RUTGERS

Laboratory for Surface Modification

Medium energy ion scattering studies of ultra-thin gate dielectrics

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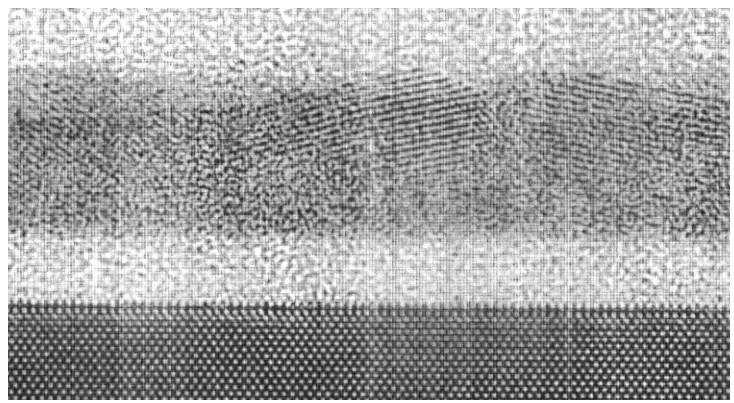


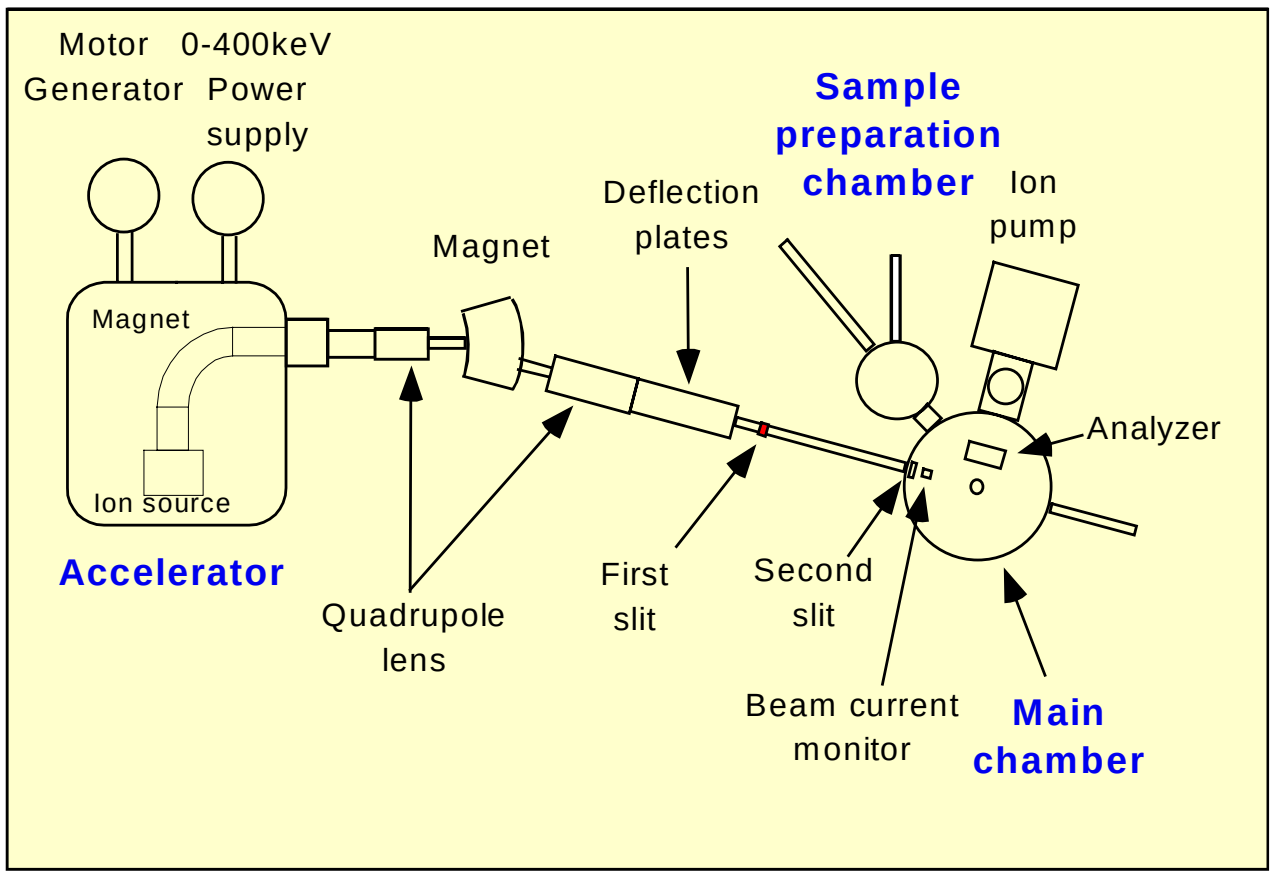
Collaborators: Lucent, IBM, NCSU, UT…

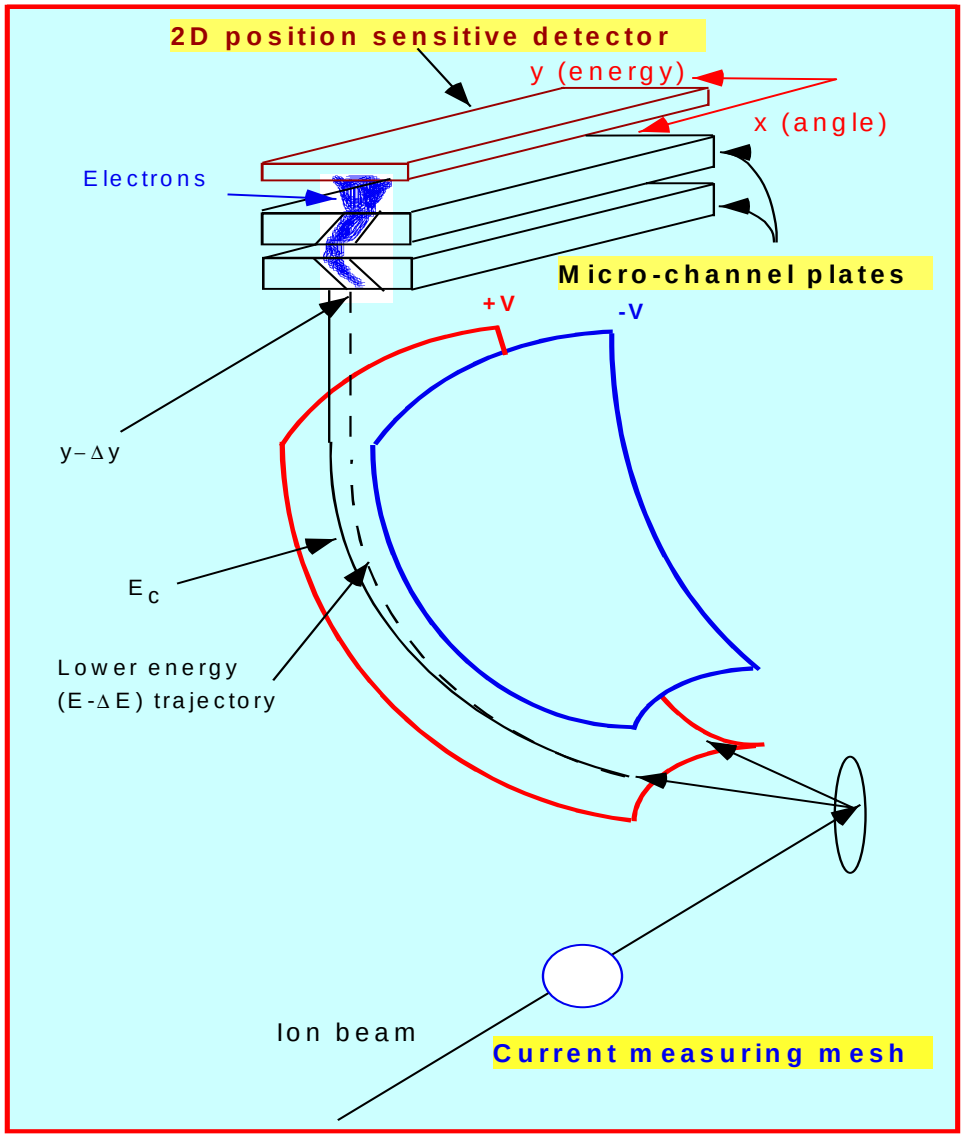
Support: SRC, NSF

Profiling method	Positive Aspects	Issues/Problems
SIMS	Depth resolution, mass separation, sensitivity	Ion yield changes Roughening/mixing
RBS	Quantification, mass resolution, Sensitivity (?)	Depth resolution poor Stopping power needed
ERD	like RBS: but good for light elements	Stopping power needed
MEIS	like RBS: but better depth resolution	Stopping power needed
NRA	Quantification, sensitivity mass resolution (?)	Depth profiling requires etchback
Resonance-NRA	Depth resolution, mass resolution (?)	Only for a few isotopes Stopping power needed
AR-XPS	Depth resolution Excellent chemical separation	Need λ's Fitting routine - soon
HRTEM STEM/EELS	True depth calibration, measures structure and composition (w/EELS)	Must work with >20nm slices
FTIR	Chemical sensitivity Can see hydrogen	Must use etchback Calibration standards
Ellipsometry	Easy to perform, non-destructive	Strongly model dependent Requires knowledge of ε_i's

Medium Energy Ion Scattering (high-resolution RBS)

- Mass (isotope) specific; quantitative – total areal density
- sub-nm depth resolution; 100 keV protons used
- electrostatic energy analysis; little beam damage





- Sensitivity:
  ≈ 10^{+12} atoms/cm^2 (Hf, Zr)
  ≈ 10^{+14} atoms/cm^2 (C, N)

- Accuracy for determining total amounts:
  ≈ 5% absolute (Hf, Zr, O)
  ≈ 2% for relative measurements
  ≈ 10% absolute (C, N)

- Depth resolution: (need density of sample)
  ≈ 3 Å near surface
  ≈ 10 Å at depth of 40 Å
  [improved by spectral simulation]

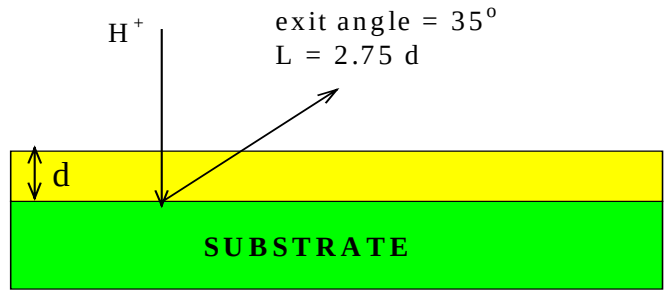
High resolution electrostatic detector

Depth resolution in MEIS depth profiling

Basic concept: Depth profile is based on the energy loss of the ions traveling through the film (stopping power $\varepsilon \propto dE/dx \propto L$).

Example: Depth resolution for ≈ 100 keV protons:

- Stopping power SiO_2 ≈ 12 eV/Å
  Si_3N_4 ≈ 20 eV/Å
  Ta_2O_5 ≈ 18 eV/Å
  Si ≈ 13 eV/Å
- Energy resolution of the spectrometer ≈ 150 eV
- 35° exit angle L = 2.75 d

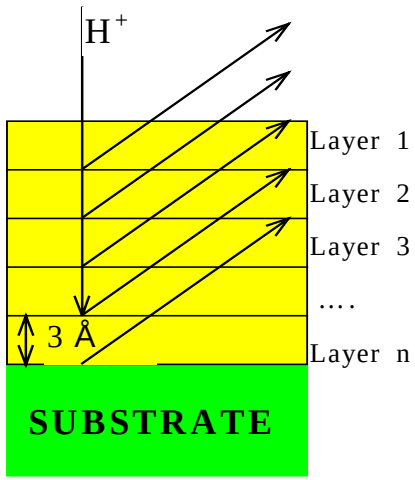


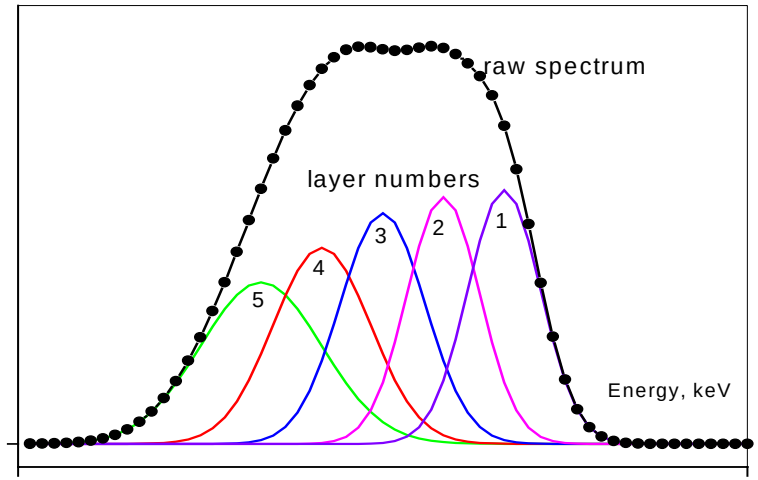
➔ "Near surface" depth resolution ≈ 3-5 Å

* Depth resolution becomes worse for deeper layers due to energy straggling ($\propto L^{1/2}$)

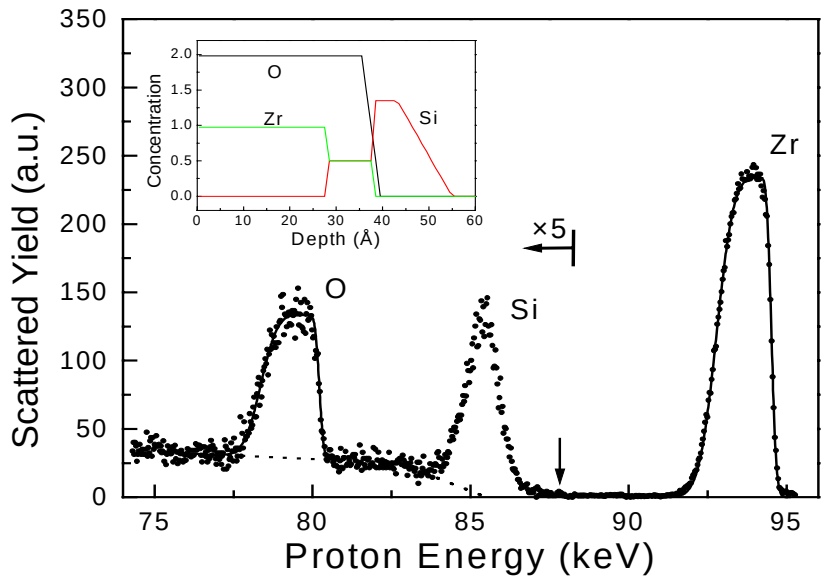
Concentration profiles obtained from energy spectra simulations

Layer model:





- Areas under each peak corresponds to the concentration of the element in a 3Å slab
- Peak shapes and positions come from energy loss, energy straggling and instrumental resolution.
- The sum of the contributions of the different layers describes the depth profile.



"Uncertainties" in the MEIS (or RBS) depth profiling analysis:

Issue/uncertainty	What they affect	Solutions
Neutralization ratio for H^+ (or other scattering particle)	**Absolute concentrations (relative concentrations are OK)**	• **Direct measurement by SSD** • **Reference samples**
"Stopping power" (energy loss) and straggling parameters of H^+ in material(s)	**"scaling" of the z (depth) axis; modeling**	• **Independent measurements of thickness by XPS, TEM...** • **Reference samples**
Non-gaussian single scat. ion energy distribution and non-statistical number of scat. loss events	**peak shape; modeling, especially at the surface**	• **Not issue for films >2nm; new basic theoretical and experimental work needed to address this for <1.5nm films**
Film thickness uniformity, roughness and compositional gradients	**may be confused with each other**	• **Angular resolved MEIS** • **Independent measurements by TEM, AFM, XPS etc.**

Other issues: Substrate/overlayer strain; channeling/blocking yield; shadow cone….

Rutgers ultrathin dielectric films and interfaces group

Past work:

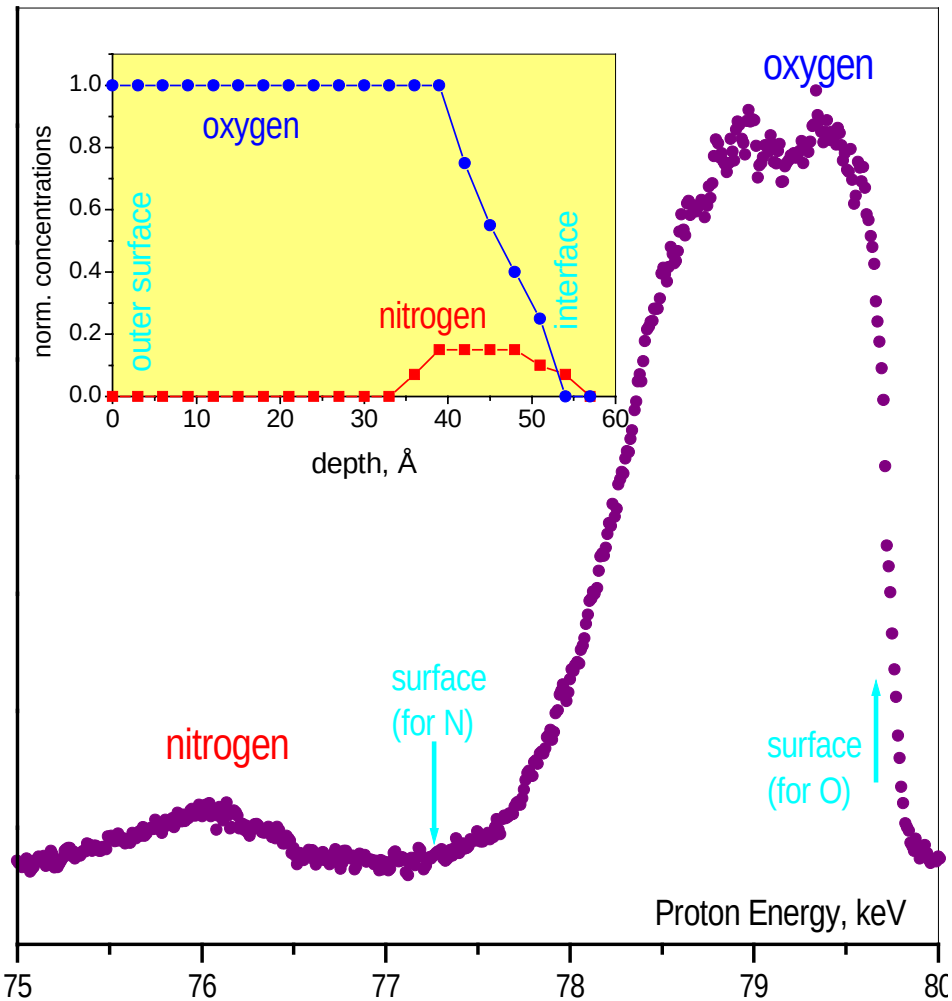
- The SiO_2/Si system: film growth chemistry, interface structure, composition and properties
- SiO_xN_y/Si: nitrogen incorporation chemistry and properties

  See, for example: E.P. Gusev, H.C. Lu, E. Garfunkel, T. Gustafsson, and M.L. Green, *Growth and Characterization of Ultrathin Nitrided Oxide Films*, IBM Journal of Research and Development, 43 (1999) 265-286; or selections from the edited book: *Fundamental Aspects of Ultrathin Dielectrics on Si-based Devices*, edited by E. Garfunkel, E. Gusev and A. Vul', Kluwer Academic Publishers, 1998.

Current work:

- High-K metal oxide dielectrics: film growth and composition, interface behavior, structure, electrical properties.…

Nitridation of 4.5nm SiO_2 on Si by NO; 950ºC, 1hr

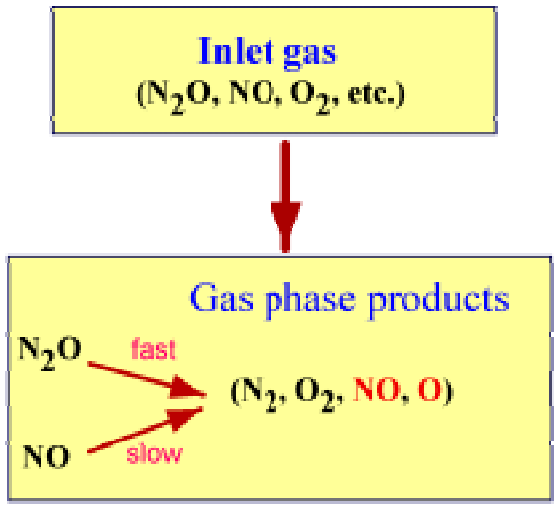


Final N content: 1.6ML

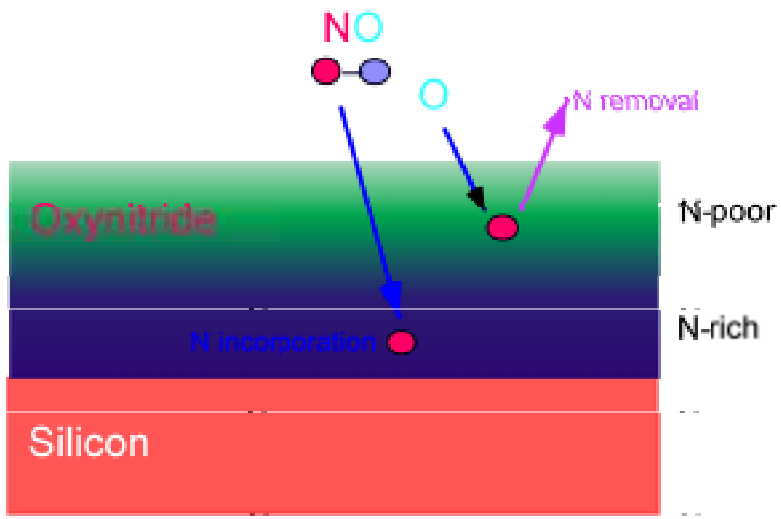
(1 ML = 6.8×10^{14} cm^{-2})

Nitrogen is located within 1.5nm of interface.

Processes relevant to the thermal oxynitridation of Si



Gas phase decomposition at high T



Short summary of our work on nitrogen chemistry in oxynitrides

- **Why nitrogen? – diffusion barrier, hot electron degradation, higher ε_k, but…**
- **MEIS - useful for depth profiling 0-5 nm oxynitrides (with >.1ML N).**
- **N_2O decomposes at reaction temperature: $N_2O \Rightarrow N_2 + O \Rightarrow NO$**
- **NO is the active (oxy)nitriding agent and reacts similar to O_2 (as in D-G).**
- **N is kinetically trapped in the film; oxide is more stable that nitride**
- **NO and N_2O differ in that: N_2O is an O source which removes N from the film**
- **N oxynitride layering can be obtained by thermal methods (e.g. $NO/O_2/NO$)**
- **Plasma and other non-thermal methods yield higher surface N concentrations**

Requirements for a high-K gate dielectric stack

Electrical

- High (>15) dielectric constant (capacitance)
- Low leakage current
- Low concentration of interface state and trapped charge defects
- High channel mobility and reliability

Physical/material

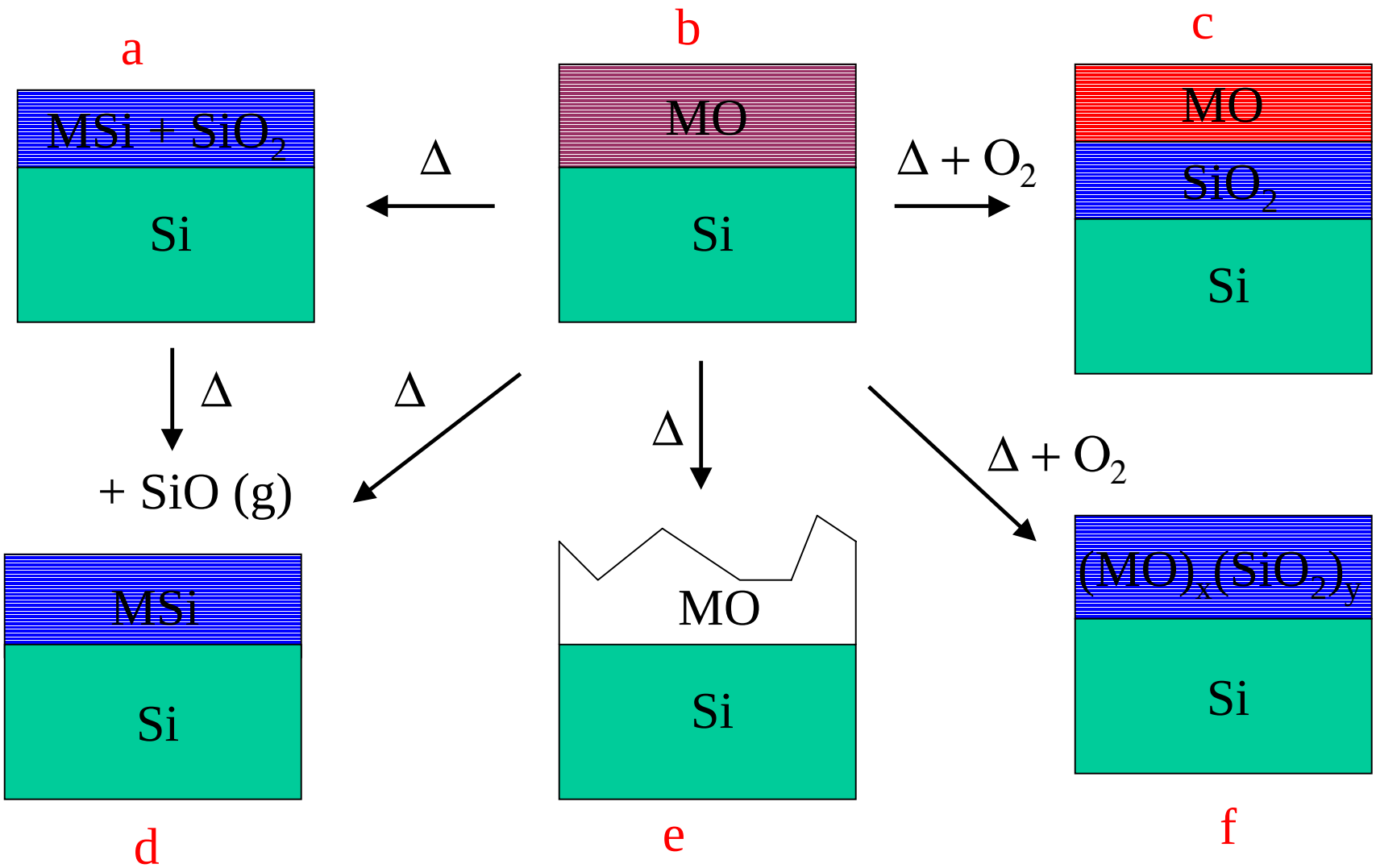
- high thermal stability; no reaction with substrate Si
- minimal roughness and crystallinity
- minimal interfacial SiO_2 **defects**
- low defect concentration; correct stoichiometry

If metal gate electrode:

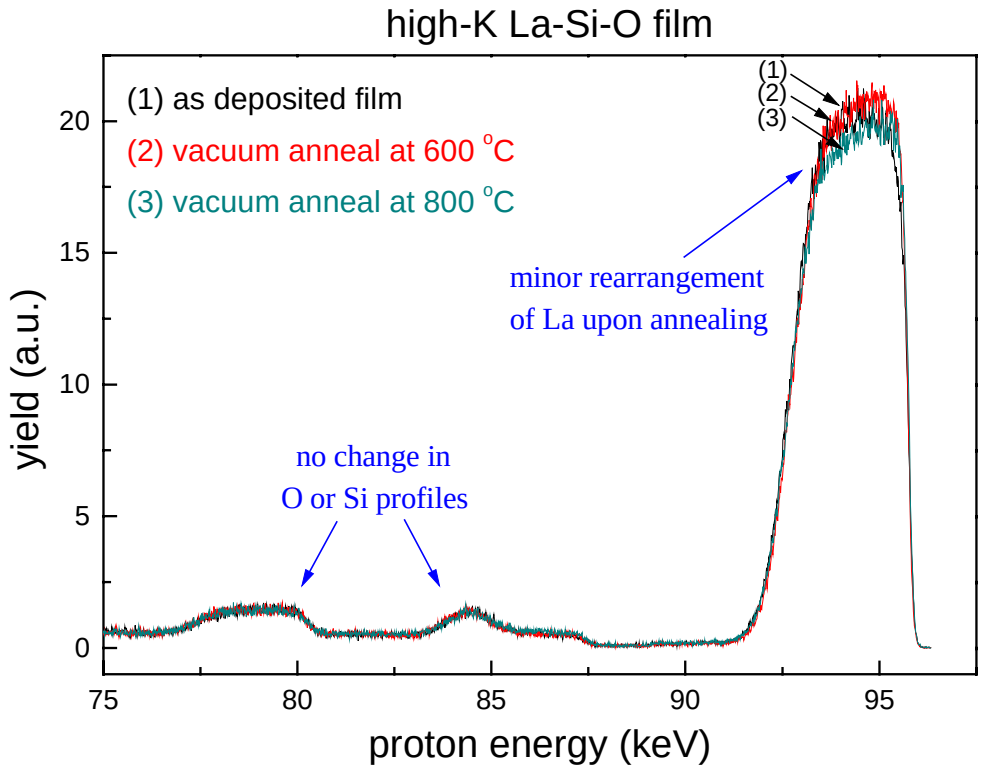
- thermal stability wrt dielectric
- appropriate barrier height

+ integration!!!

Metal oxide reactions on silicon



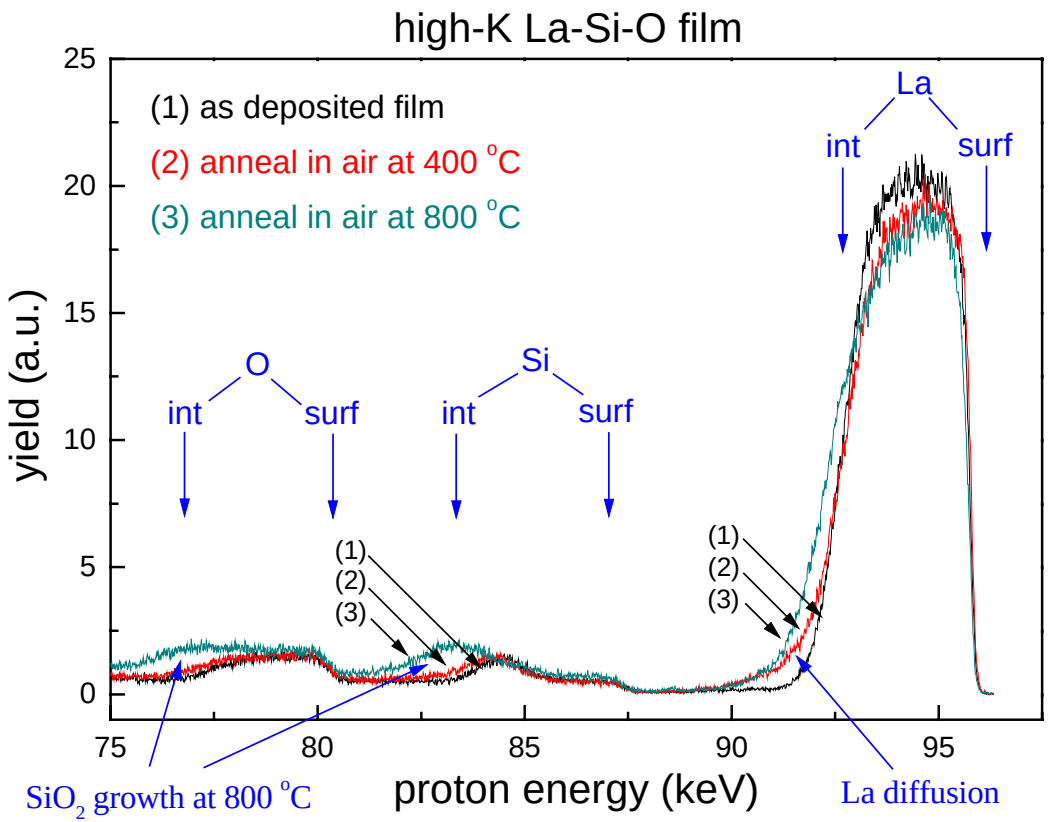
MEIS spectra of La_2SiO_5 before and after vacuum anneal to 800°C (w/NCSU)



- Annealing up to 800 °C in vacuum shows no significant change in MEIS spectra.
- Surface remains flat by AFM.

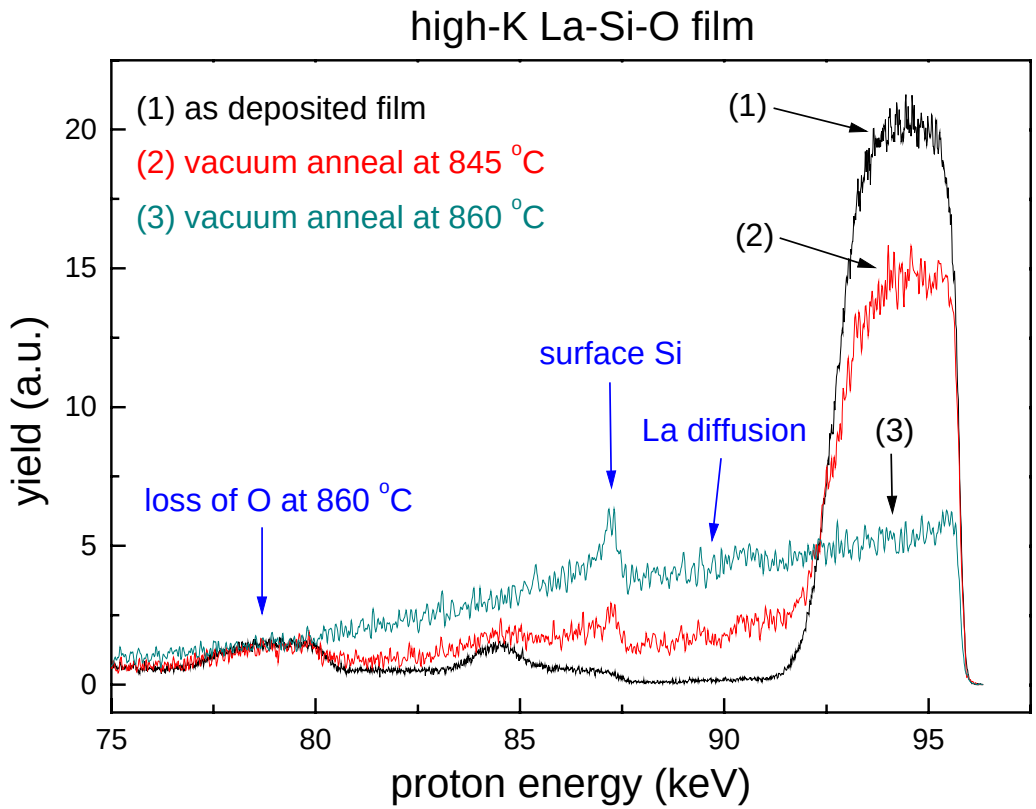
MEIS spectra of La_2SiO_5 before and after in-air anneal

- stoichiometry and thickness consistent with other analyses
- 400°C anneal leads to minor broadening of the La, O and Si distributions
- 800°C anneal shows significant SiO_2 growth at interface
- La diffusion towards the Si substrate



MEIS spectra of La_2SiO_5 before and after vacuum anneal to >800 °C

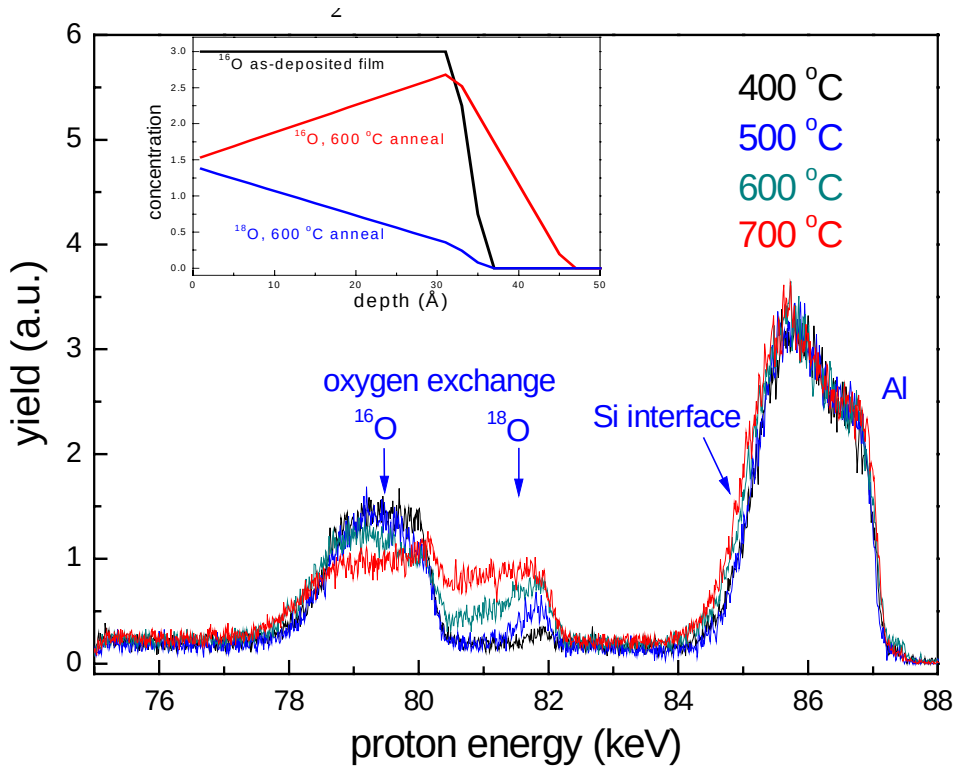
- Annealing to >800 °C in vacuum shows significant change in MEIS spectra. Silicon surface peak grows substantially and La diffuses away from the surface.
- Model is O loss by SiO desorption from film.



Oxygen exchange in 30Å Al_2O_3 annealed in 3 Torr $^{18}O_2$

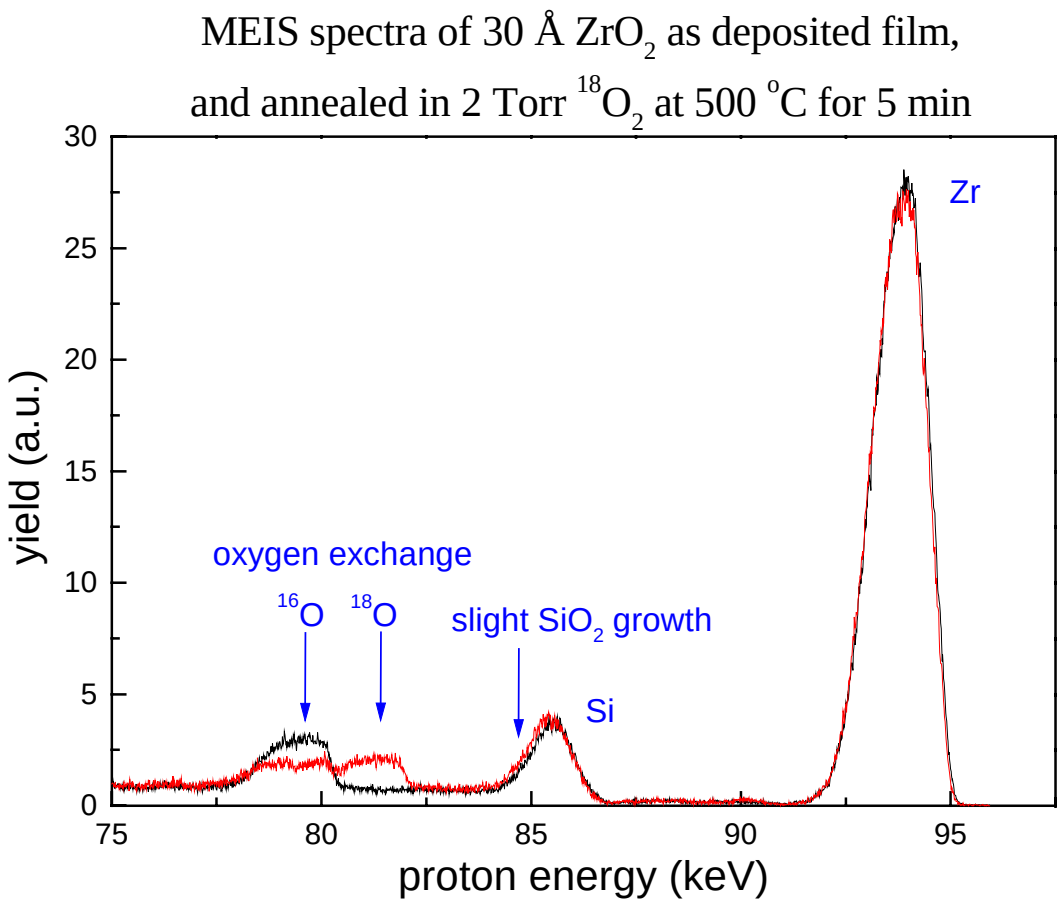
- O exchange throughout the Al_2O_3 film. Exchange commences at the surface and moves in deeper.
- Si oxide grows at the interface.

Prep.	Tot. O [ML]	^{16}O [ML]	^{18}O [ML]
as-dep	35	35	0
400 ^{o}C	37	36	1
500 ^{o}C	36	33	3
600 ^{o}C	41	31	10
700 ^{o}C	43	24	19



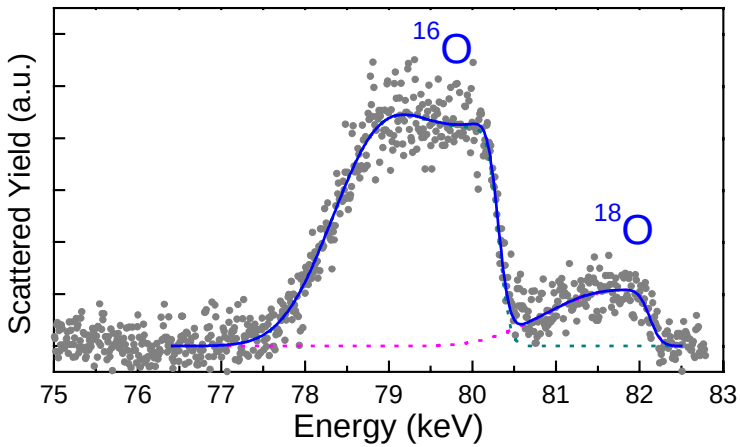
MEIS results for 30Å as-deposited ZrO_2 annealed in 2 Torr $^{18}O_2$ at 500°C for 5 min. (w/UT)

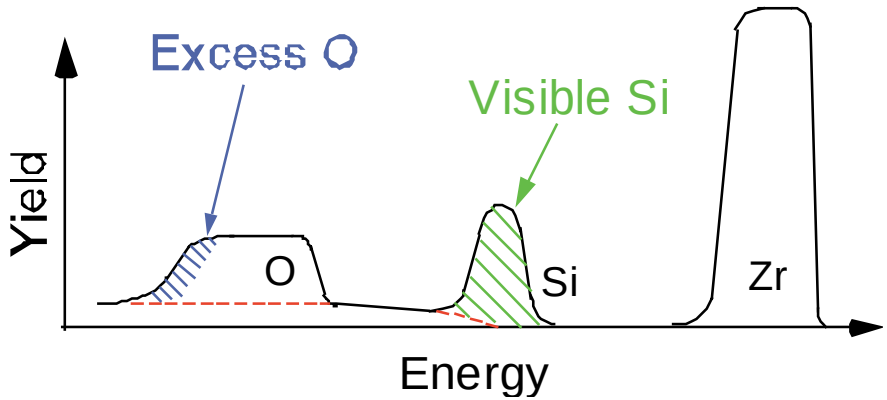
- No change in Zr distribution for annealing up to 900 °C.
- Remains flat by AFM after $^{18}O_2$ anneal.
- high O exchange in the ZrO_2 film by 500 °C.
- Si oxide grows at the interface.

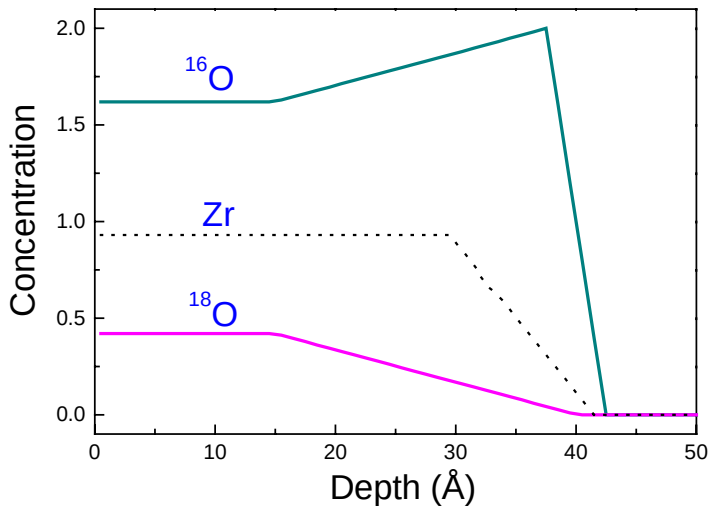


Some methods to examine oxygen exchange and interfacial SiO_2 growth

1 Torr $^{18}O_2$ - 300 ^{o}C - 5 min



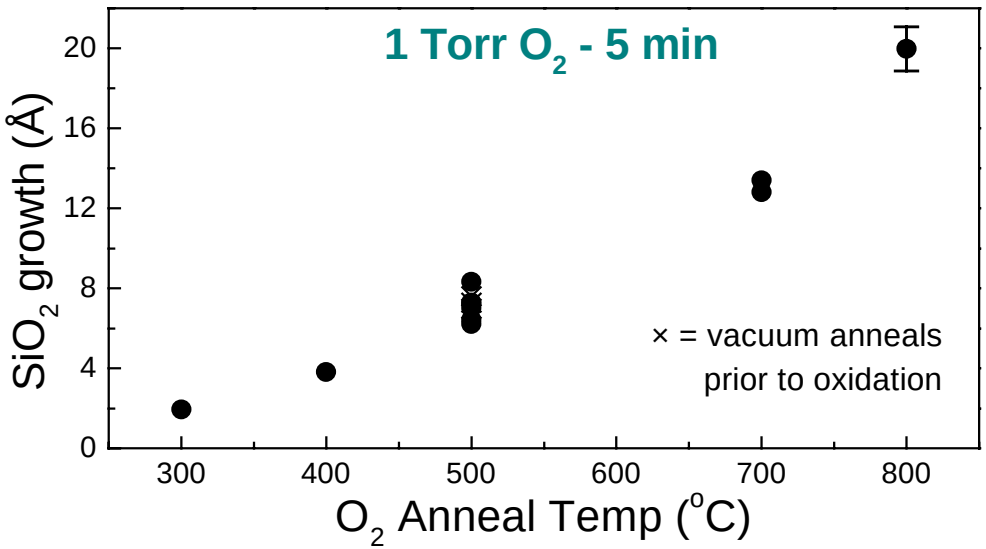




2-3 Torr $^{18}O_2$ anneal at T ≈500 ^{o}C for 5 min

Oxide	Thickness [Å]	$^{18}O/O_{tot}$
Al_2O_3	30	0.083
$(Y_2O_3)_x(SiO_2)_y$	13	0.24
ZrO_2	30	0.50
HfO_2	25	0.56

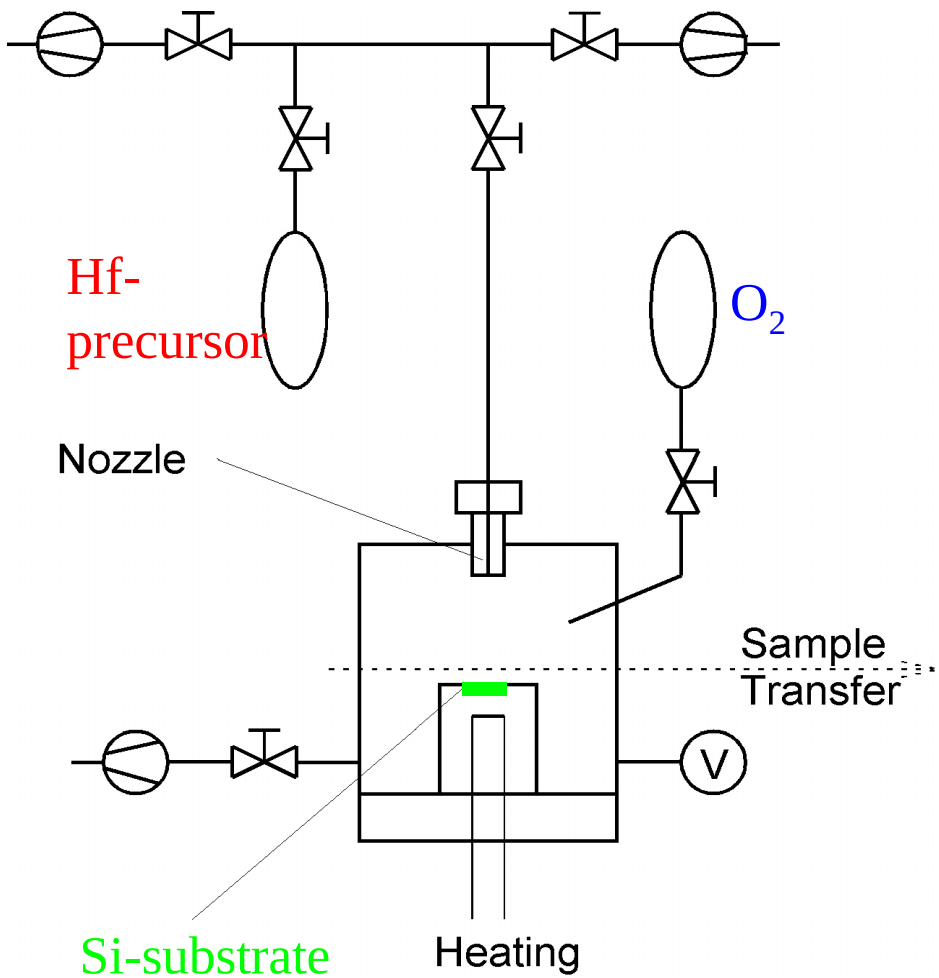
SiO_2 growth at ZrO_2/Si interface during oxygen anneal



- SiO_2 interface growth strongly T-dependent
- SiO_2 growth rate faster than DG-like growth (O_2 on Si).
- No significant pressure or time dependence in Torr, minutes range (implying saturated; try 10^{-6} - 10^{-3} Torr anneals)
- ZrO_2 presumed to act as O_2 dissociation catalyst and fast ion conductor source of O atoms

Schematic of CVD system

CVD (ALCVD) system is part of a complex UHV system, that includes a thermal processing chamber and XPS analysis.



Growth and properties of CVD-grown HfO_2 films

Growth parameters

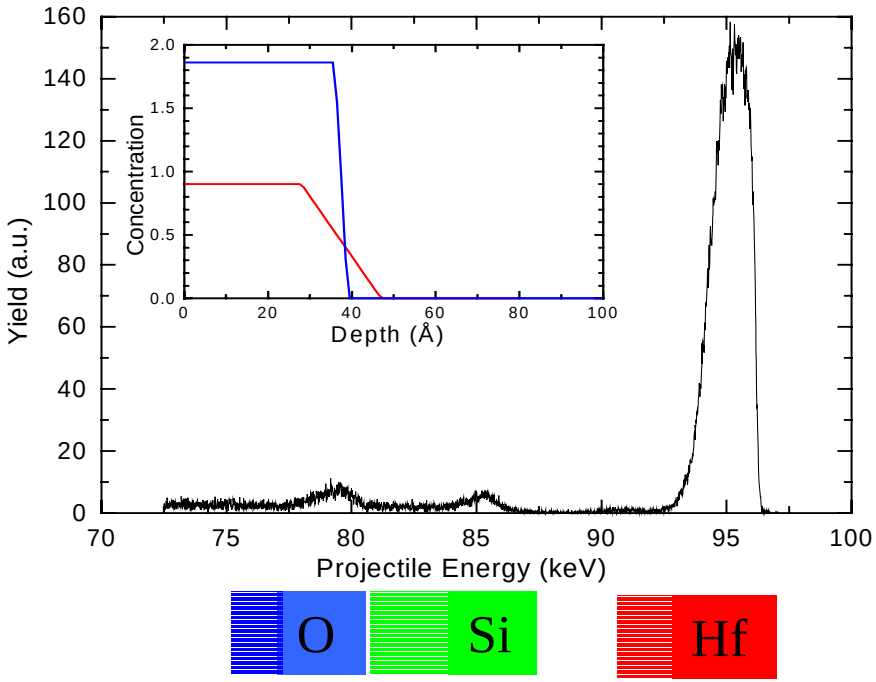
Substrate temperature T_S	250-450 ºC
Precursor temperature	25-50 ºC (for t-butoxide)
Time	20-600 s

Analysis

XRD:	Amorphous structure
XPS:	Surface carbon
RBS/MEIS:	Stoichiometric HfO_2
	Growth rate 1-5 Å/s
AFM:	Surface roughness ≈ 2 Å
Electrical:	Leakage current (acceptable)
	Dielectric constant (18-20)

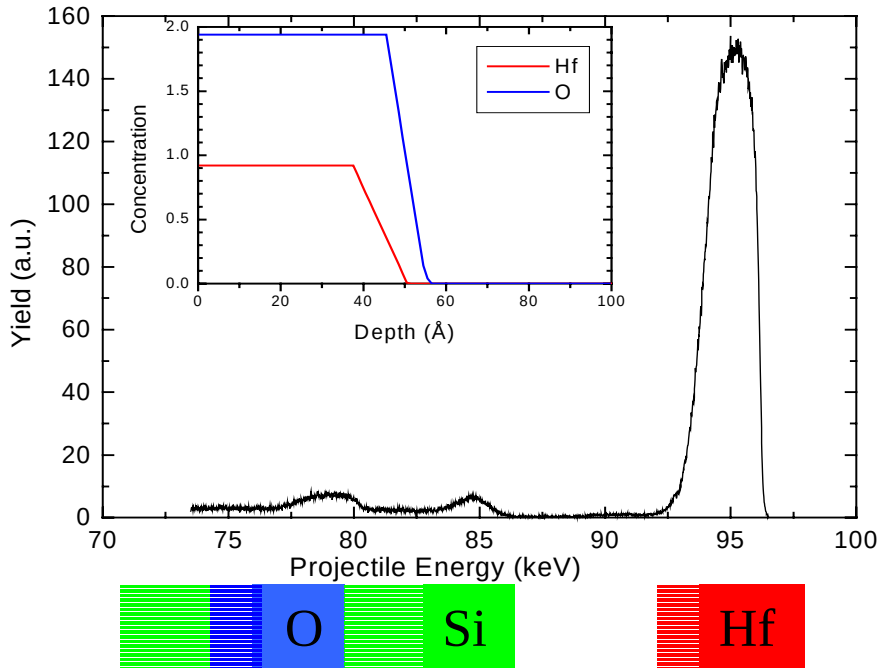
Various starting surface configurations examined: Si-H, SiO_2, Si_3N_4

40 Å HfO_2 grown on HF-cleaned Si



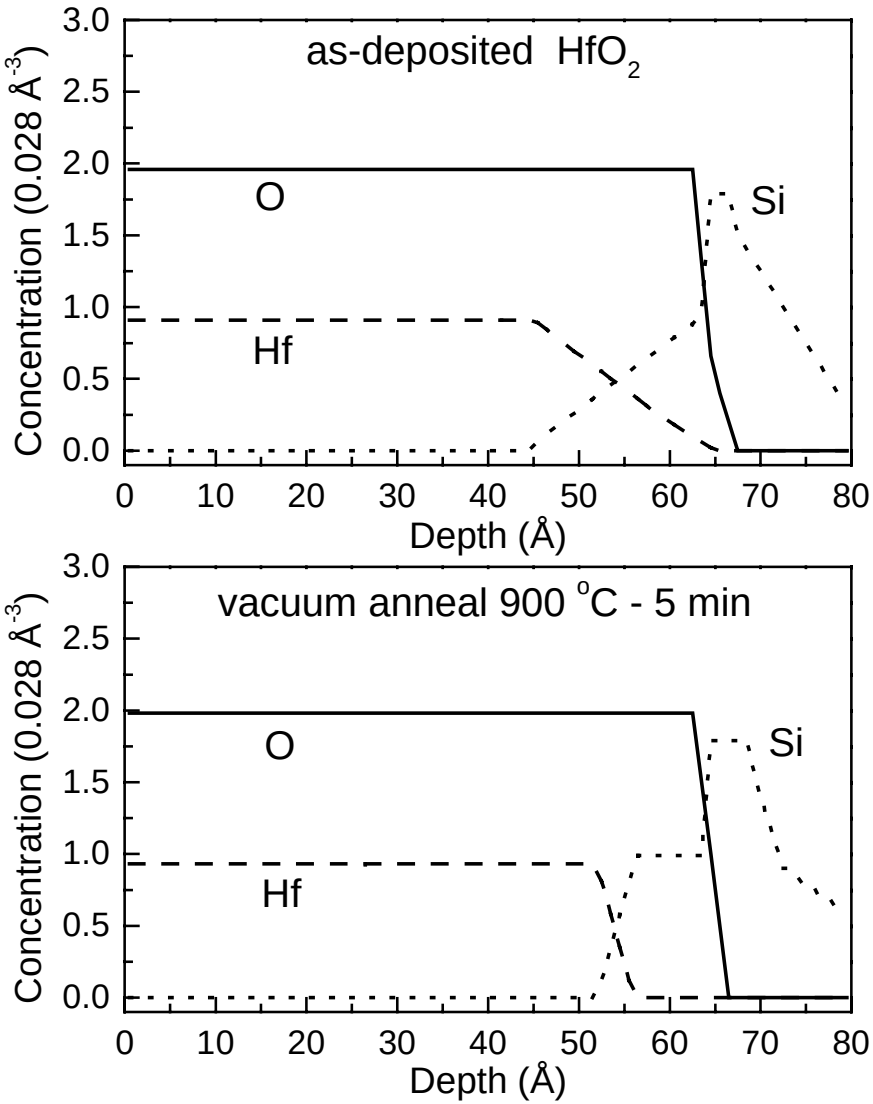
- MEIS analysis showed little interfacial SiO_2 and (probable) silicide formation
- Poor electrical characteristics …

45 Å HfO_2 grown on 12 Å SiO_xN_y



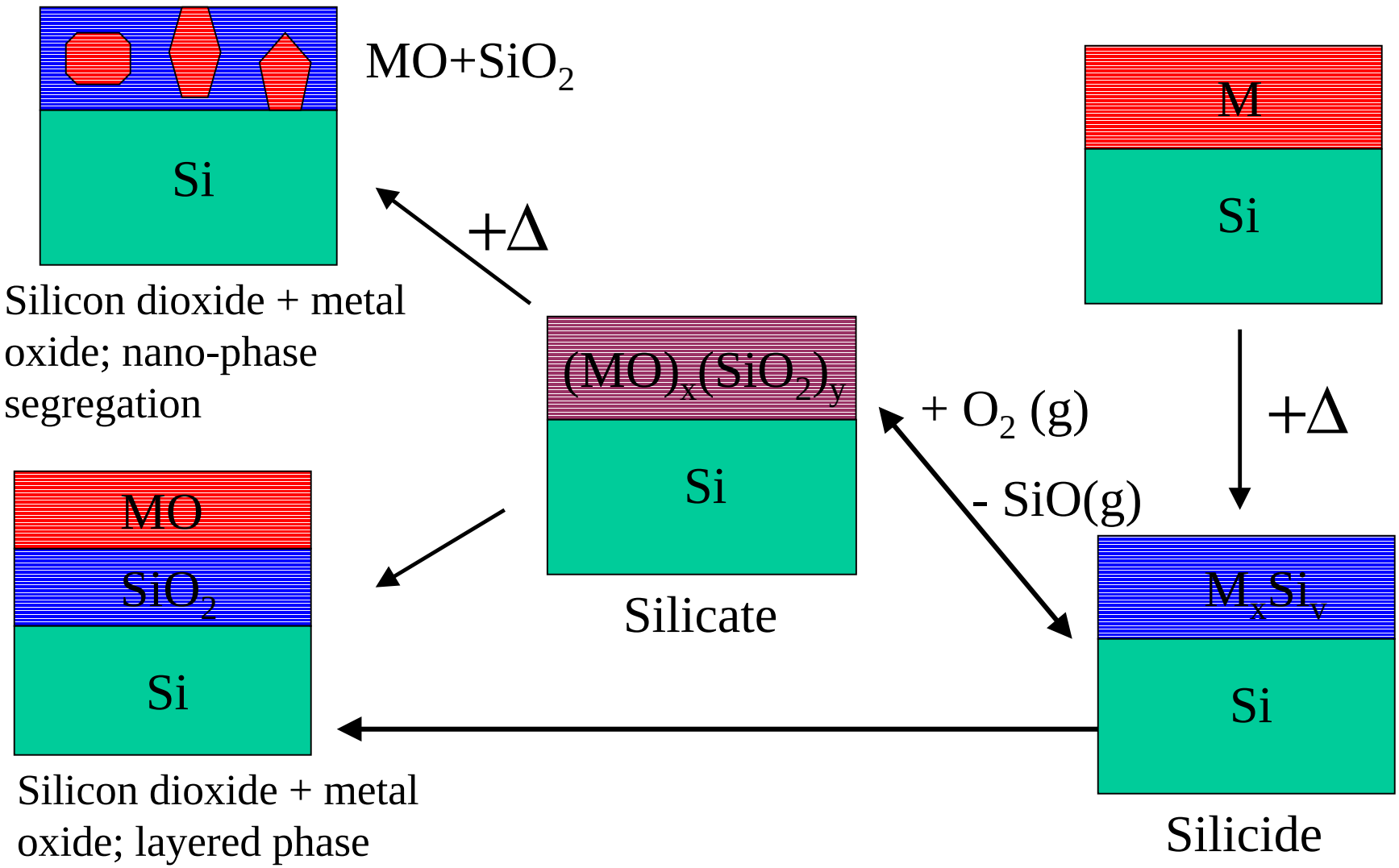
- MEIS analysis showed interfacial SiO_2 and no silicide formation
- Promising electrical characteristics …equivalent SiO_2 thickness ~20Å

Effect of anneal on interface composition for $HfO_2/SiO_x/Si$ system



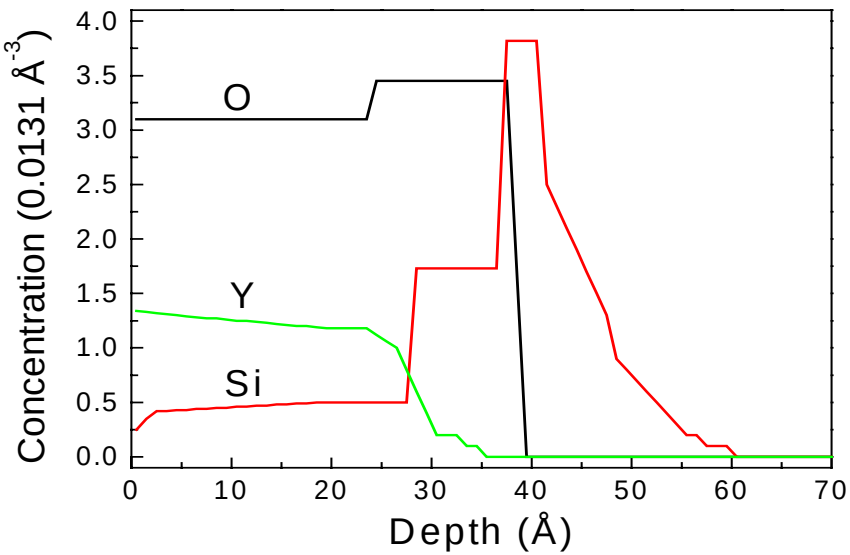
MEIS depth profiles of as-deposited and vacuum annealed 50Å HfO_2 films on Si(100). An initial graded Hf-silicate interfacial layer appears to sharpen and form a more stoichiometric SiO_2 phase after annealing. Phase segregation?

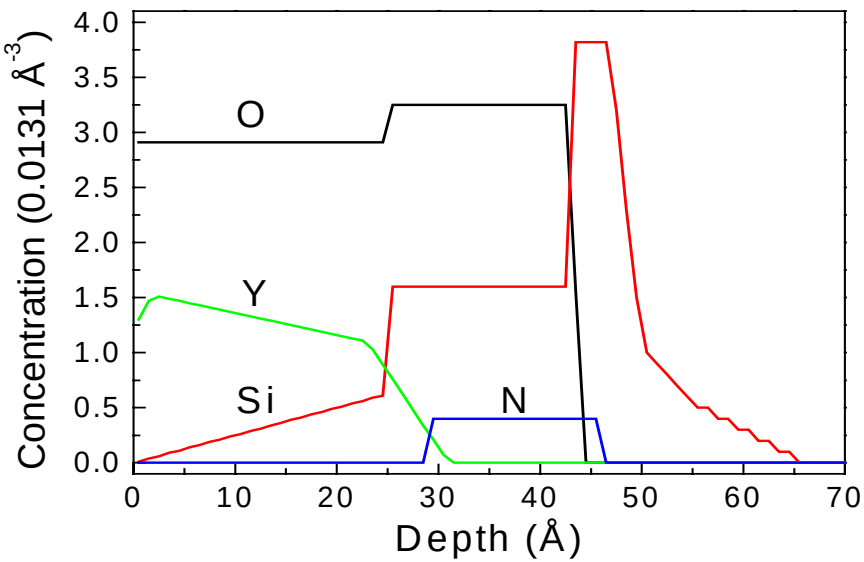
Other M-Si-O reactions



Y_2O_3 + SiO_2 films (w/NCSU)

- Amount and distribution of Si and Y in the film change for different interface compositions, and growth/anneal conditions.
- N profiles obtained for N_2O processed substrates.



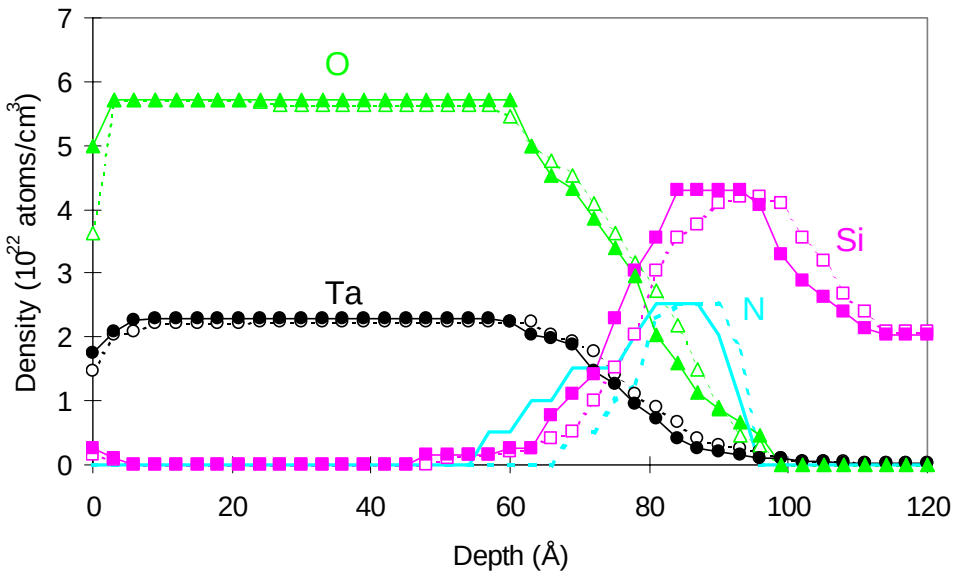


- sputtering ~8 Å of Y onto HF-last Si, followed by oxidation, leads to silicate formation: $(Y_2O_3)/(SiO_2)$ ~ 3/2

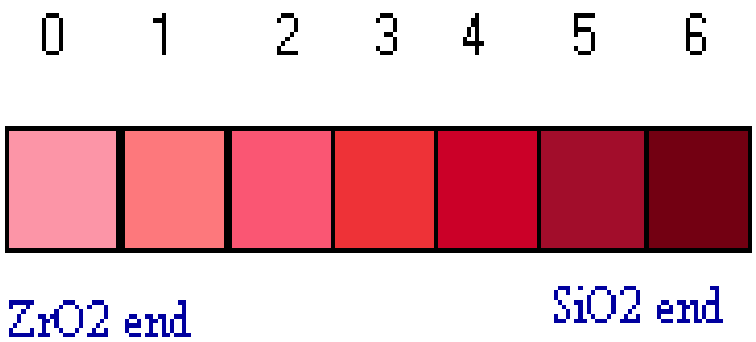
- metal sputtered onto SiO_xN_y, followed by oxidation, leads to reduced silicate formation – SiN is diffusion barrier

MEIS yield change on nitrided sample after 700°C anneal

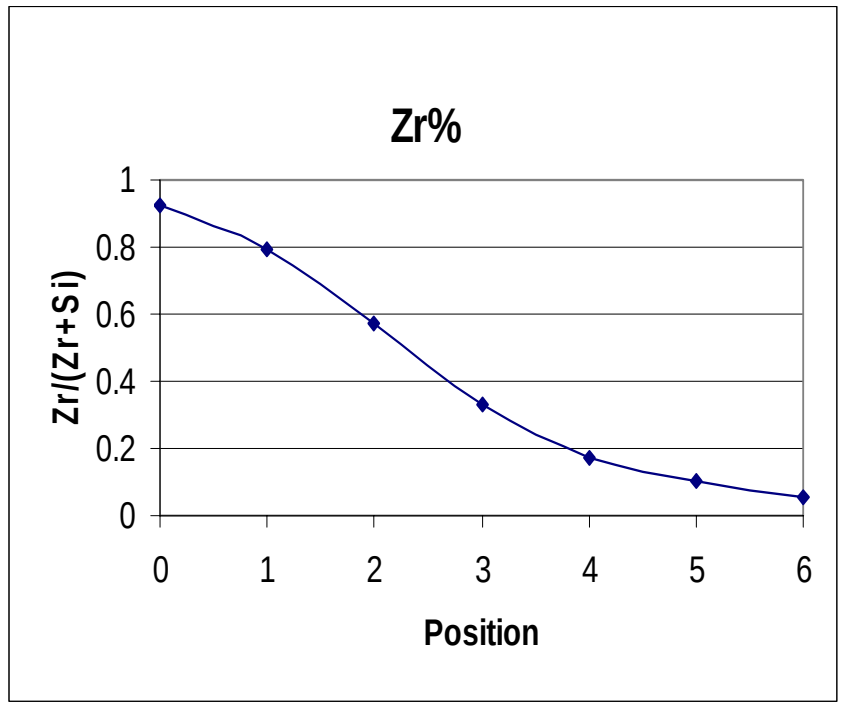
- Little change in overlayer or interface of Ta_2O_5/SiN/Si sample following 700C anneal.
- SiN interface more stable than SiO interface for TaO_x/Si reactions



ZrO_2 + SiO_2 variable composition "compositionally spread" film on Si (w/Lucent)

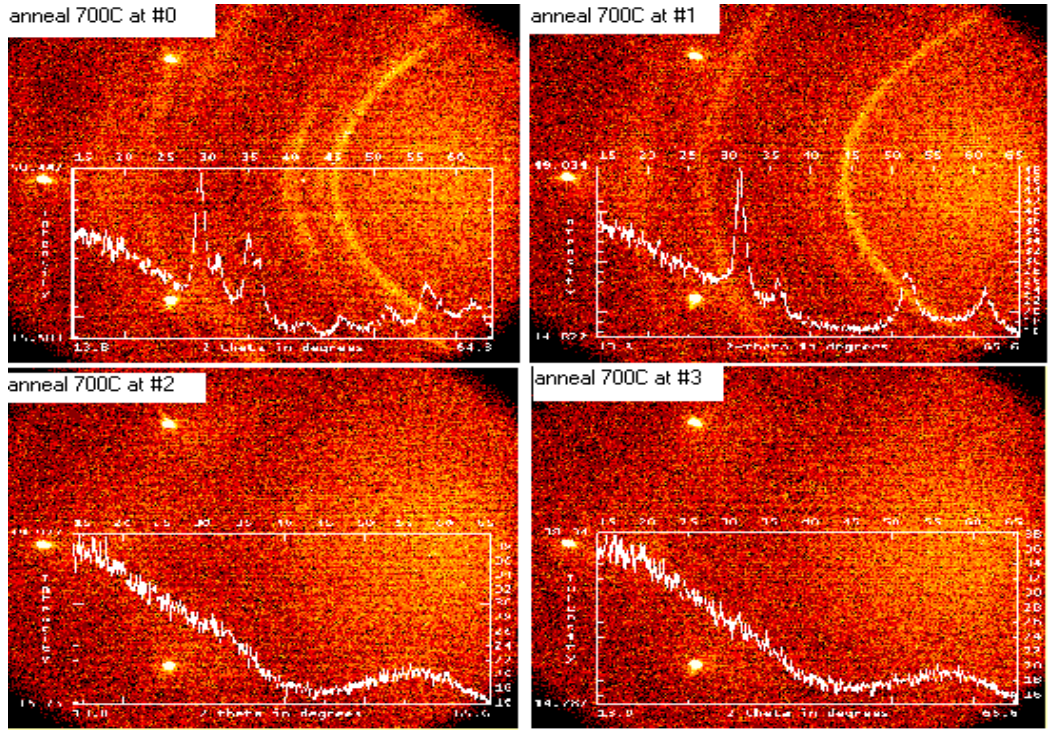


- Electrical
- X-Ray diffraction
- RBS, MEIS
- XPS
- AFM, current imaging

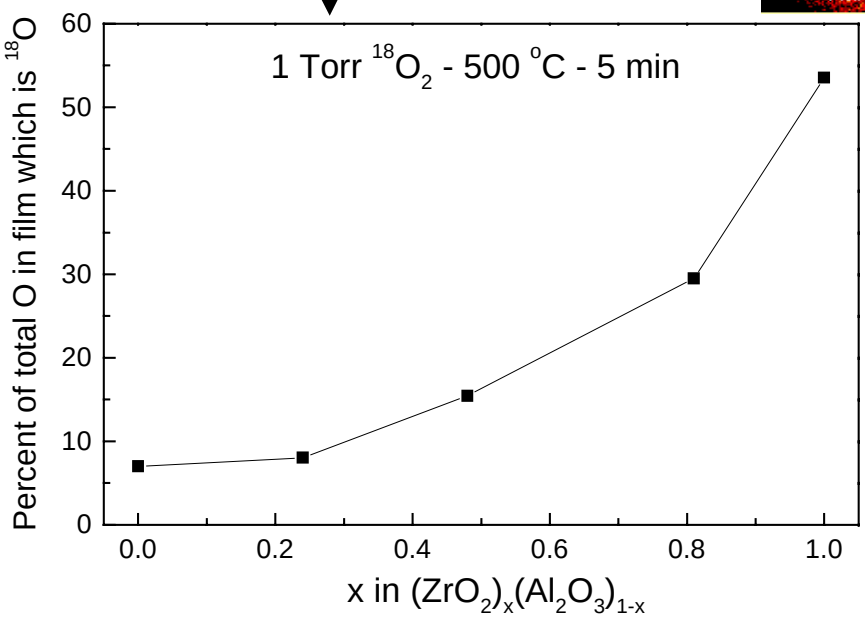


Zr/(Zr+Si) ratio in the Zr-Si-O sample as determined by XPS (agrees with RBS)

Zr-Si-O and Zr-Al-O systems: crystallinity and O exchange vs composition



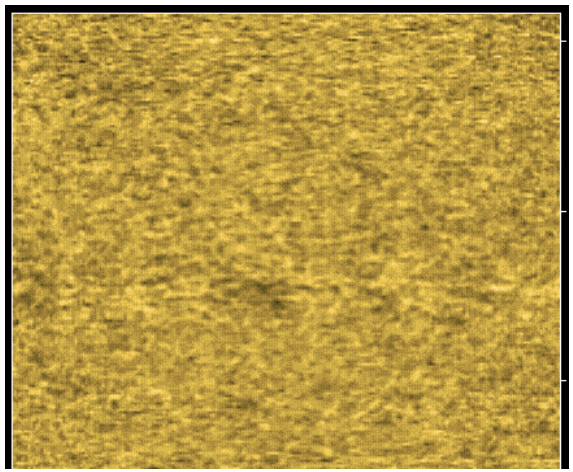
Percentage of oxygen exchanged in high-K films with compositions varying from pure Al_2O_3 to pure ZrO_2



Mixed ZrO_2-SiO_2 films.
After anneal to 700ºC.
Thickness: 800Å.
Composition (%Zr):
#0: 92% #1: 79% #2: 57% #3: 33%

Topographic and scanning current imaging of 5nm Ta_2O_5 film

a



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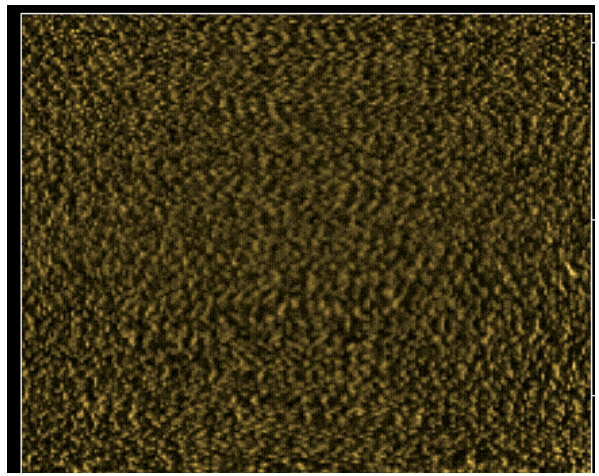
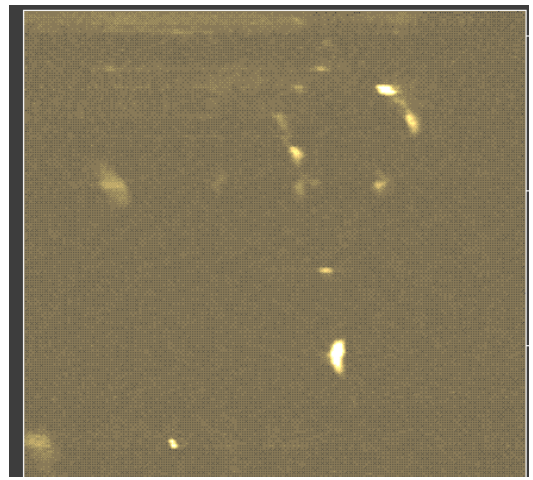


c



- Topographic image (a) flat (150x130nm area); 2-3Å rms roughness.
- Current image (b) for as-deposited film uniform - same area as (a): flat background w/~300 femtoamp noise level (at ~3V bias).
- Annealing to 800ºC (c) leads to hot spots (nanoamp local current with <2V bias), with no direct correlation to roughening.

Summary

- As-deposited high-K films compositionally graded/layered with SiO_2 at the interface.
- Anneals: some improvements, but … crystallization, SiO_x growth, phase changes…
- Isotopic labeling studies: significant oxygen exchange.
- SiO_2 interface growth is very T dependent, and appears to be self-limiting.
  (Challenge is to find P_i, T, t phase space range that optimizes properties.)
- As-deposited high-K films usually flat, but many roughen upon annealing (>800ºC).
- Nitride or other barrier layers and alloying slows interdiffusion and recrystallization.

Current work:

CVD, ALCVD, compositional spread methods….
Buffer and graded layers
Special H and Al depth profiling
Understand defects and breakdown – scanning current imaging
Gate metallization – interfaces and offset voltage
Theoretical modeling