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

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

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

Motivation and background

- SiC: Very promising for high temperature, high power, and high radiation environments
  - MOSFET devices limited by poor channel carrier mobility and reliability
  - Best device μ_{FE}: SiC ~ 125 $\frac{cm^2}{V \cdot s}$ (a-face P passivation)[◊]; Si ~ 600 $\frac{cm^2}{V \cdot s}$ (uniaxial <100> strain)[◊]
  - 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]
  - Other results (XPS, MEIS, etc.) suggest more abrupt transition[2,3,4,5]
  - What is NO post oxidation annealing really changing about the interface structurally and chemically?

[1] J. Taillon, L. Salamanca-Riba, *et al.*, J. Appl. Phys. 113, 044517 (2013).
[2] H. Watanabe, *et al.*, Appl. Phys. Lett., 99(2), 021907 (2011).
[3] P. Tanner, *et al.*, J. Electron. Mater., 28(2), 109 (1999).
[4] P. Jamet, *et al.*, J. Appl. Phys., 90(10), 5058 (2001).
[5] X. Zhu, *et al.*, Appl. Phys. Lett., 97(7), 071908 (2010).

Central questions

How do the structure and chemistry of the 4H-SiC/SiO_2 interface change under NO anneal?

What do these changes tell us about the effects of the passivation process?

Outline

- Depth profiles and XPS
  - Development and refinement of SiO_2 spin-etch technique
  - Initial results from XPS depth profiles
- TEM-EELS on miscut samples
  - Analysis of oxidized and NO annealed samples with various crystallographic orientations
- Future areas of inquiry
  - TEM investigation of interfacial roughness
  - Further XPS depth profiles, valence band modeling, etc.

SPIN-ETCH DEVELOPMENT FOR DEPTH PROFILES

Motivation for XPS "spin-etch" depth profiles

- By etching very close to the interface and performing angle-resolved XPS (ARXPS), we can learn about the differences caused by an NO post-oxidation anneal in a depth-sensitive manner

- Most etching/profiling techniques however, cause extreme modifications of the surface being investigated
  - Sputtering – not an option due to induced damage and preferential oxygen removal
  - Dip etching – difficult to control, and leaves significant residue

- How to faithfully profile the interfacial region?
  - Need a technique that will not significantly modify interface or cause damage to underlying structure

Spin-etch Profiling

- Developed by Grunthaner, Grunthaner, and Vasquez for use on Si/SiO_2 interfaces in the 1970s[1,2]
- Further refined by Fenner *et al.* in the 1980s[3]
- Dropwise etching of SiO_2 proven to be a highly controllable technique, with very little contamination of surface compared to other methods

Sample and treatment	C (ML)	O (ML)	F (ML)
Spin etched with HPLC grade			
etch native oxide	0.025 ± 0.005	0.005 ± 0.002	0.010 ± 0.002
etch thermal oxide	0.037 ± 0.013	0.005 ± 0.001	0.008 ± 0.002
Spin etched with USP-grade			
etch native oxide	0.052	0.011	0.042
Dip-etched native oxide			
with HPLC grade	0.19	0.16	<0.002
with technical grade	0.25	0.13	0.10
Si(111) cleaved in UHV			
10 min afterwards	0.007	0.0008	...
Ar^+-ion sputtering			
while at 600 °C	0.16	0.11	...

Order of magnitude improvement in surface residue, as measured by XPS[3] (reported in monolayers)

[1] F. J. Grunthaner, P. J. Grunthaner, R. P. Vasquez, B. F. Lewis, J. Maserjian and A. Madhukar, J. Vac. Sci. Technol., 16(5), 1443 (1979)
[2] R. P. Vasquez and F. J. Grunthaner, J. Appl. Phys., 52(5), 3509 (1981).
[3] D. B. Fenner, D. K. Biegelsen and R. D. Bringans, J. Appl. Phys., 66(1), 419 (1989).

Etching experimental setup

- Small samples (1 x 0.5 cm) spinning at 3000 rpm on vacuum chuck
- Etchant solution is 10:1:1 ratio of EtOH:H_2O:49.5% HF
- Rinse sample with alcohol and H_2O before etching
- Manually pipette 25 µL drops in groups of 5 drops (each group is 1 "step")
- Dry sample using N_2 blow gun after each step

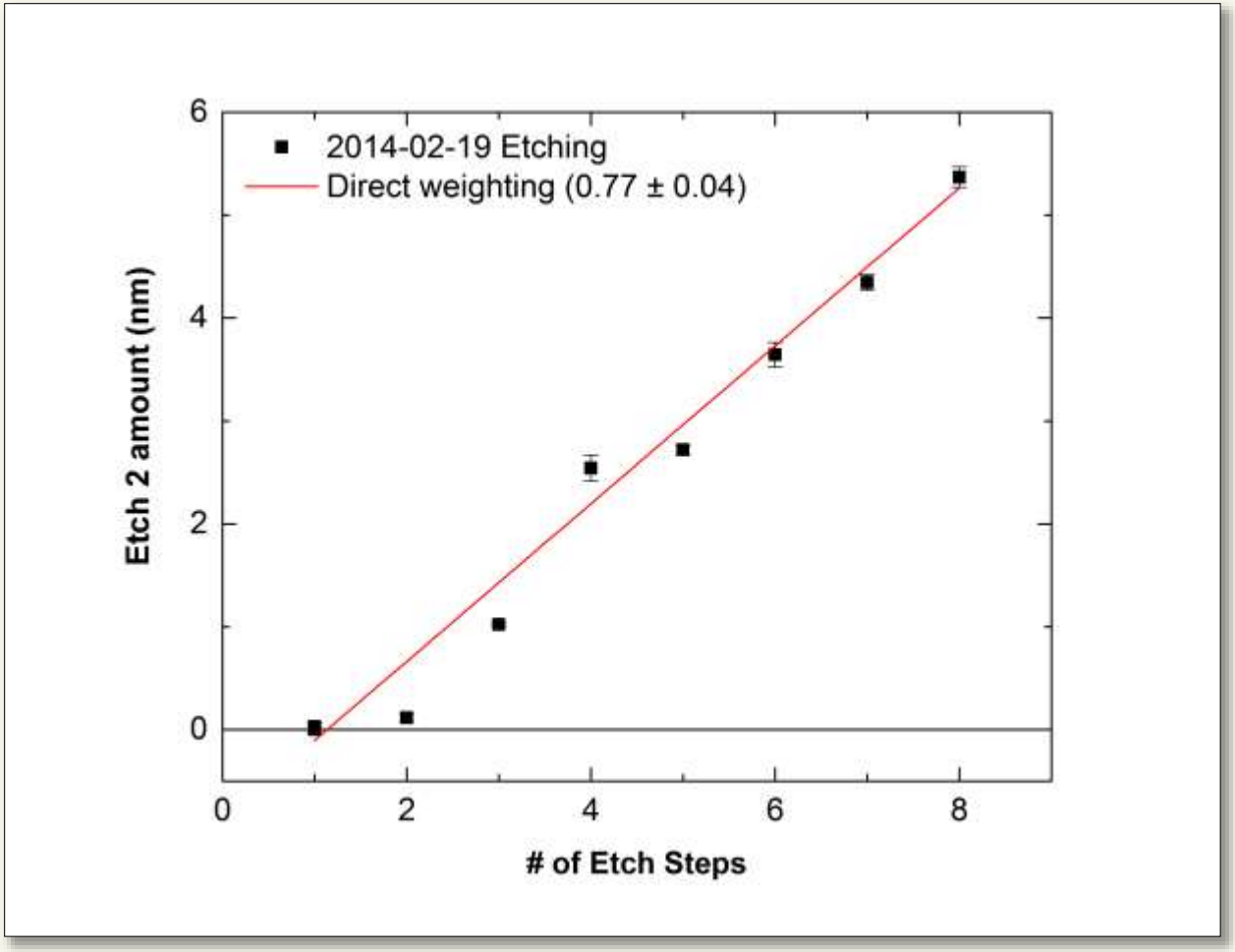
- Controls explored:
  - Number of steps
  - Oxide type (wet or dry SiO_2 on Si)
  - Time etchant is left before drying
  - Time between etch steps

UMD process refinement

- Refine techniques on similarly-sized SiO_2/Si samples

1) Measure SiO_2 thickness profile using ellipsometry
2) Etch, changing some parameter to control
3) Remeasure SiO_2 thickness profile, taking etched amount as data point

Results – control via number of etch steps

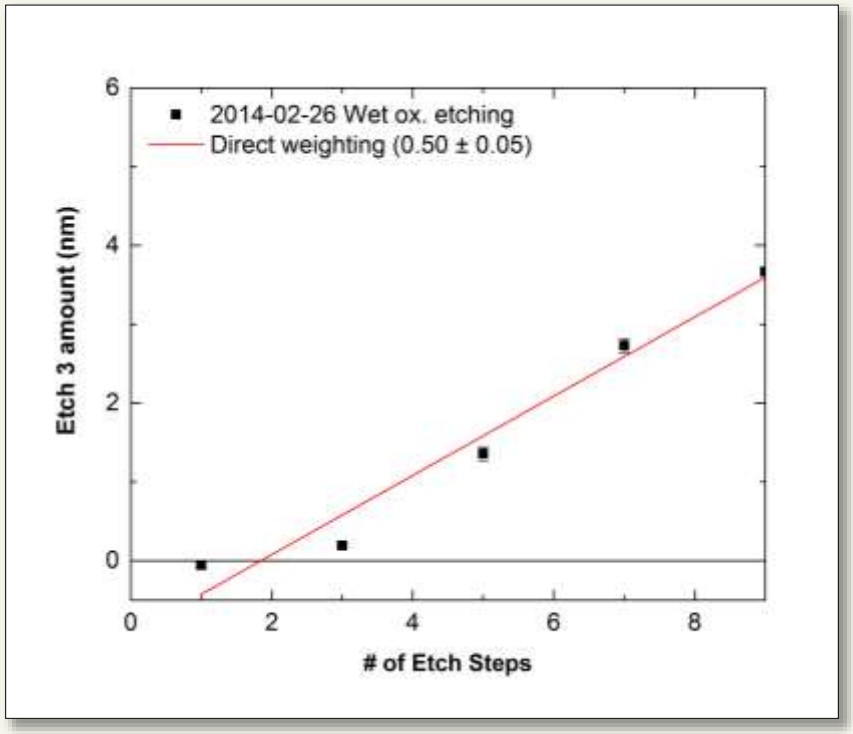


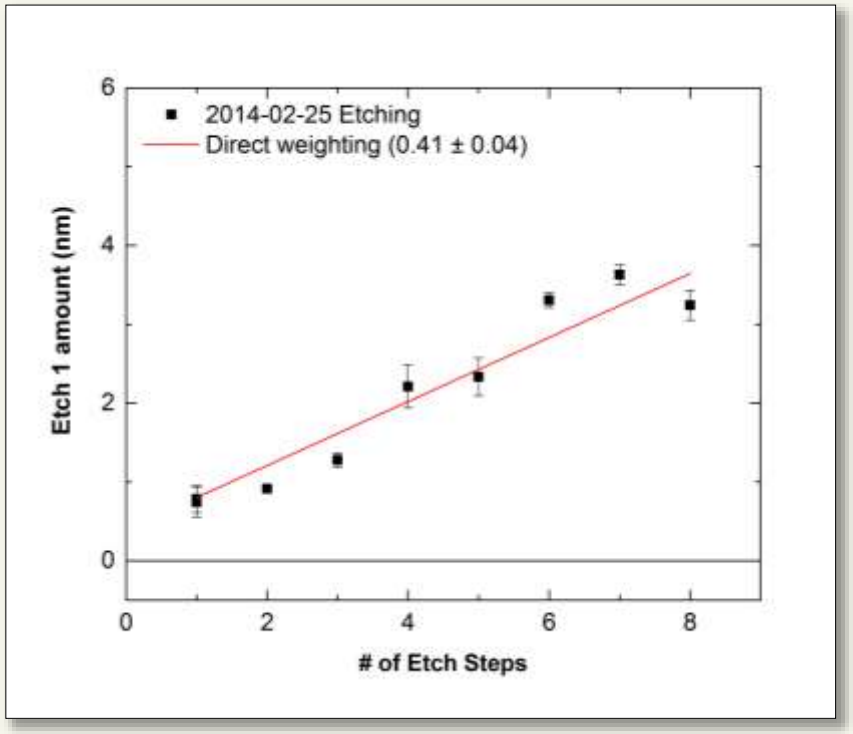
"Long" exposure (~15 seconds between etch steps)

Wet thermal oxide

0.8 nm removed per step

Results – control via number of etch steps

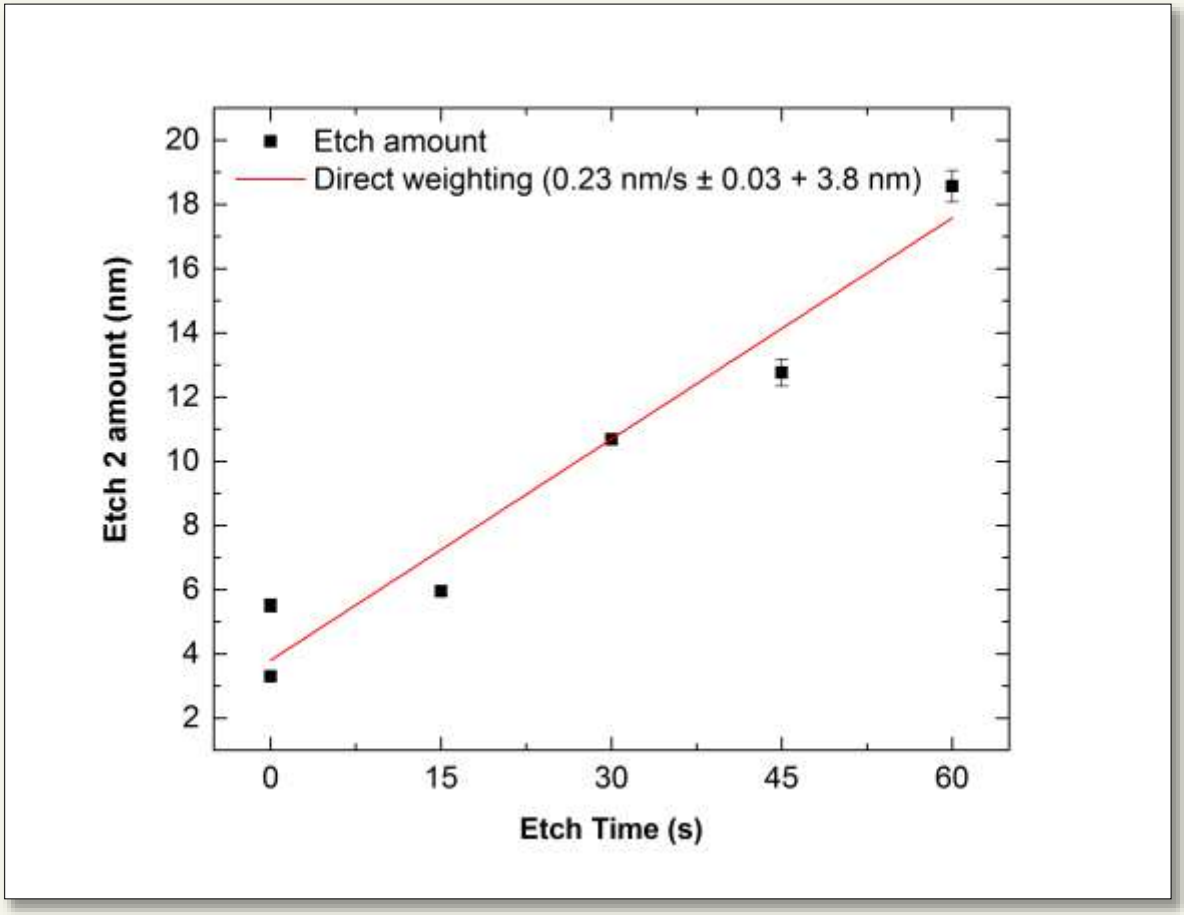




"Short" exposure
(~2 seconds between steps)
Wet thermal oxide
0.5 nm removed per step

"Short" exposure
(~2 seconds between steps)
Dry thermal oxide
0.4 nm removed per step

Results – control via etching time



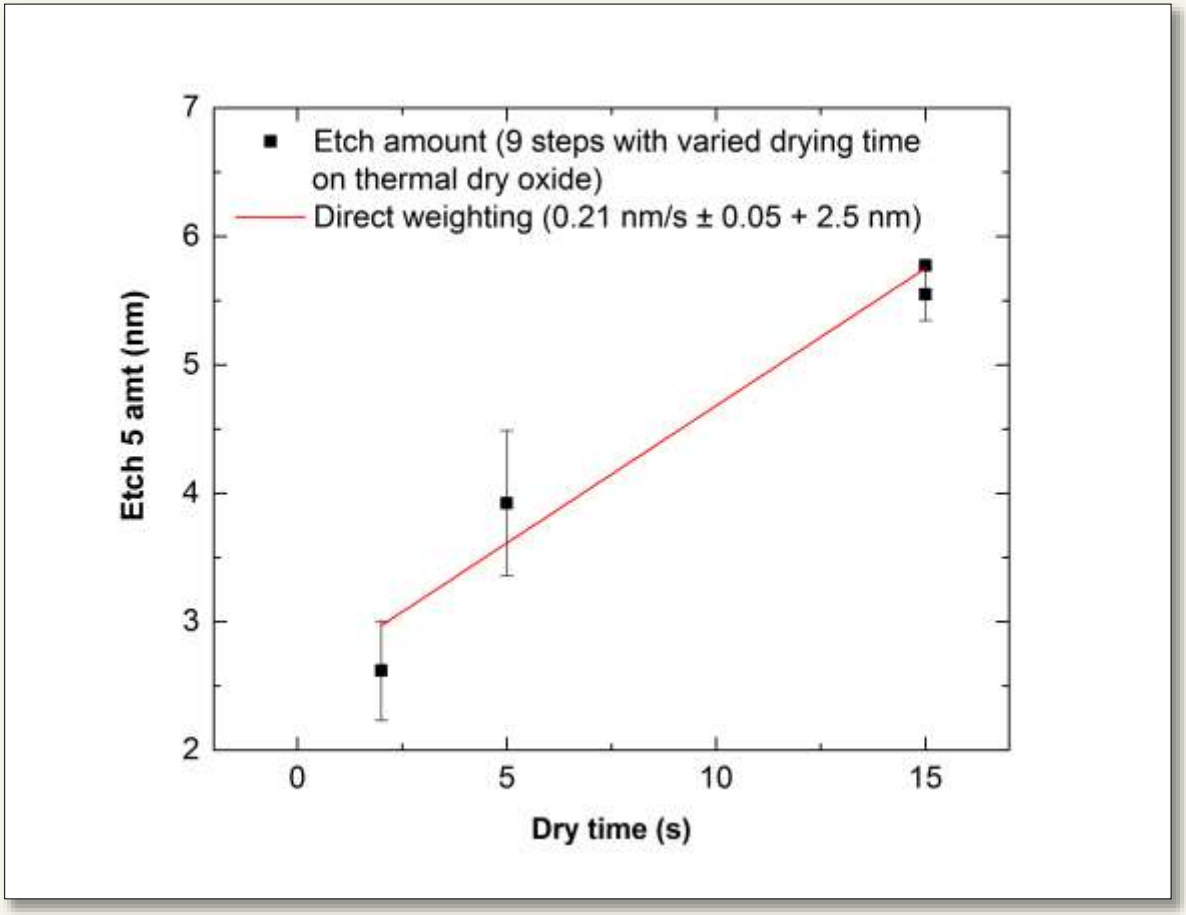
Controlled amount of time left on spinner after 9 "short" etch steps

Dry thermal oxide

0.2 nm removed per second remaining on spinner

Indicates additional etching, without introduction of more etchant; **vapor phase etching** means process timing is important

Results – control via etching time



Controlled duration of each step by varying time between each step from 2 to 15 seconds; 9 steps

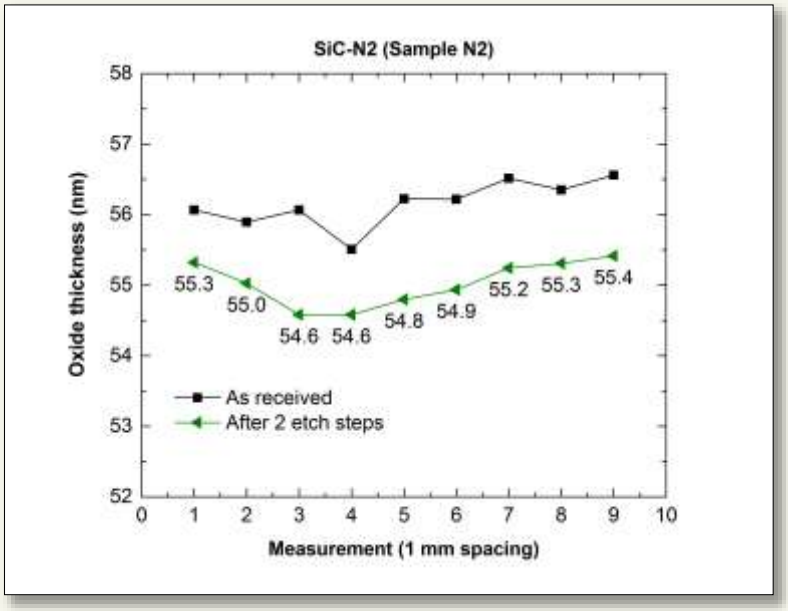
Dry thermal oxide

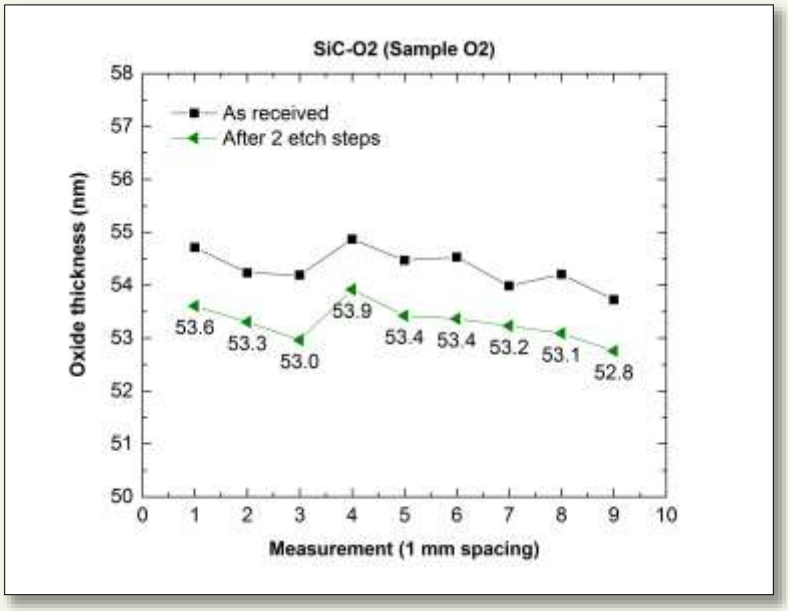
0.2 nm removed per second of step time

Again, indicates that timing of process is critical, likely due to vapor effects

Uniformity of etch

- Spin etch process retains original oxide profile, indicating uniform etching
- Plots below show ellipsometry measurements of oxide thickness across SiC samples after 2 etch steps, retaining oxide profile





Process limitations

- Spin-etch is extremely effective at removing material from 1 monolayer up to about 10 nm
  - Beyond this, unintended edge effects, accelerated etching, and cumulative error make the method unreliable
  - It is expected that a dip etch (for large-scale removal) followed by spin-etch would retain the desirous characteristics while being more efficient
- Trying to remove too much SiO_2 at once caused unintended over-etching of SiC samples for XPS analysis

INITIAL XPS RESULTS

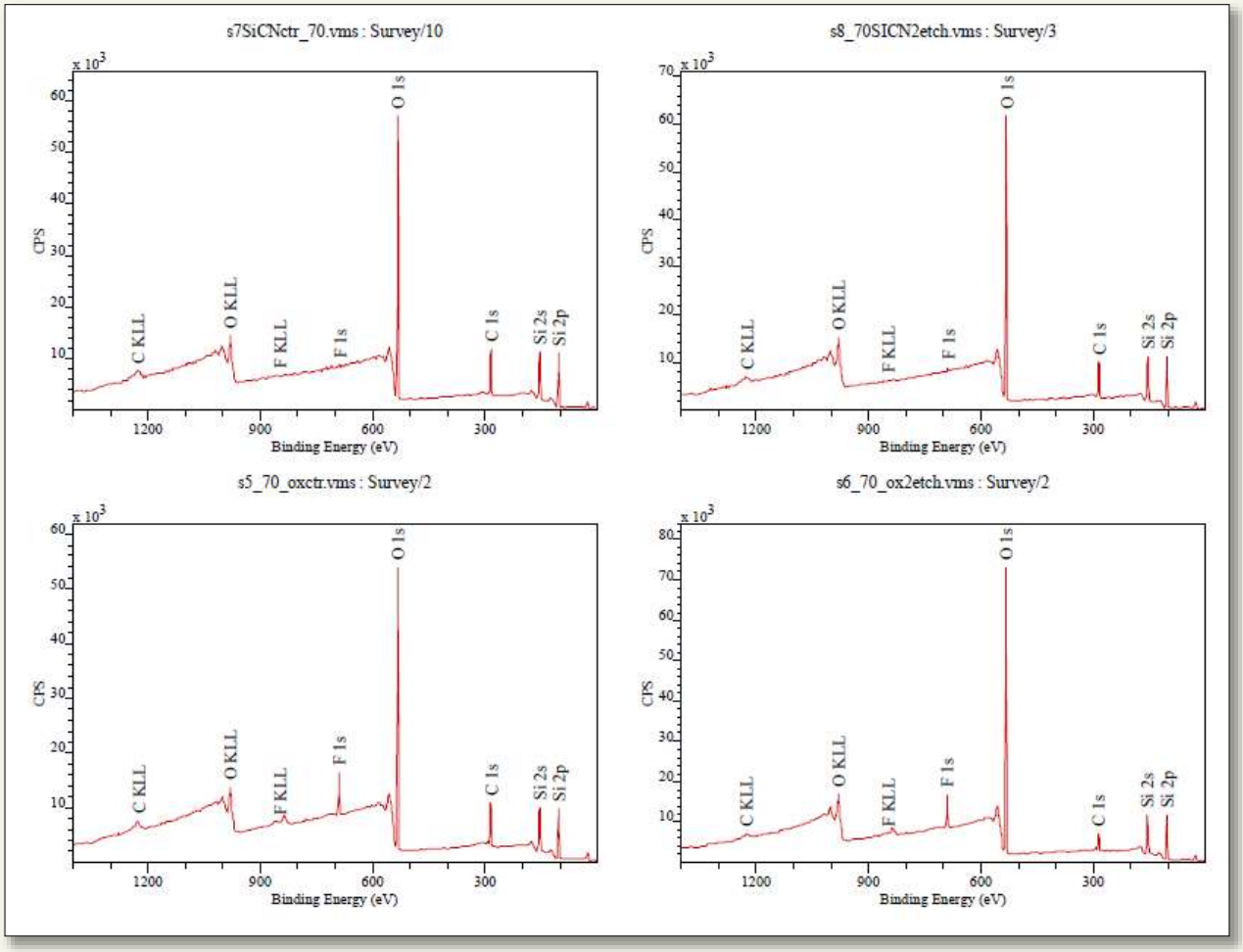
Samples investigated

- 4 SiC/SiO_2 samples were provided by Rutgers
  - All are n-type with 10^{16} cm^{-3} doping
  - Two samples were just oxidized (labeled O1 and O2)
  - Two samples received 2hr NO post-oxidation anneal (labeled N1 and N2)
  - Starting oxide thicknesses were ~55nm

- First test was to see if there was any perceptible effect of our spin-etch process in the XPS
  - Two of the samples were etched very slightly (about 2nm removed)
  - Two were cleaned (EtOH rinse) and analyzed as received

Etch effects – XPS Survey Spectra

SiC – N1
As-received



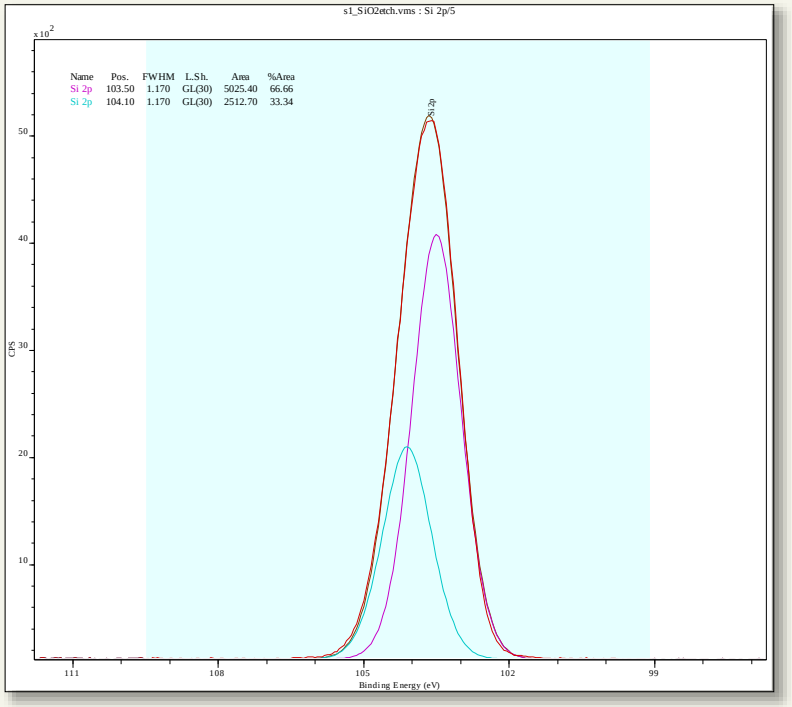
SiC – N2
After 2 etches

SiC – O1
As-received

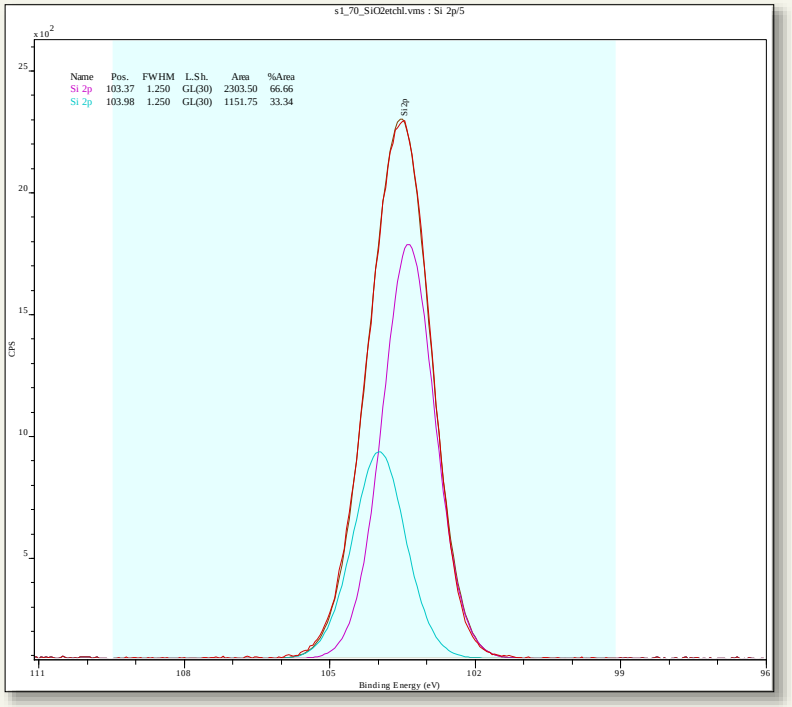
SiC – O2
After 2 etches

- No immediately observable effect of spin-etch on XPS survey scans

Etch effects – Si 2p signal



0 degrees

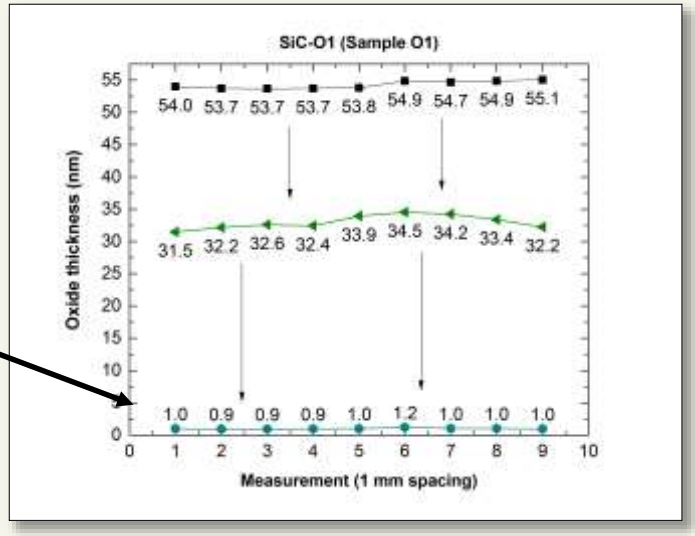


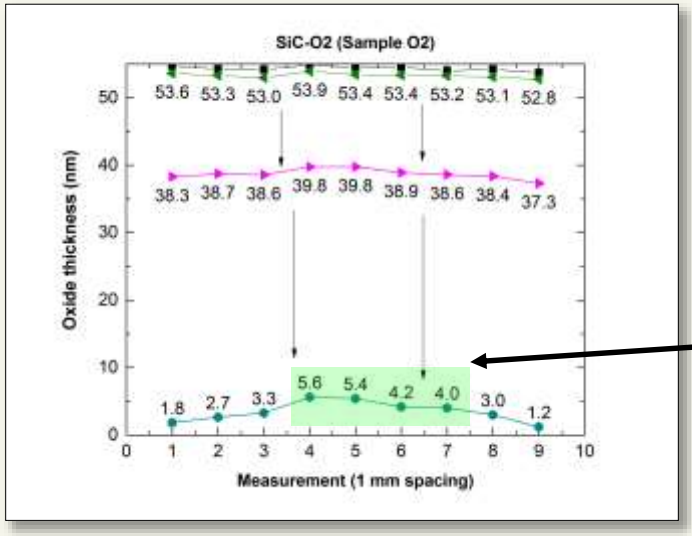
70 degrees

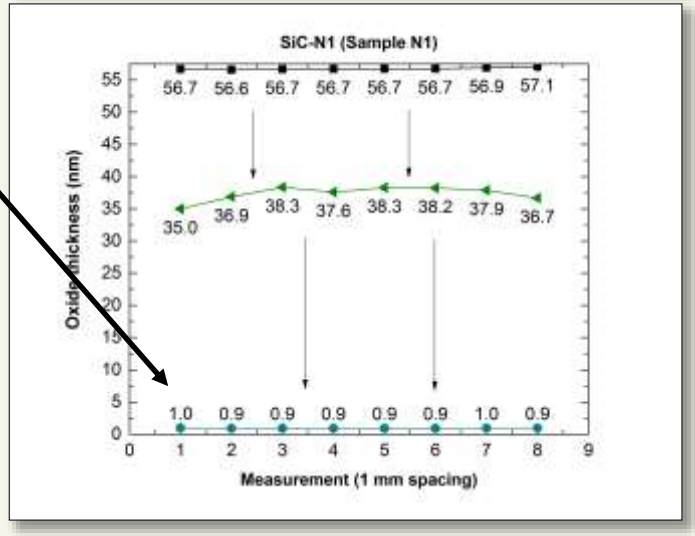
- Two distinct angle measurements from same sample (etched with 2 steps)
- Si 2*p* signal in thick SiO_2 (that was etched with two steps) looks exactly as expected for normal bulk SiO_2, indicating that the spin-etch does not chemically modify the Si

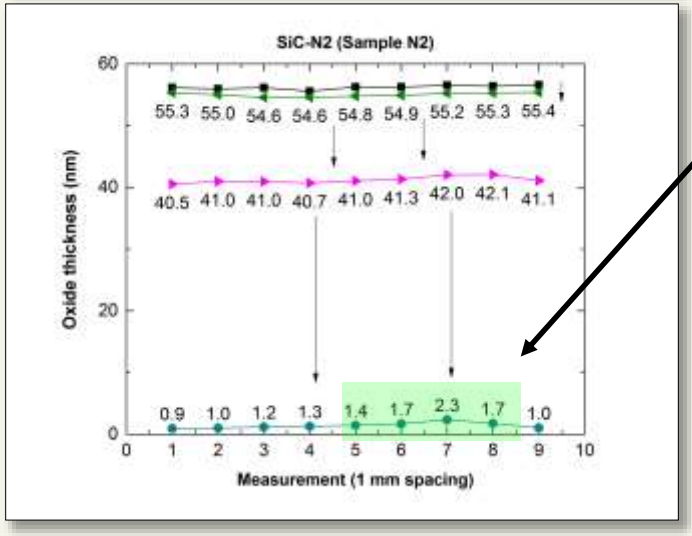
SiC sample oxide profiles (ellipsometry)

Accidentally stripped all oxide





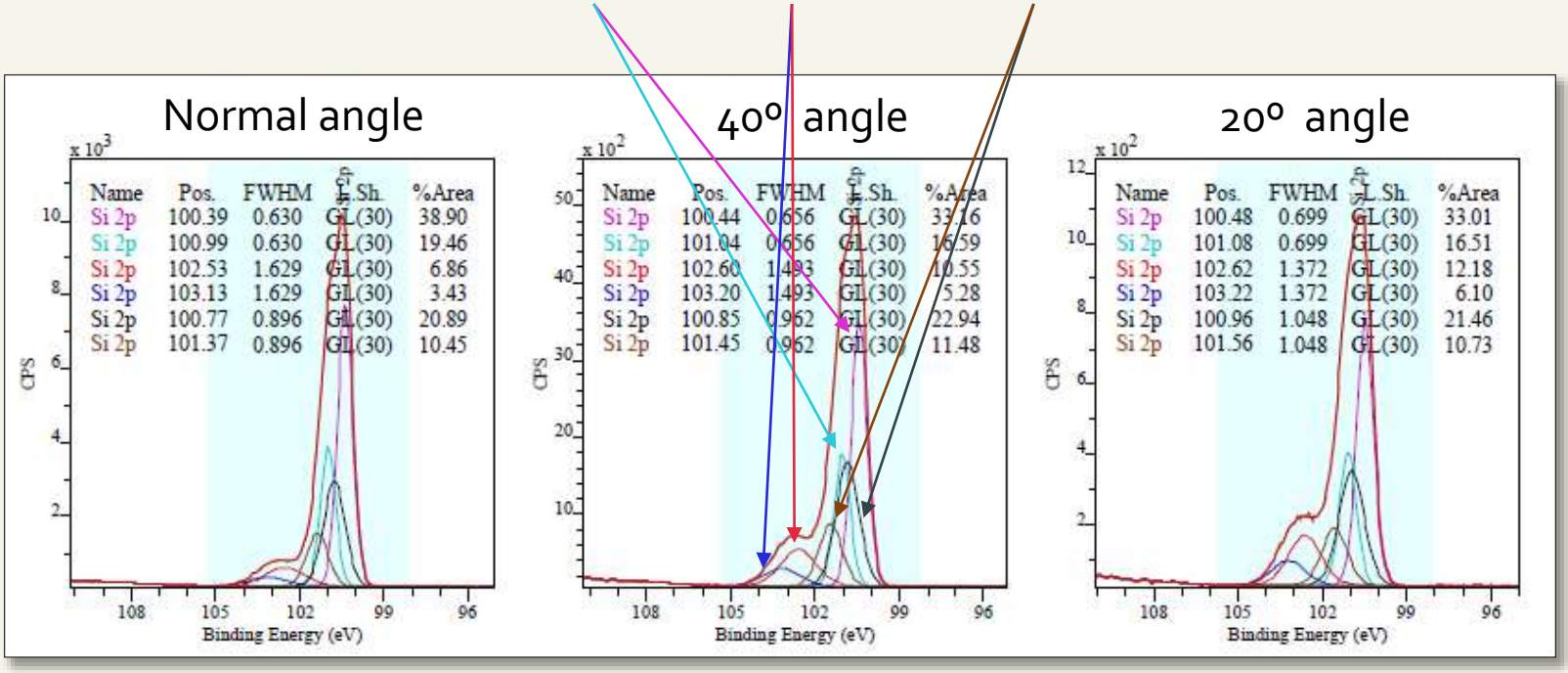




Areas of analysis for XPS

XPS Results – Si 2*p*

- Fit Si 2*p* with spin-orbit split components
  - Constrain fit by known physical phenomena to reduce spurious peak fits
  - 3 components found: Substrate, oxide, and substrate surface/interface



Sample O1 – completely etched oxidized SiC sample

XPS Results – Si $2p^{3}/_{2}$

- Looking at the peak position (binding energy) for each sample, we can see something interesting:

Sample	Substrate (I_o)	Oxide(I_o)	Substrate surface (I_s)
O1 – normal	102.5	102.5	100.8
O1 – 40°	102.6	102.6	100.9
O1 – 20°	102.6	102.6	100.9
N1 – normal	102.3	102.1	100.7
N1 – 40°	102.4	102.4	100.8
N1 – 20°	102.5	102.5	100.9
O2 – normal	103.1	103.1	100.7
O2 – 40°	103.2	103.2	100.7
O2 – 20°	103.2	103.2	100.9
N2 – normal	103.0	103.0	100.7
N2 – 40°	102.9	102.9	100.7
N2 – 20°	103.0	103.0	100.8

Thin oxide layers

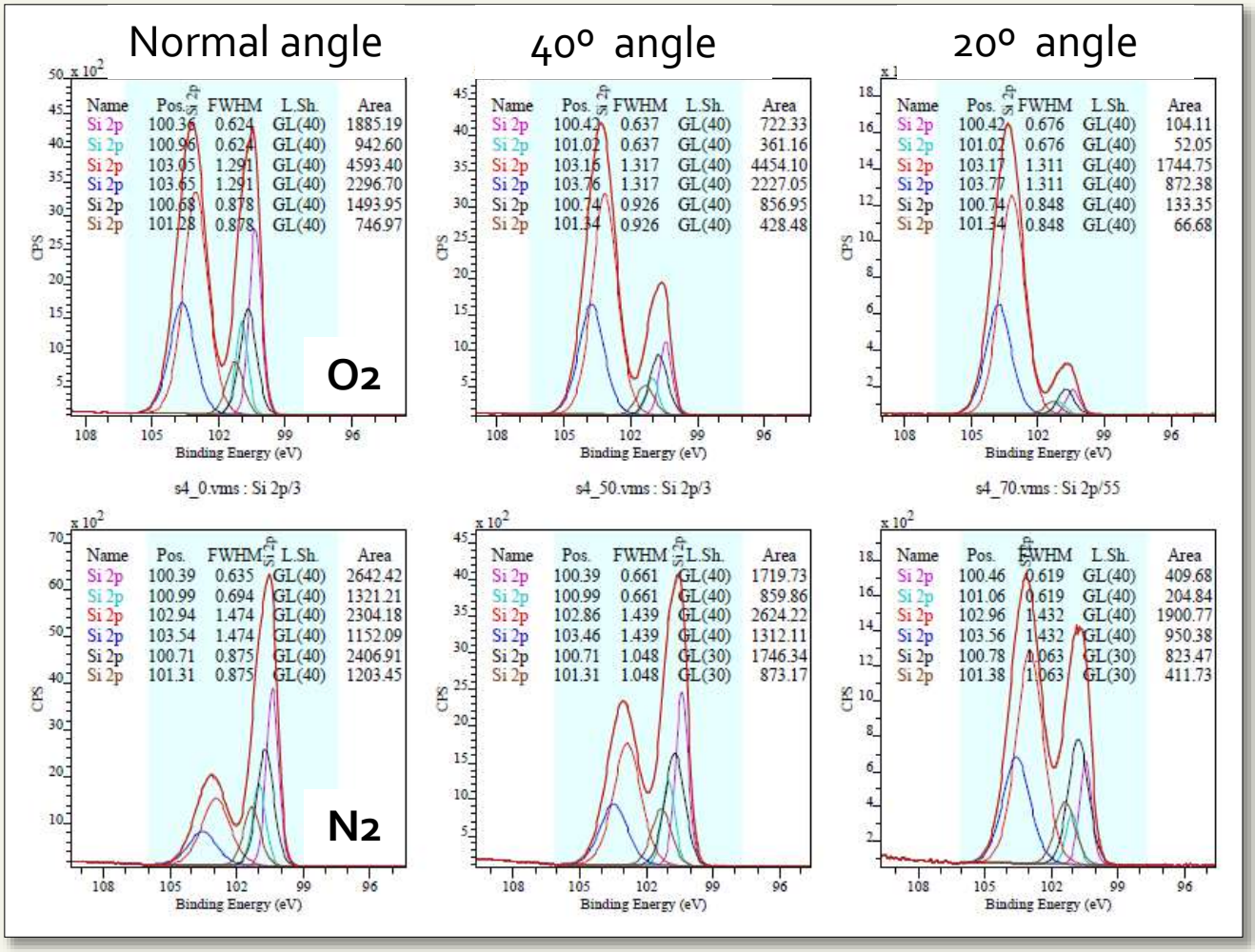
"Thicker" oxide layers

We can determine these samples were completely etched, and have reformed a "native oxide" that is at a lower binding energy

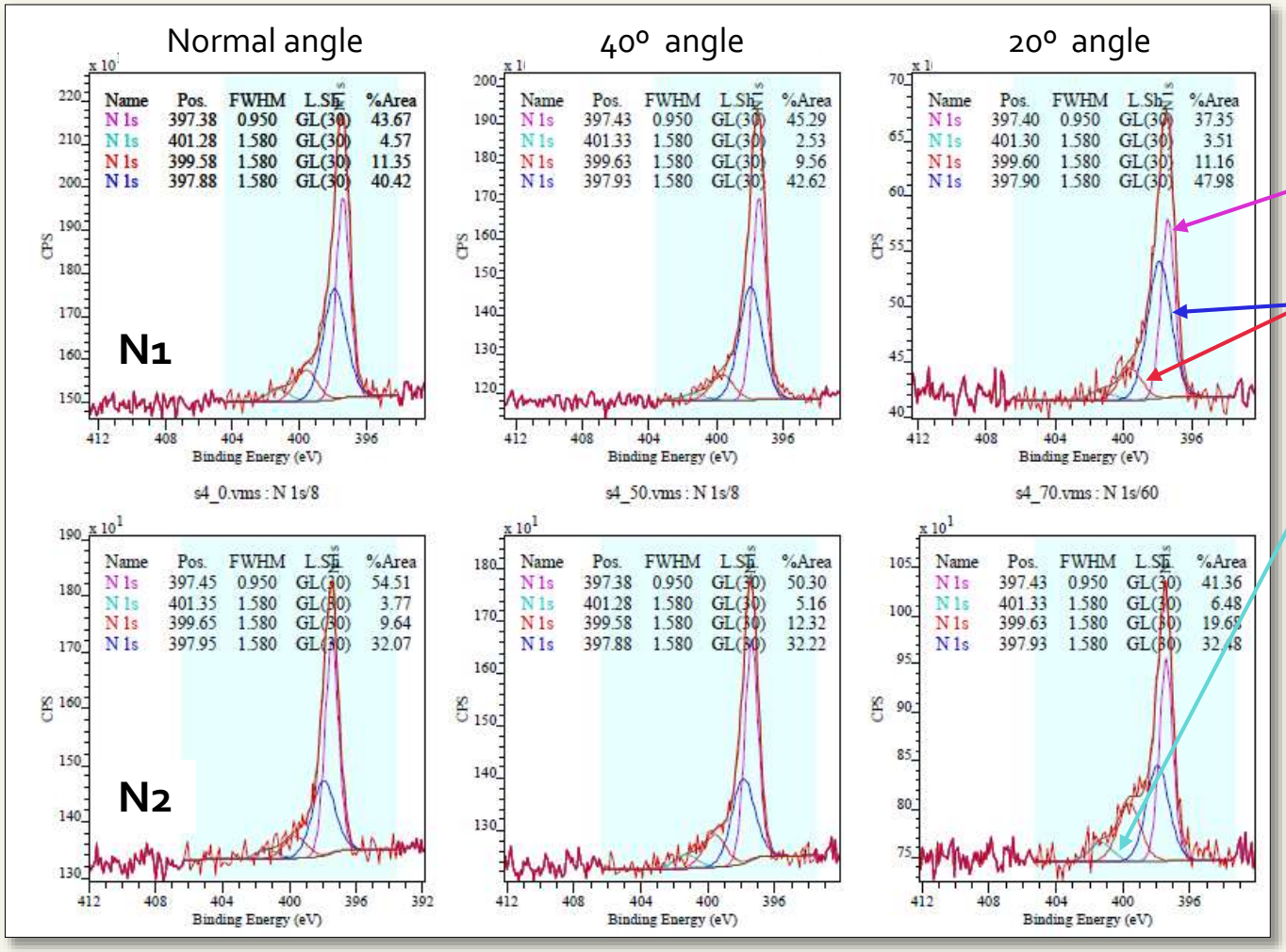
These samples are at the normal SiO_2 binding energy, so some of the true oxide remains

XPS – Si 2*p*

- 2*p* signals for Si in samples with thicker oxide do not show any evidence of "suboxide" or "native" oxide states
- Also no apparent influence of N in the Si 2*p*, but we might not expect to see it anyway due to the low concentration



XPS N 1*s*



- 4 components found in constrained fit
- Primary fit is consistent with silicon nitride-like bonding
- Other peaks likely to be successively more oxygen bonding
- See an additional component at high energy (compared to paper) but we're not ready to identify it with any certainty

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

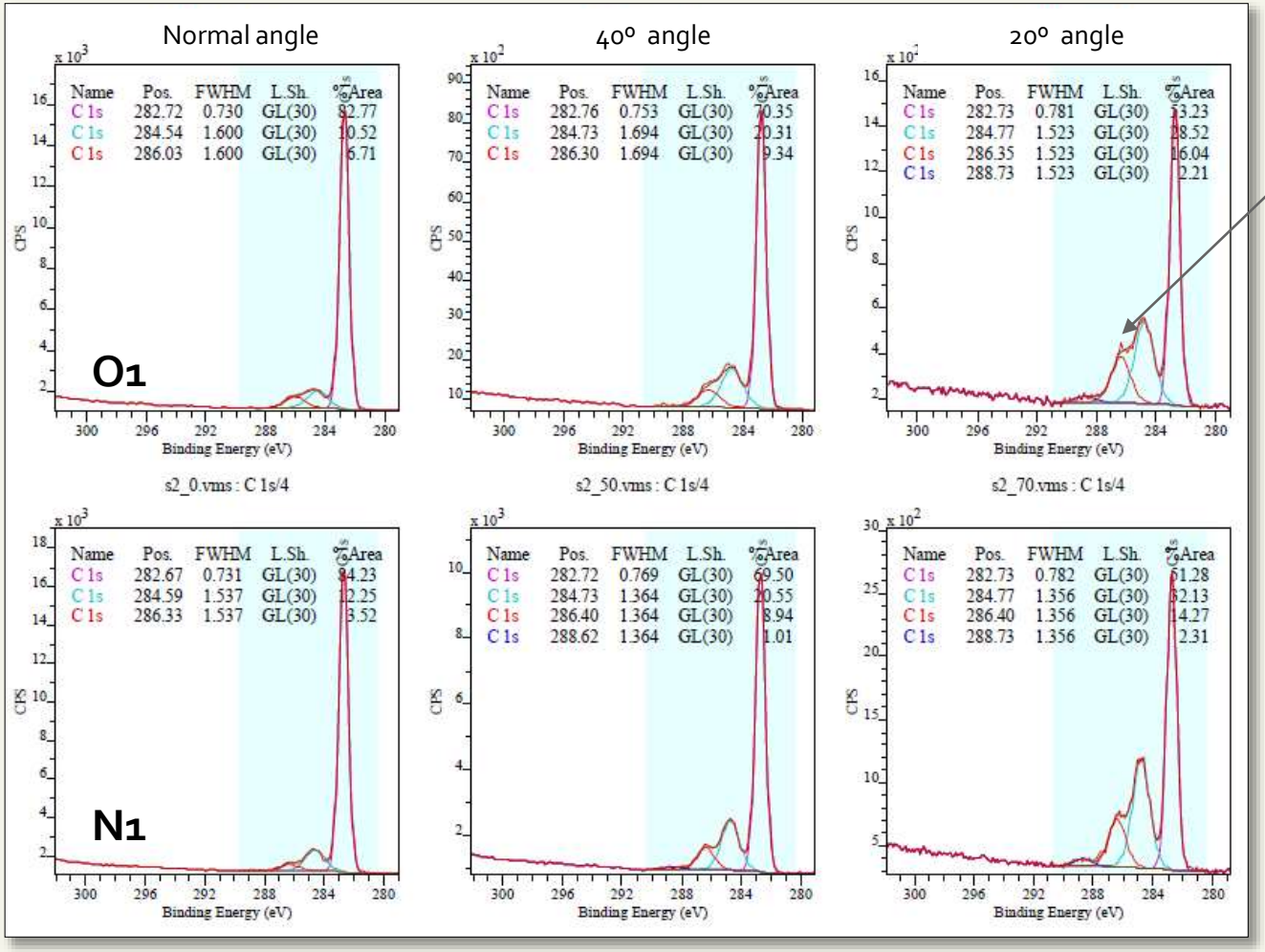
XPS N 1s

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

- 4 components found in constrained fit
- Primary fit is consistent with silicon nitride-like bonding
- Other peaks likely to be successively more oxygen bonding
- See an additional component at high energy (compared to paper) but we're not ready to identify it with any certainty
- 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 (like the recent paper from Rutgers[1])

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

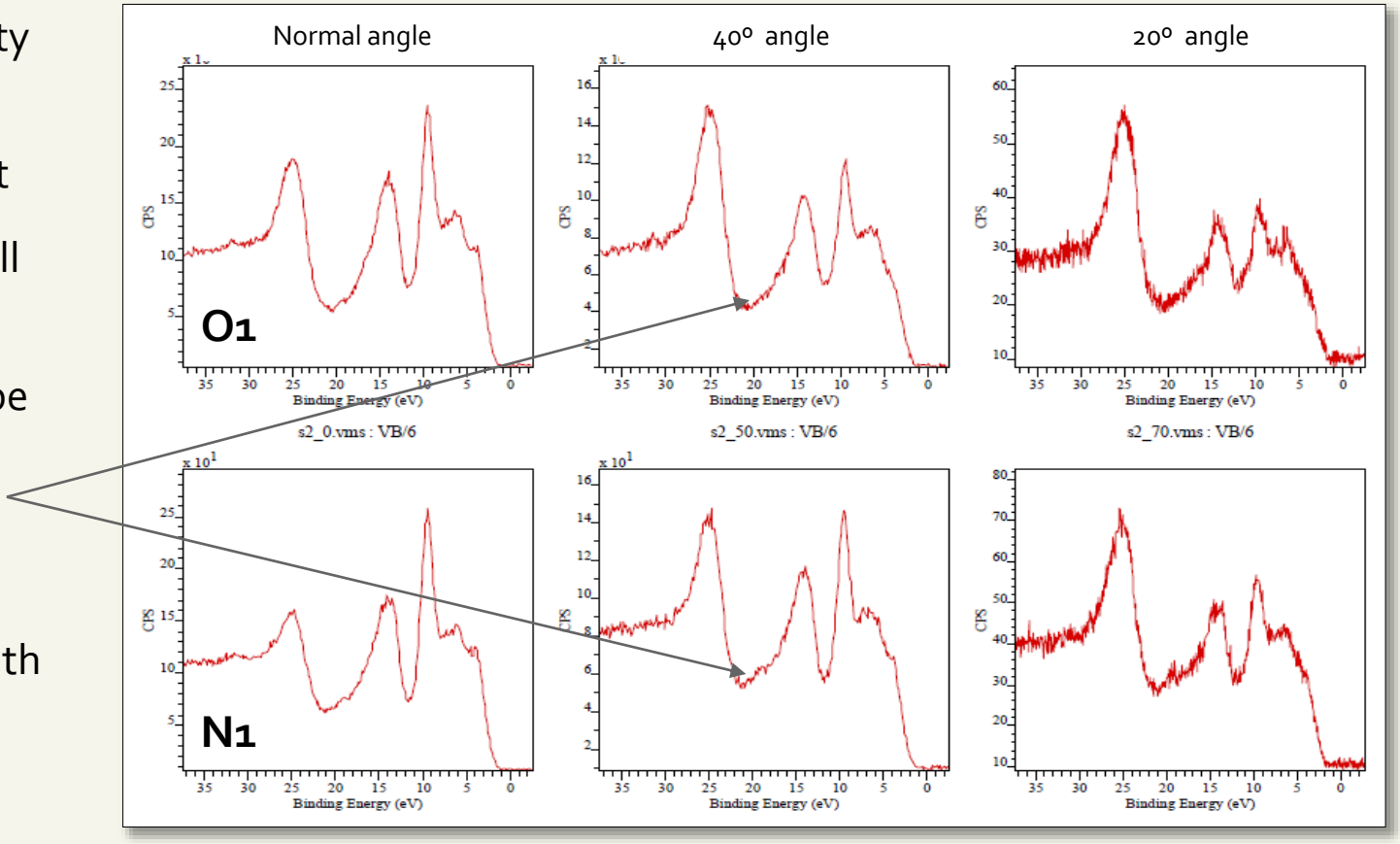
XPS C 1*s*



- Appears there is more C bonded to higher electronegativity atoms than we would expect from just contamination
- Possible C-O bonding at the interface
- Appears that NO anneal might reduce C-O peak (and perhaps C-O defect), but this needs more investigation

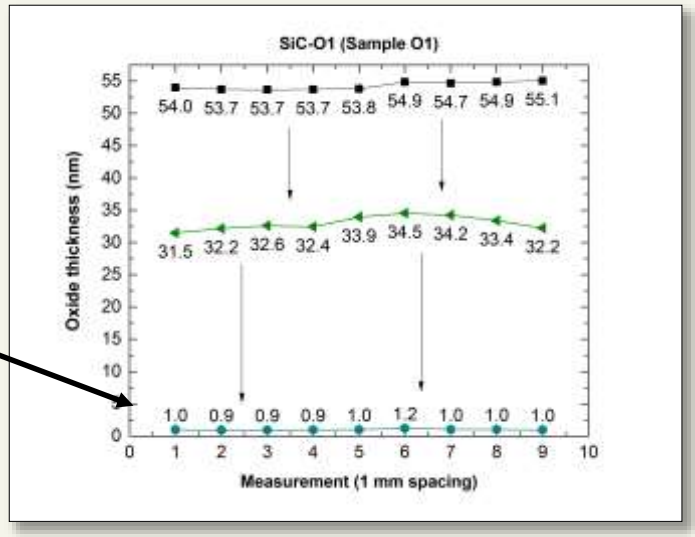
XPS valence band

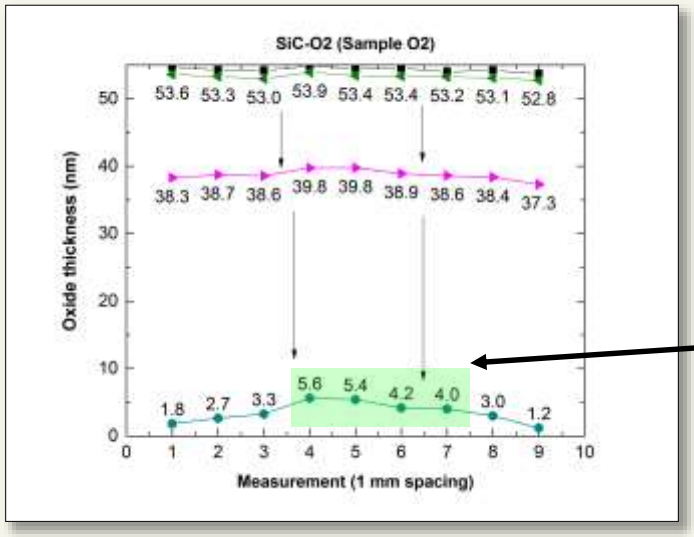
- Valence band is related to density of states
- Lots of information, but difficult to interpret and will need modeling
- Possible small differences (to be analyzed using principle component analysis)
- Future collaboration with N. Goldsman's group to investigate further

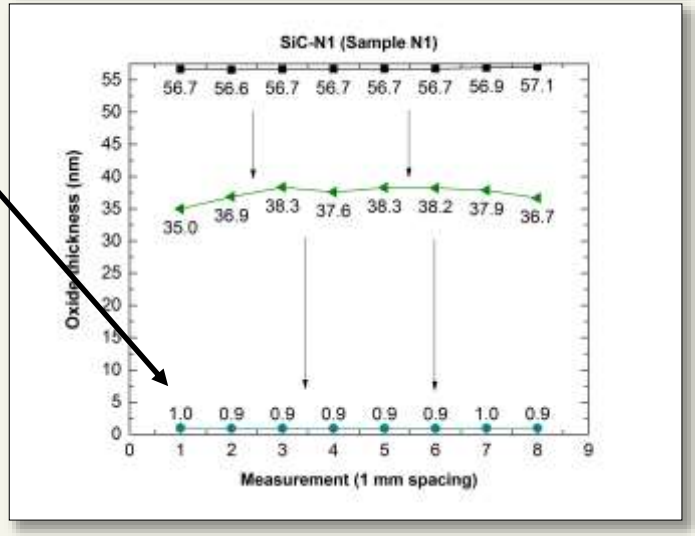


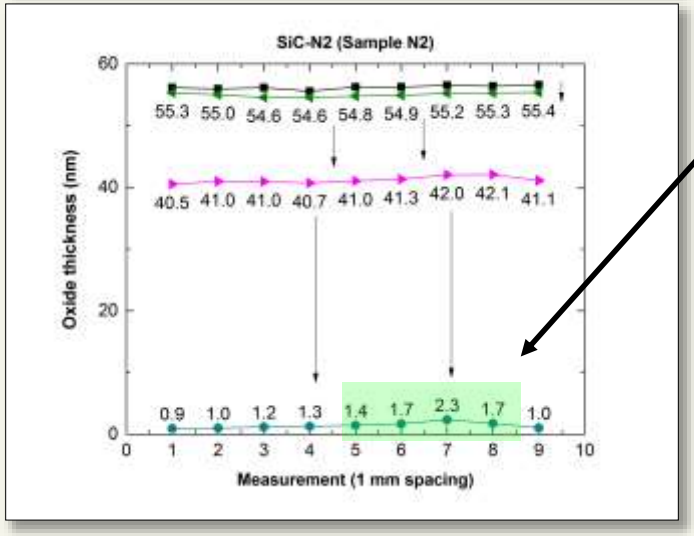
SiC sample oxide profiles (ellipsometry)

Accidentally stripped all oxide



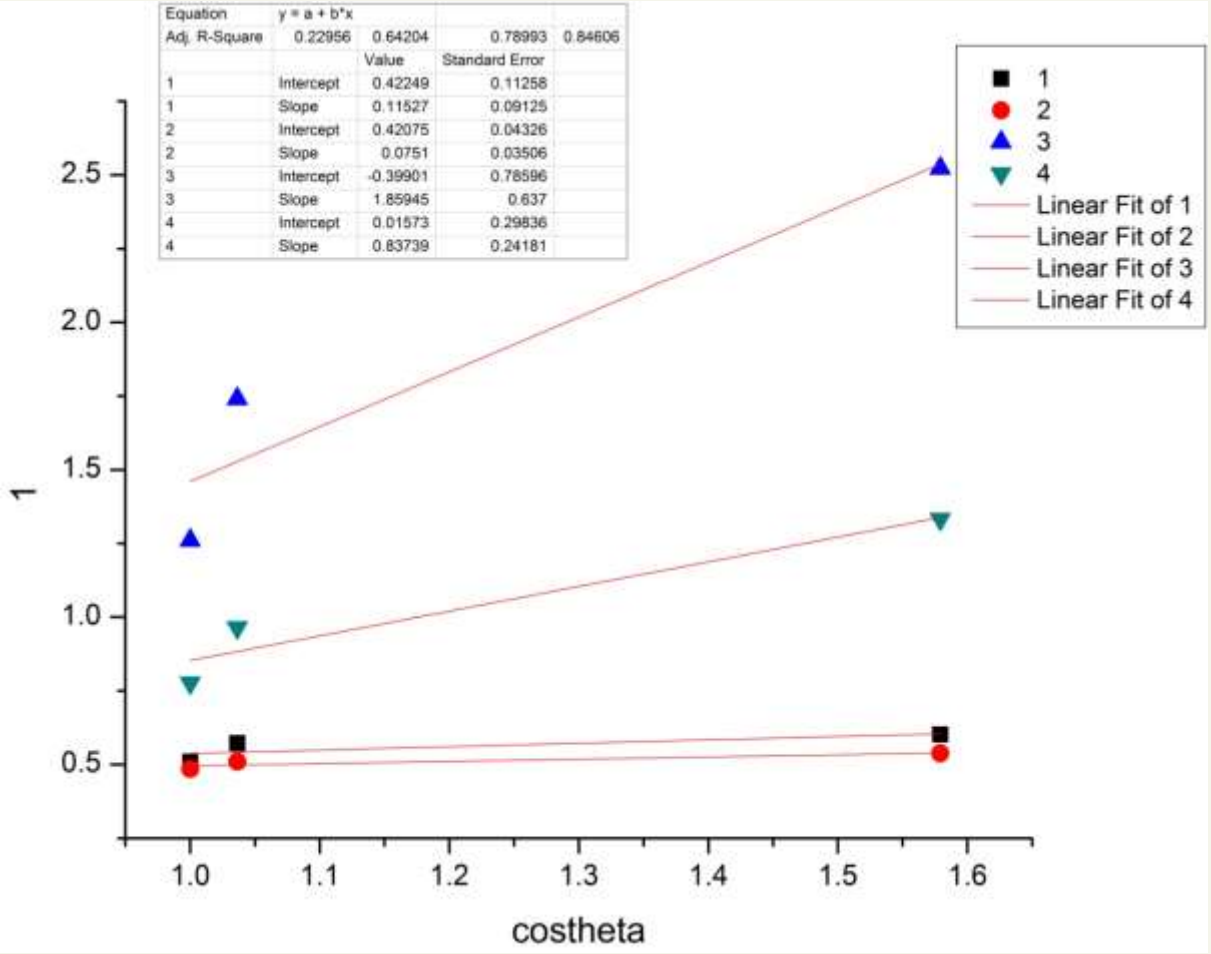






Areas of analysis for XPS

XPS oxide thickness compared to ellipsometry



Slope of line from different angle measurements is related to thickness and mean free path of electrons

$Slope = d/\lambda_{SiO_2}$

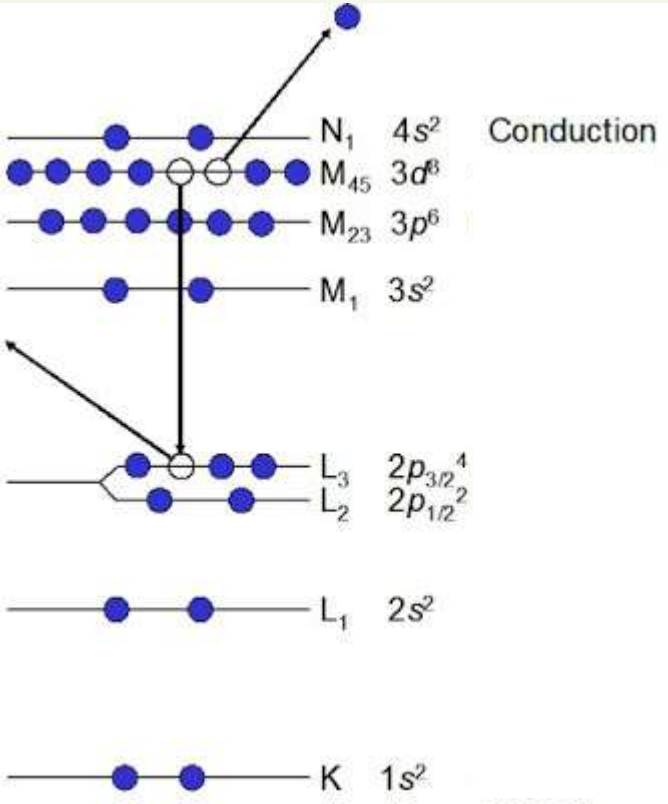
	XPS d	***Ellips. d***
O1 =	0.38 nm	~ 0.9 nm
N1 =	0.25 nm	~ 1.0 nm
O2 =	6.13 nm	~ 5.4 nm
N2 =	2.76 nm	~ 2.0 nm

Auger parameter

- Auger emission:
  - Additional electron emitted caused by absorption of the energy created when another electron falls down to fill a hole left by the photoemission process
- Energy of this electron can vary
  - Many pathways for the emission to occur
- Auger parameter
  - Relatively obscure XPS measurement
  - Difference between the kinetic energy (E_k) of the Auger transition and the E_k of the core level photoelectron that caused the transition:

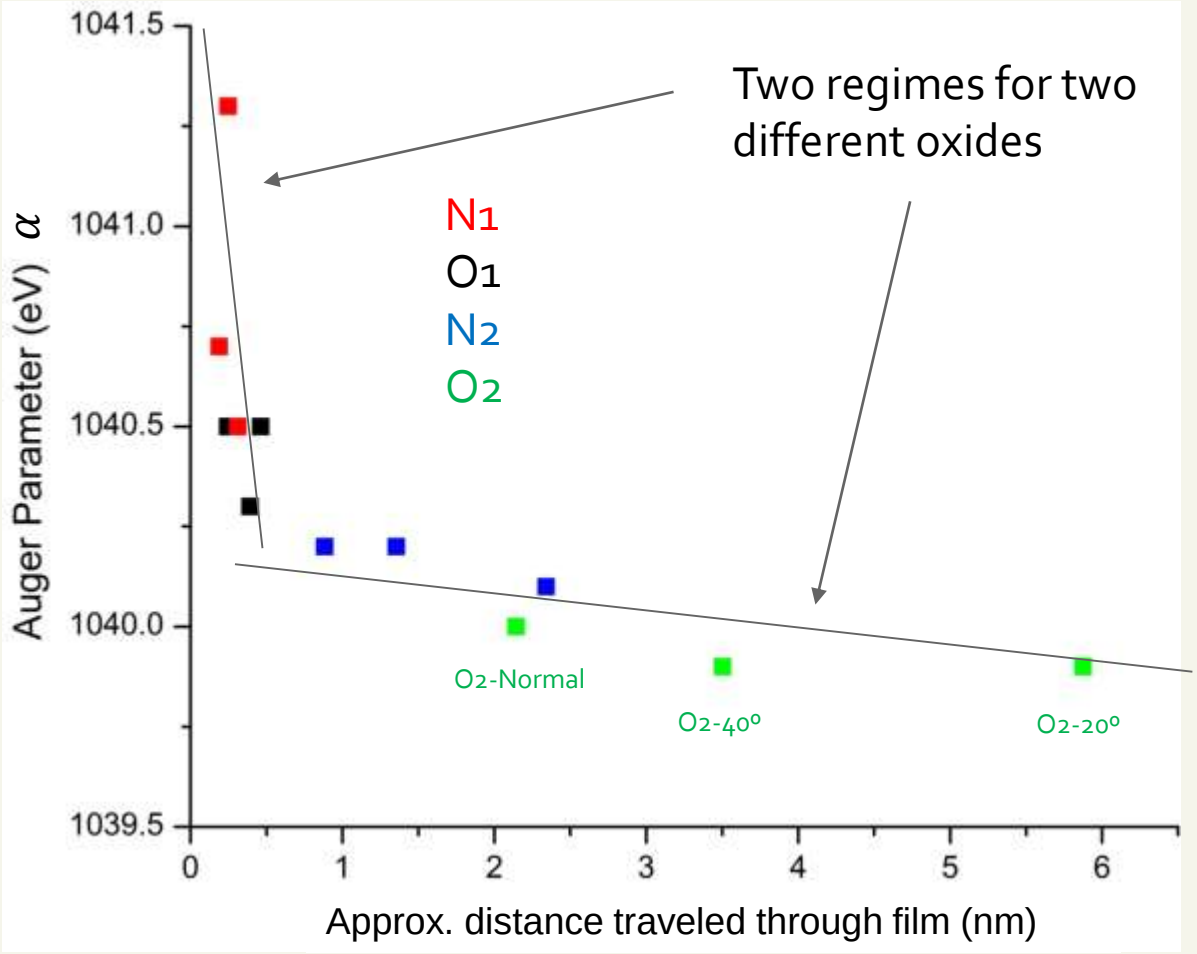
$$\alpha = E_k(C_1C_2C_3) - E_k(C)$$

  - Auger parameter is proportional to the amount of polarization of the bonds around the atom



http://www.xpsfitting.com/2012/08/auger-peaks-and-auger-parameter.html

Auger parameter



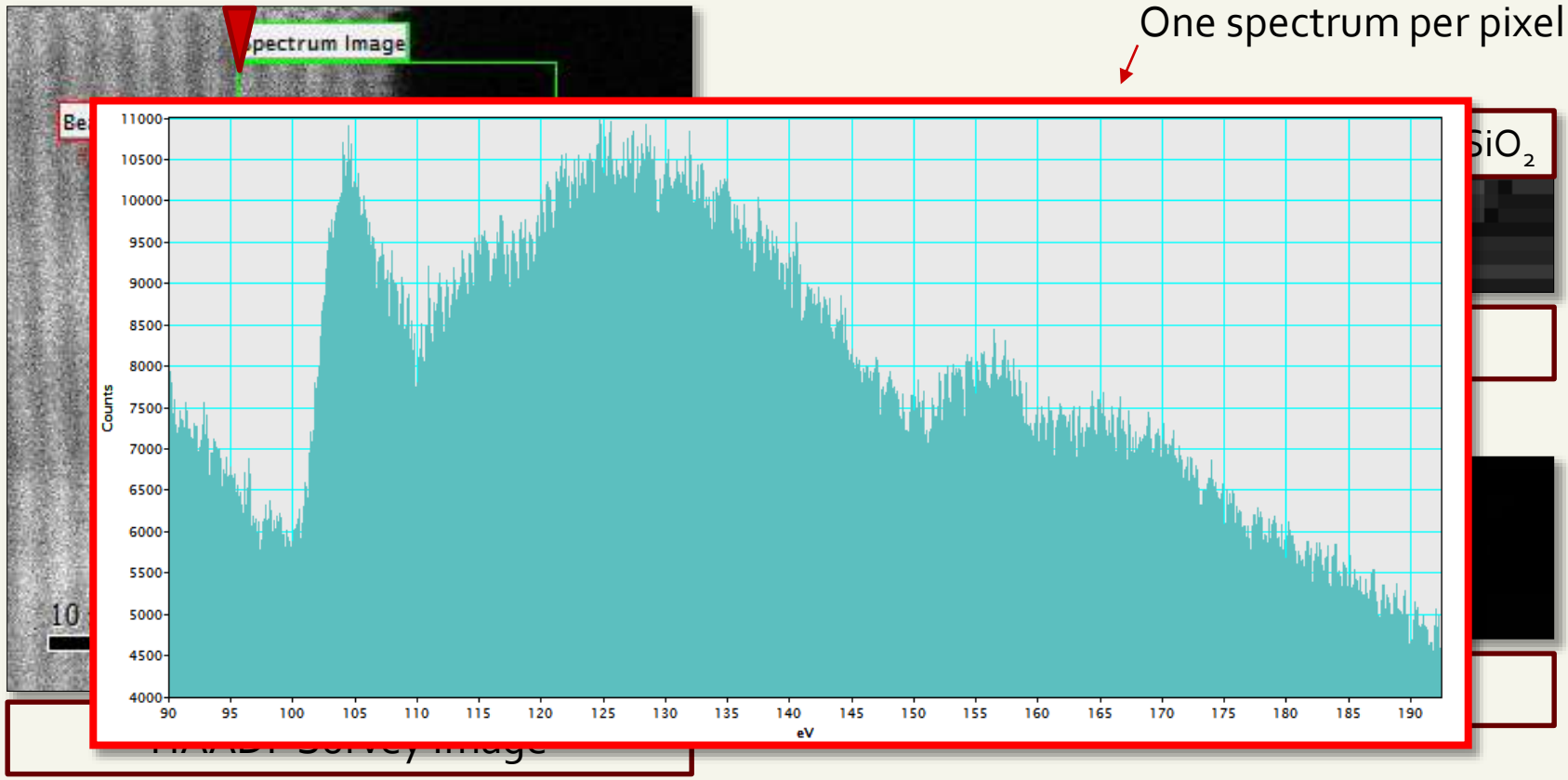
- Using the angle resolved measurements, we can plot α vs the distance the photoelectron travels through the film
- It appears that the less the distance through the film (closer to interface), α increases
- α for NO samples is always slightly higher
- Interesting phenomenon that has not been observed before that we are actively investigating further

XPS Summary

- Spin-etch does not seem to create artefacts in the data
- At room temperature, SiC forms a native oxide with different binding energies than typical SiO_2
- None of these different bonding energies (or "suboxide states") were observed near the interface in the Si 2p signals
- N 1*s* peak confirms that N is located mostly in SiC, and is located near interface, with many bonding configurations
- C 1*s* peak suggests that additional C-O bonding near interface and possible reduction of C-O bonding upon NO anneal
- Valence band spectra show little difference, but more work being done
- Auger parameter suggests significant change in oxide character while approaching interface, but much more work being done

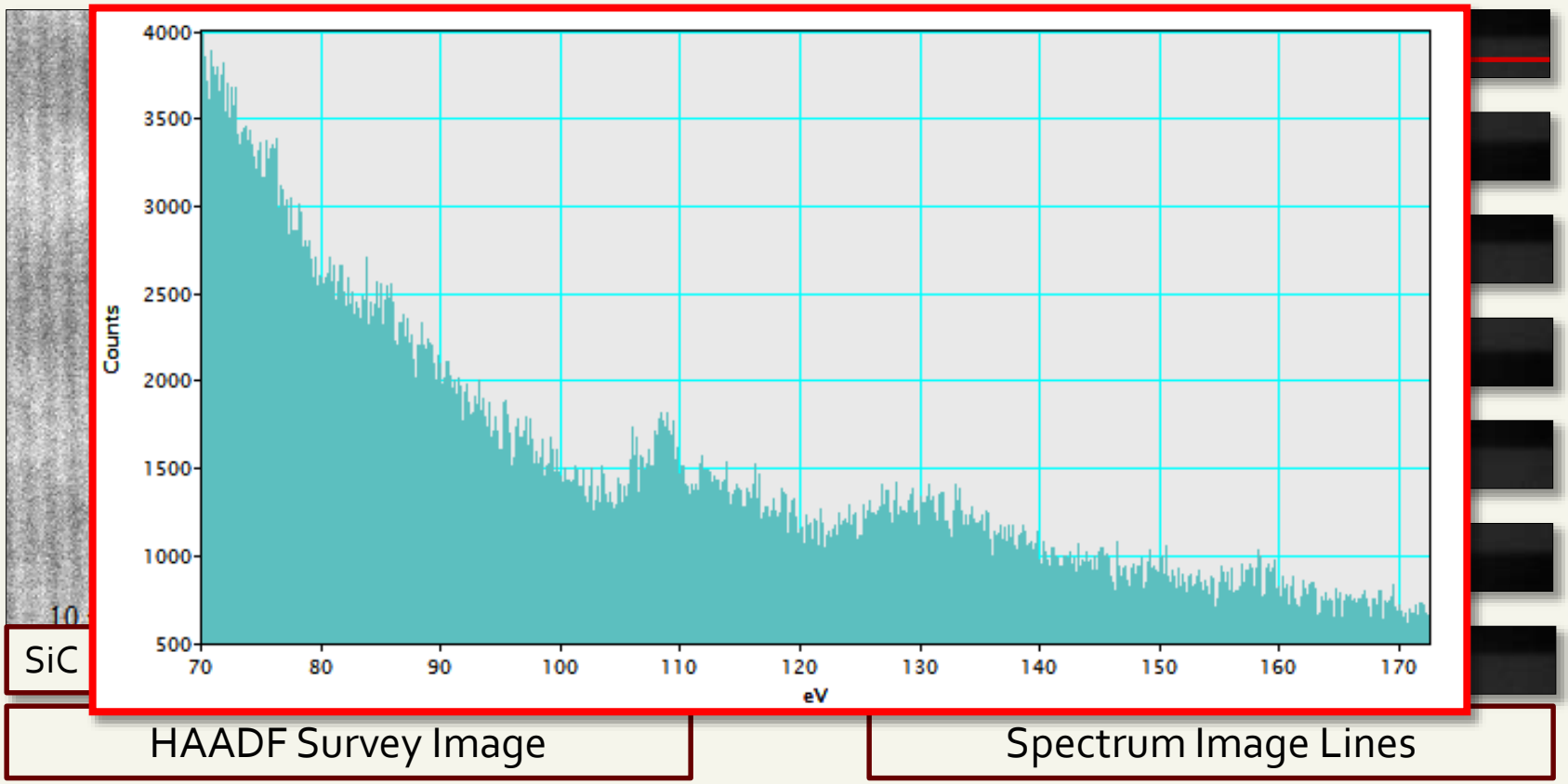
STEM-EELS OF MISCUT SAMPLES

Spectrum Imaging - areas



Spectrum Imaging - lines

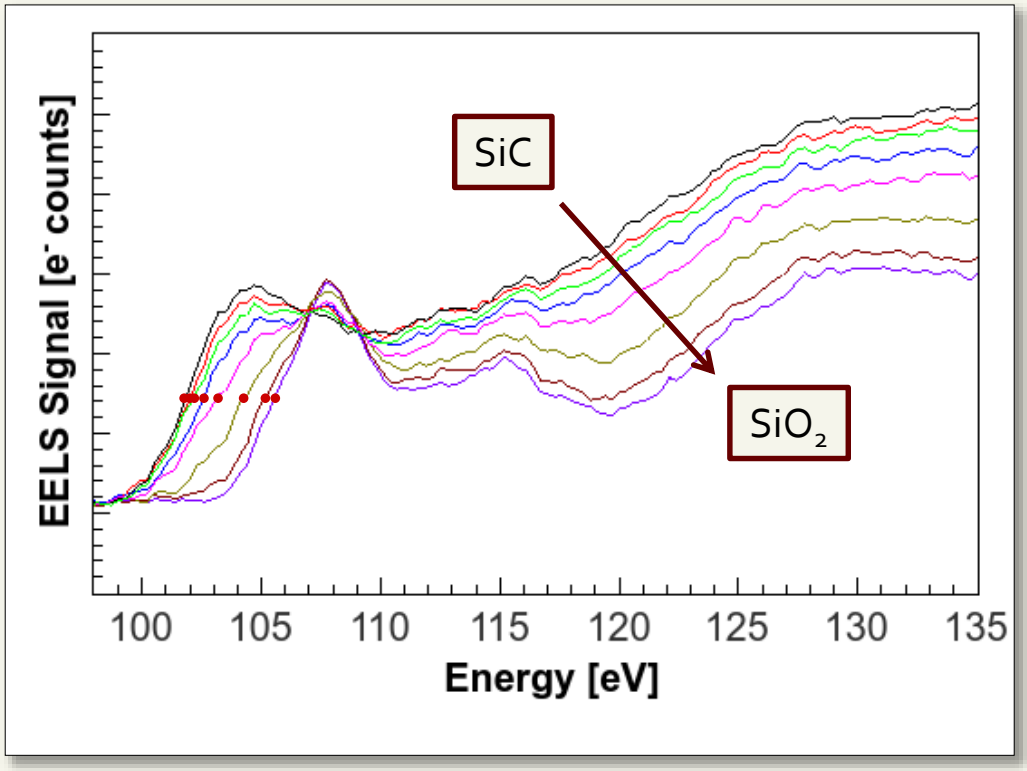
One spectrum per line



HAADF Survey Image

Spectrum Image Lines

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

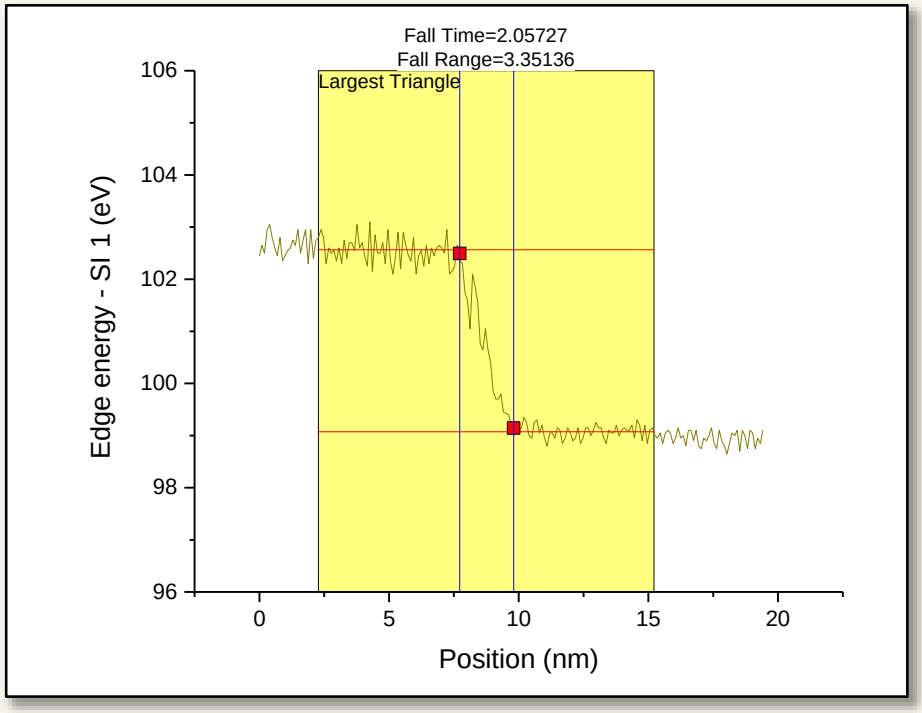


- EELS fine structure (ELNES) reflects local unoccupied density of states
  - Semiconductor → insulator
  - Edge onset → minimum energy needed to excite core shell e^-
  - Band gap widens, core levels depressed relative to E_F[1]
    - Charge transfer from Si → C/O
    - Onset shifts to higher energy

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

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

- 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



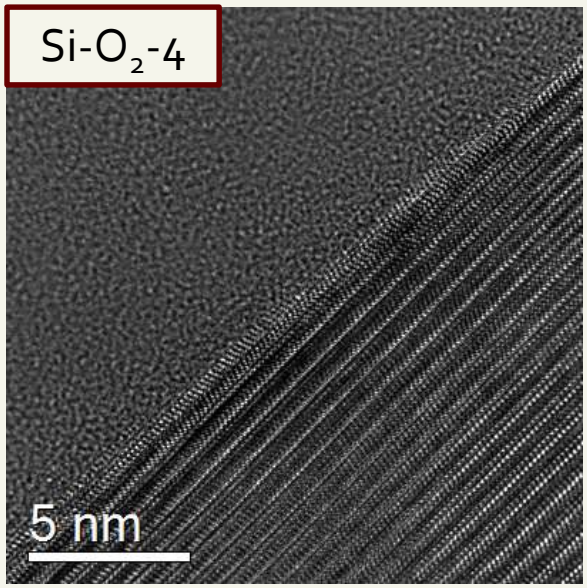
Example from new sample Si-O_2-o

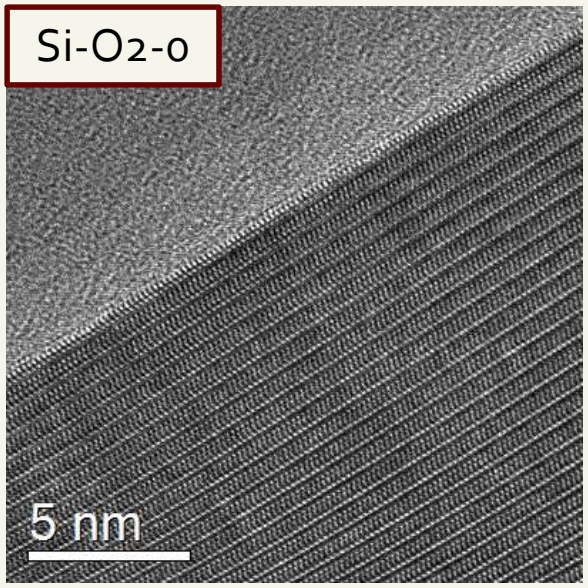
[1] D. Muller, P. Batson, and J. Silcox, Physical Review B **58**, 11970 (1998).

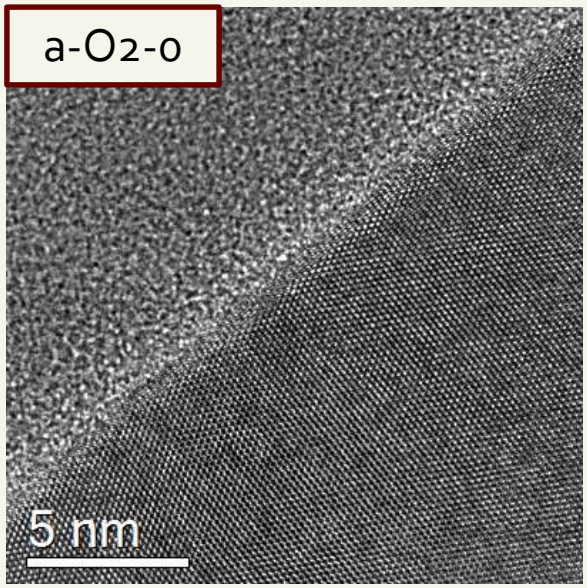
Samples investigated

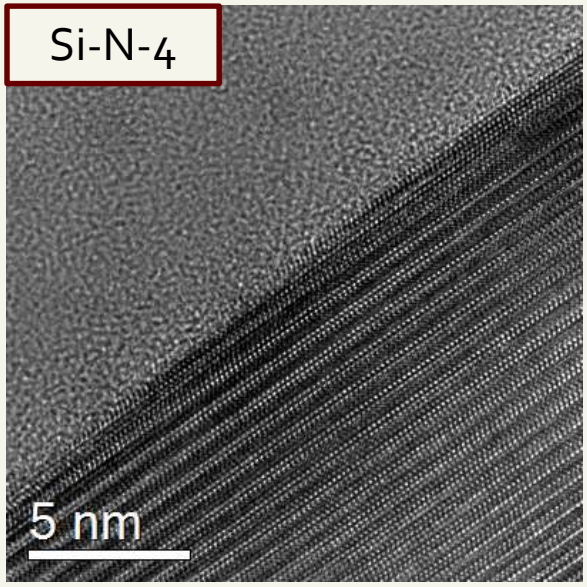
- 2 x 3 matrix aimed at comparing substrate orientation (and miscut) with processing conditions:
  - NO POA is for 2hr, all SiC substrates are n-type, SiO_2 ~60nm thick

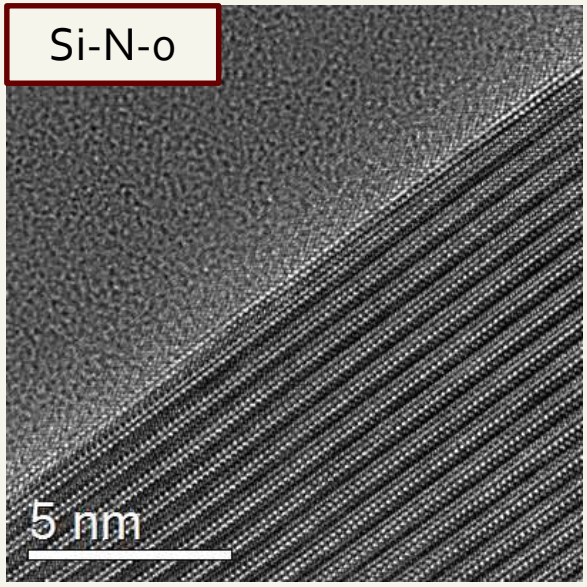
Sample Labels:	**Only oxidized**	**NO Post-annealed**
Si-face on-axis	Si-O_2-0	Si-N-0
Si-face miscut (4°)	Si-O_2-4	Si-N-4
a-face on-axis	a-O_2-0	a-N-0

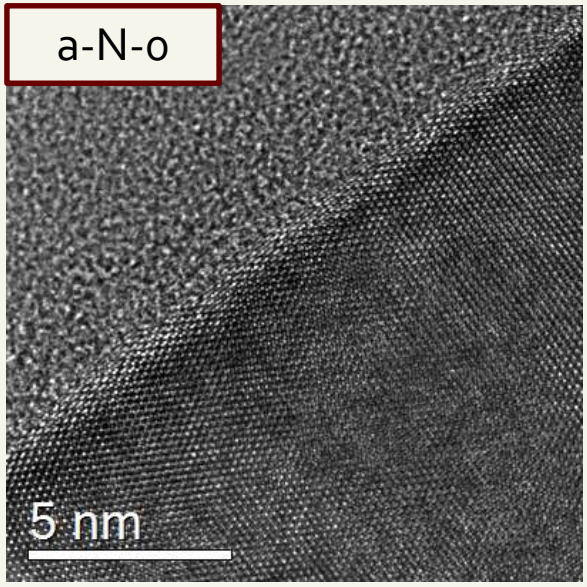

Si-O_2-4
5 nm


Si-O2-0
5 nm

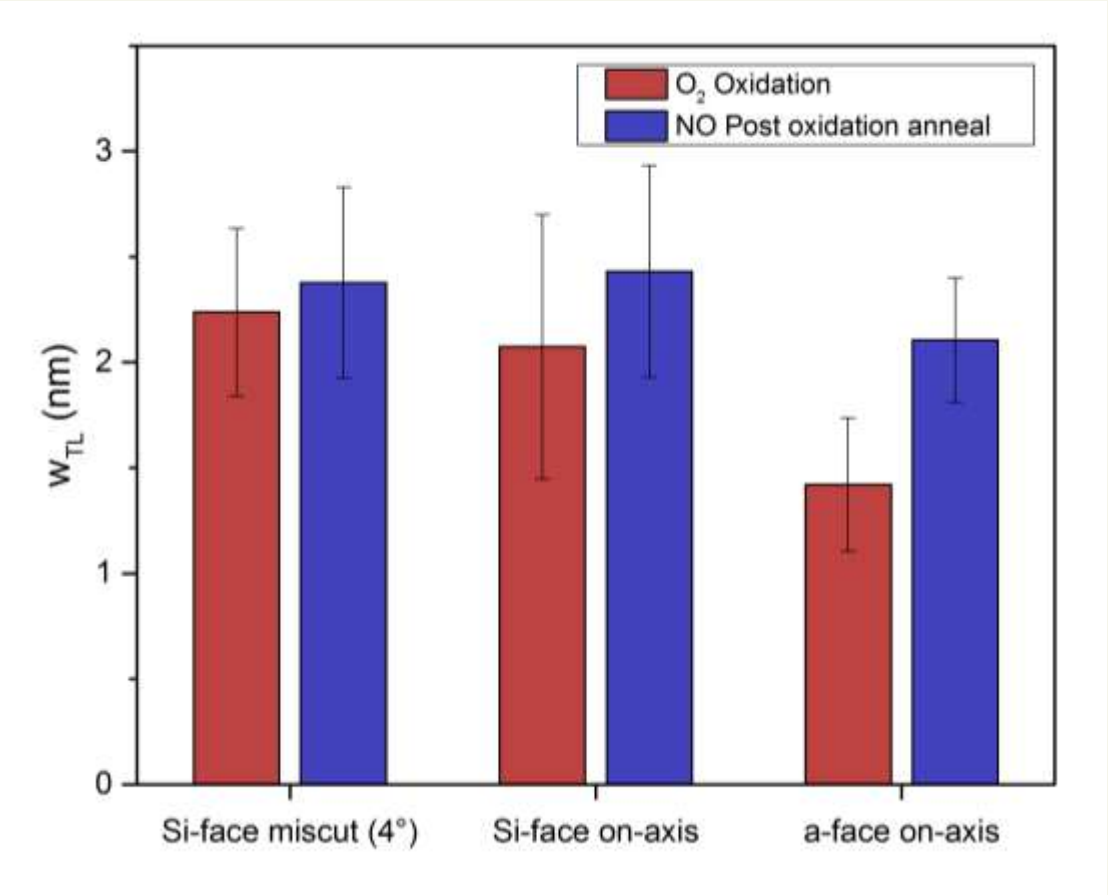

a-O2-0
5 nm


Si-N-4
5 nm


Si-N-0
5 nm


a-N-0
5 nm

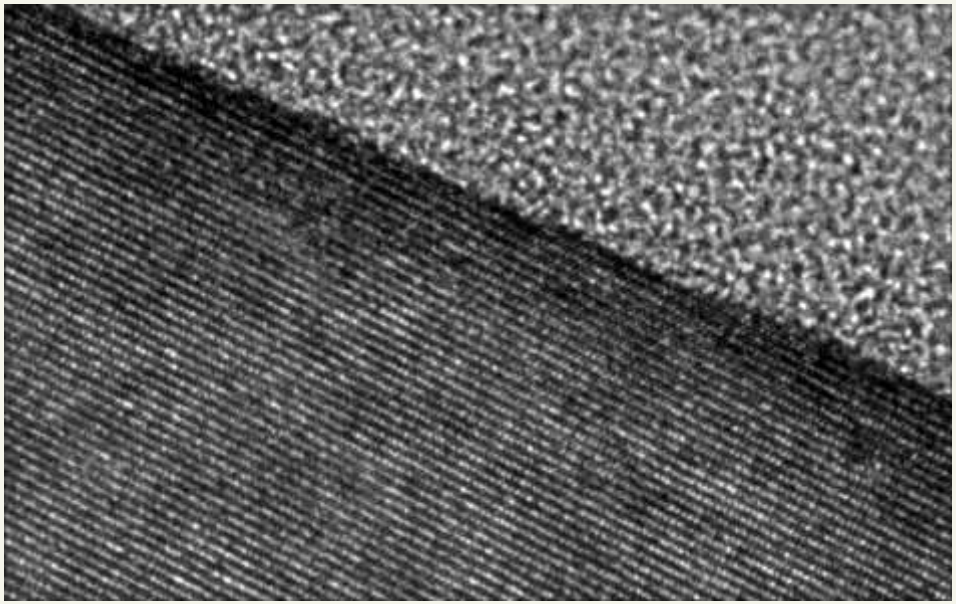
w_{TL} measurements



- 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/Vs for Si-face
  - 85 cm^2/Vs for a-face

FUTURE WORK

Roughness from HRTEM reconstructions



$$G(\boldsymbol{u}) = T(\boldsymbol{u})F(\boldsymbol{u})$$

$$G(\boldsymbol{u}) = A(\boldsymbol{u})E(\boldsymbol{u})2\sin\chi(\boldsymbol{u})\,F(\boldsymbol{u})$$

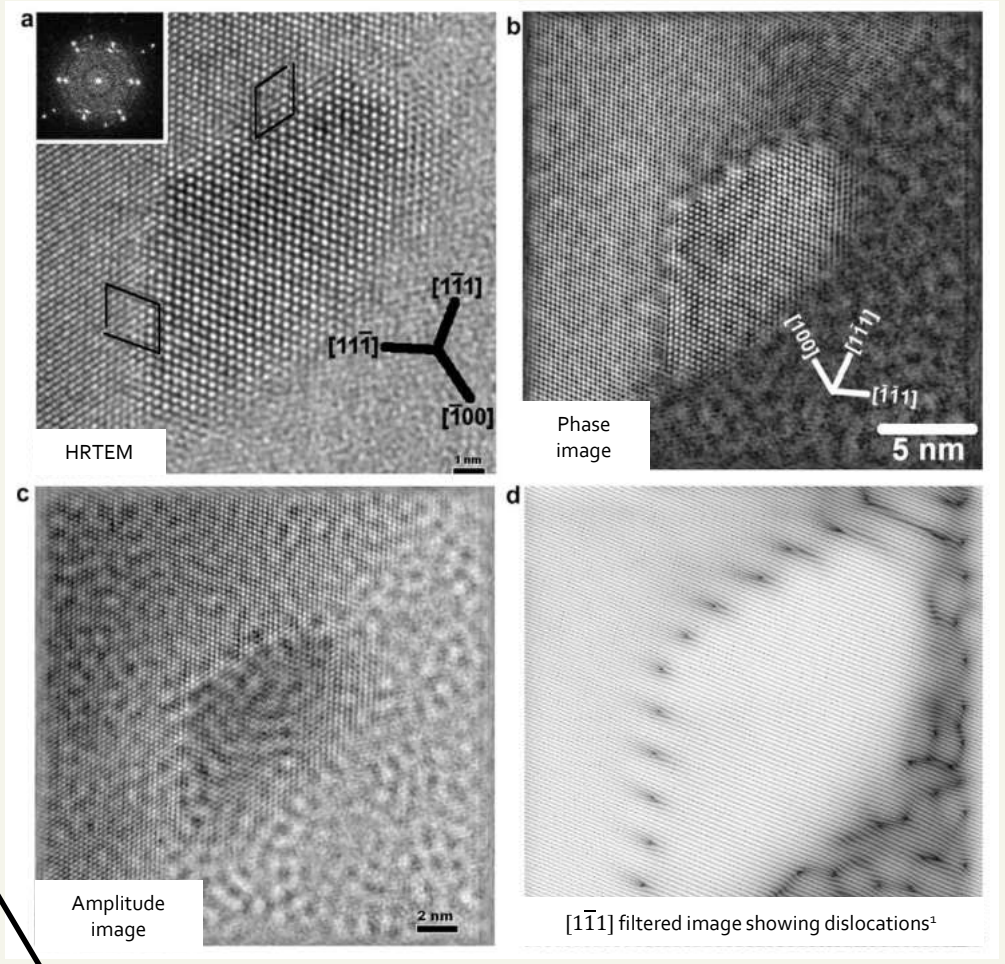
$$\chi(u,\Delta f) = \pi(\boldsymbol{\Delta f})\lambda u^2 + \frac{1}{2}\pi C_s\lambda^3 u^4$$

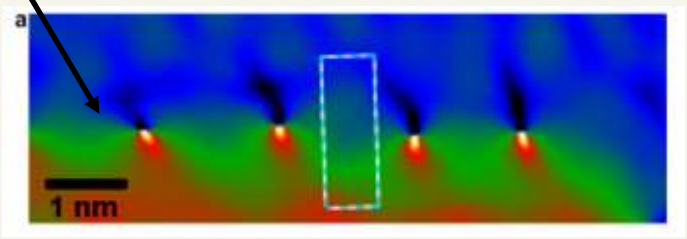
- Roughness of interface can be used to calculate power spectrum of interface
  - Estimation of surface scattering-limited mobility possible from this [1,2]
- How to measure?
  - Difficult to digitize based on single image
  - HRTEM focal series reconstruction allows extraction of pure wave function phase
  - Could also accomplish this through electron holography

[1] Goodnick, S., *et al.*, Physical Review B, **32**, 8171–8186 (1985).
[2] Zhao, Y., *et al.*, IEEE Electron Device Letters, **30**, 987–989 (2009).

Strain measurement: geometric phase analysis

- Utilizing reconstructed phase, can measure strain captured in the interface
- Has been used to measure strain at misfit dislocations in Al-Pb interfaces[1]
- Currently working on implementation of this method, but results are not ready yet





Experimental quantitative strain map[1]

[1] H. Rösner, C. T. Koch and G. Wilde, Acta Mater., 58(1), 162 (2010).

Conclusions

- Spin-etch technique has been developed and used to do initial XPS profiles
- XPS results show some interesting ledes for future investigation
  - N bonding states, valence band differences, auger parameter of oxide
- STEM-EELS results on miscut samples show unexpected results that require additional thought/analysis
  - Roughness and strain measurements at the SiC/SiO_2 interfaces in these samples are underway

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- ARL Contracts W911NF-11-2-0044 and W911NF-07-2-0046.
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THANK YOU

Questions and comments?