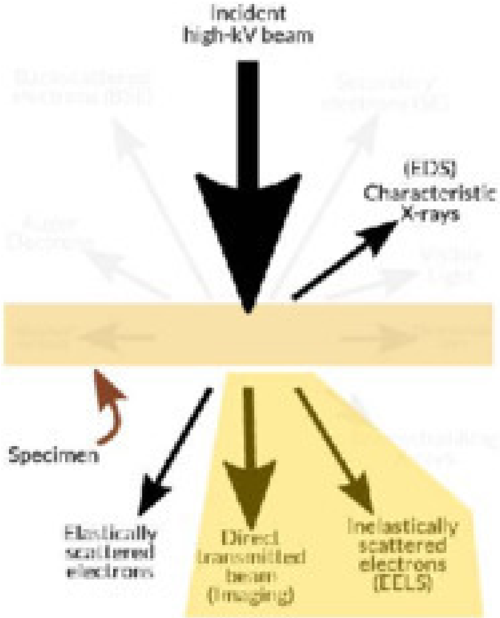
Brief introduction to TEM



JEOL JEM-2100F



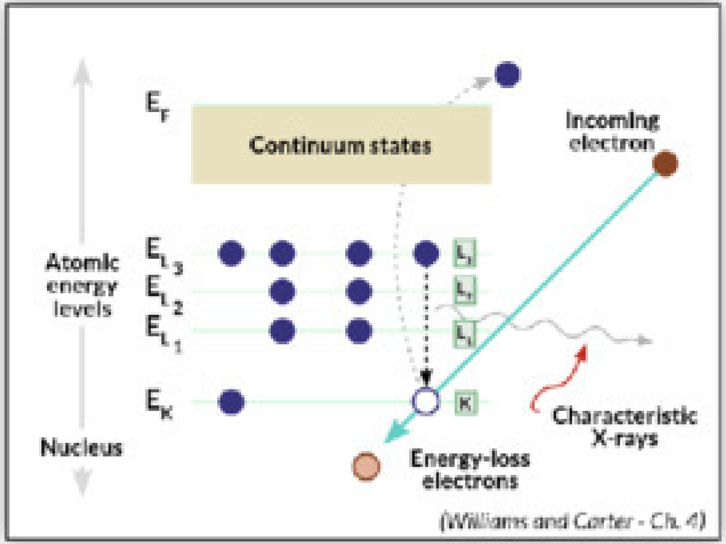
TEM Schematic



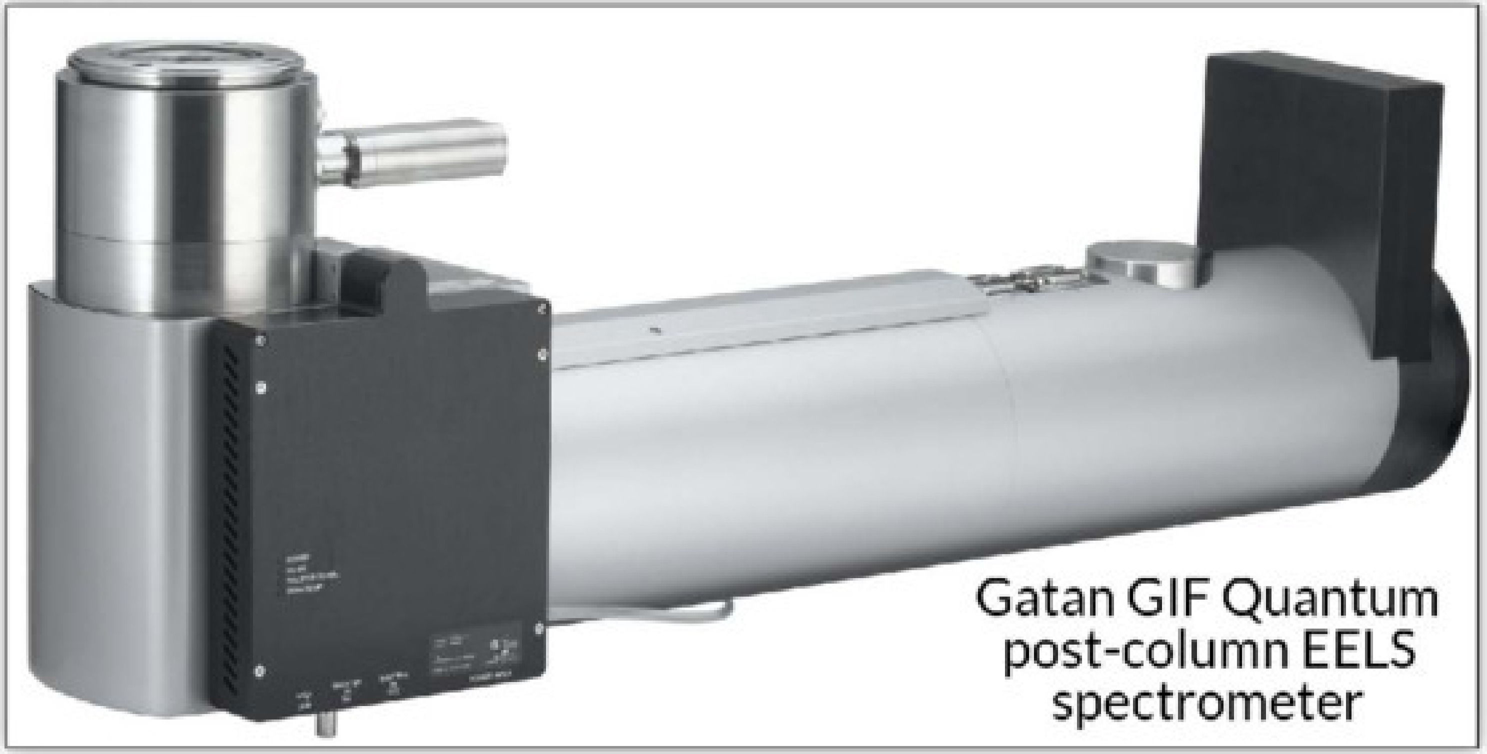
Electron-sample interactions
(adapted from Williams and Carter, 2009)

Fundamental process

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

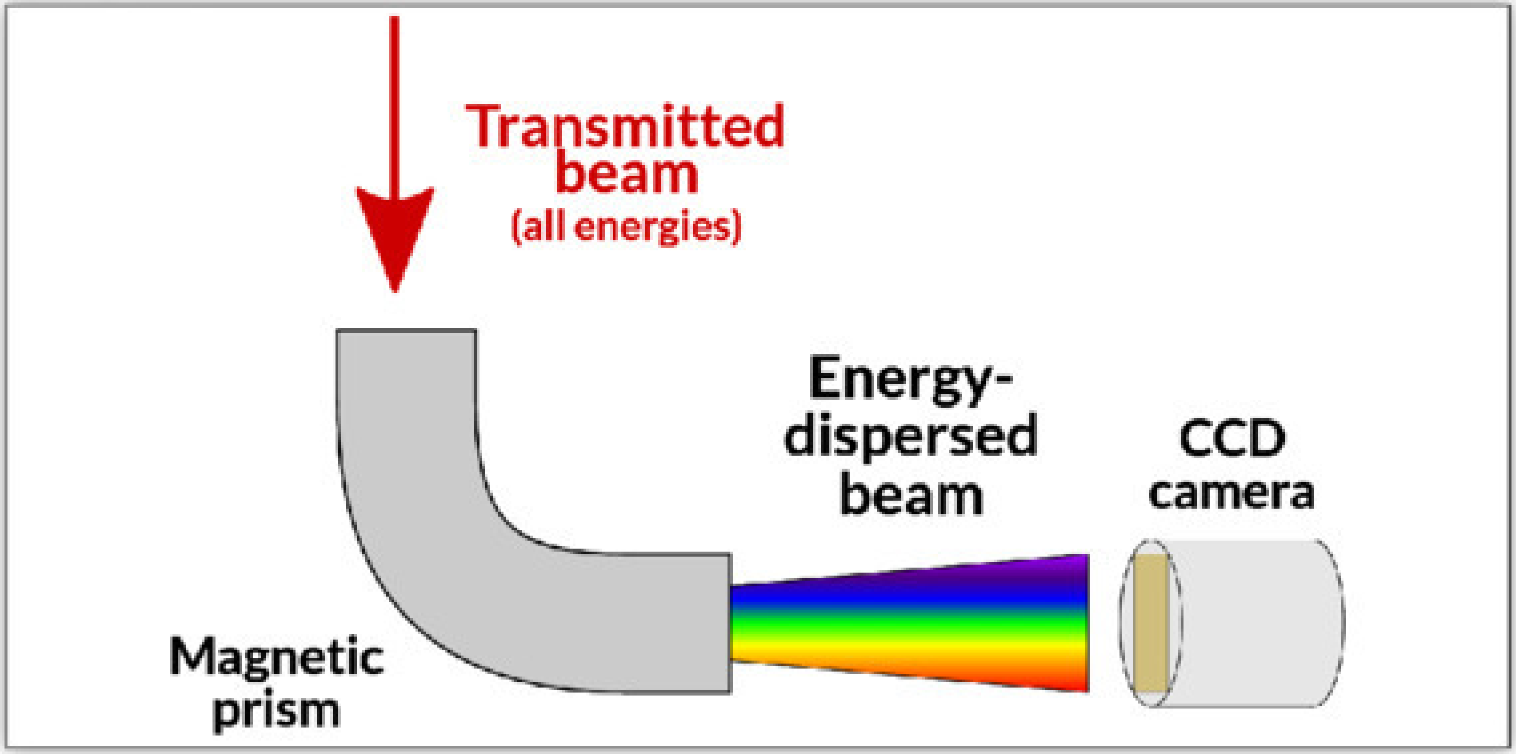


EELS Instrumentation

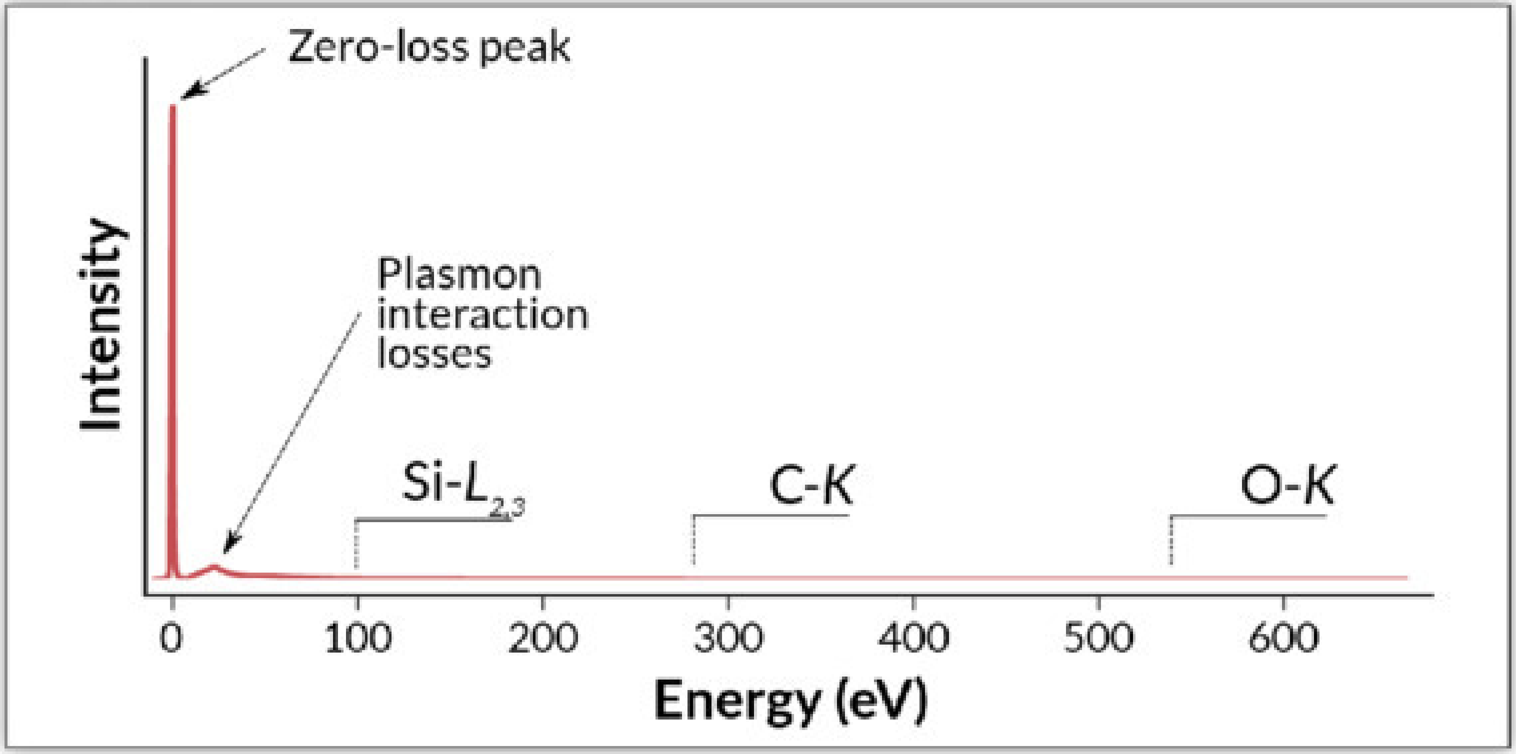


Gatan GIF Quantum
post-column EELS
spectrometer

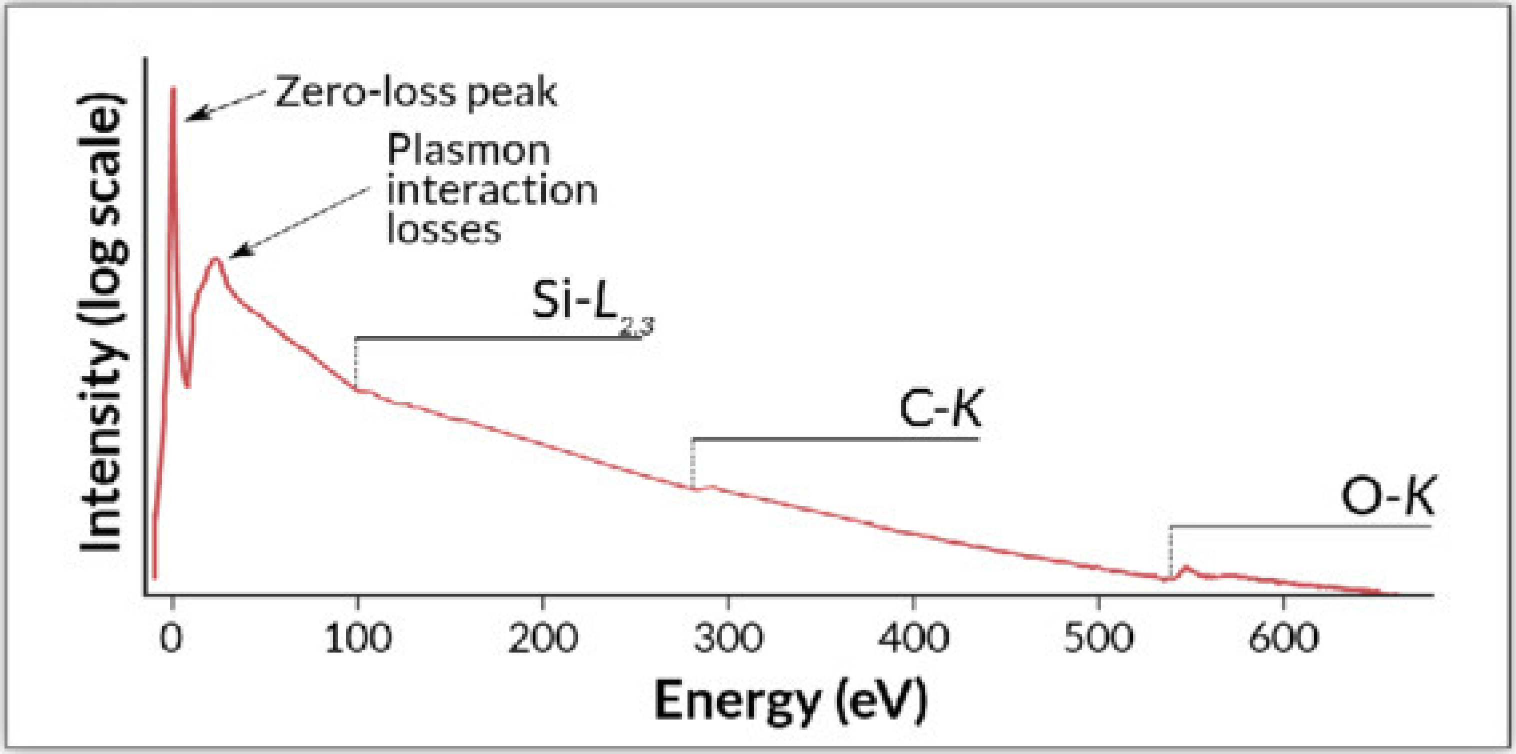
EELS Instrumentation



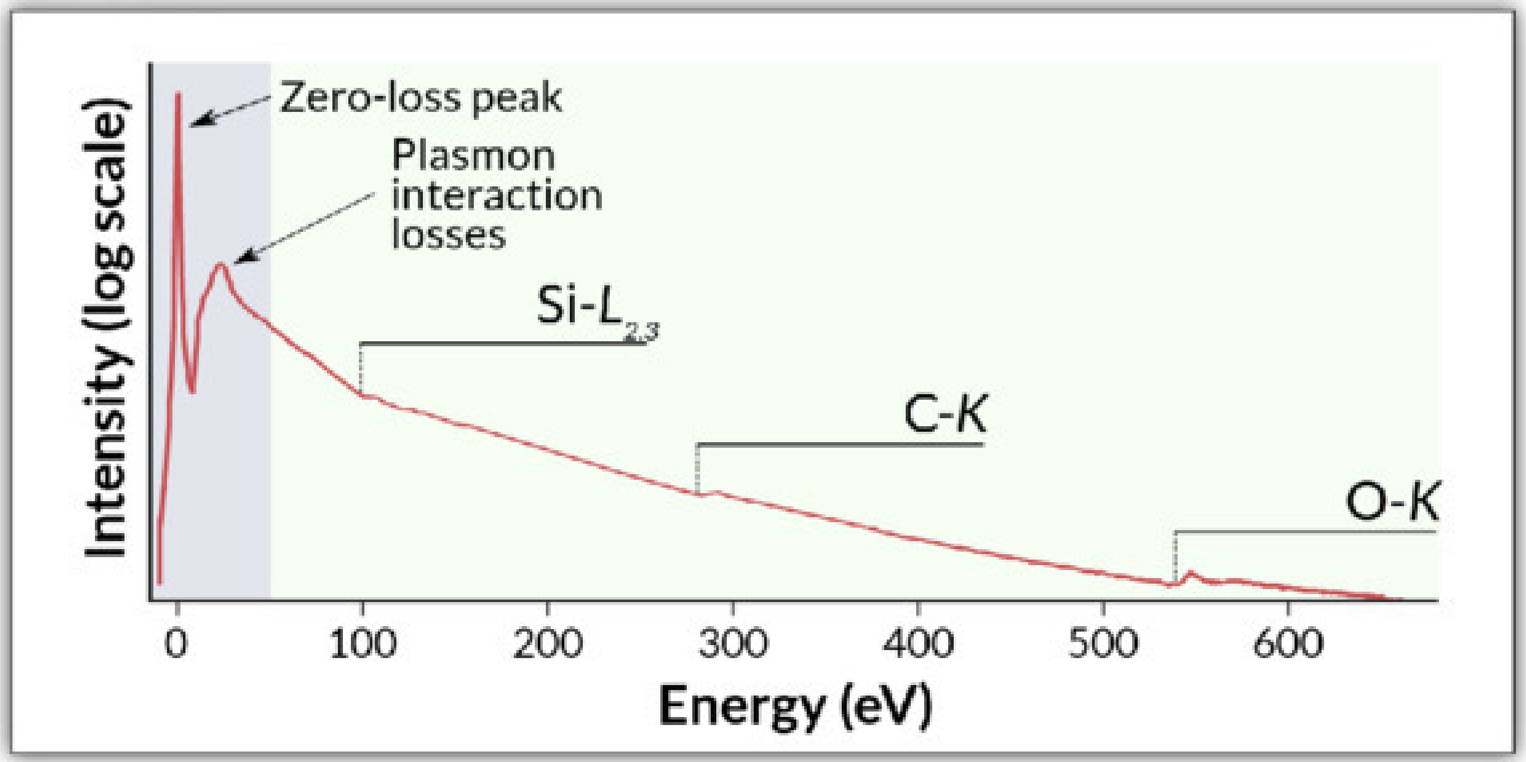
Example EELS spectra



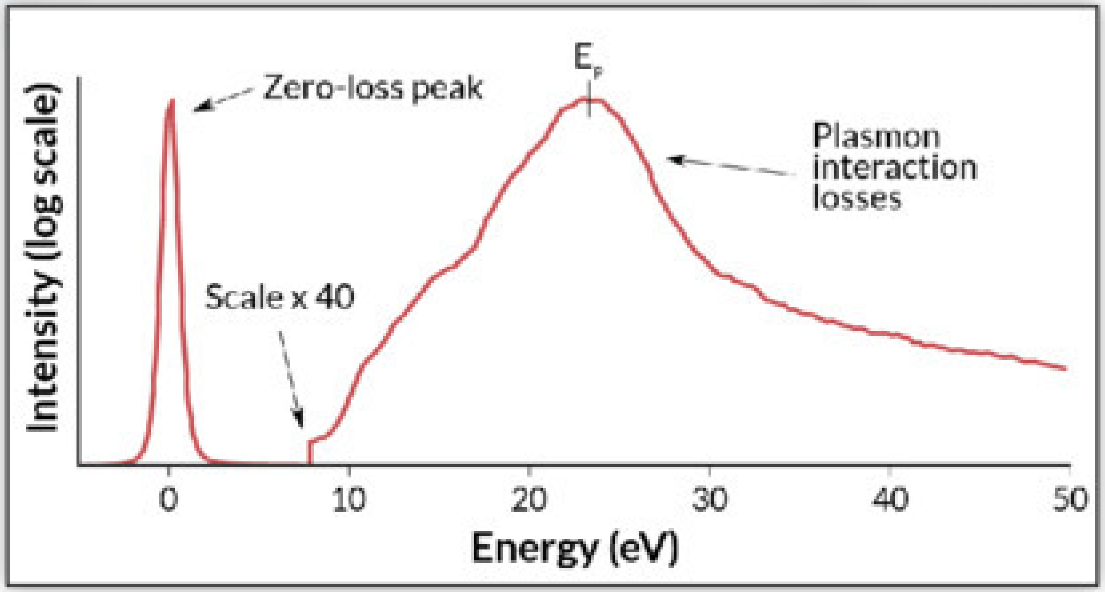
Example EELS spectra



Example EELS spectra



Low-loss EEL spectra



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

Why Microscopy?

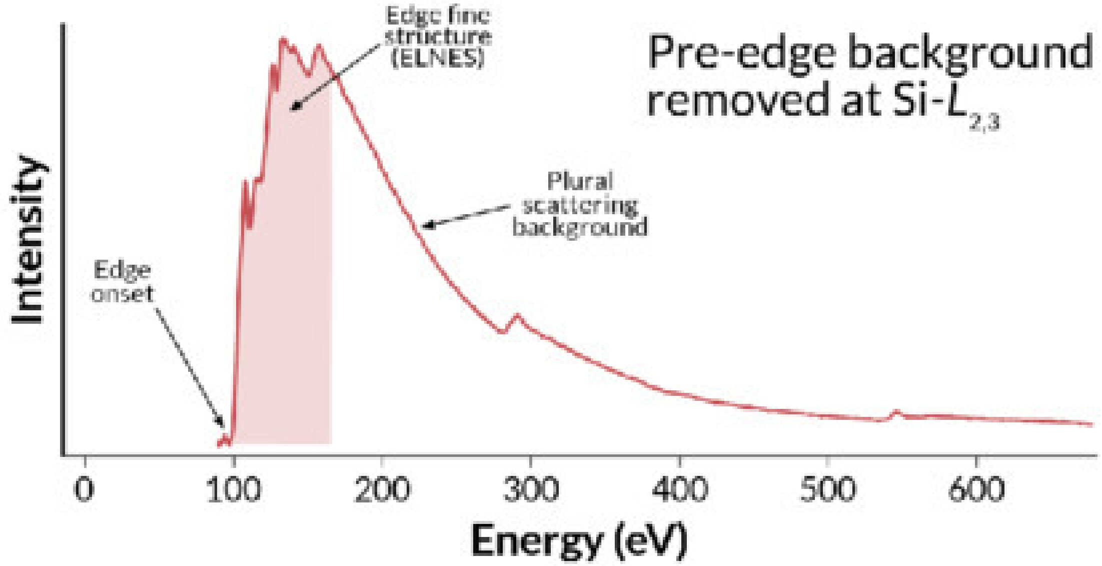
Seeing is believing!

8x Optical

JWST

First TEM (Ruska and Knoll)

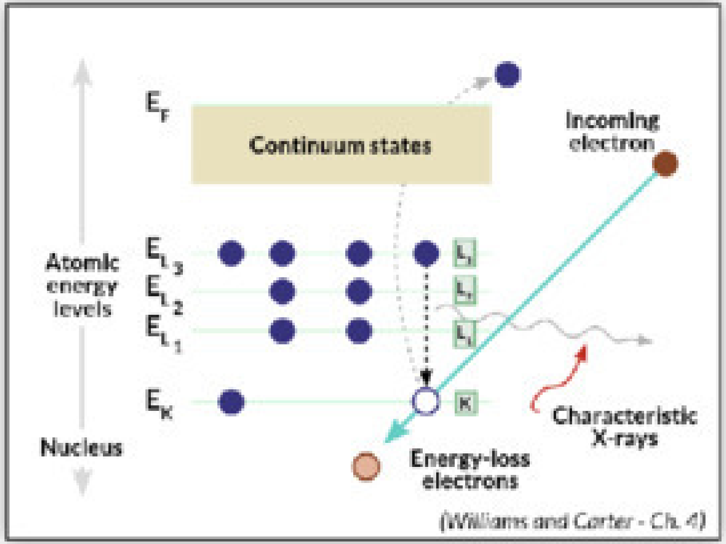
Core-loss EEL spectra



- **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

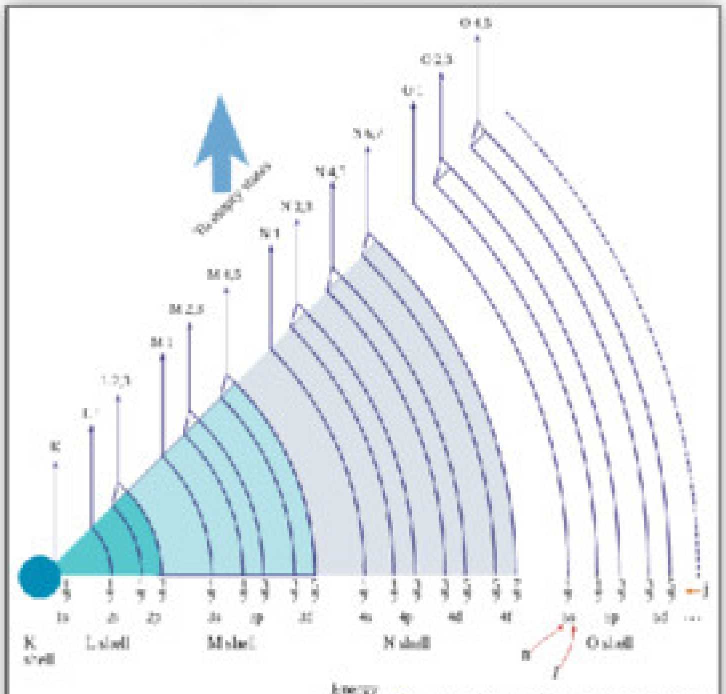
EELS core-loss edges

- **Excitations of core-level electrons into empty states**



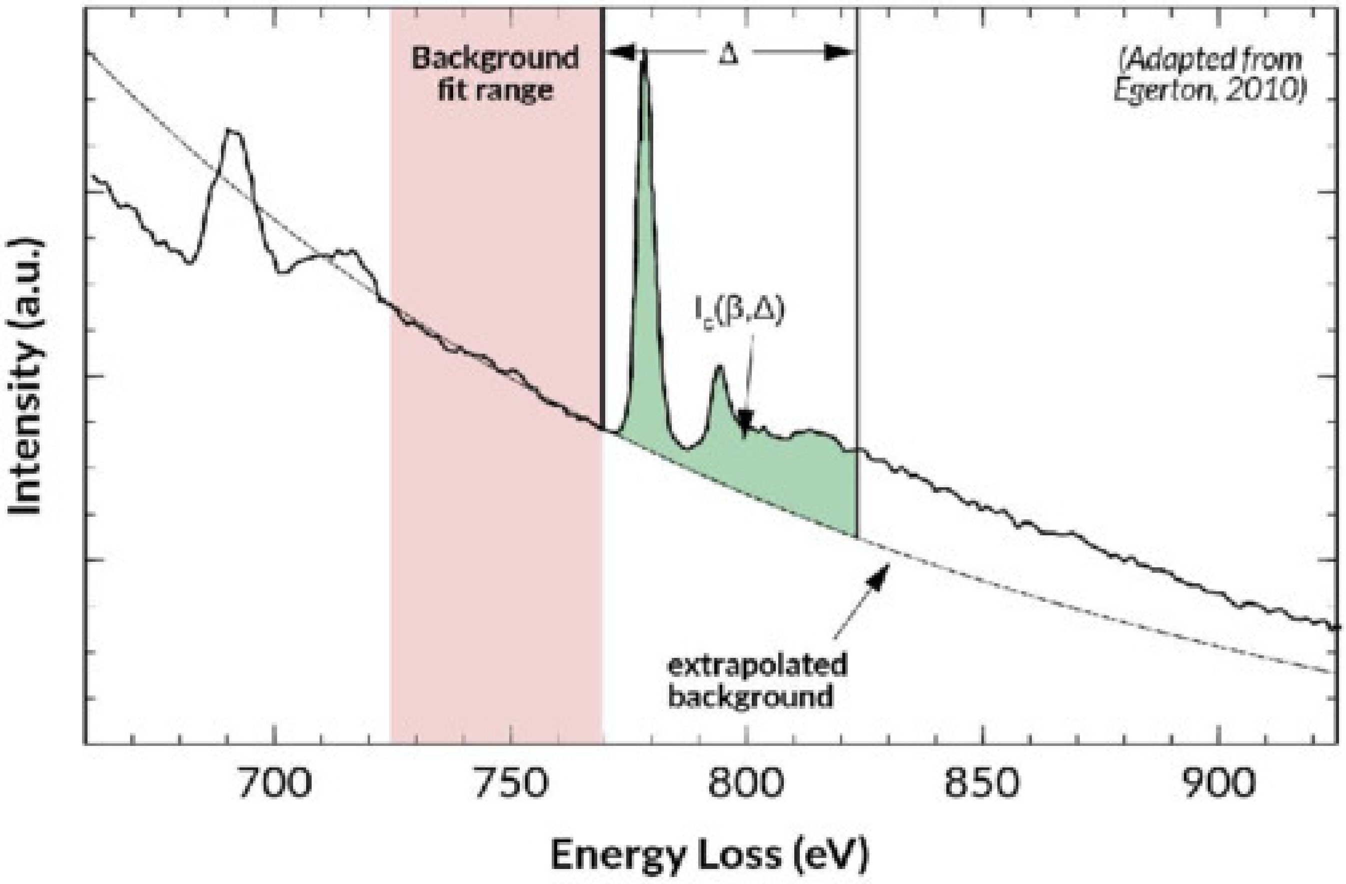
EELS core-loss edges

- **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.



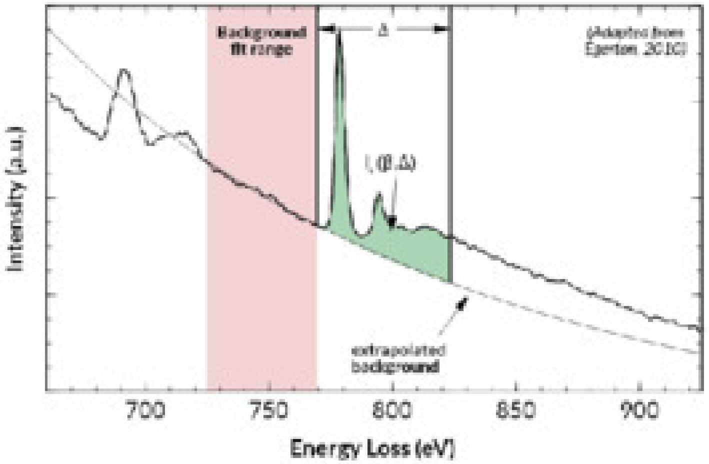
(Williams and Carter, 2009)

EELS composition quantification

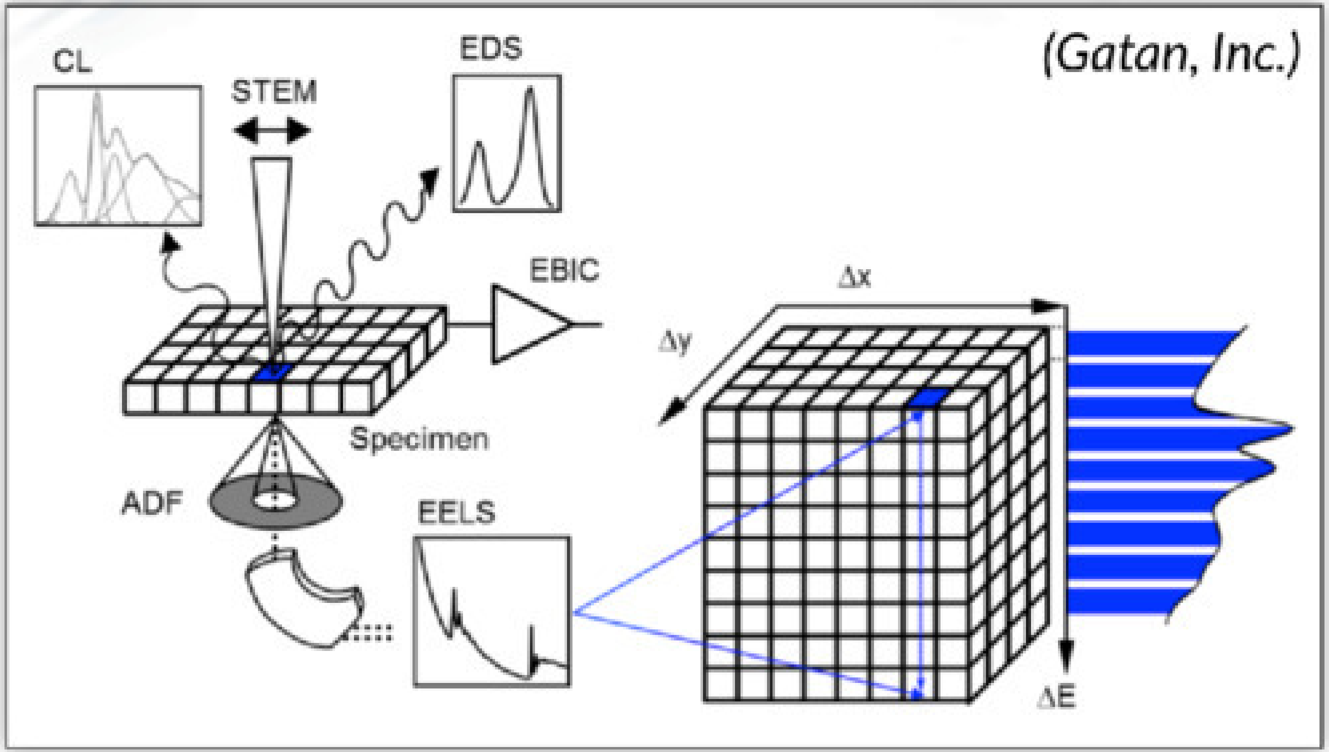


EELS composition quantification

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



Spectrum imaging



Three-dimensional data collection process

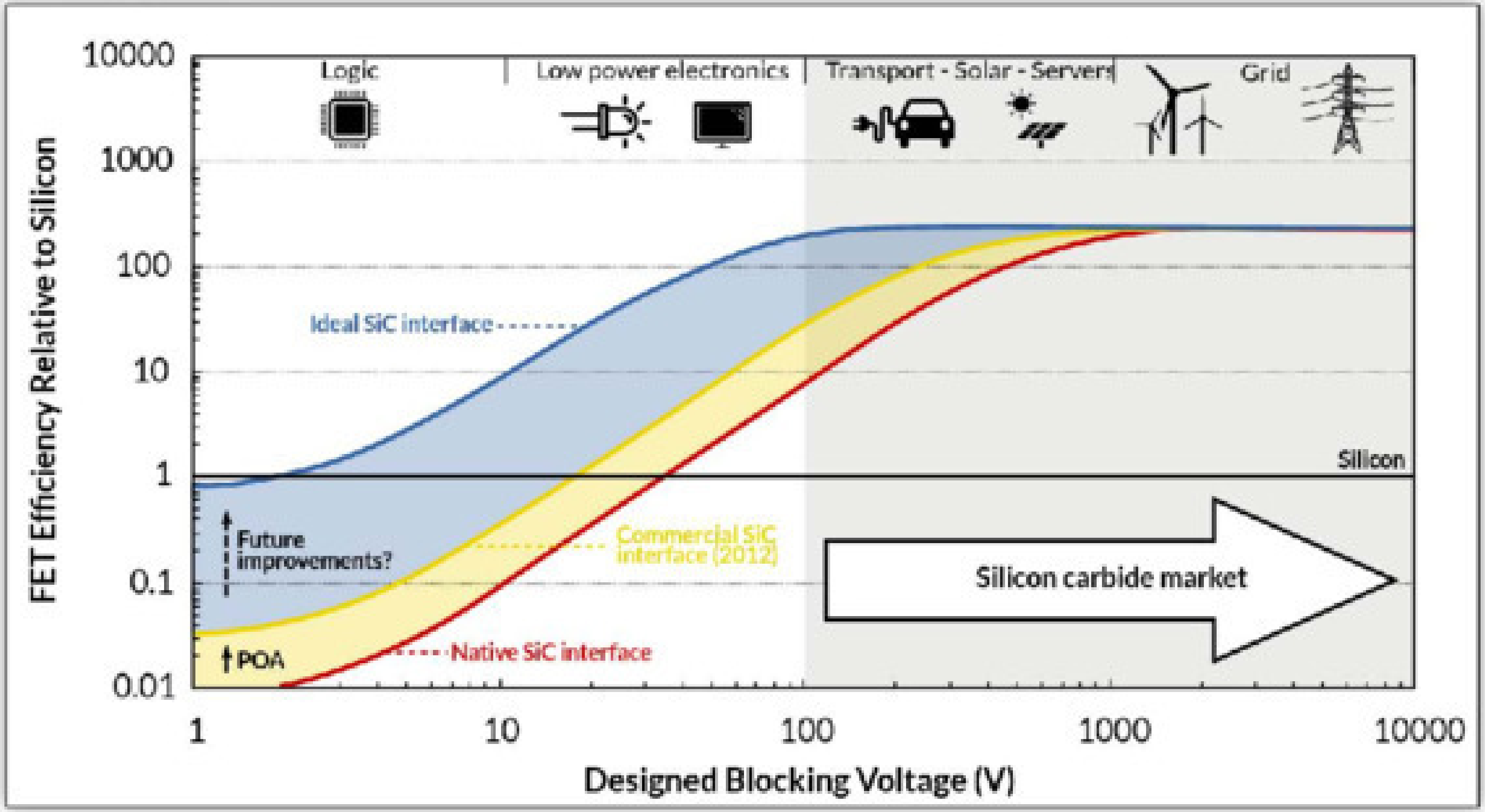
Some Real-world Examples

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_2
  - Lighter and more efficient than Si in high power

SiC promise


Logic
Low power electronics
Transport - Solar - Servers
Grid
FET Efficiency Relative to Silicon
10000
1000
100
10
1
0.1
0.01
Ideal SiC interface
Silicon
Future improvements?
Commercial SiC interface (2012)
Silicon carbide market
POA
Native SiC interface
1
10
100
1000
10000
Designed Blocking Voltage (V)

Why *Electron* Microscopy?

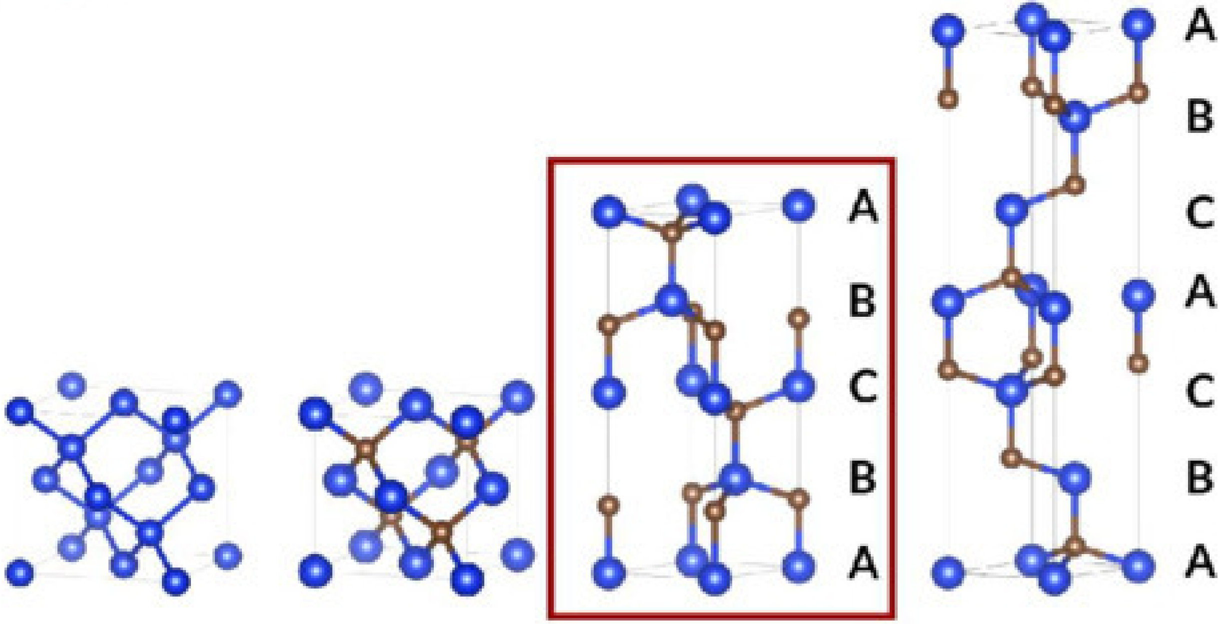
Dramatic resolution improvement compared to visible light (or x-rays)...

Rayleigh Criterion:

δ (resolution) $\approx 0.61\lambda$ (wavelength)

	Wavelength	Best Resolution
Visible Light	380 nm to 750 nm	≈ 200 nm*
X-rays	0.01 nm to 10 nm	≈ 20 nm
Electrons	0.002 nm to 0.004 nm	0.055 nm

SiC structure

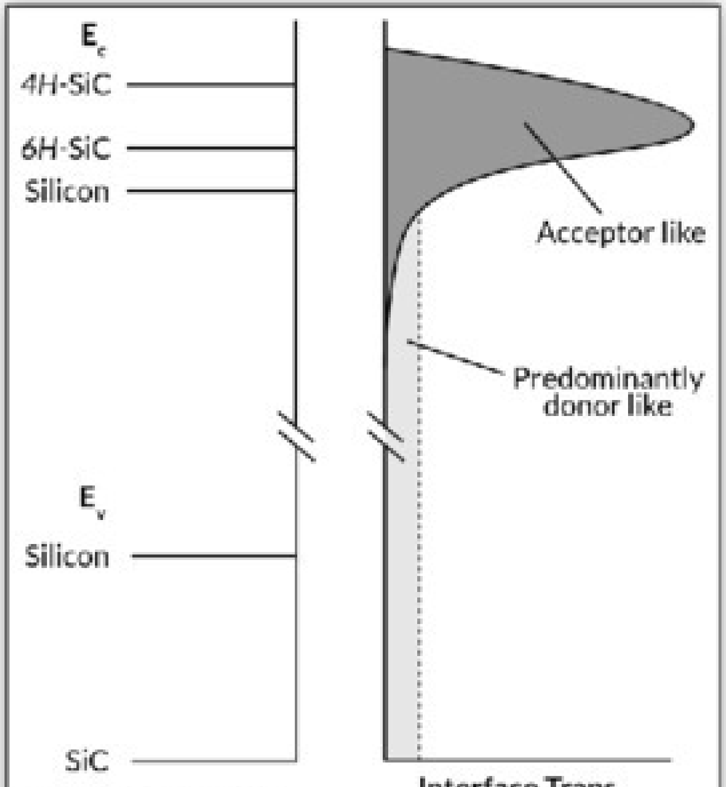


Silicon 3C-SiC 4H-SiC 6H-SiC

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

Issues facing SiC

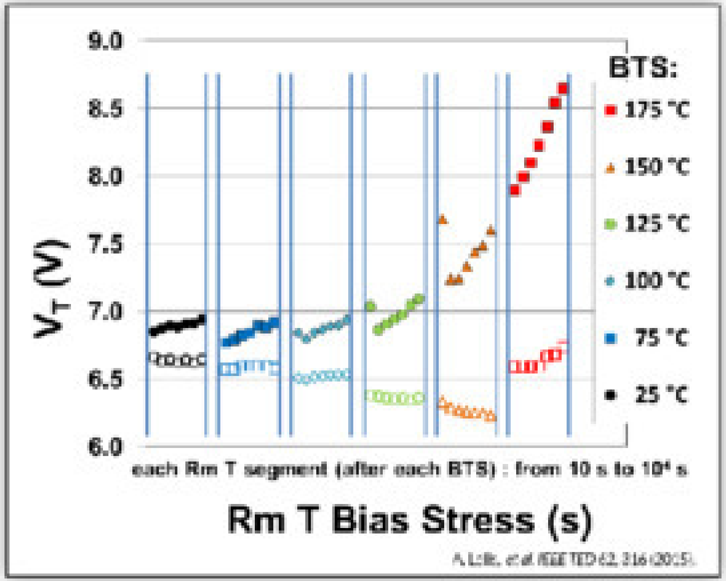
- **High wafer cost**
  - Orders of magnitude higher than Si
- **Low device mobility (μ_e)**
  - Interface traps within E_g of 4H-SiC limit mobility to about 1% of bulk value



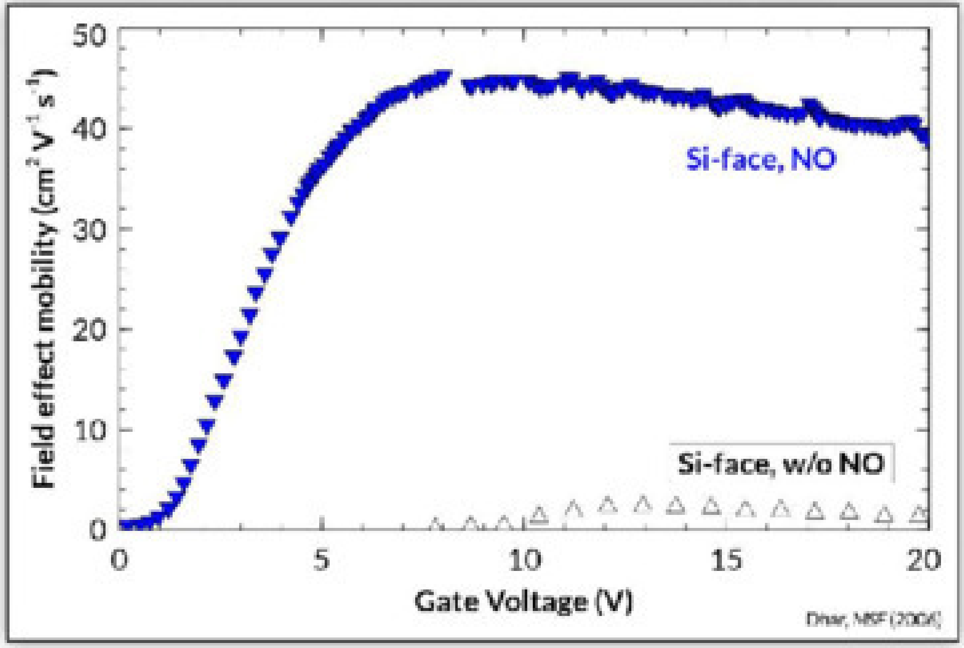
(Adapted from Schörner, 1999)

Issues facing SiC

- **High wafer cost**
  - Orders of magnitude higher than Si
- **Low device mobility (μ_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



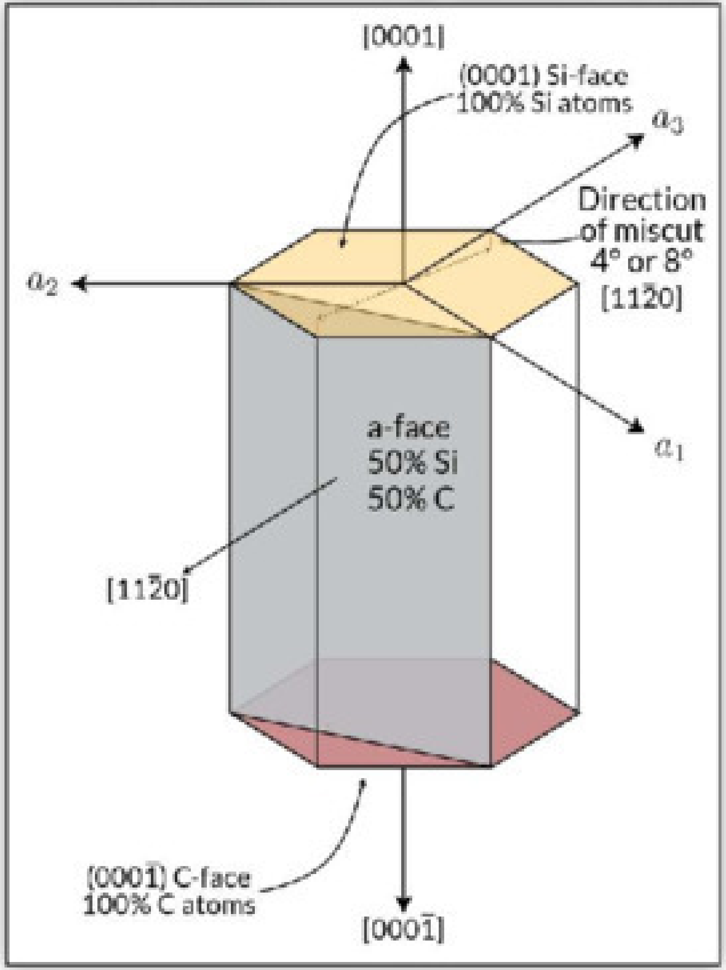
How to improve μ_e?



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

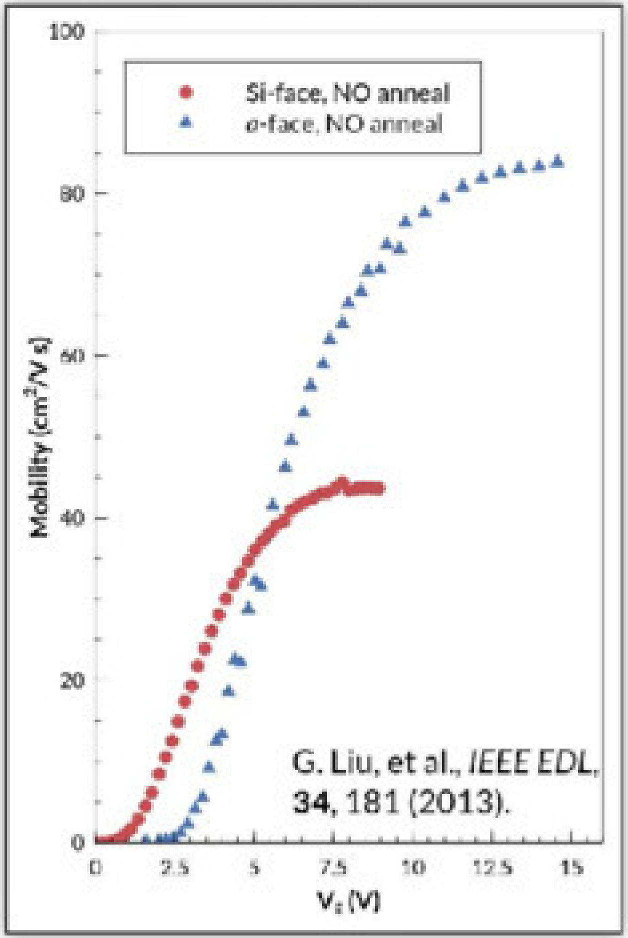
How to improve μ_e?

- **Change substrate orientation**
  - Relevant for trench MOSFET designs



How to improve μ_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



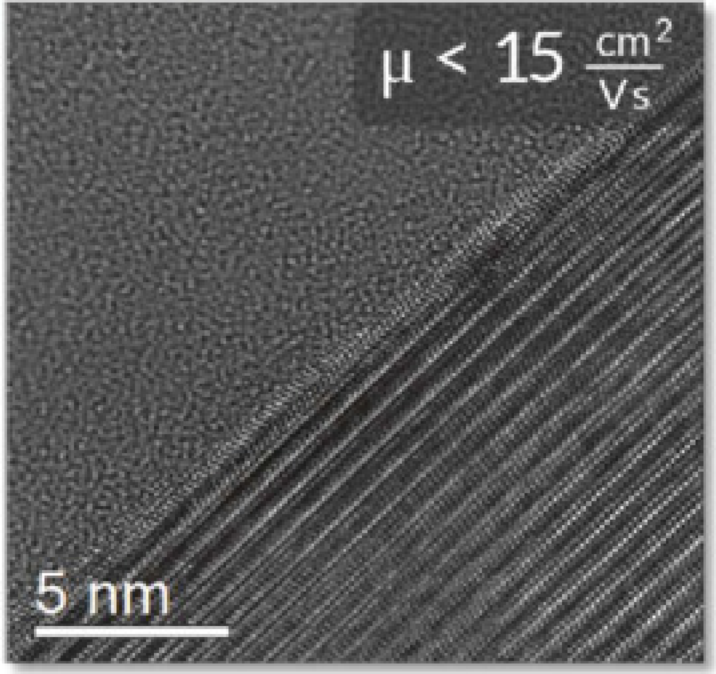
G. Liu, et al., *IEEE EDL*, **34**, 181 (2013).

Opportunities for TEM

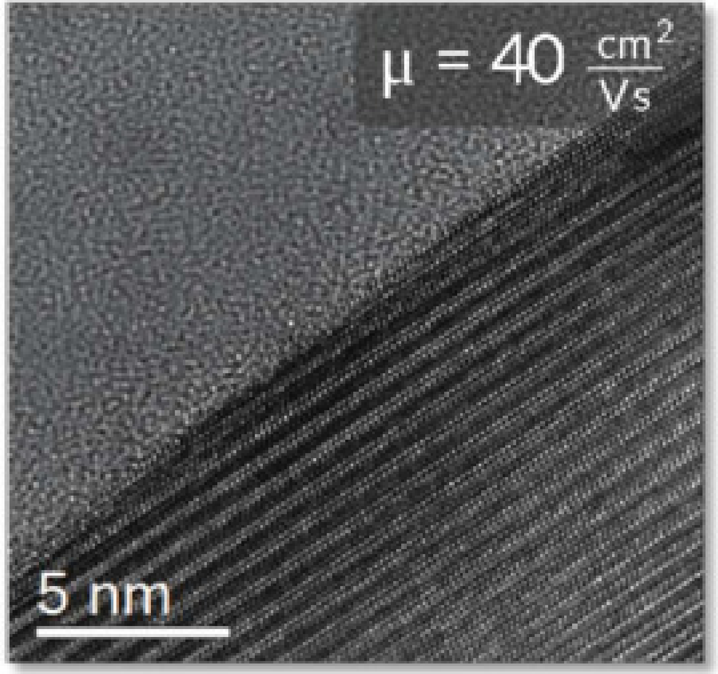
- **Structure and chemical states at the interface are unclear**
  - Nitrogen is there, but how is it incorporated?
  - Are there distinct chemical states (a "transition layer")?
- **Effects of processing conditions and device orientation**
  - Does NO-annealing work differently on different surfaces?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

Effect of NO-anneal time on interfacial width

Investigating transition layer



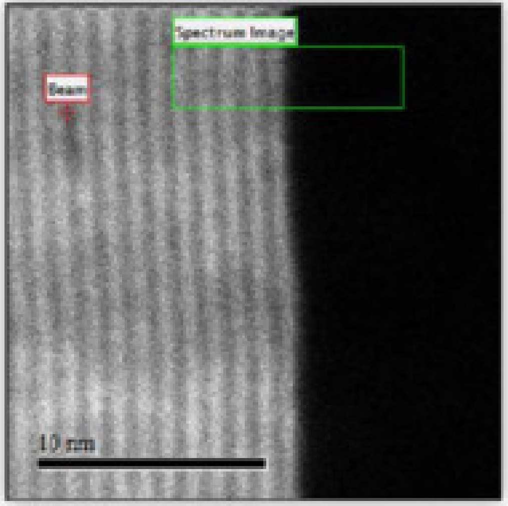
O_2 Oxidation



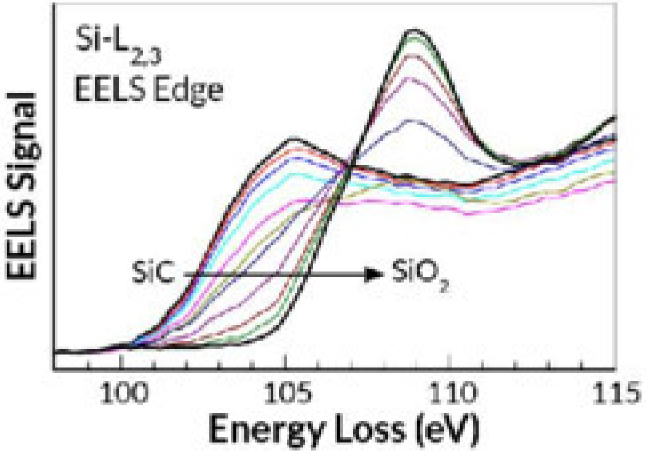
2hr NO POA

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

Interfacial characterization



HAADF-STEM

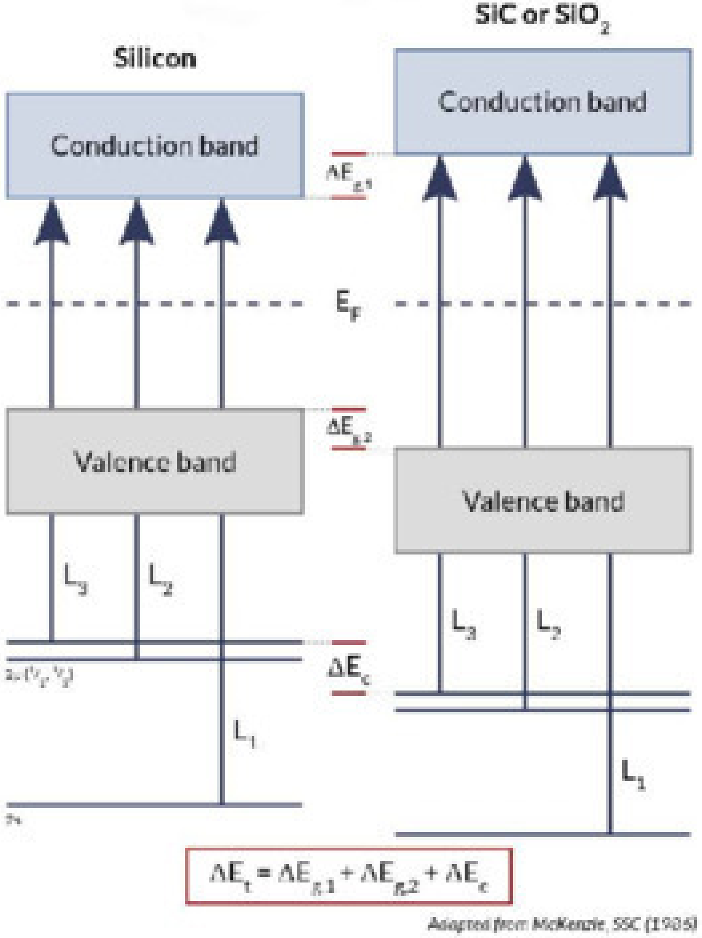


Si-$L_{2,3}$ edge at interface

Basics of Transmission Electron Microscopy

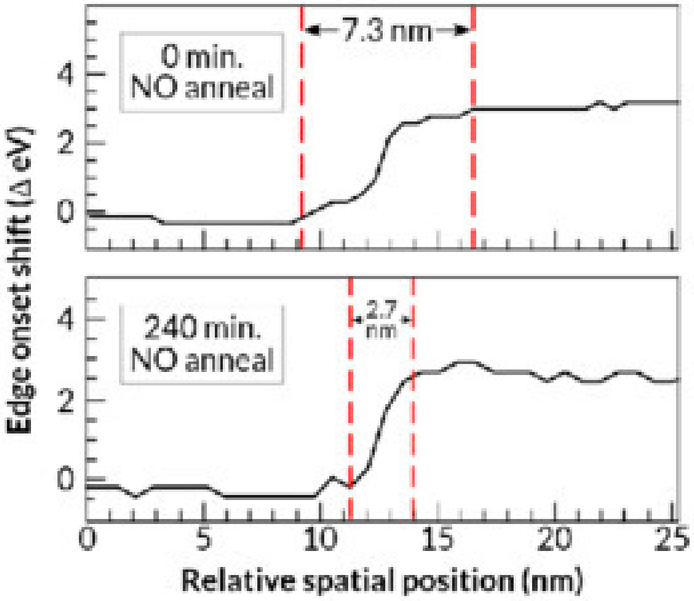
Core-level shifts

- **Between semiconductor and insulator, band diagram shifts**
  - Bandgap grows, core levels depressed
  - ΔE_t corresponds to observed EELS edge onset shift

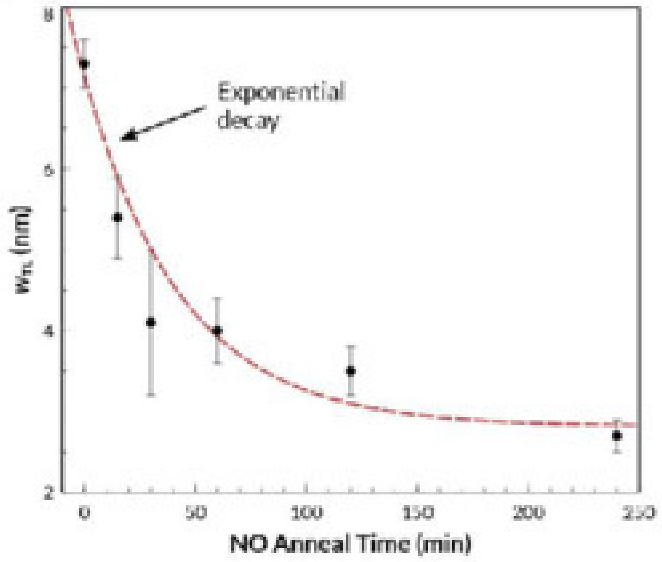


Interfacial characterization

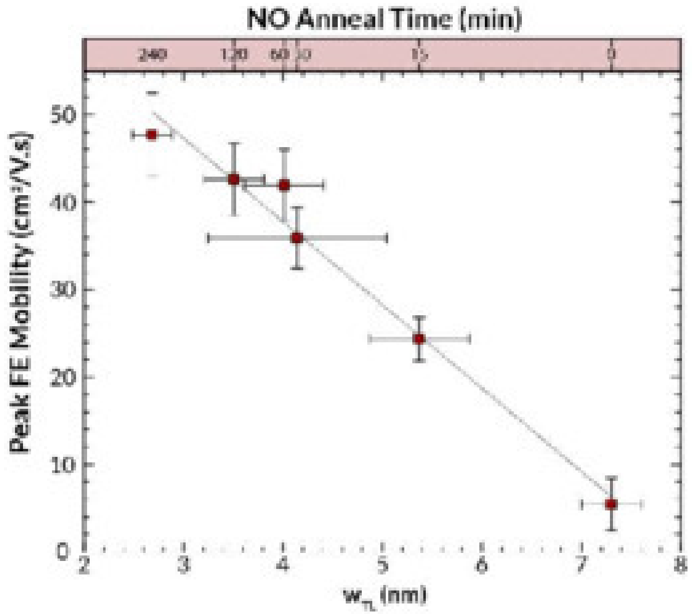
- **Change in onset energy of edge reflects change in bandgap (roughly)**
  - Probes bonding configuration of silicon atoms
  - Measure onset energy as function of NO-annealing time
  - Width of transition region defined as w_{TL}



NO time series results



w_{TL} decreases with NO anneal time

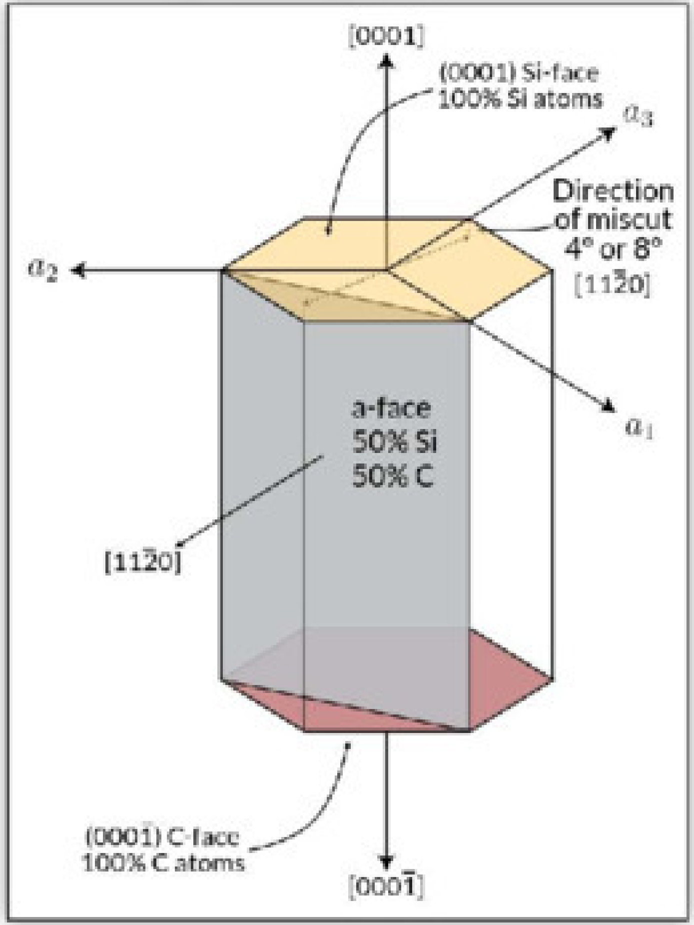


w_{TL} inversely related to μ_c

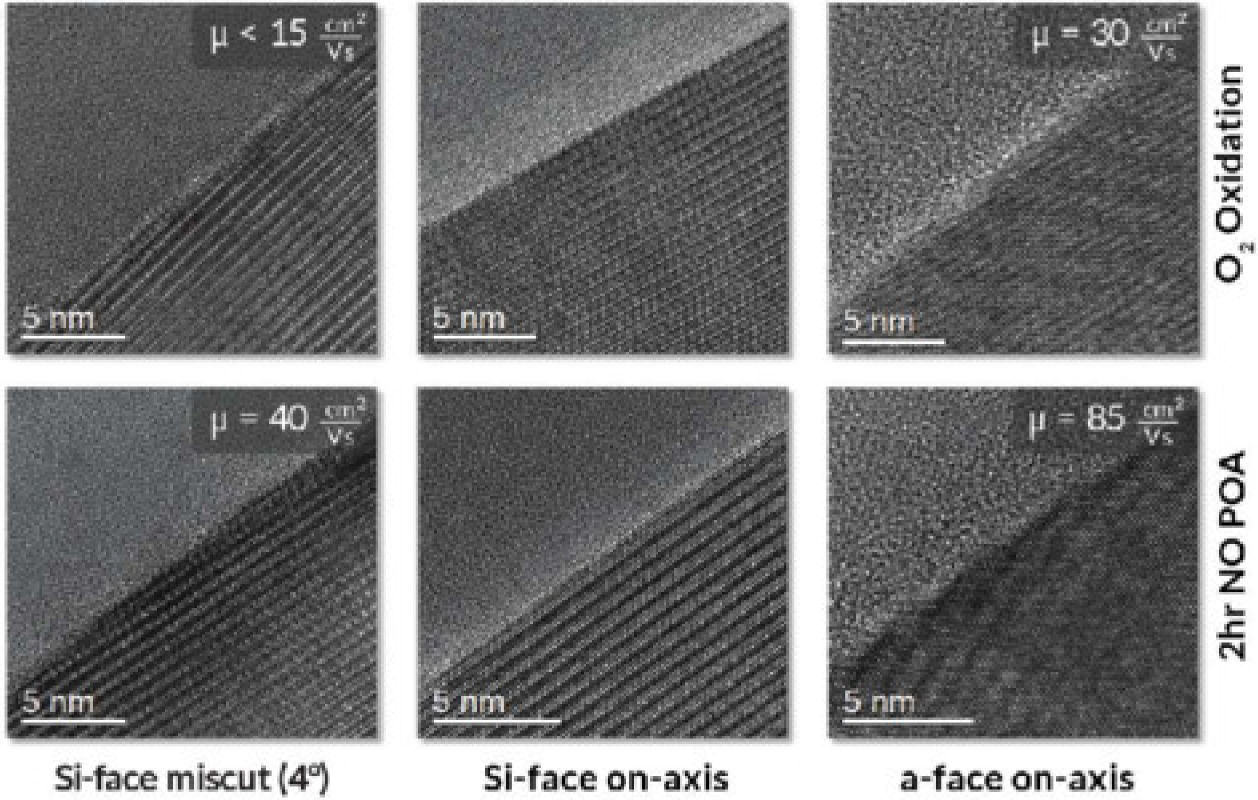
SiC substrate orientation effects

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

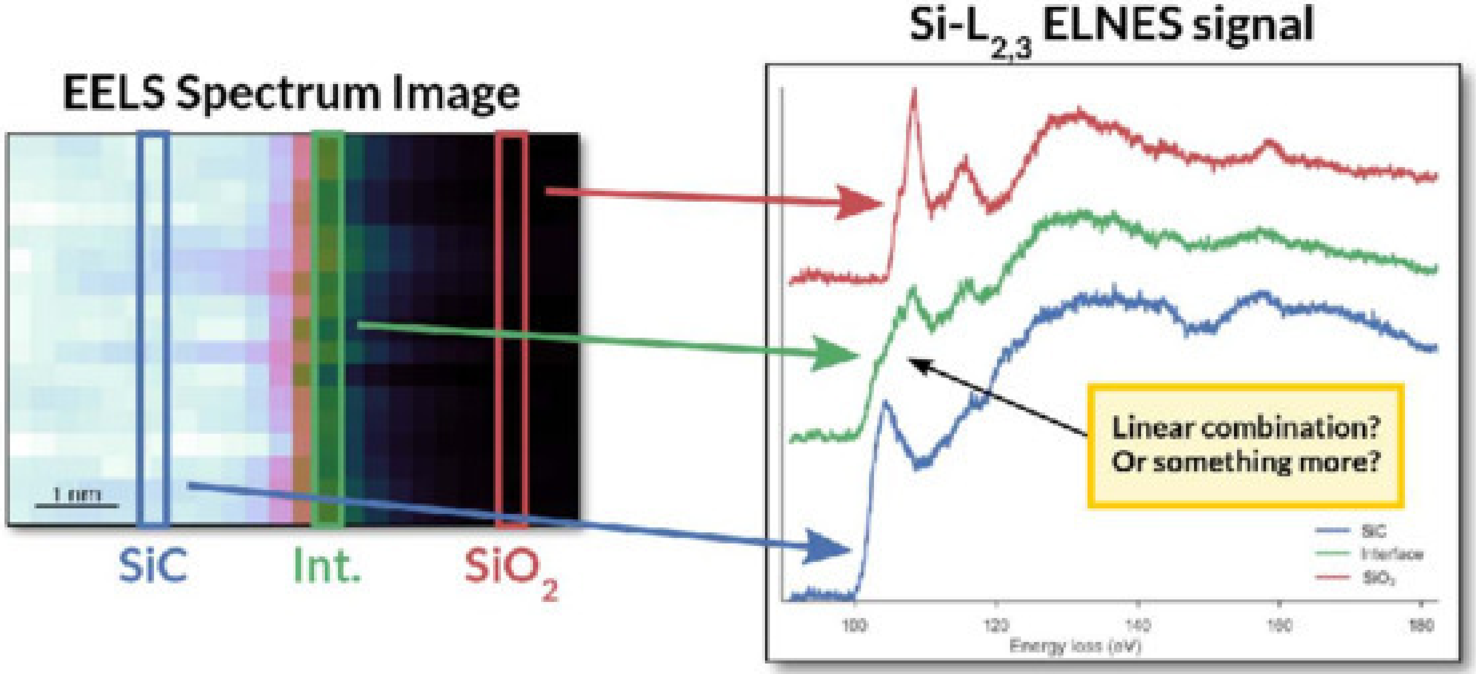


HRTEM results



- Like before, little structural evidence of interfacial states

EELS analysis



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

Hyperspectral decomposition

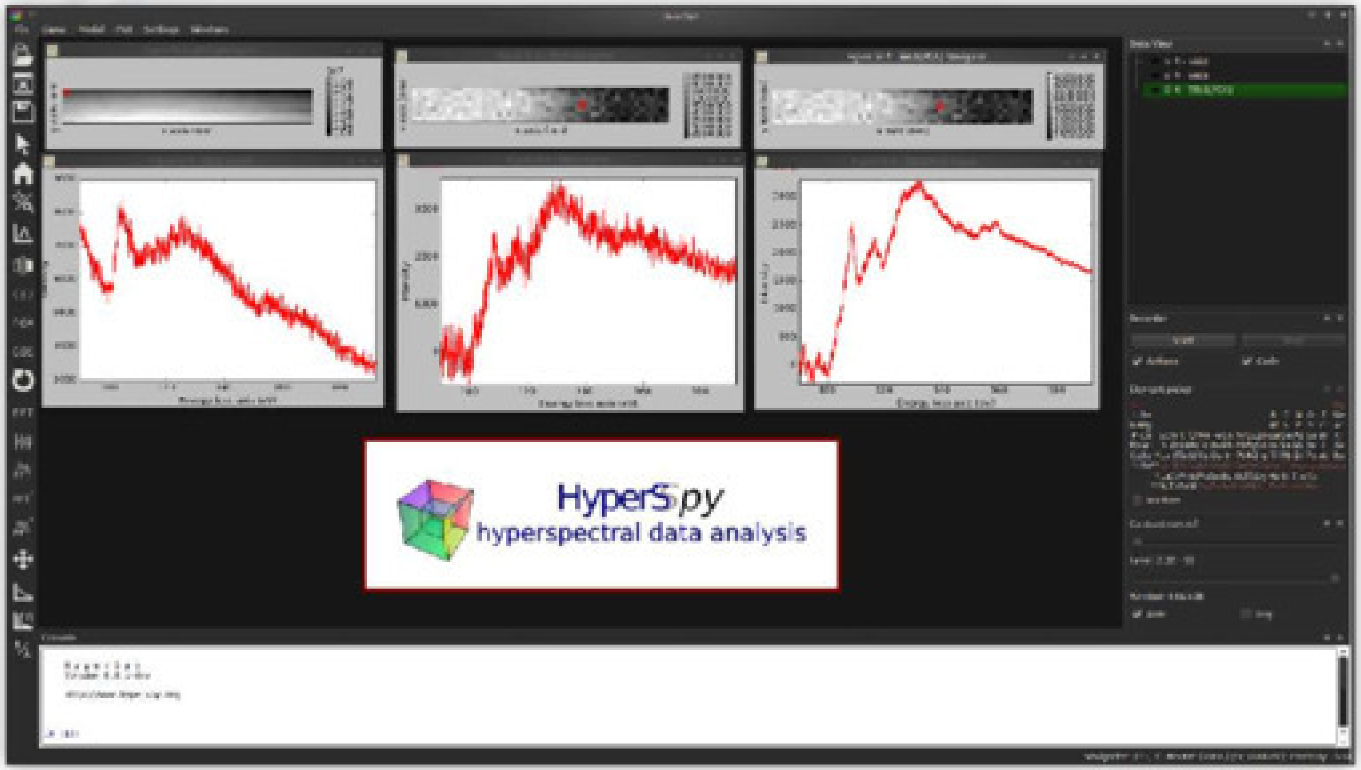
- **Technique to recover multiple unknown signals from a spectrum image**
- **Consider a spectrum image as a matrix, and use matrix decomposition:**

$$\text{Data} = \text{Scores} \times \text{Loadings}$$

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

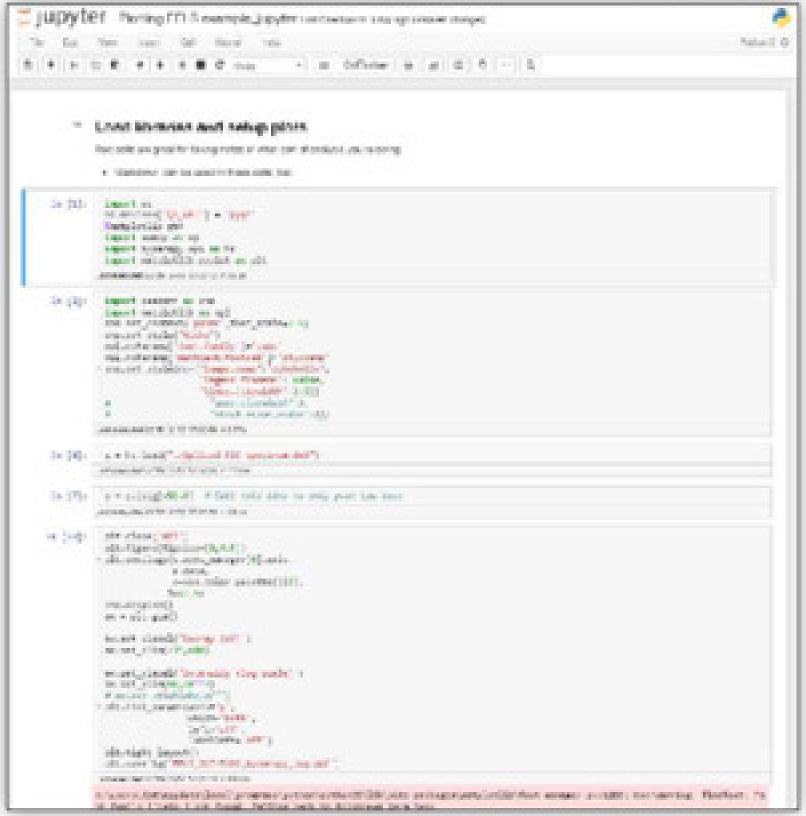
- **Any decomposition strategy can be used**
  - Non-negative Matrix Factorization (NMF) suitable for EELS data
  - Unbiased; unsupervised; only assumption is positivity of data

Hyperspectral software tool



- [HyperSpy](#): **Open-source hyperspectral data analysis tool**
  - Easy access to PCA, ICA, NMF, and signal modeling

Hyperspectral software tool

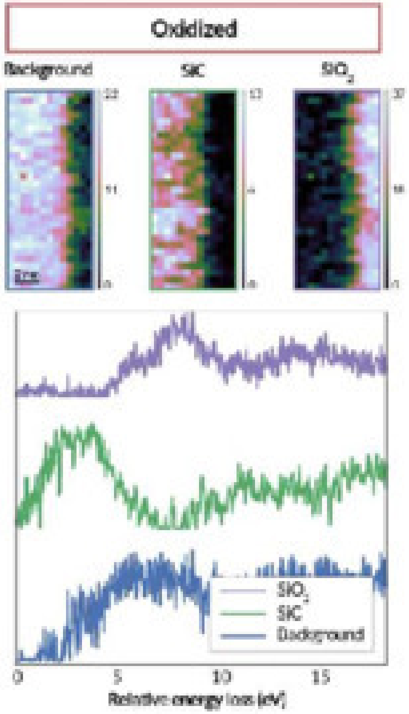


- **[HyperSpy](#): Open-source hyperspectral data analysis tool**
  - Can be used in Jupyter notebook for complete reproducibility

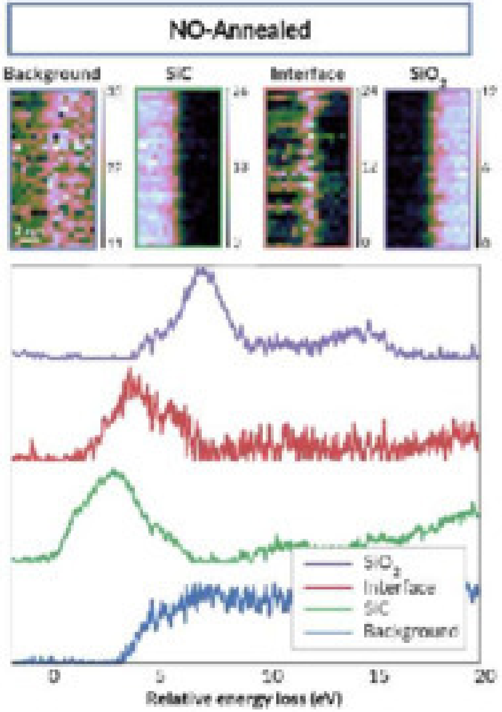
Brief history of TEM

- **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

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



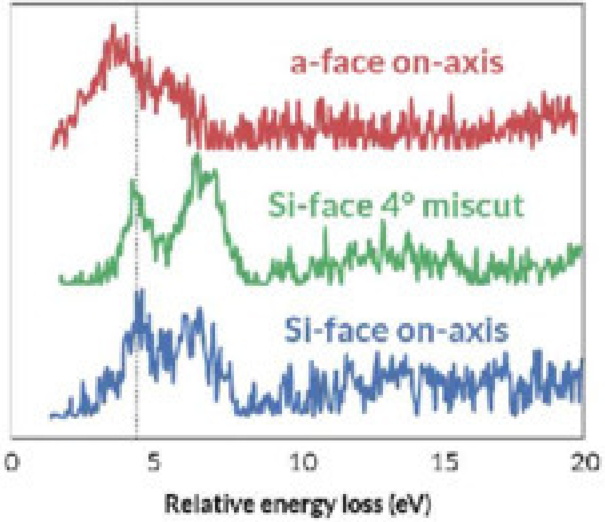
a-face on-axis



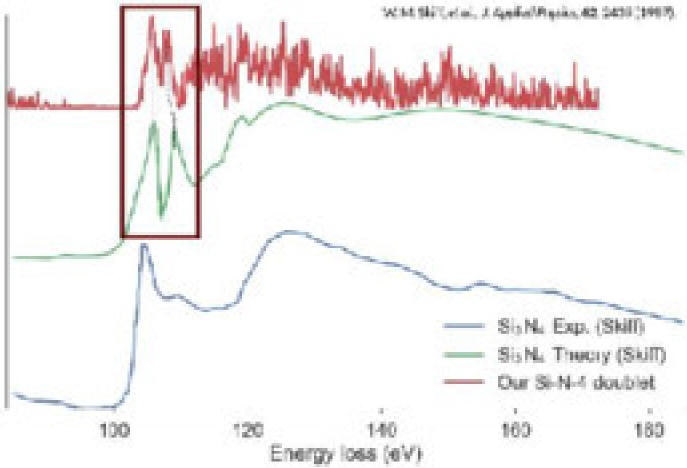
a-face on-axis

- **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 Si_3N_4

Analysis of Si-$L_{2,3}$ signal

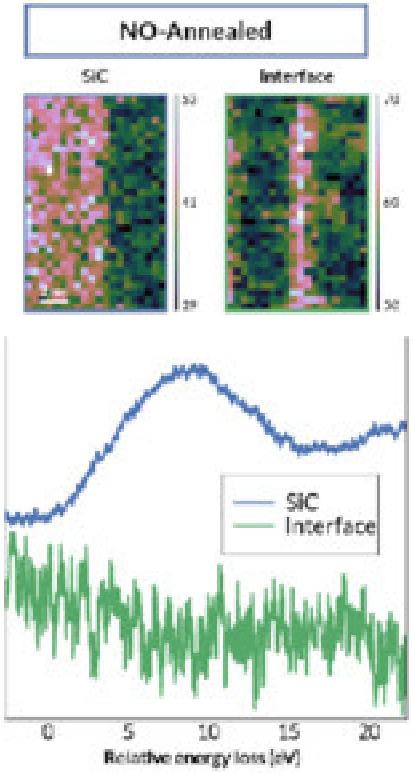


Effect of substrate orientation



Comparison to Si_3N_4 literature

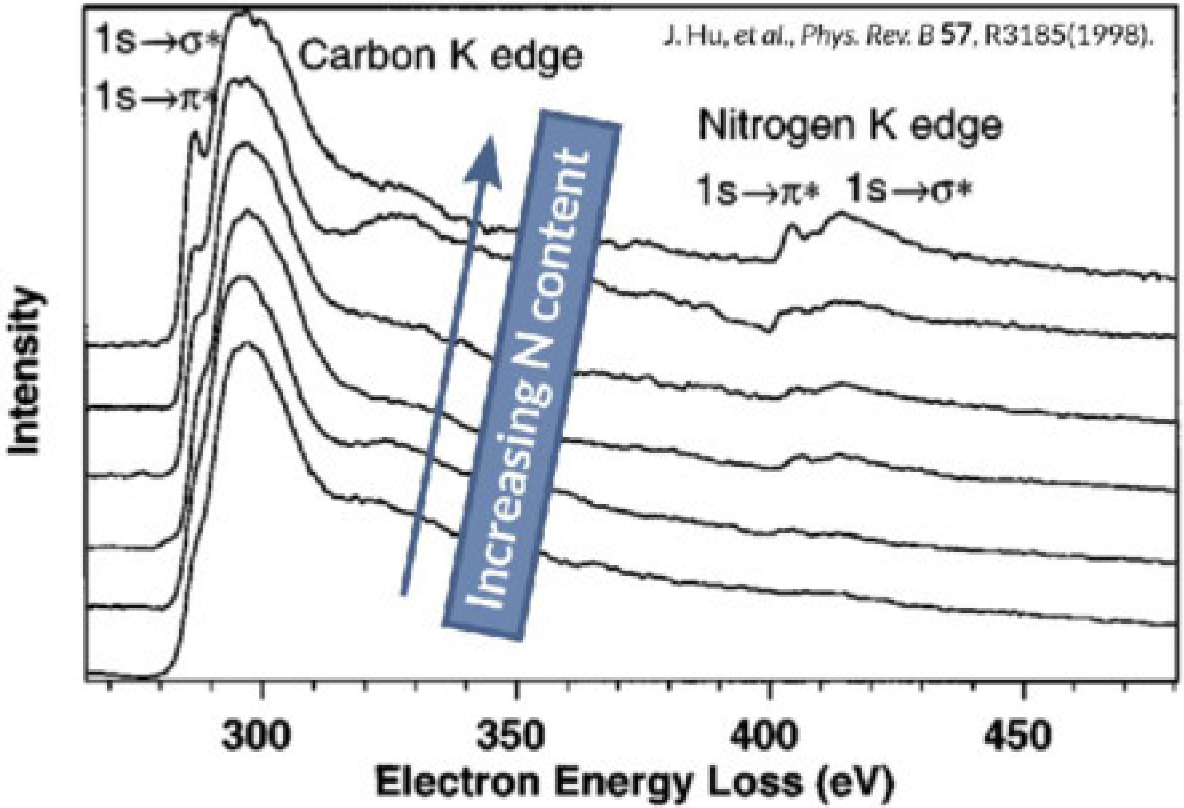
Decomposing C-K signal



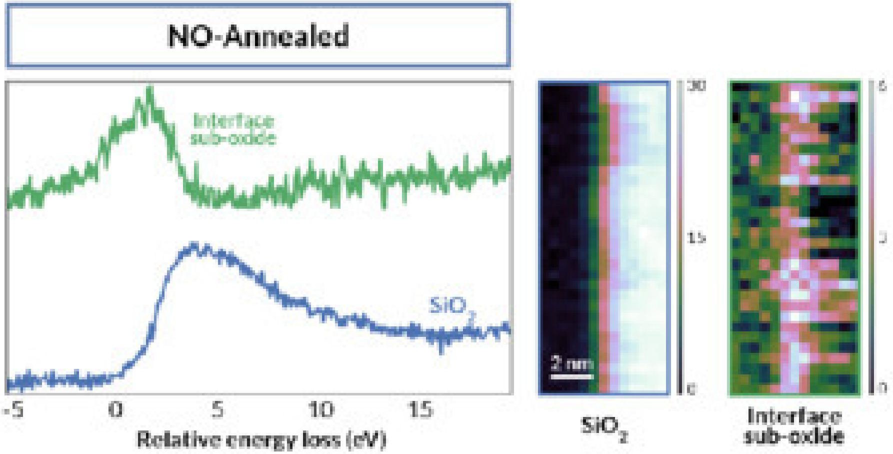
a-face on-axis

- **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-$L_{2,3}$ results
- **Interfacial state has pre-edge intensity**
  - Indicative of sp^2-like bonding
  - Influence of nitrogen is apparent

Analysis of C-K signal



Decomposing O-K signal



- Only sample with interface is a-face NO
- Interface has edge onset 2 eV to 3 eV below SiO_2
  - Reduced bandgap
  - Increased dielectric constant
  - Enhanced mobility
- Only clue as to enhanced mobility on the a-face
  - Silicon/carbon oxynitride configuration

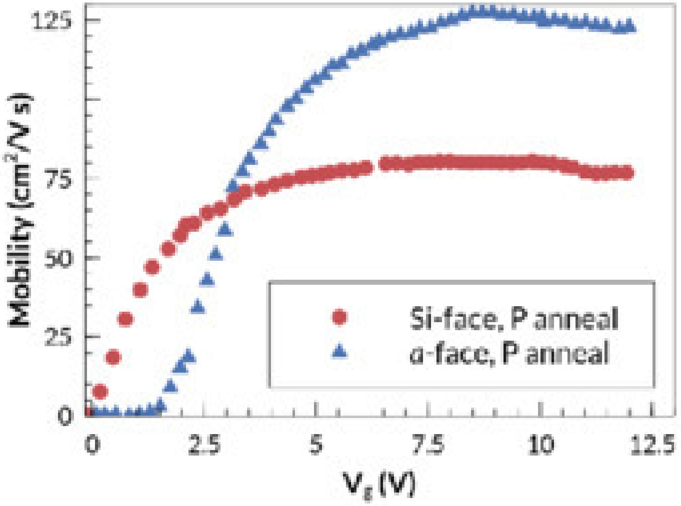
Orientation effects summary

- **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

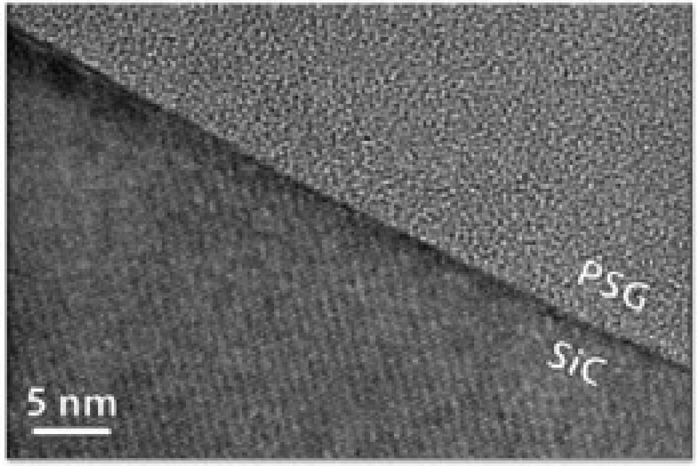
Motivation

- "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?

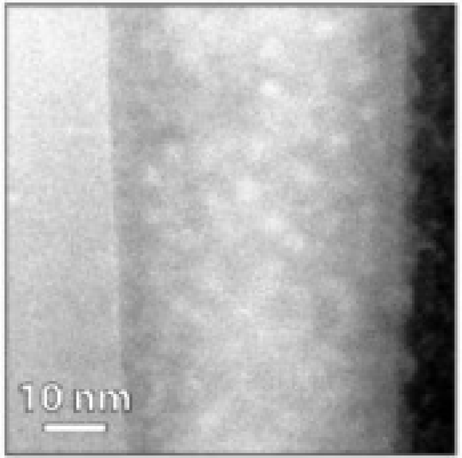


High μ in P-annealed devices
(G. Liu, 2013)

Phosphorus imaging results

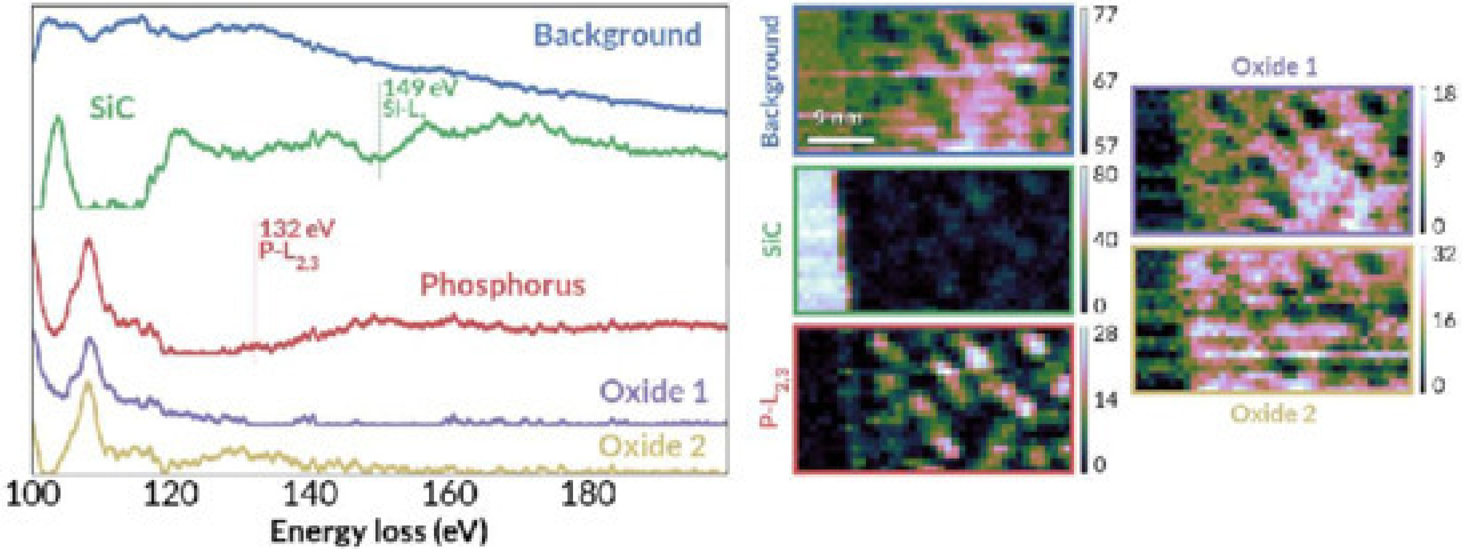


HRTEM of P-annealed interface



HAADF-STEM of same interface

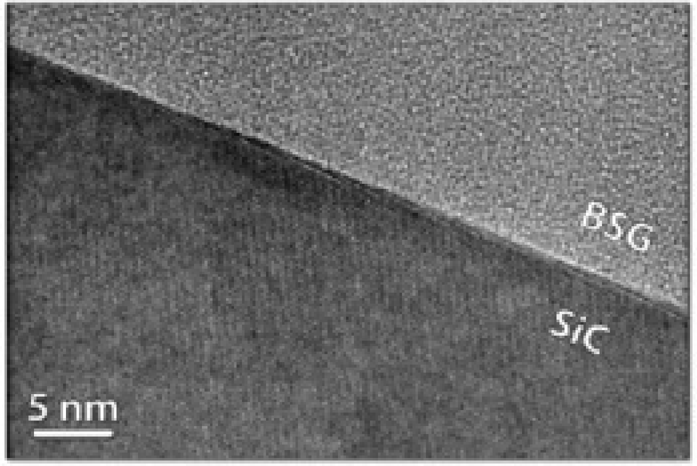
Phosphorus EELS results



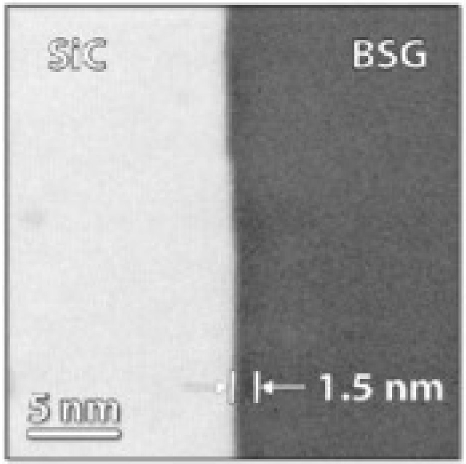
Bright spots in HAADF-STEM image correspond to P-rich clusters

Brief introduction to TEM

Boron imaging results

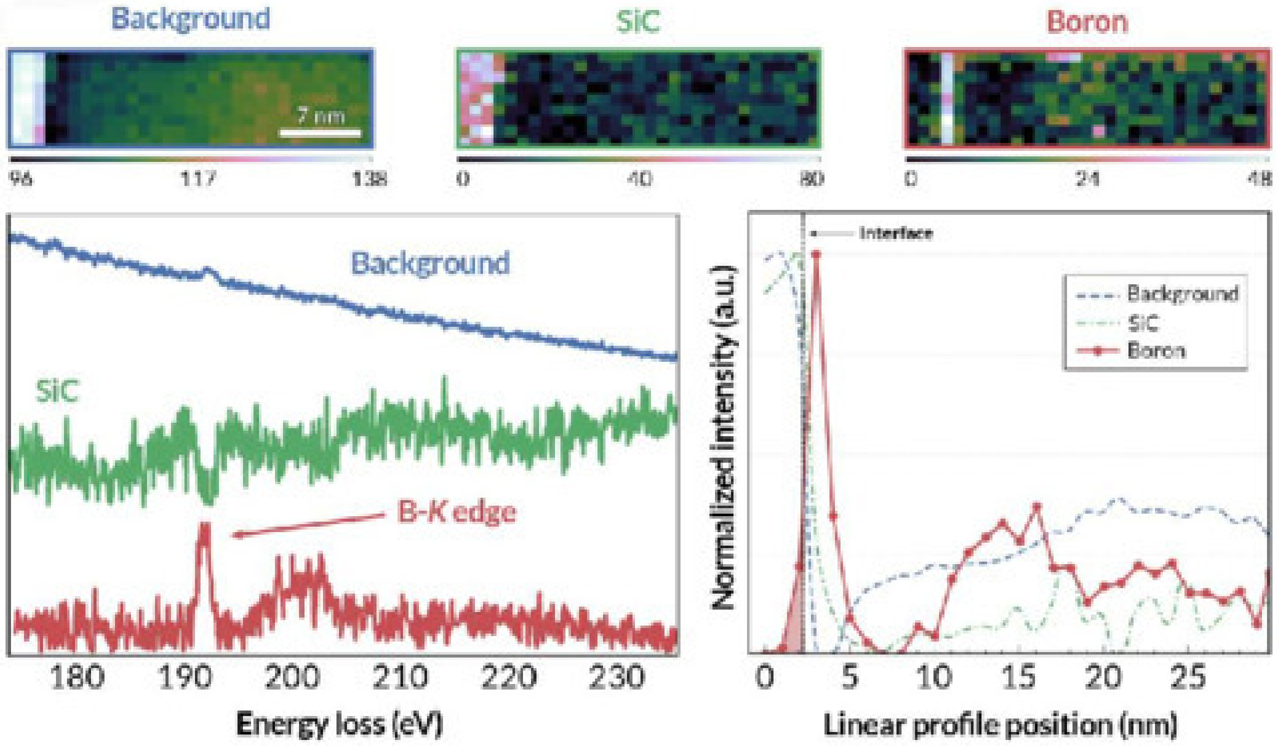


HRTEM of B-annealed interface



HAADF-STEM of same interface

Boron EELS results



Boron accumulates at interface, but some distributed throughout oxide

"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

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)

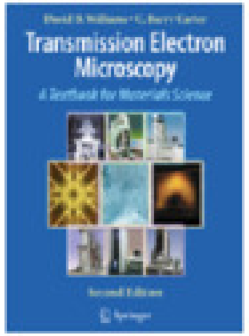
Summary

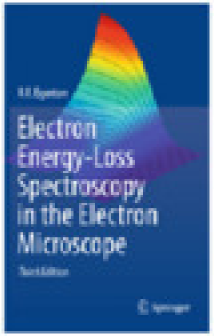
- **TEM is a powerful and versatile technique for materials analysis**
  - Conventional, scanning, and high-angle imaging
  - Sample preparation using FIB/SEM
  - Analytical strategies (EELS)
- **Data analysis methods:**
  - Machine learning tools enable new avenues of inquiry

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

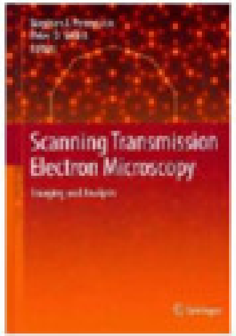
More reading (1):

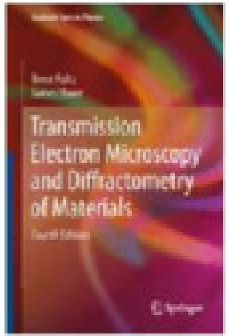


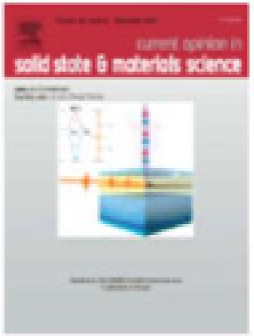


- *Transmission Electron Microscopy: A Textbook for Materials Science*, David Williams and Barry Carter (2009) - link
- *Electron Energy-Loss Spectroscopy in the Electron Microscope*, Ray Egerton (2011) - link
- *Introduction to Focused Ion Beams*, Lucille Giannuzzi (2005) - link

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

Acknowledgments

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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

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  - Aivars Lelis - ARL
  - Eric Wachsman - UMD

Thank you

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References

- D. Williams and C. Carter, Transmission Electron Microscopy, 2nd ed. New York, NY: Springer Science, 2009.
- FEI Company, https://www.fei.com/image-gallery/logic-device2011/.
- T. Hoshino & S. Matsui, 47th International Conference on Electron, Ion and Photon Beam Technology and Nanofabrication (2003).
- J. Rozen, "Energy efficiency in high power electronics: role and challenges of silicon carbide interface," in Human Photonics International Forum, Saitama University, 2012.
- R. Schörner, P. Friedrichs, D. Peters, and D. Stephani, "Significantly improved performance of MOSFETs on silicon carbide using the 15R-SiC polytype," IEEE Electron Device Letters, vol. 20, no. 5, pp. 241–244, May 1999.
- A. J. Lelis, R. Green, D. B. Habersat, and M. El, "Basic mechanisms of threshold-voltage instability and implications for reliability testing of SiC MOSFETs," IEEE Transactions on Electron Devices, vol. 62, no. 2, pp. 316–323, Feb. 2015.
- S. Dhar, S. Wang, A. Ahyi, T. Isaacs-Smith, S. T. Pantelides, J. R. Williams, and L. C. Feldman, "Nitrogen and hydrogen induced trap passivation at the SiO2/4H-SiC interface," Materials Science Forum, vol. 527-529, pp. 949-954, 2006.
- T. S. Zheleva, A. J. Lelis, G. Duscher, F. Liu, I. Levin, and M. K. Das, "Transition layers at the SiO2 /SiC interface," Applied Physics Letters, vol. 93, no. 2, p. 022 108, 2008.
- P. Liu, G. Li, G. Duscher, Y. Sharma, A. C. Ahyi, T. Isaacs-Smith, J. R. Williams, and S.Dhar, "Roughness of the SiC/SiO2 vicinal interface and atomic structure of the transition layers", Journal of Vacuum Science and Technology A, 32, 060603 (2014).
- Y. Xu, X. Zhu, H. D. Lee, C. Xu, S. M. Shubeita, A. C. Ahyi, Y. Sharma, J. R. Williams, W. Lu, S. Ceesay, B. R. Tuttle, A. Wan, S. T. Pantelides, T. Gustafsson, E. L. Garfunkel, and L. C. Feldman, "Atomic state and characterization of nitrogen at the SiC/SiO2 interface," Journal of Applied Physics, vol. 115, no. 3, p. 033 502, Jan. 2014.
- L. I. Johansson, C. Virojanadara, T. Eickhof, and W. Drube, "Properties of the SiO2/SiC interface investigated by angle resolved studies of the Si 2p and Si 1s levels and the Si KLL Auger transitions," Surface Science, vol. 529, no. 3, pp. 515–526, 2003.
- H. Watanabe, T. Hosoi, T. Kirino, Y. Kagei, Y. Uenishi, A. Chanthaphan, A. Yoshigoe, Y. Teraoka, and T. Shimura, "Synchrotron x-ray photoelectron spectroscopy study on thermally grown SiO2/4H-SiC(0001) interface and its correlation with electrical properties," Applied Physics Letters, vol. 99, no. 2, p. 021 907, 2011.
- G. Liu, A. C. Ahyi, Y. Xu, T. Isaacs-Smith, Y. K. Sharma, J. R. Williams, L. C. Feldman, and S. Dhar, "Enhanced inversion mobility on 4H-SiC (11-20) using phosphorus and nitrogen interface passivation," IEEE Electron Device Letters, vol. 34, no. 2, pp. 181–183, Feb. 2013.
- S. Dhar, "Nitrogen and hydrogen induced trap passivation at the SiO2/4H-SiC interface," PhD thesis, Vanderbilt University, 2005, p. 147.
- W. M. Skiff, R. W. Carpenter, and S. H. Lin, "Near-edge fine-structure analysis of core-shell electronic absorption edges in silicon and its refractory compounds with the use of electron-energy-loss microspectroscopy," Journal of Applied Physics, vol. 62, no. 1987, pp. 2439–2449, 1987.