CHARACTERIZATION OF THE OXIDE-SEMICONDUCTOR INTERFACE IN 4H-SiC/SiO₂ STRUCTURES USING TEM AND XPS*

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Outline

- Motivation behind analytical microscopy of SiC microelectronics
  - Impacts of NO post-annealing

- TEM-EELS from a collection of SiC/SiO₂ interfaces
  - Previous findings related to the transition layer
  - HRTEM, hyperspectral imaging, machine learning techniques for signal deconvolution
  - Significant changes in interface character after NO-anneal

- Correlation with XPS results
  - What differences are observed with an NO-anneal?

- Conclusions: What’s next?
Motivation and background

• SiC: Very promising for high temperature, high power, and high radiation environments
  • Limited by poor channel carrier mobility and reliability
  • Typical device $\mu_{FE}$: 4H-SiC before NO anneal: $< 10 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1}$; after NO anneal: $\sim 45 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1}$; bulk value: $\sim 1,000 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1}$
  • Electrically active defects at the SiC/SiO$_2$ interface inhibit devices during channel inversion
  • Other defects significantly affect the reliability and stability of devices over time

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

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TEM-EELS EXPERIMENTS
EELS Spectrum Imaging

One spectrum per line

SiC

SiO$_2$

Si-L$_{2,3}$

HAADF Survey Image

Spectrum Image Lines
Si-$L_{2,3}$ chemical shift

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

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1 D. Muller, Ultramicroscopy 78, 163 (1999).
Si-$L_{2,3}$ chemical shift – measuring $\nu_{\text{TL}}$

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

NO-anneal results (previous results)

- $w_{TL}$ correlates inverse-linearly $\mu_{FE}$

- NO-anneal removes/passivates mobility-limiting defects
  - Compositionally and electronically

**Conclusions:**
- $w_{TL}$ decreases with increasing NO anneal time
  - New chemical shift of Si-$L_{2,3}$ edge onset was most reliable method
  - No excess C on either side of interface

Samples investigated – TEM/EELS

- 2 x 3 matrix aimed at comparing substrate orientation (and miscut) with processing conditions:
  - NO POA is for 2hr, all SiC substrates are n-type, SiO$_2$~60 nm thick

<table>
<thead>
<tr>
<th>Sample Labels</th>
<th>Only oxidized</th>
<th>NO Post-annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-face on-axis</td>
<td>Si-O$_2$-0</td>
<td>Si-N-0</td>
</tr>
<tr>
<td>Si-face miscut (4°)</td>
<td>Si-O$_2$-4</td>
<td>Si-N-4</td>
</tr>
<tr>
<td>a-face on-axis</td>
<td>a-O$_2$-0</td>
<td>a-N-0</td>
</tr>
</tbody>
</table>
HRTEM of Si-face and α-face with and without NO annealing

Without NO-anneal

Si-face

Miscut = 4°

Si-face

Miscut = 4°

Si-face

Miscut = 0°

With 2hr NO-anneal

Si-face

Miscut = 4°

Si-face

Miscut = 0°

α-face

Miscut = 0°
$w_{TL}$ measurements

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

Hyperspectral signal decomposition – machine learning

- Si-$L_{2,3}$
- Low-loss EELS
- Phosphosilicate glass samples
HyperSpy for analytical microscopy

- Open source
  hyperspectral analysis package for Python
  - GUI and/or web notebook (traceability!)

- Data-agnostic, but...
  - Specialized routines for EDS and EELS

- Easy access to PCA, ICA, and signal modeling

http://hyperspy.org

DOI: 10.5281/zenodo.16850
Decomposition analysis

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

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

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

Example applied to Olivetti faces

What features are found most often in the training set?
Decomposition of Si-$L_{2,3}$
Interface components at NO-annealed interfaces

- Simple sum improves S/N, but cannot detect faint or overlapping signals
Interface components at NO-annealed interfaces

- Signal decomposition (NMF) is much more powerful
- Significant detection of unique orthogonal component at interface
- New component that is distinct from SiO$_2$ and SiC was observed
- Non-linear combination of signals!
Interface components at NO-annealed interfaces

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- Non-linear combination of signals!

Component average width: 
“$w_{TL}$” = $1.97 \pm 0.25$nm

Measured from chem. shift: 
$w_{TL} = 2.11 \pm 0.11$nm

Good agreement!
Decomposed Si-L$_{2,3}$ comparison of interface components

<table>
<thead>
<tr>
<th>Face / Treatment</th>
<th>O$_2$ oxidation</th>
<th>O$_2$ oxidation + NO POA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-face 4° miscut (Si-X-4)</td>
<td><img src="image1" alt="Graph" /></td>
<td><img src="image2" alt="Graph" /></td>
</tr>
<tr>
<td>Si-face no miscut (Si-X-0)</td>
<td><img src="image3" alt="Graph" /></td>
<td><img src="image4" alt="Graph" /></td>
</tr>
<tr>
<td>a-face no miscut (a-X-0)</td>
<td><img src="image5" alt="Graph" /></td>
<td><img src="image6" alt="Graph" /></td>
</tr>
</tbody>
</table>
What does it mean?

- Si₃N₄ theory and experiment (Skiff et al.)
  - Calculated ΔE between doublet peaks 3.4 eV compared to our 2.08 eV
- Not SiO₂ or SiC
  - Those were also identified, and peak positions do not match
- Effect of N-bonding
  - Si-C-N-O bonding configurations?
  - Likely that this is evidence of N-bonding at interface
  - DFT modeling will reveal further details

Decomposition of Low-loss EELS signal
Low-loss EELS

• Reveals information originating from inelastic scattering by outer shell electrons
  • Plasmon interactions
    • (Collective oscillations of electrons within the sample: bulk, surface, interface, etc.)
  • Energy related to valence e\(^{-}\) density
  • Width is indicative of the damping effect of single electron transitions
  • Information about dielectric response
  • Can be used for spectral “fingerprinting”
$O_2$ oxidation – decomposition loadings
Decomposed plasmon spectra at SiC/SiO$_2$ interface - Loadings

NO post-anneal – decomposition loadings
Low-loss Interface component - comparison

- O₂ oxidation
- NO post-anneal (2hr)
Low-loss decomposition results

• **Results:**
  
  • Interface components observed for all samples investigated
  
  • Specific component shapes appear very similar
    
    • Limited NO impact in this range of spectrum

  • Finite transition layer regardless of interface/treatment

• “$w_{TL}$” from low-loss component $\approx 2.2$nm
Decomposition of Phosphosilicate glass (PSG)
Phosphorus PSG process – decomposition analysis

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

![STEM signal during acquisition](image1)

a-face PSG sample (STEM data):

- Initially thought contamination...
- ...but maybe there’s more.
PSG decomposition results

Si-face PSG STEM and EELS:
PSG decomposition results

a-face PSG STEM and EELS:
PSG decomposition results

a-face PSG STEM and EELS:

PSG decomposition results

• **Results:**
  • “Clusters” observed in STEM imaging are not contamination or sample preparation artifacts, as initially thought
  • P is not evenly distributed throughout the PSG
  • Rather, appears to be P inclusions within SiO$_2$

• Are newer PSG samples similar?
  • Further analysis of PSG process (see Sarit’s talk)

a-face PSG sample (STEM data):

- as acquired
- enhanced contrast
XPS DEPTH PROFILING
XPS N 1s

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

### XPS N 1s

<table>
<thead>
<tr>
<th>Measurement</th>
<th>C 1s %</th>
<th>N 1s %</th>
<th>O 1s %</th>
<th>Si 2p %</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1 - normal</td>
<td>40.95</td>
<td>1.67</td>
<td>9.56</td>
<td>47.82</td>
</tr>
<tr>
<td>N1 – 40°</td>
<td>41.43</td>
<td>2.66</td>
<td>16.44</td>
<td>39.47</td>
</tr>
<tr>
<td>N1 – 20°</td>
<td>41.20</td>
<td>2.73</td>
<td>20.59</td>
<td>35.49</td>
</tr>
<tr>
<td>N2 – normal</td>
<td>29.92</td>
<td>1.01</td>
<td>21.80</td>
<td>47.28</td>
</tr>
<tr>
<td>N2 – 40°</td>
<td>33.59</td>
<td>1.37</td>
<td>29.46</td>
<td>35.58</td>
</tr>
<tr>
<td>N2 – 20°</td>
<td>36.28</td>
<td>1.45</td>
<td>33.57</td>
<td>28.70</td>
</tr>
</tbody>
</table>

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

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XPS Elemental Ratios

• Looking at absolute elemental ratios is not always accurate/ideal
  • Hydrocarbon contamination
  • Normalizing by appropriate signal

• Example:
  • Si 2p quantification

![All Si-2p](image)

<table>
<thead>
<tr>
<th>SiC</th>
<th>SiO₂</th>
<th>Interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding energy (eV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>108</td>
<td>106</td>
<td>104</td>
</tr>
<tr>
<td>102</td>
<td>101</td>
<td>100</td>
</tr>
</tbody>
</table>
With proper normalization, XPS reveals approximately expected stoichiometry.

Best normalization by Si in SiC

O ratio ≈ 1.5... lower than expected

N as expected

2.4 x10^{14} \text{ cm}^{-2}
Summary

• The shift of the Si-L$_{2,3}$ edge is a good indicator of the width of the transition region in 4H SiC/SiO$_2$.
  • Newer devices do not follow previously observed trend
  • Measuring interface width does not reveal what is happening inside
• Decomposition of Si-L$_{2,3}$ EELS edge reveals a chemically/electrically distinct interface state
  • Likely significant impacts on mobility and performance
  • Spatial distribution matches measurements of $w_{TL}$
• Decomposition of low-loss EELS shows same-sized interface component
  • Not dependent on NO anneal
• XPS indicates Si$_3$N$_4$-like N bonding at the interface, with N incorporated primarily at interface
• PSG passivation does not cause a uniform PSG dielectric (clusters of P within oxide)

Future work

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

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• And many others…
THANK YOU

Questions/comments/discussion?