The Abdus Salam
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SCHOOL ON ION BEAM ANALYSIS AND ACCELERATOR APPLICATIONS

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MEIS - applications

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Laboratory for Surface Modification

Structure and composition of ultrathin films using MEIS

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Applied Materials: C. Czarnik et al.

IMEC/Intel: W.Tsai et al.

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Vanderbilt: Y. W. Song, L. Feldman

Penn State: V. Vaithyanathan, D.G. Schlom

Singapore: M.-Y. Ho, H. Gong et al.

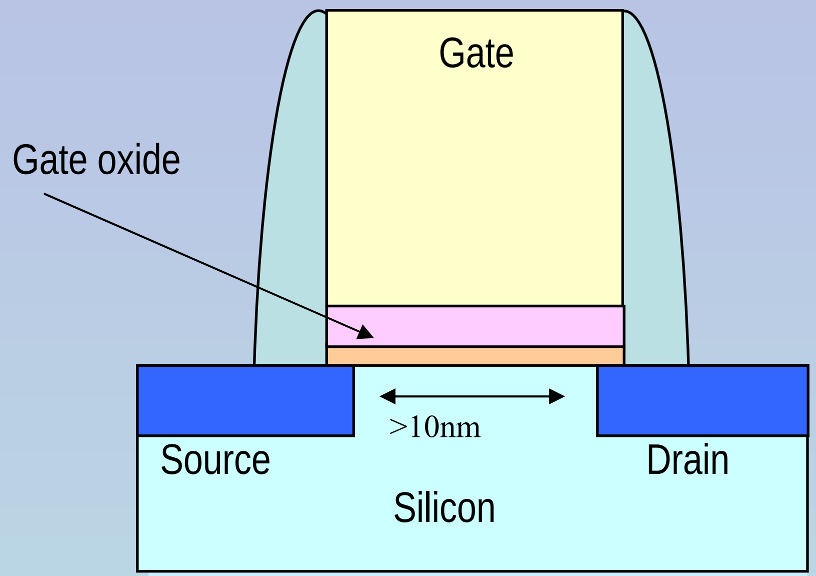
Berlin: G. Schiwietz

Porto Alegre: H. Budinov, P. L. Grande

Why interest in ultrathin analysis?

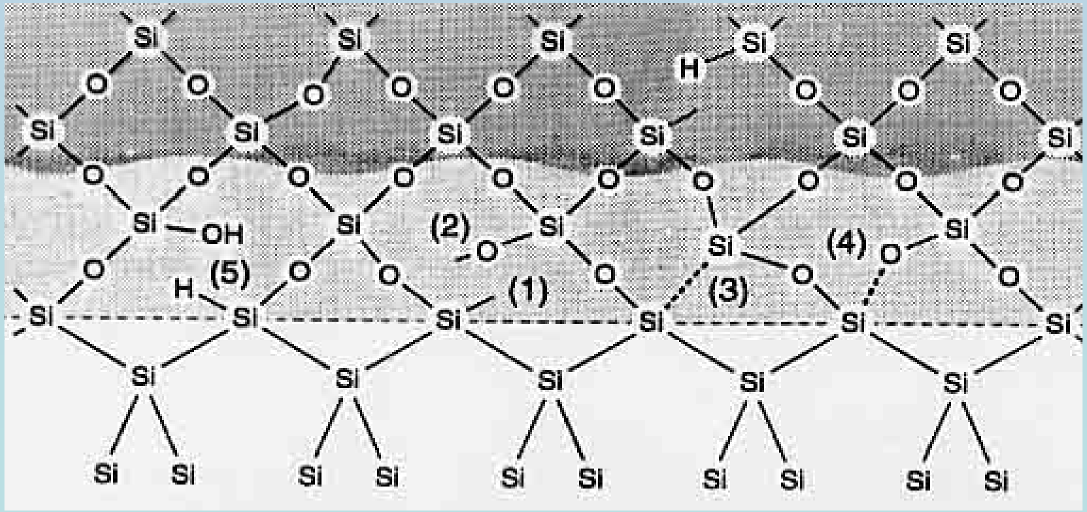
The SiO_2/Si system: interface of choice in microelectronics for 40+ years

Moore's law says that the gateoxide thickness will soon be too small (~ 1 nm) due to large leakage currents from quantum mechanical tunneling

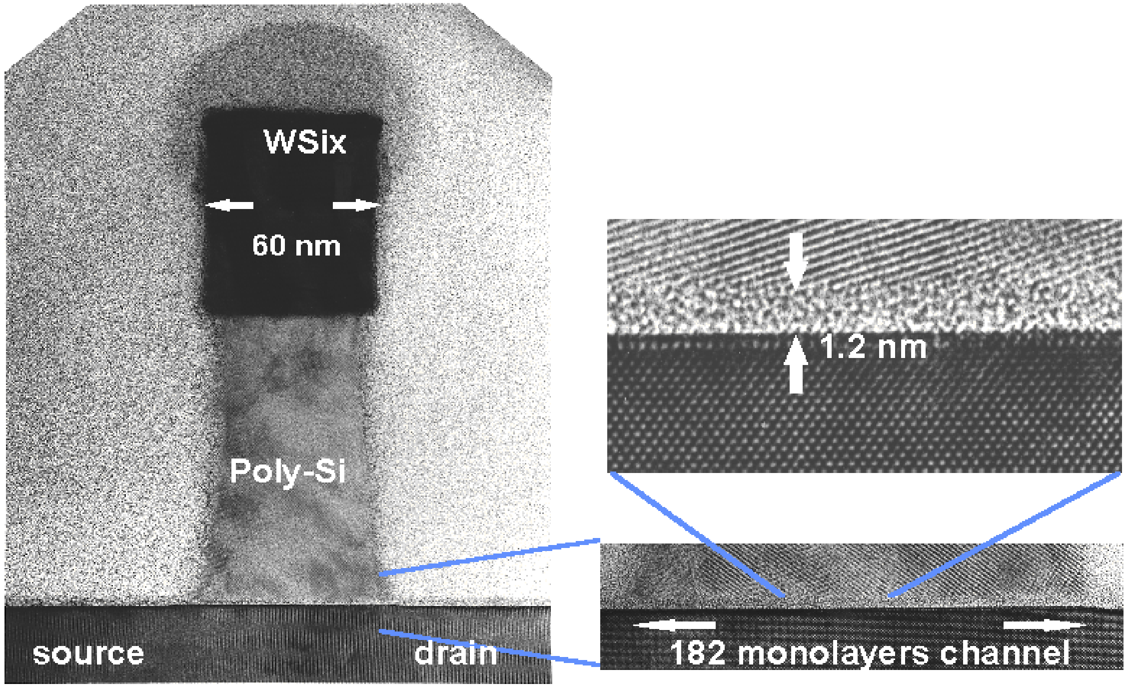


CMOS Gate Structure

SiO_2 needs to be replaced by a higher dielectric constant material ("high-k")



Towards Sub - 0.1 μm Technology



Dielectric properties of some materials

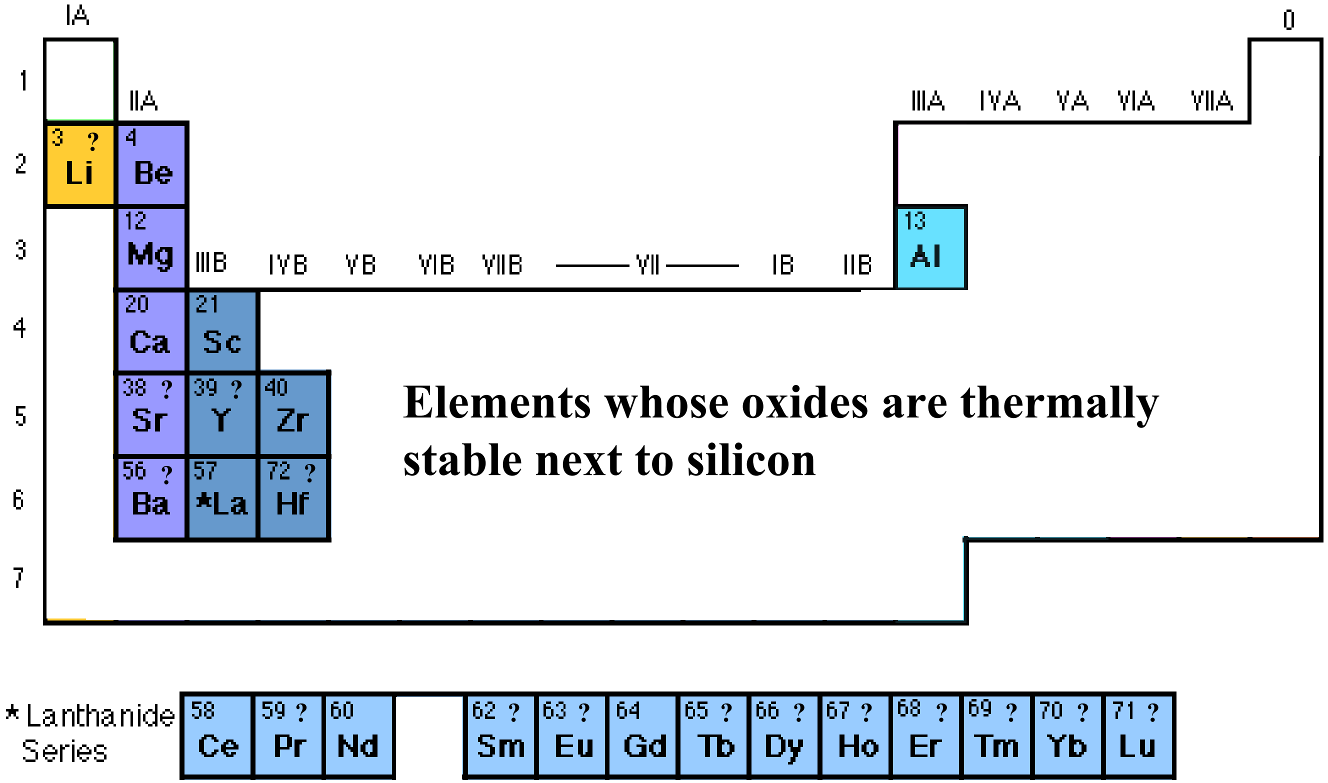
Material	Permittivity (k)	Thickness equivalent to 10 Å SiO_2
Vacuum/Air	1	~3Å
SiO_2	~3.8	10Å
Si_3N_4	~7.8	~20Å
Al_2O_3	~9	~30Å
ZrO_2, HfO_2	~20-30	~50-75Å
Ta_2O_5, TiO_2	~25-60	~60-140Å
$SrTiO_3$	~60	~140Å

Thermal stability:

$Si + M_xO_y \rightarrow M + SiO_2$

$Si + M_xO_y \rightarrow MSi_z + SiO_2$ (or silicate)

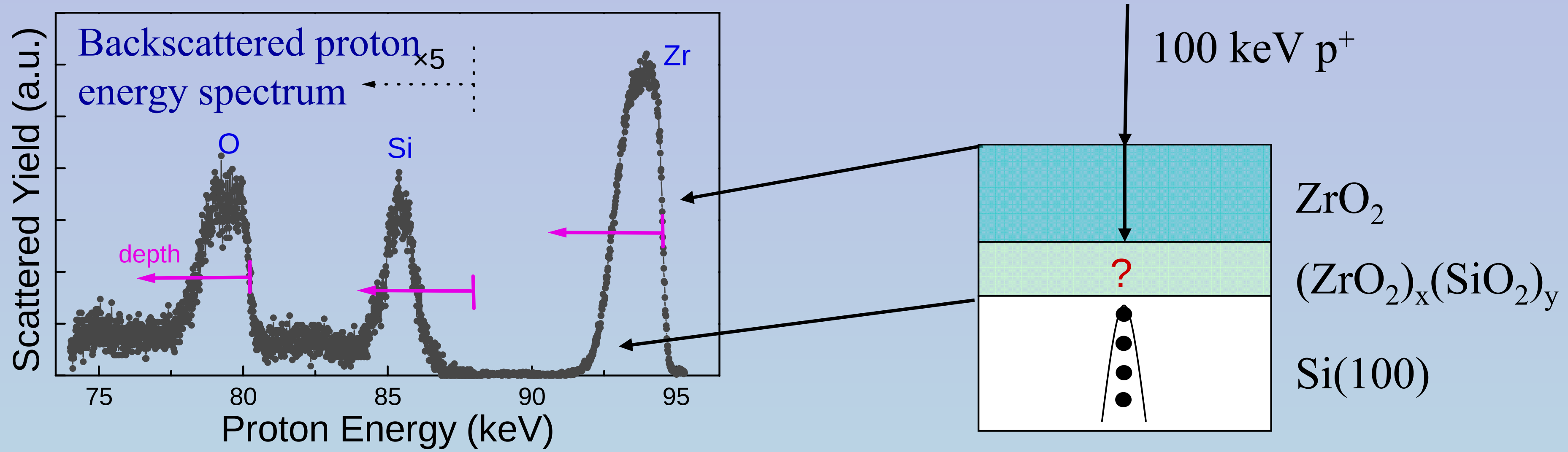
$\Delta G>0$ @1000°K

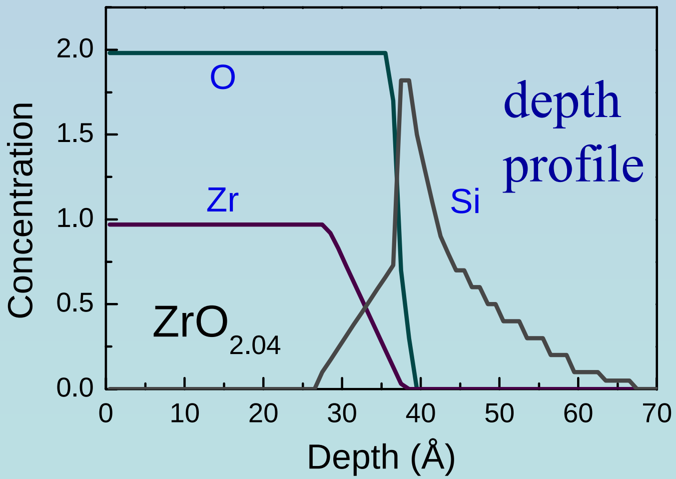


Elements whose oxides are thermally stable next to silicon

Hubbard and Schlom, 1996

Spectra and information content

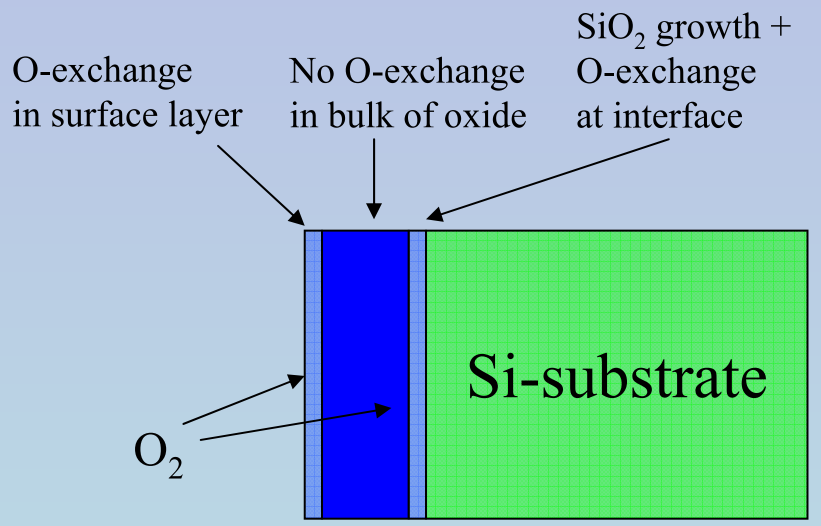




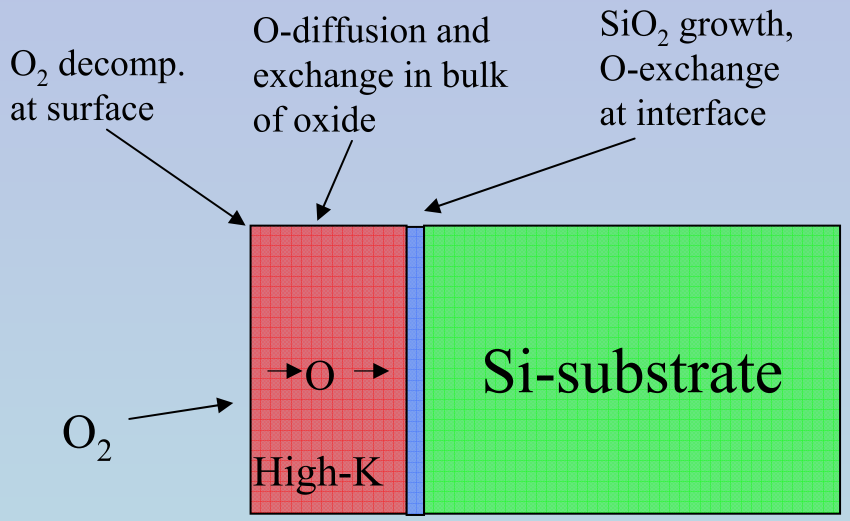
- **Sensitivity**:
  ≈ 10^{+12} atoms/cm^2 (Hf, Zr)
  ≈ 10^{+14} atoms/cm^2 (C, N)
- **Accuracy** for determining total amounts:
  ≈ 5% absolute (Hf, Zr, O), ≈ 2% relative
  ≈ 10% absolute (C, N)
- **Depth resolution**: (need density)
  ≈ 3 Å near surface
  ≈ 8 Å at depth of 40 Å

Isotope studies of diffusion in oxides

Oxygen (O_2) transport in SiO_2



Atomic oxygen (O) transport in high-K films



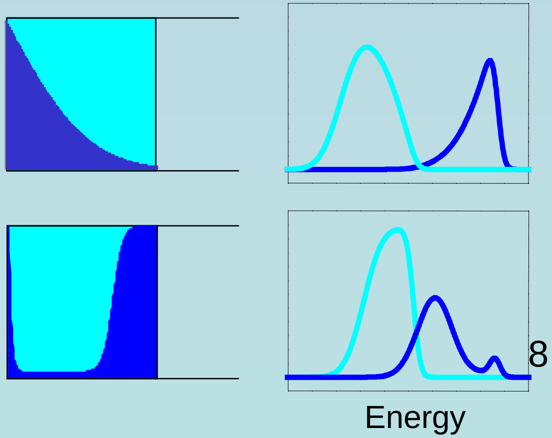
<u>SiO_2 films:</u>

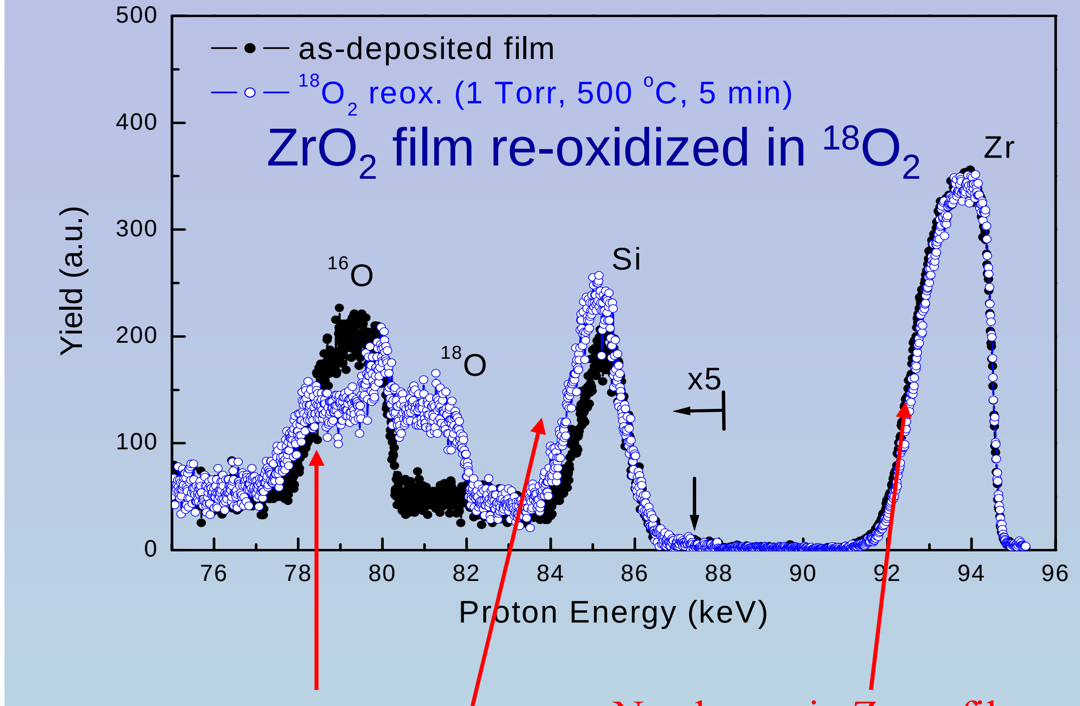
- amorphous after annealing
- molecular O_2 transport in SiO_2
- decomposition by SiO desorption

<u>High-K films (except Al_2O_3):</u>

- tend to crystallize at low T
- high oxygen mobility

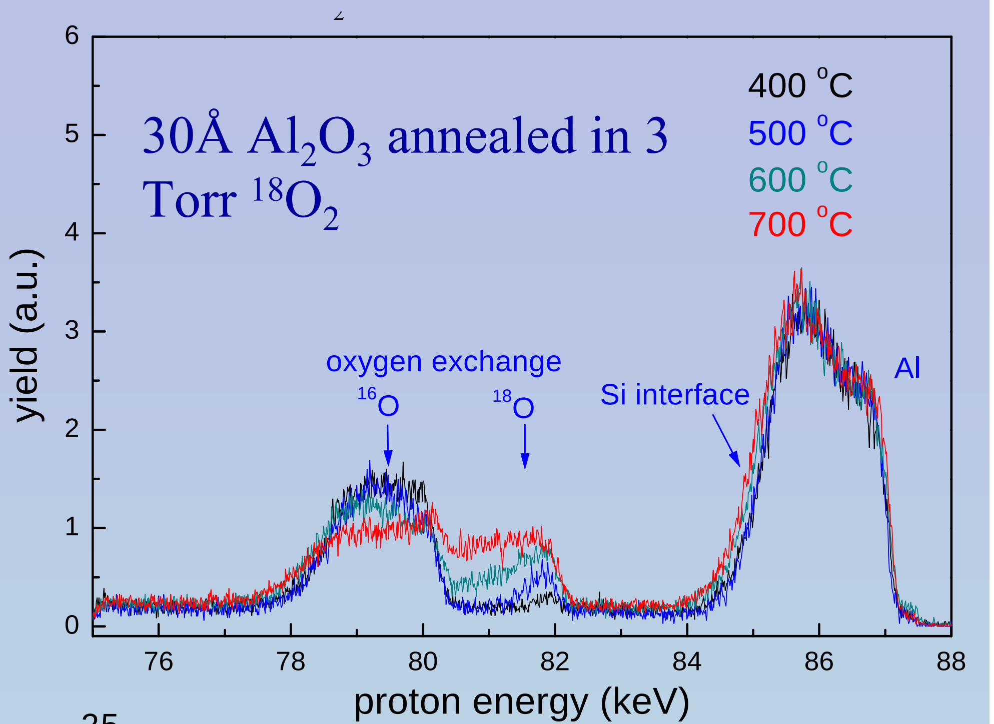
Isotope tracer studies

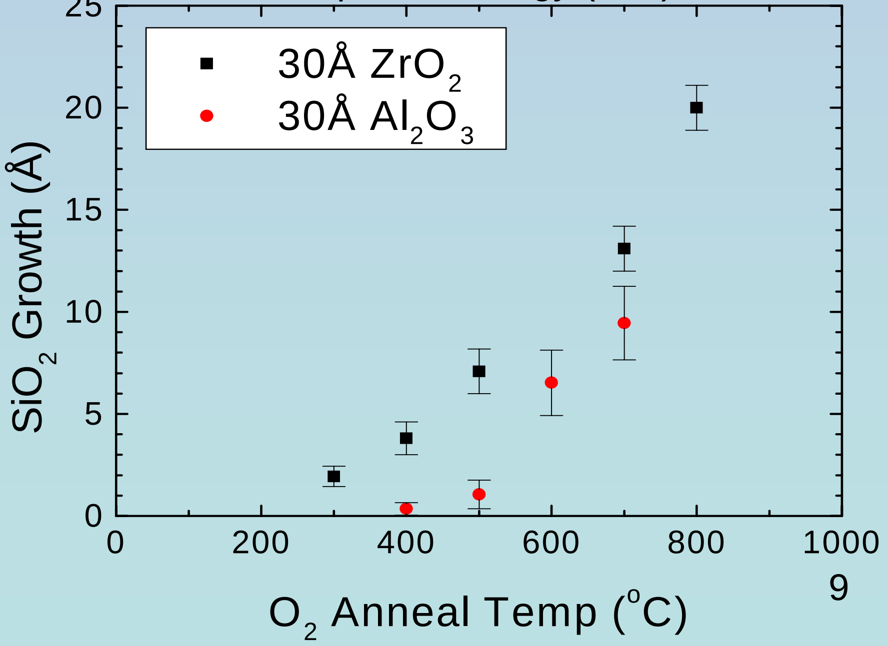




Deeper O and Si

No change in Zr profile
Surface flat by AFM

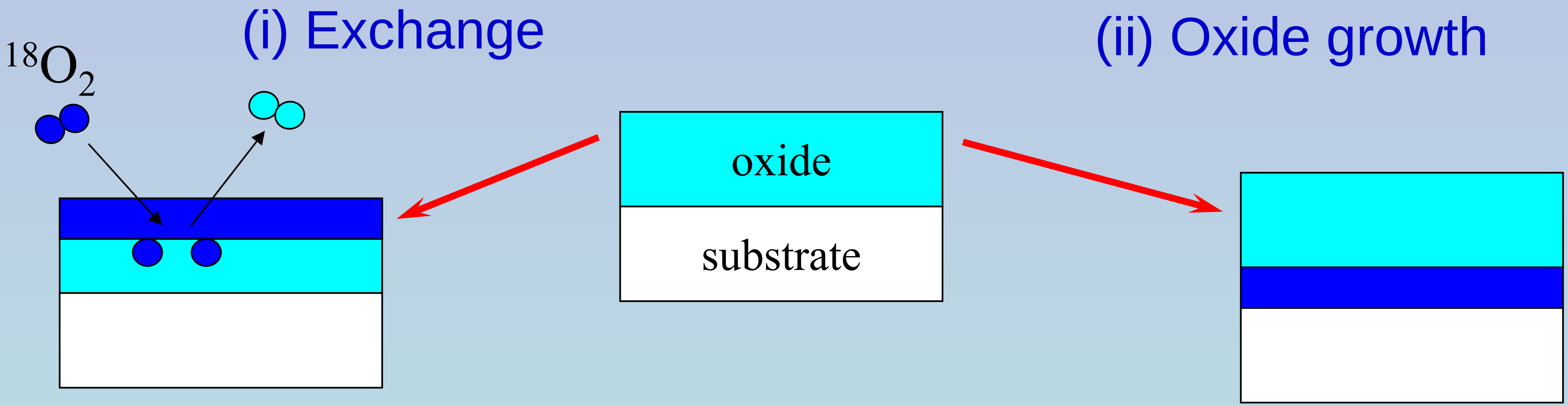




- Significant interfacial SiO$_2$ growth for ZrO$_2$, less for Al$_2$O$_3$
- Dramatic oxygen exchange: ^{18}O incorporation and ^{16}O removal
- SiO$_2$ growth rate faster than for O$_2$ on Si
- Growth faster under ZrO$_2$ than Al$_2$O$_3$

Oxygen reactions with and diffusion in hafnium oxide and silicate films

At least two reactions are possible:



(i) Exchange

(ii) Oxide growth

$^{18}O_2$

oxide

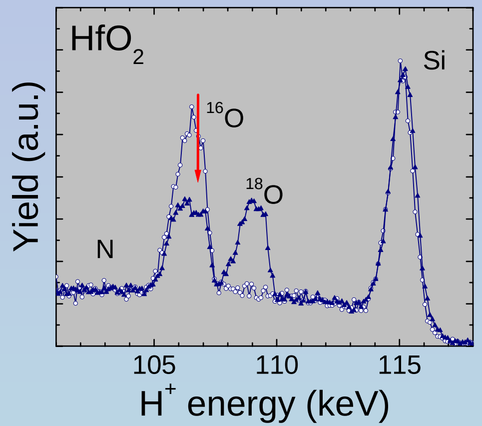
substrate

Is the transport atomic (fast, for high-κ systems) or molecular (slow, SiO_2)? What is the mechanism?

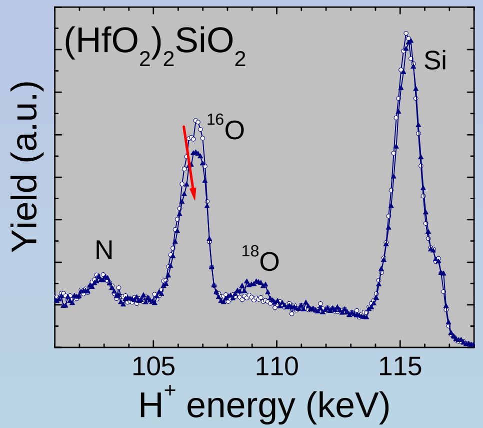
What is the influence of composition on the rate of transport?

Oxygen reaction: effects of composition

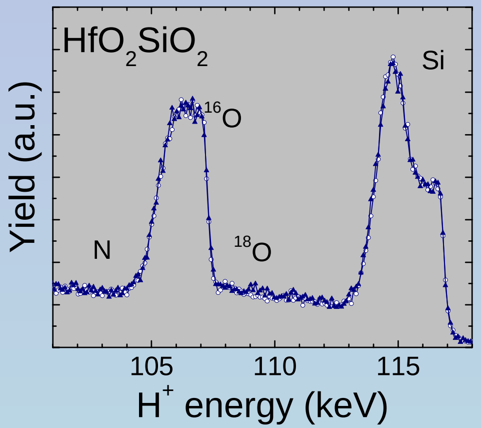
$HfO_2(SiO_2)_x$ re-oxidation in ^{18}O: 500°C, 10^{-2} Torr, 30 min



$x = 0\%$



33%

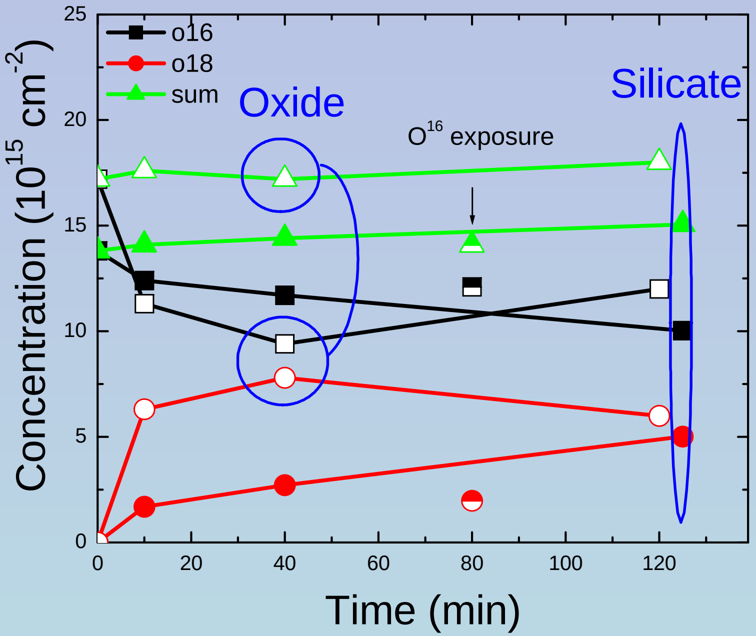


50%

- strong exchange reaction even at 500°C: ^{16}O loss, but the same total O concentration
- no change in width of ^{16}O and Si peaks (no formation of interfacial oxide)
- exchange rate decreases with increase of SiO_2 fraction x
- 50% of SiO_2 in $HfO_2(SiO_2)_x$ is enough for almost full suppression of oxygen exchange

Kinetics of oxygen exchange with gas phase

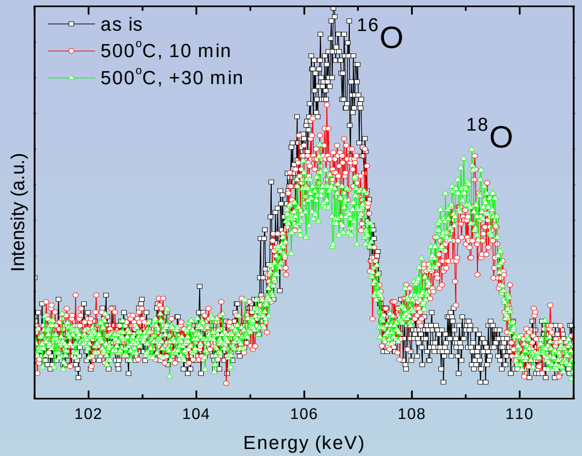
Oxidation conditions: $^{18}O_2$, 10^{-2}Torr, 490°C



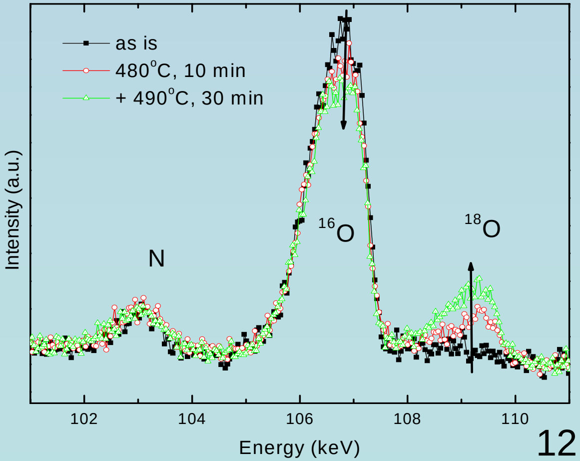
open symbols: HfO_2 (0%)

solid symbols: $(HfO_2)_2(SiO_2)$ (33%)

HfO_2

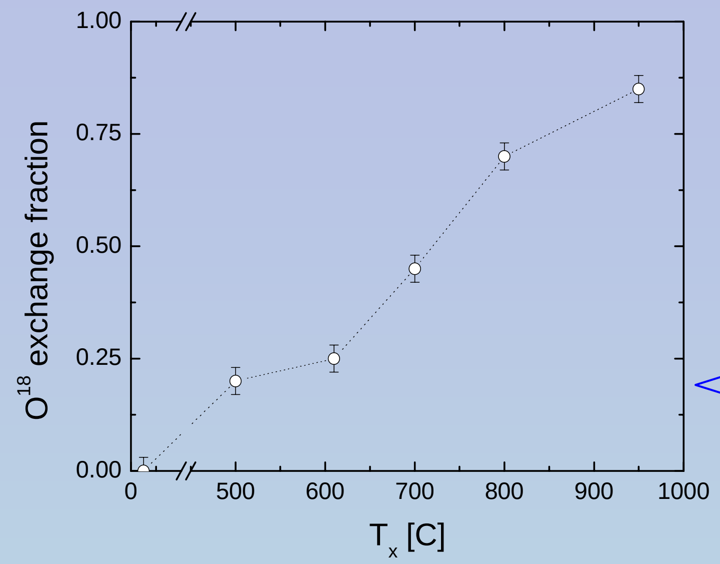


$(HfO_2)_2(SiO_2)$



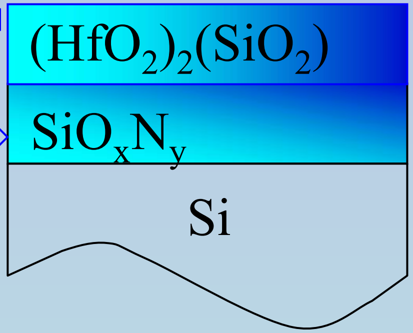
- **Hf oxide has a faster exchange rate than Hf silicates (reaches >90% of its final value in 10 min)**
- **^{18}O incorporation at 490°C is predominately due to exchange with gas phase, no/very little interface reaction**
- **^{16}O and ^{18}O peaks have similar shapes, implying relatively uniform isotope intermixing**
- **The small reduction of ^{18}O after ^{16}O exposure indicates random network exchange**

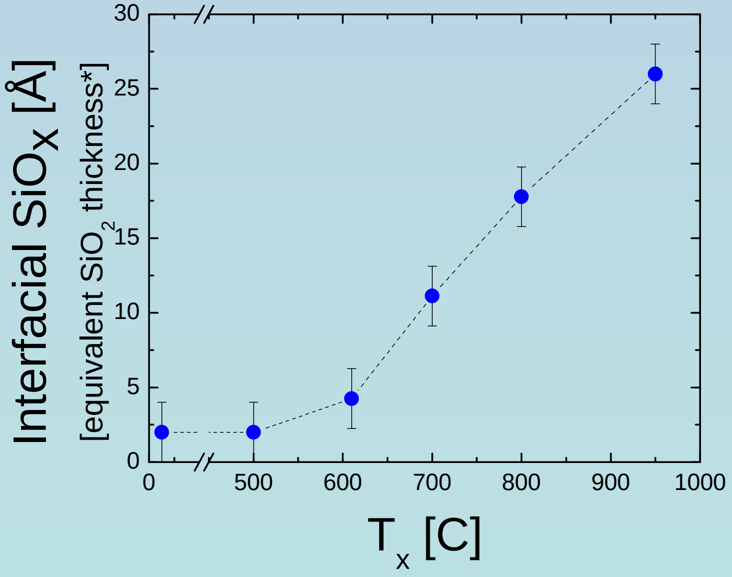
Temperature dependence of oxidation (I)



The sample was oxidized in $^{18}O_2$ (500ºC, 10^{-2} Torr, 30 min) after short anneal to 500ºC in UHV

O^{18} exchange fraction = $[O^{18}]/([O^{18}]+[O^{16}])$ in $(HfO_2)_2(SiO_2)$ film

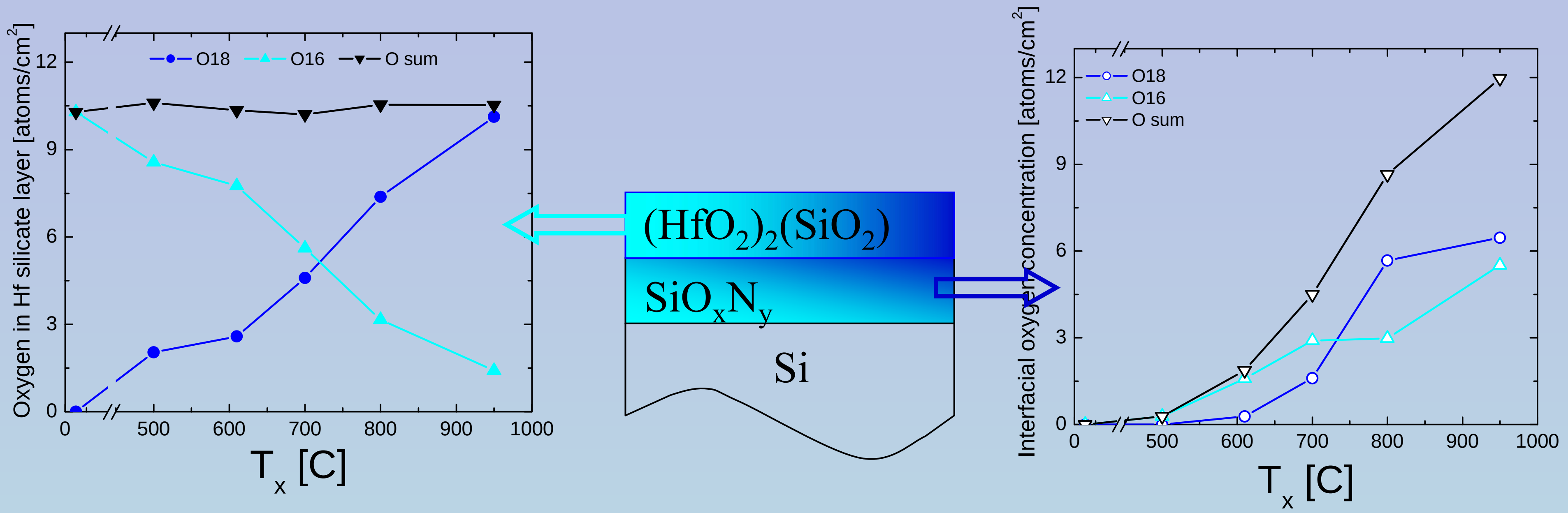




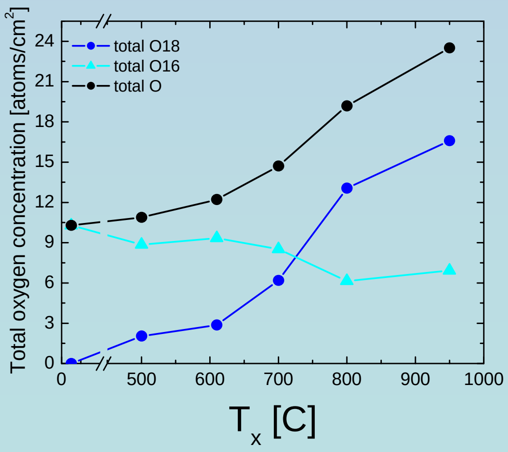
*** Thicknesses of interfacial SiO_xN_y layers were scaled to the SiO_2 layer thickness with equal amounts of oxygen**

- ^{18}O exchange in $(HfO_2)_2(SiO_2)$ film increases with T_{anneal}
- Interfacial SiO_2 growth is observed for T_x>610ºC

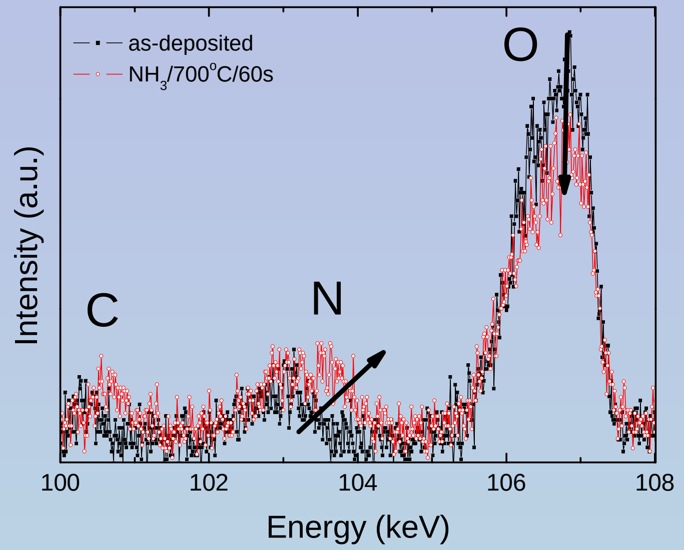
Exchange and growth temperature dependence (II)



- **Due to exchange reactions, the ^{18}O <u>in $(HfO_2)_2(SiO_2)$ layers</u> increases, ^{16}O decreases, with the total oxygen content constant.**
- **There is higher ^{16}O density <u>*at the interface*</u> ($^{16}O/^{18}O$ >1) at T_x=500-700°C (oxygen or vacancy exchange mechanism)**
- **<u>*Interface*</u> $^{16}O/^{18}O$ changes at T_x≥800°C due to**
  (a) higher ^{18}O equilibrium concentration
  (b) opening of direct paths through $(HfO_2)_2(SiO_2)$



Presence of nitrogen in high-κ film



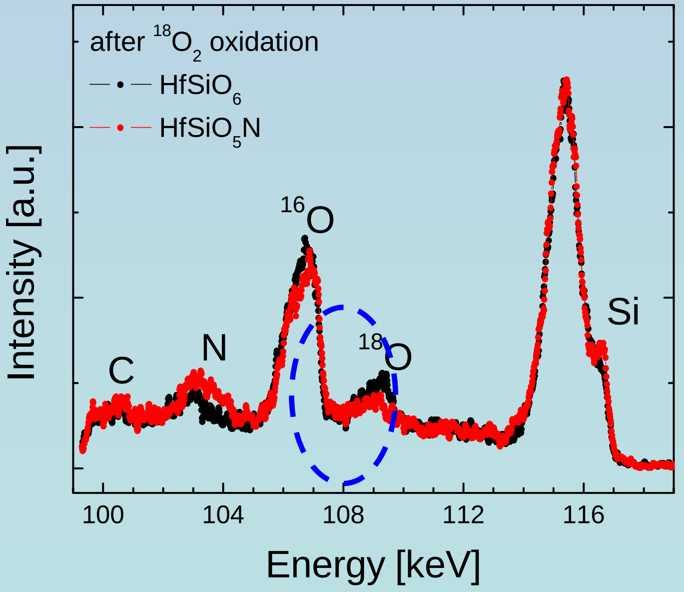
- $(HfO_2)_2(SiO_2)$ films have been submitted to various post growth anneals (NH_3, N_2, O_2, T_{anneal} =500-700ºC)
- only annealing in NH_3/700ºC/60s results in nitrogen incorporation in $HfSiO_6$ with oxygen removal (final composition of **$HfSiO_5N$ (O : N = 5:1)**)

Sample	as grown	annealed in NH_3
N content, 10^{15} cm^{-2}	2.59	4.09

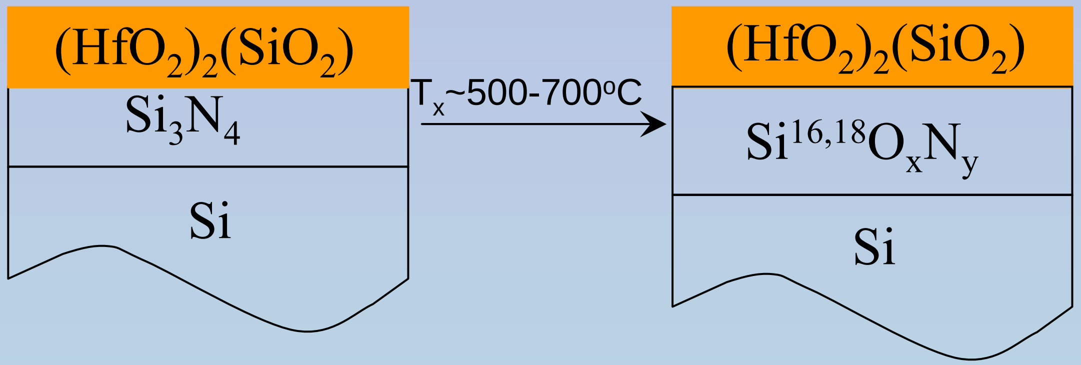
- Nitrogen incorporation into the $HfSiO_x$ film **reduces** oxygen exchange in the film:

After ^{18}O oxidation

Sample	as grown	annealed in NH_3
^{18}O content, 10^{15}cm^{-2}	2.55	2.1



Si_3N_4 layer nitrogen diffusion during ^{18}O annealing



$(HfO_2)_2(SiO_2)$

Si_3N_4

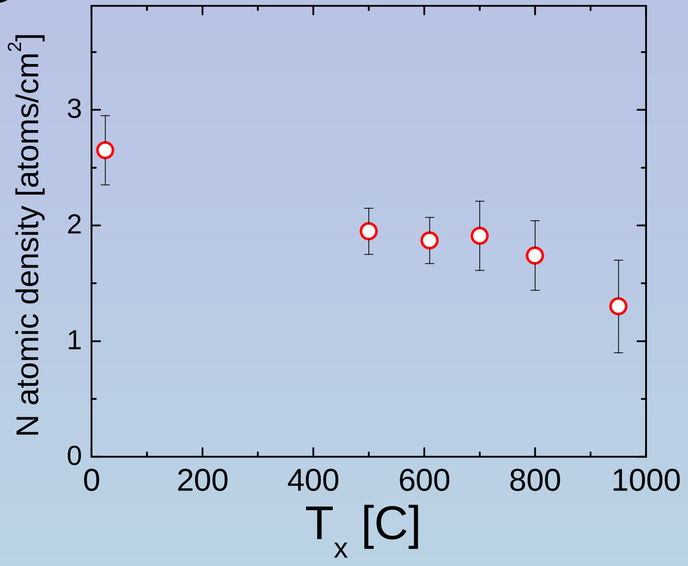
Si

T_x~500-700°C

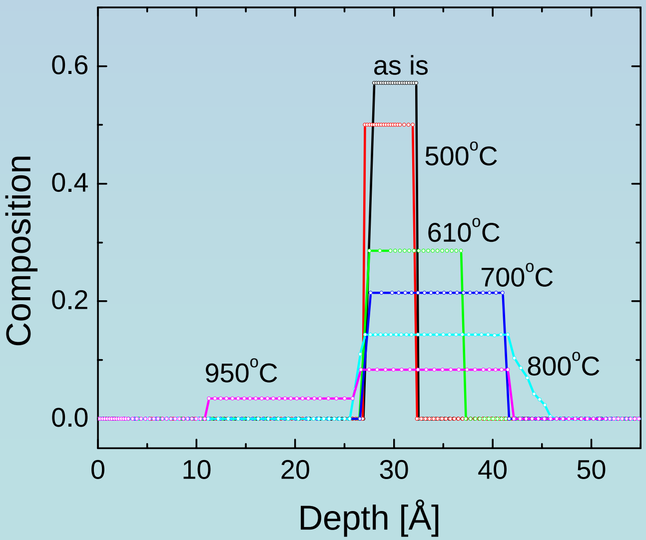
$(HfO_2)_2(SiO_2)$

$Si^{16,18}O_xN_y$

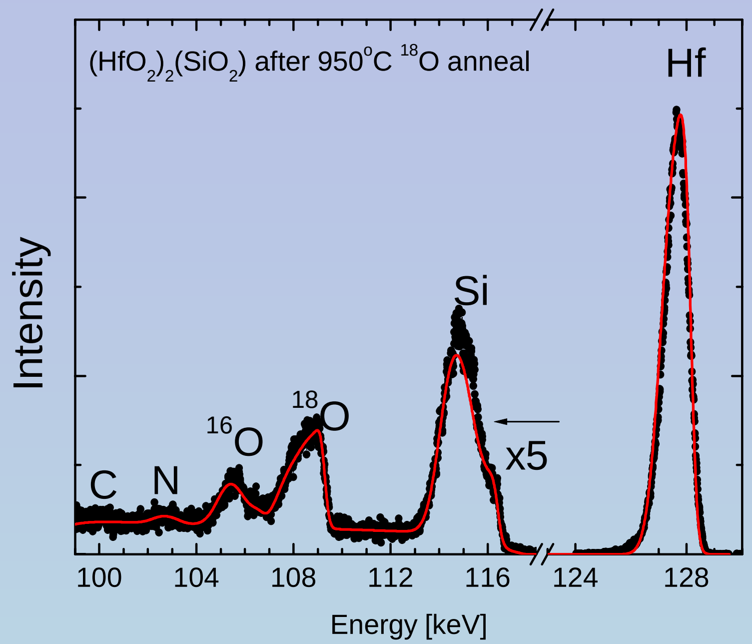
Si



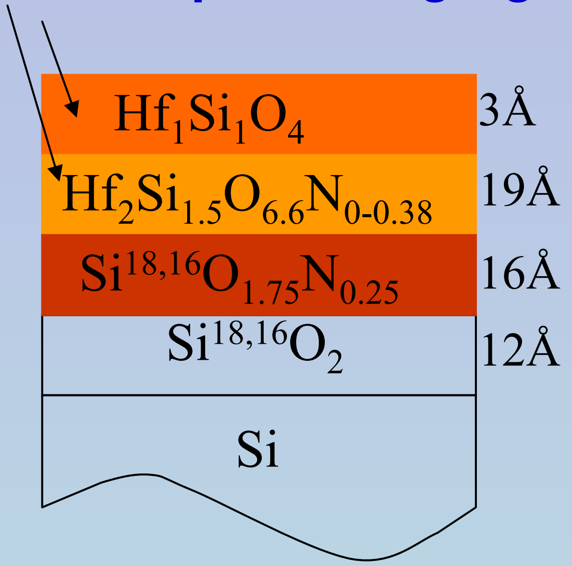
- **Nitrogen atomic density is constant at $T_x \leq 700^oC$, oxygen diffusion causes some O/N intermixing at T_x~610-700°C at the interface**
- **Nitrogen distribution broadens. Possible loss at $T_x > 800^oC$, presumably via diffusion towards the top surface and nitrogen loss from near-surface region**



^{18}O oxidation anneal at 950°C



Possible phase segregation



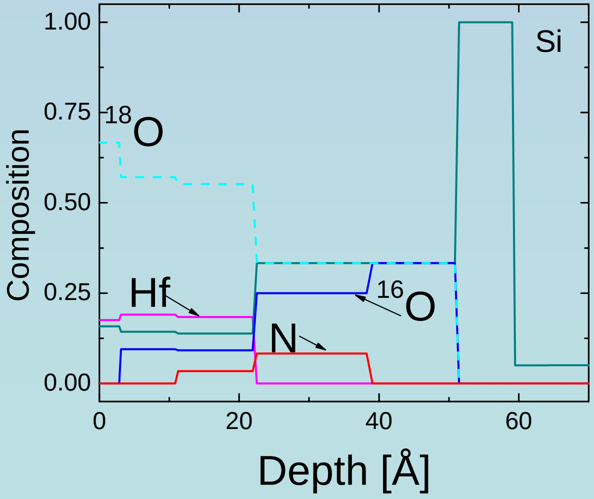
$Hf_1Si_1O_4$ 3Å

$Hf_2Si_{1.5}O_{6.6}N_{0-0.38}$ 19Å

$Si^{18,16}O_{1.75}N_{0.25}$ 16Å

$Si^{18,16}O_2$ 12Å

Si

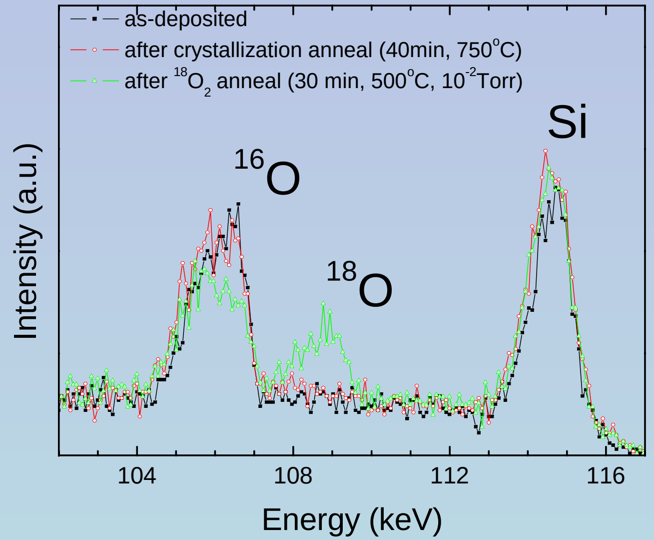


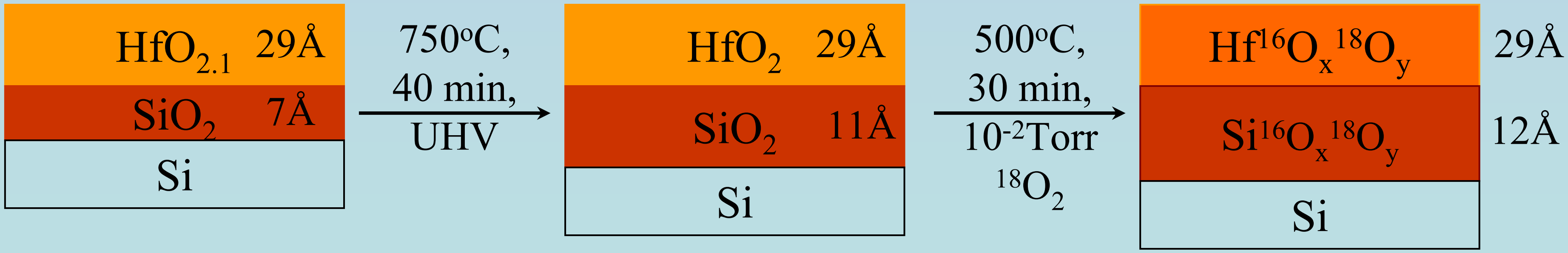
- almost complete exchange of ^{16}O by ^{18}O in the silicate layer
- possible phase segregation of the silicate layer with SiO_2 enrichment of the top surface layer

Shown depth profile is for illustration only, as lateral inhomogeneity may occur

Effects of film crystallization

To determine effect of crystallinity of the high-κ film, a 30Å HfO_2/6Å SiO_2/Si(001) stack was subjected to crystallization anneal prior to oxidation in $^{18}O_2$





$HfO_{2.1}$ 29Å

SiO_2 7Å

Si

750°C,
40 min,
UHV

HfO_2 29Å

SiO_2 11Å

Si

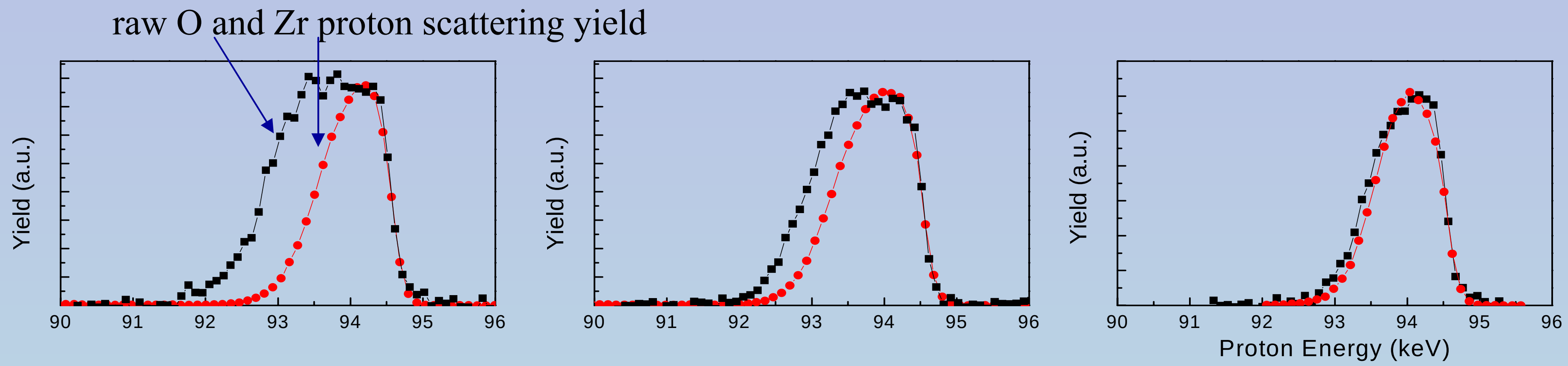
500°C,
30 min,
10^{-2}Torr
$^{18}O_2$

$Hf^{16}O_x{}^{18}O_y$ 29Å

$Si^{16}O_x{}^{18}O_y$ 12Å

Si

Interfacial SiO_2 content by MEIS

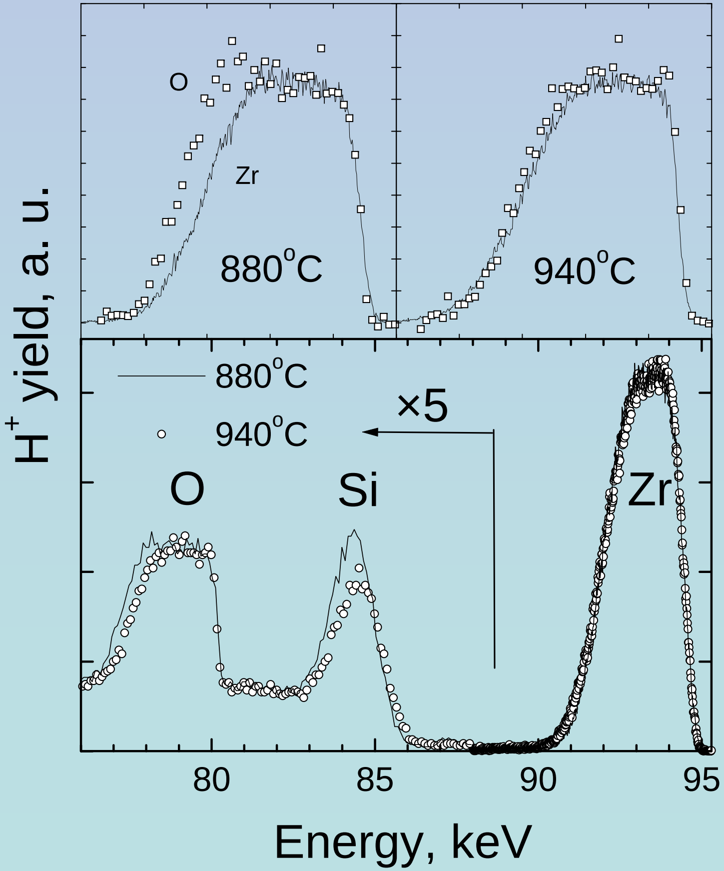


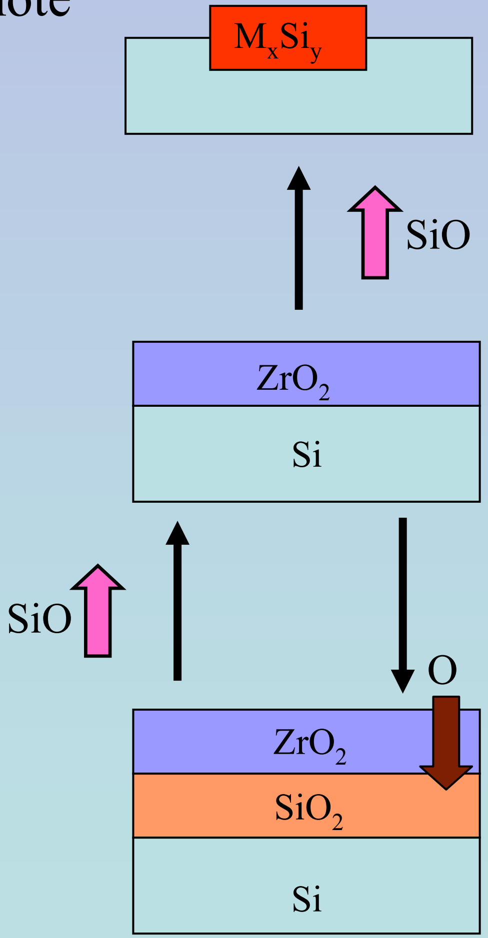
raw O and Zr proton scattering yield

- Normalize O and M peak position (to surface scattering energy) and heights.
- Can use to quantify excess (or missing) O in raw data
- $ZrO_2/SiO_2/Si$ –process-dependent interface SiO_2 thickness

Fine control of SiO_2 interface - can we controllably remove SiO_2 and not high-K oxide?

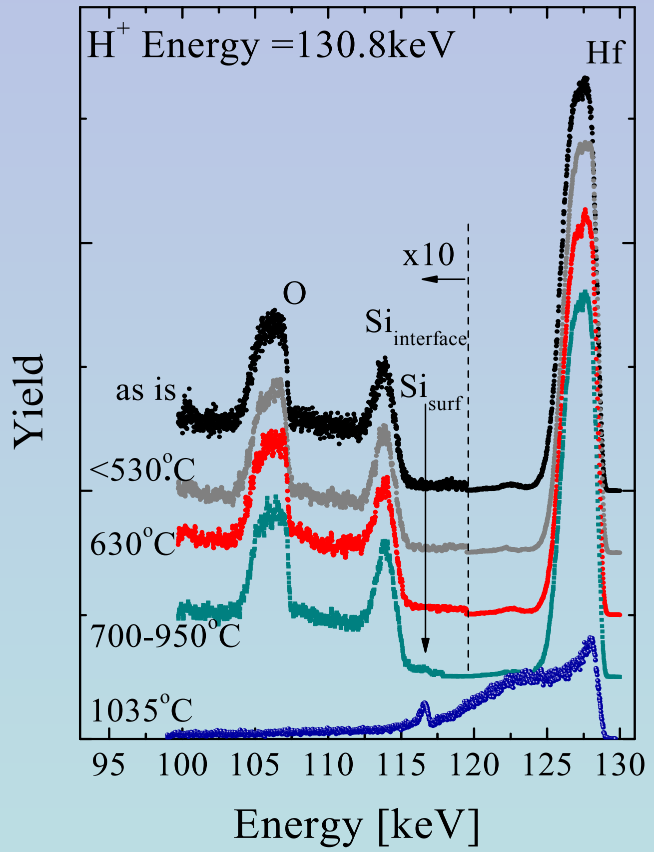
Interfacial SiO_2 desorption (as SiO) by vacuum annealing; note MO_x has not yet decomposed in this case.



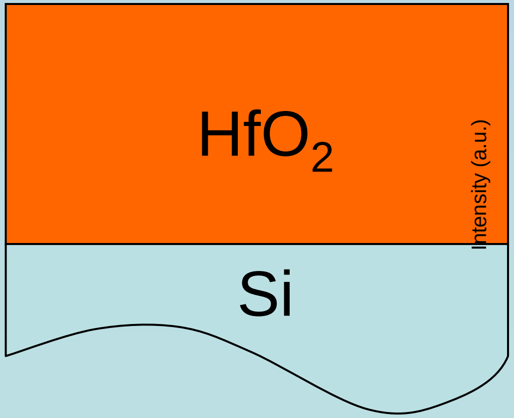


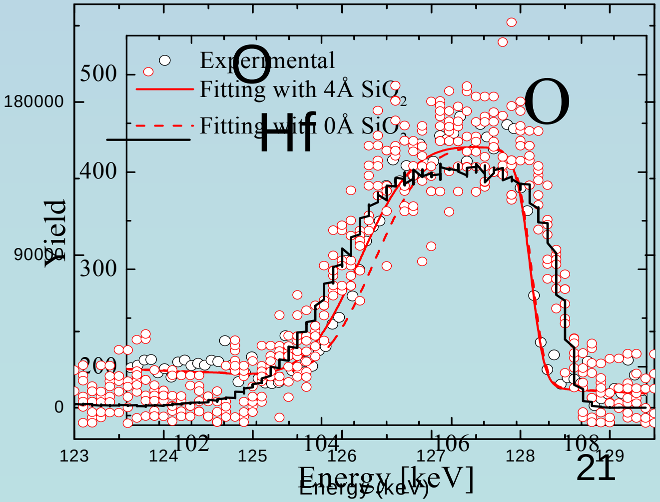
One approach to interface control: Grow in UHV

MEIS spectra for MBE grown HfO_2 on Si(001) after UHV anneals



- ✓ No SiO_2 layer on HfO_2/Si interface, stable to anneal in UHV to ≤530°C
- ✓ growth of thin (~4Å) SiO_2 interfacial SiO_2 layer at T~630°C
- ✓ complete film disintegration only above ~1020°C
- ✓ Broadening of the O peak and a small increase of the Si peak indicate interfacial SiO_2 formation

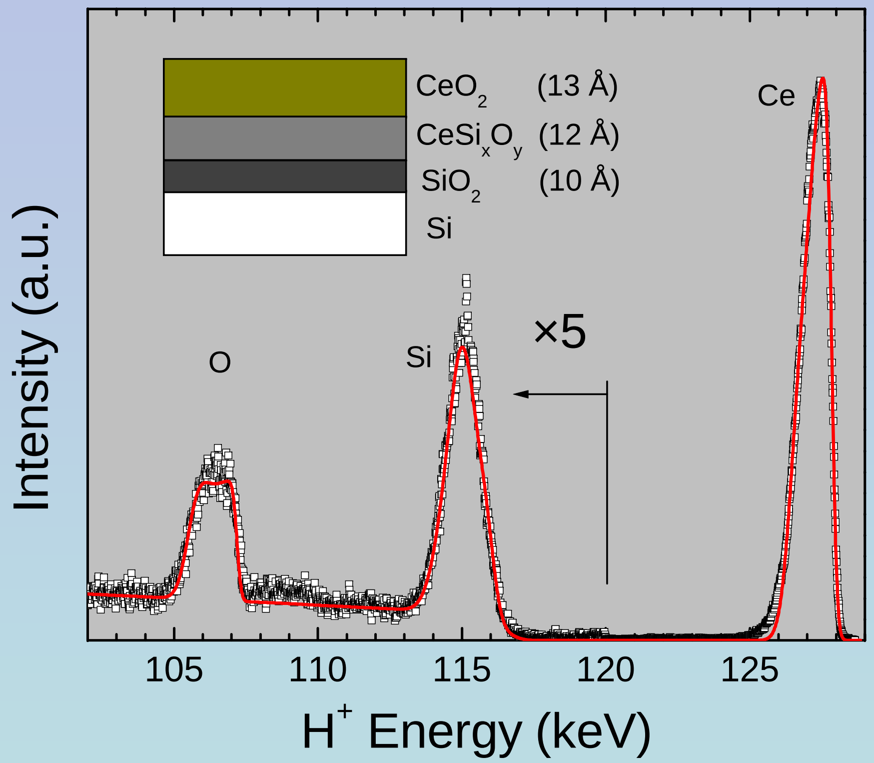




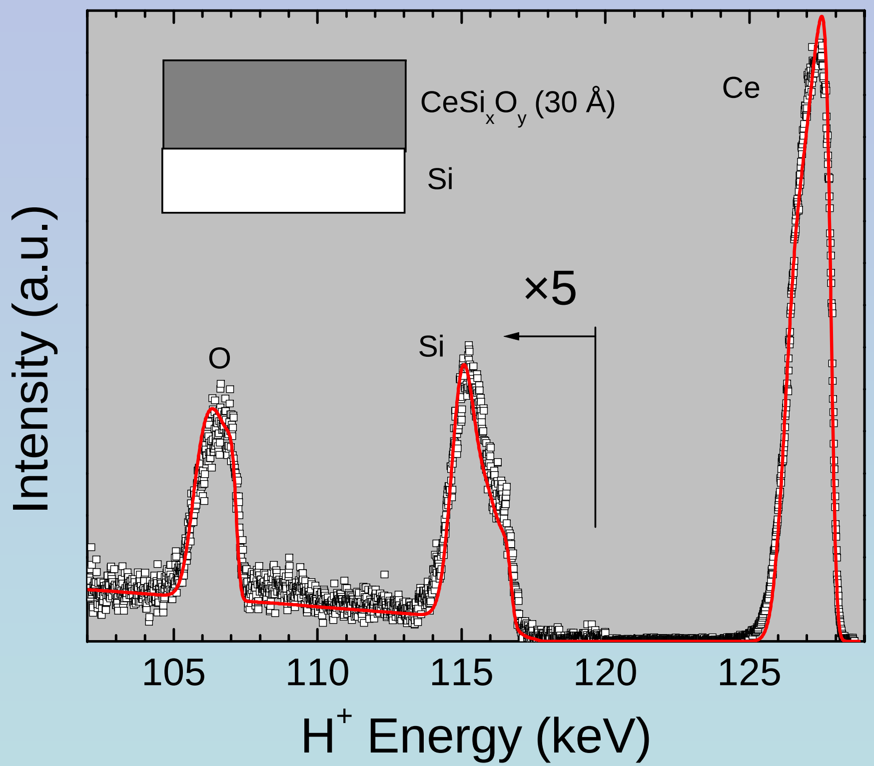
(with R. Kwo, National Tsing Hua University, Taiwan)

Oxygen interaction with cerium oxide films

Sample I: as-grown



Sample II: Sample I annealed to 750°C 10 min



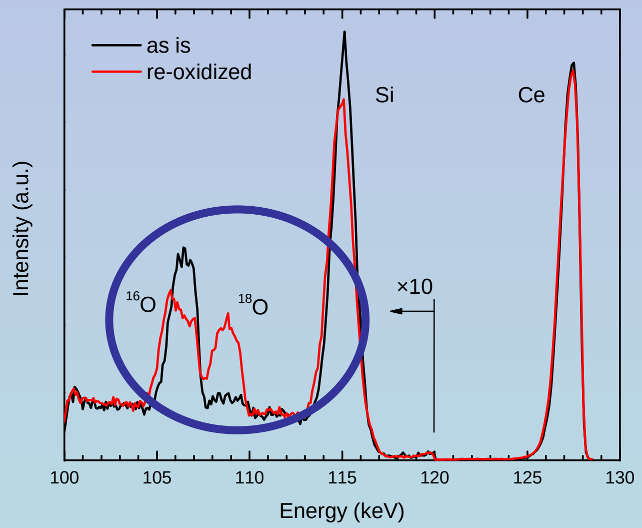
- interfacial Ce^{4+} is reduced to Ce^{3+} state
- interfacial SiO_2 and silicate

- dissolution of interfacial SiO_2 with formation of a thick silicate film

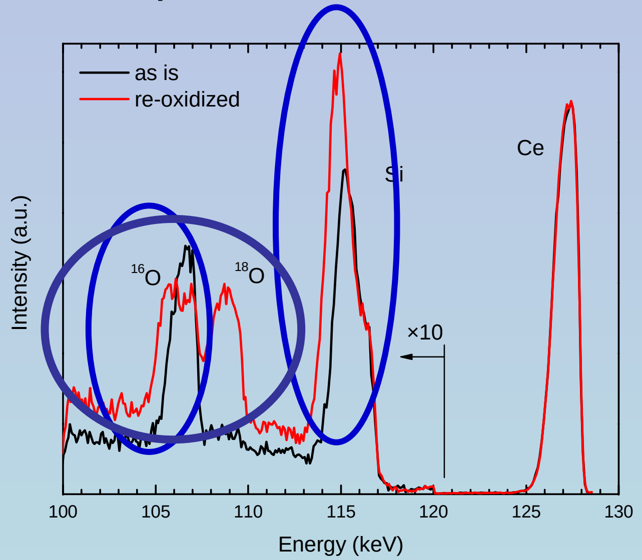
Isotopic study of Ce oxide re-oxidation

10^{-2} torr $^{18}O_2$, 500°C, 15 min H^+ 130.75keV; 125.3°

Sample I “Ce oxide”



Sample II: Ce silicate



- the oxygen content in the films increases upon re-oxidation for both samples
- much more rapid interface growth than Hf silicate case
- the Si yield increases for the silicate, consistent with SiO_2 formation
- broadening and lowering of ^{16}O peak suggests oxygen transport via place exchange mechanism

Influence of gate metals on the chemical stability of oxide stacks

Defects in high−κ gate stacks seem to be strongly dependent upon gate metal and thermal treatment.

Gate metal:

- **can be oxygen source: W/HfO_2/Si**

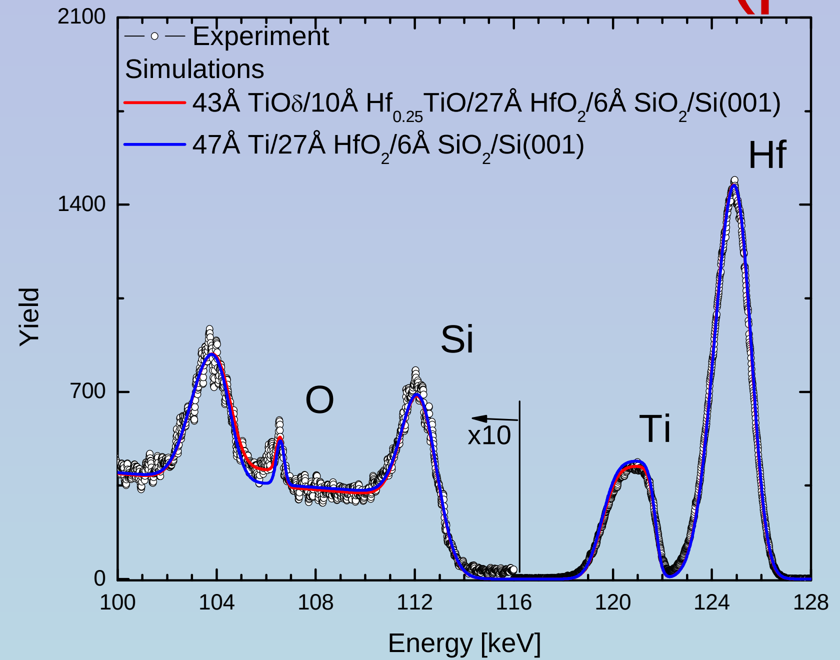
  (E.J. Preisler, S. Guha, M. Copel *et al., APL* 85 (2004) 6230)
- **can be oxygen acceptor: Ti/HfO_2 (ZrO_2)/Si**

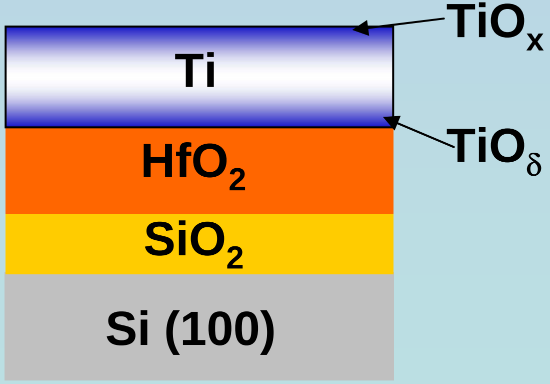
  (H. Kim, P.C. McIntyre, C.O.Chui *et al., JAP* 96 (2004) 3467)
- **can induce positive charge: Re/HfO_2/Si**

  (Shift of E_{Fermi})

Ti/HfO_2/Si(001) - mechanism?

Composition of initial gate stack (pre-anneal)





TiO_x

Ti

TiO_δ

HfO_2

SiO_2

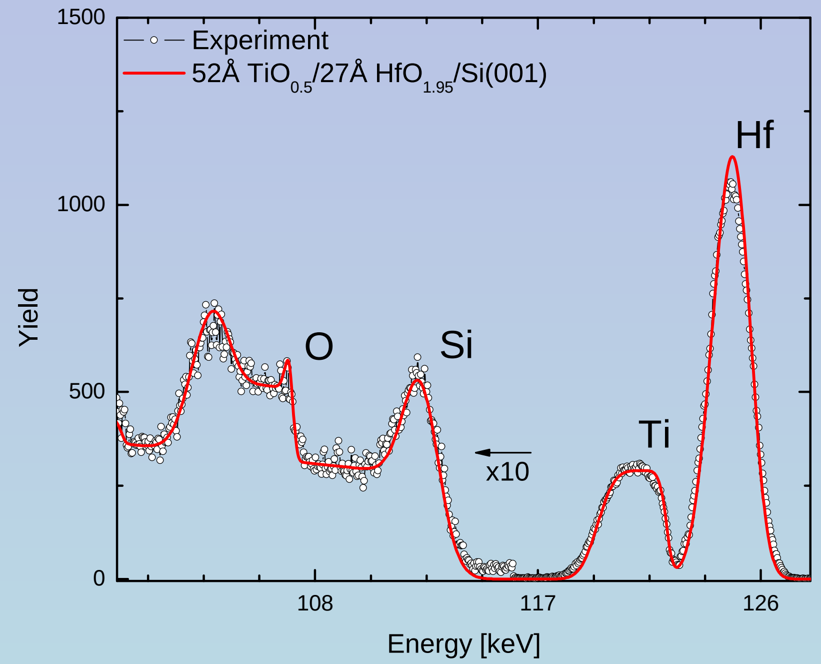
Si (100)

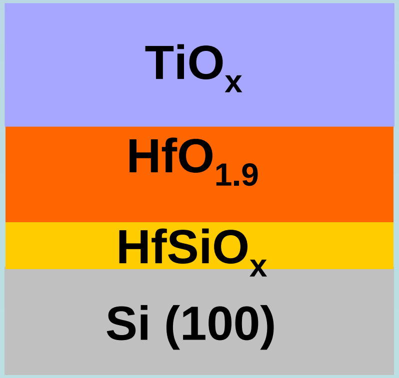
- ~45Å Ti was deposited at RT, p~1×10^{-8} Torr
- MEIS measurements were done within 14 hrs of deposition
- Ti layer oxidizes on the surface and at Ti/HfO_2 interface
- possible intermixing at TiO_x/HfO_2 interface
- partial depletion of oxygen from HfO_2 layer

$HfO_2 + Ti \rightarrow HfO_{2-x} + V_O + TiO_x$

- simulations indicate that there is still detectable amount of SiO_2 remaining at the HfO_2/Si(001) interface

Compositional profile after anneal to 300ºC





TiO_x

$HfO_{1.9}$

$HfSiO_x$

Si (100)

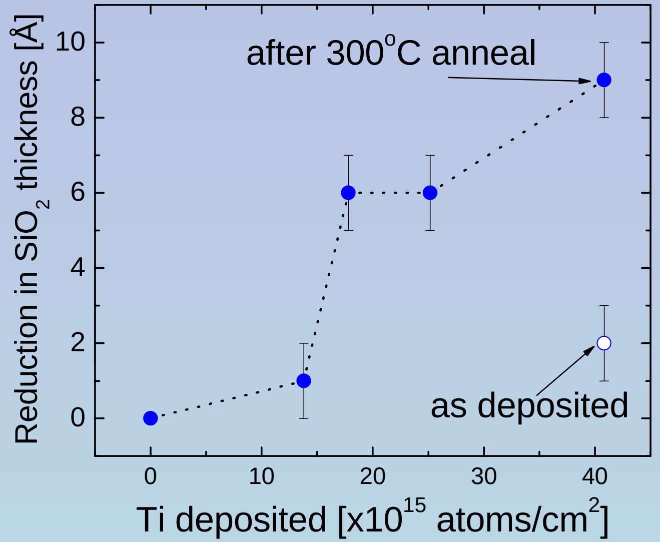
- Lowing and broadening of Ti peak with growth of O yields for the Ti region indicate Ti oxidation

  - $Ti + xO \Rightarrow TiO_x$

- Decrease of Si surface peak and decrease of the width of O peak indicate partial removal of SiO_2 layer

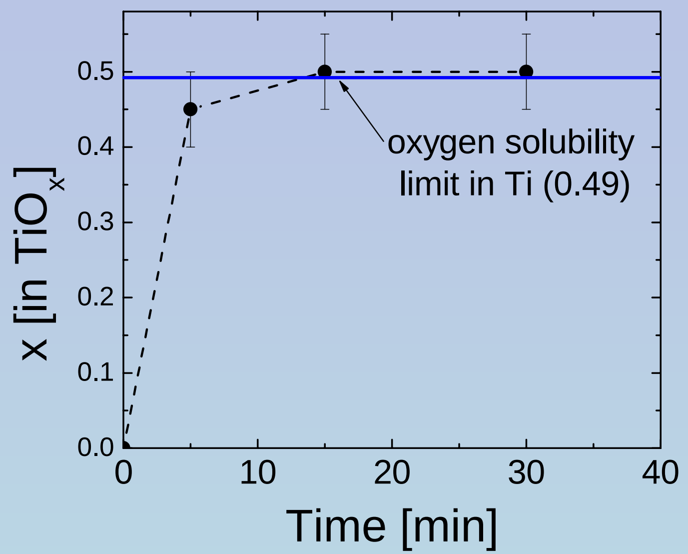
- Incorporation of some of the Si initially present in the interfacial SiO_2 layer in the high-κ layer and oxidation of the Ti layer at the Ti/HfO_2 interface changes stack capacitance in comparison to an ideal TiOδ/HfO_2/Si structure

Ti thickness issues



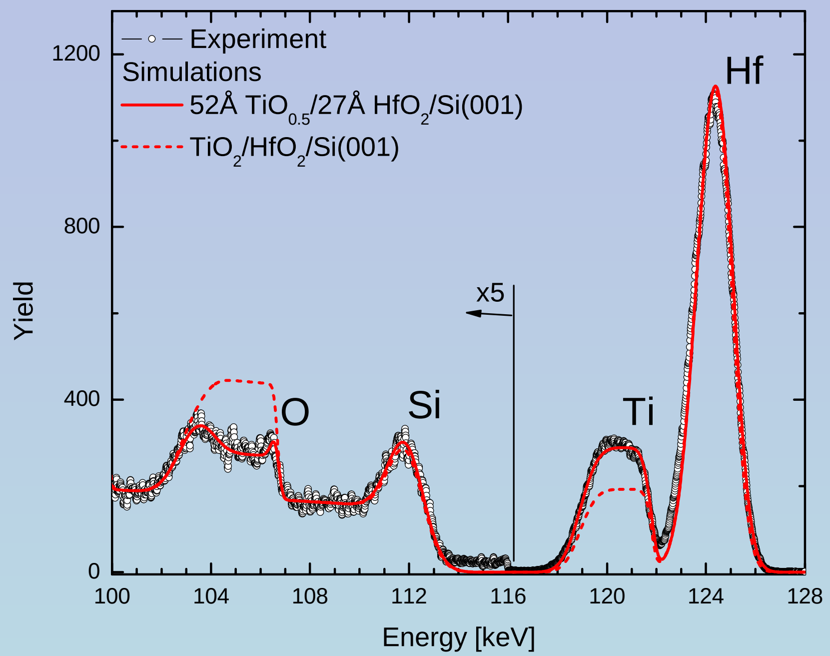
- Ti thickness should exceed some minimal value for SiO_2 reduction to start
- Thicker Ti films stacks show SiO_2 layer reduction even without low T anneal

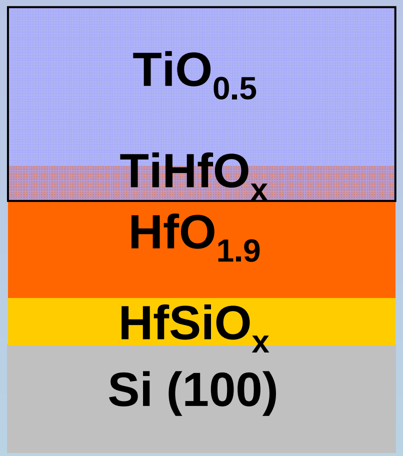
Oxygen diffusion kinetics



- O transport through HfO_2 is fast
- amount of O incorporated into the bulk of Ti overlayer never exceeds O solubility limit in Ti (no strong chemical bonding…)

Compositional profile after air exposure





$TiO_{0.5}$

$TiHfO_x$

$HfO_{1.9}$

$HfSiO_x$

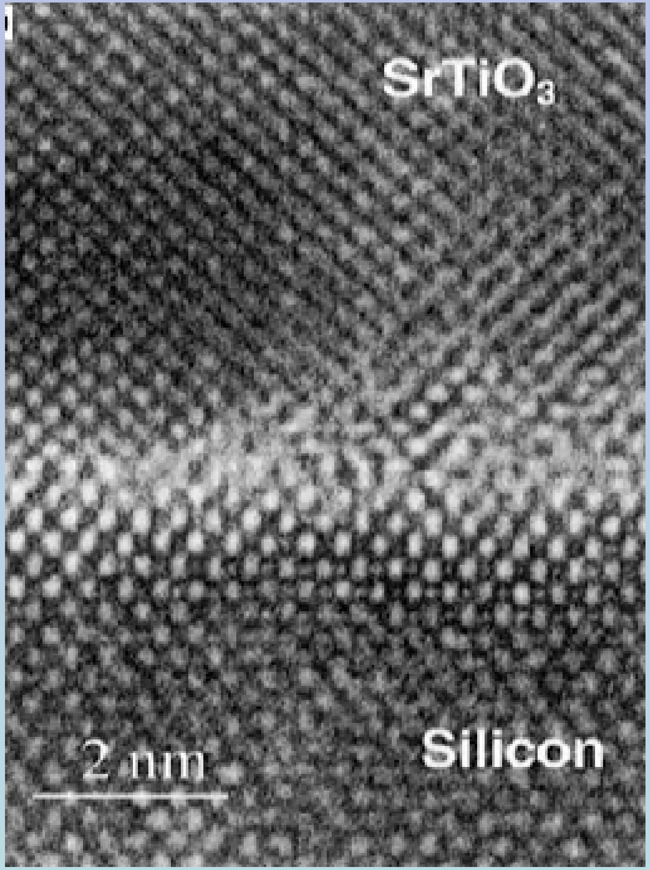
Si (100)

- Further Ti oxidation in the surface layer
- Complete Ti layer oxidation to TiO_2 is not achieved (dashed line),
- Hf oxide layer remains slightly oxygen depleted: oxygen vacancies can affect electrical measurements

Summary (so far)

- Oxygen incorporation and /or exchange rates are a strong function of film composition: different interaction mechanisms with oxygen for Hf and Ce compounds
- Exchange and growth rates are strong functions of temperature
- Nitrogen incorporation into the high-k film reduces oxygen exchange
- Increasing film crystallinity enhances oxygen exchange, presumably (?) by opening more permeable diffusive pathways via crystallite grain boundaries

Epitaxial oxide material integrated with Si



Epitaxial oxides on Si
grown by molecular beam epitaxy
Droopad R., Yu Z.Y., Ramdani J., *et.al*
J. CRYSTAL GROWTH 227, 936 (2001)

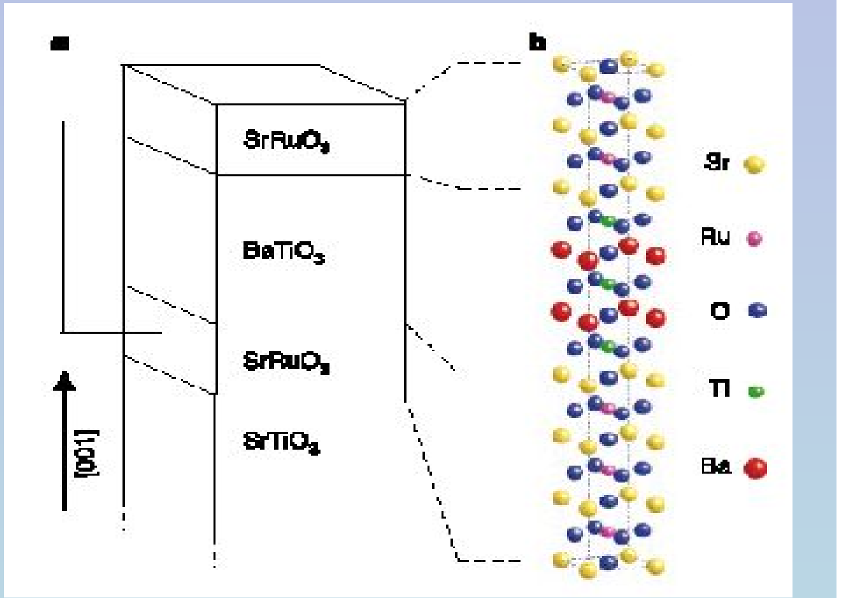
- **Epitaxial structures may afford controllable interfaces (no dangling bonds…)**
- **Thermal stability**
- **Dielectric constants**
- **Lattice match?**

1. Sc_2O_3/Si(111)
2. $SrTiO_3$/Si(001)

Motivation

Possible applications

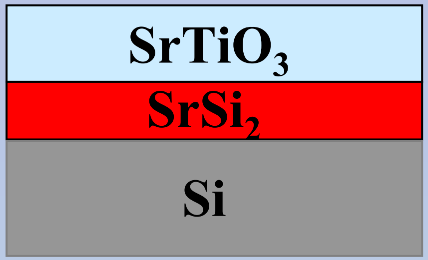
- gate oxide in Si CMOS technology:
  - high κ results in low equivalent oxide thickness
  - nearly defect-free interface results in large carrier mobility
  - crystallinity results in better stability and reliability
- ferroelectric and high-T_c heterostructures

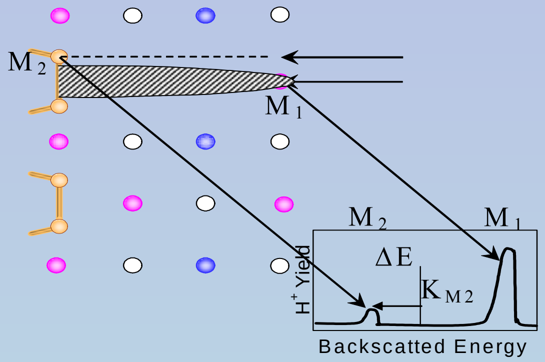


Challenges

- chemically unstable interface with Si
- formation of ***low-κ*** (a-SiO$_2$, silicates) layer at the interface
- low band offsets
- difference in expansion thermal coefficients

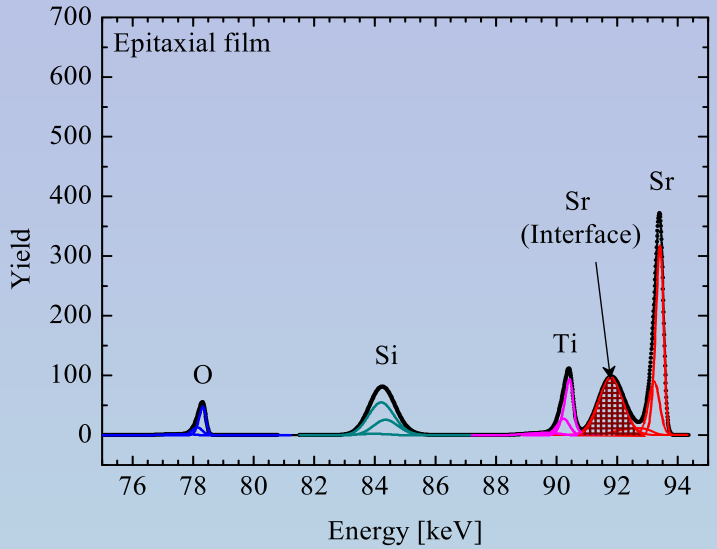
MEIS Yields: Epitaxial *vs* Amorphous

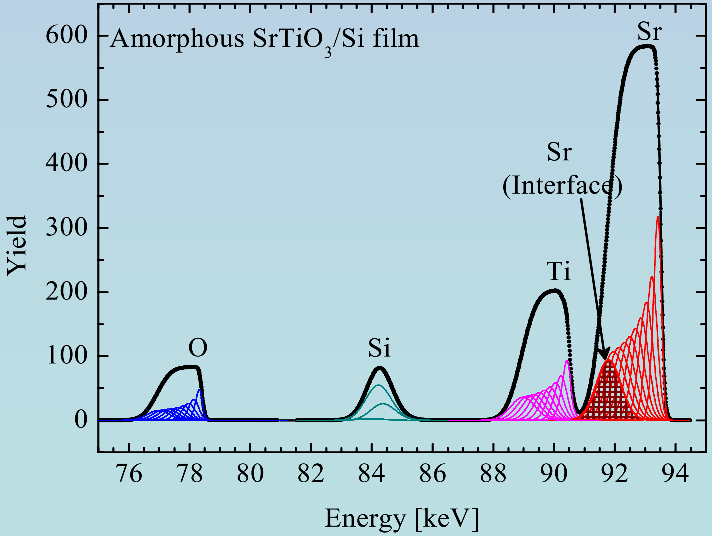




- When an incident beam is aligned with a low-index axis of an epitaxial film, the spectrum mainly reflects the surface composition

- Easier to investigate interface chemical composition of epitaxial films than amorphous ones

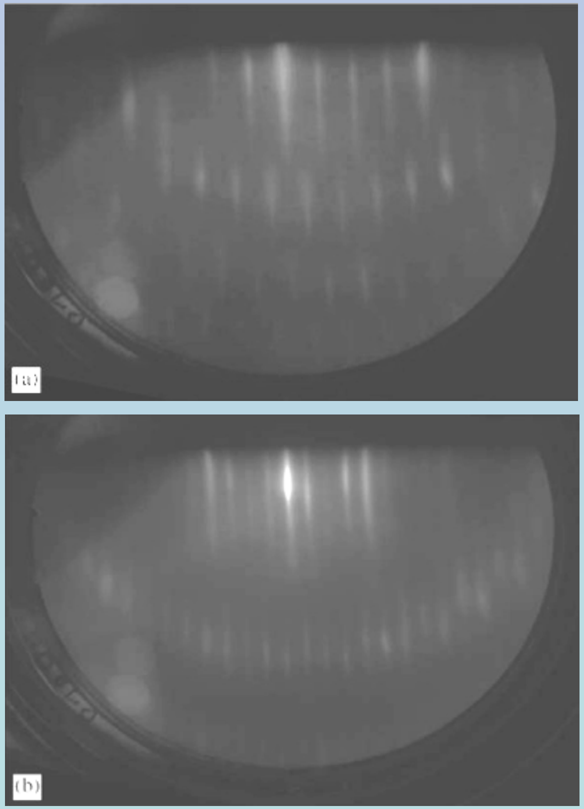




Sc_2O_3 films grown on Si(111): Growth Details

- 50-80Å Sc_2O_3 films were grown on Si(111) using MBE (electron beam evaporation of a pure Sc_2O_3 at substrate T~770^{o}C)
- Initial SiO_2 was removed from the surface by annealing in UHV at Tx~950^{o}C, (7x7) reconstructed Si(111) surface
- HREED indicate that the films have the same in-plane symmetry as the Si(111) substrate

$\Rightarrow$ Epitaxial growth



C. P. Chen, M. Hong, J. Kwo, et al, *J. Crystal Growth* 278 (2005) 638
M. Hong, A. R. Kortan, P. Chang, et al, *APL* (submitted)

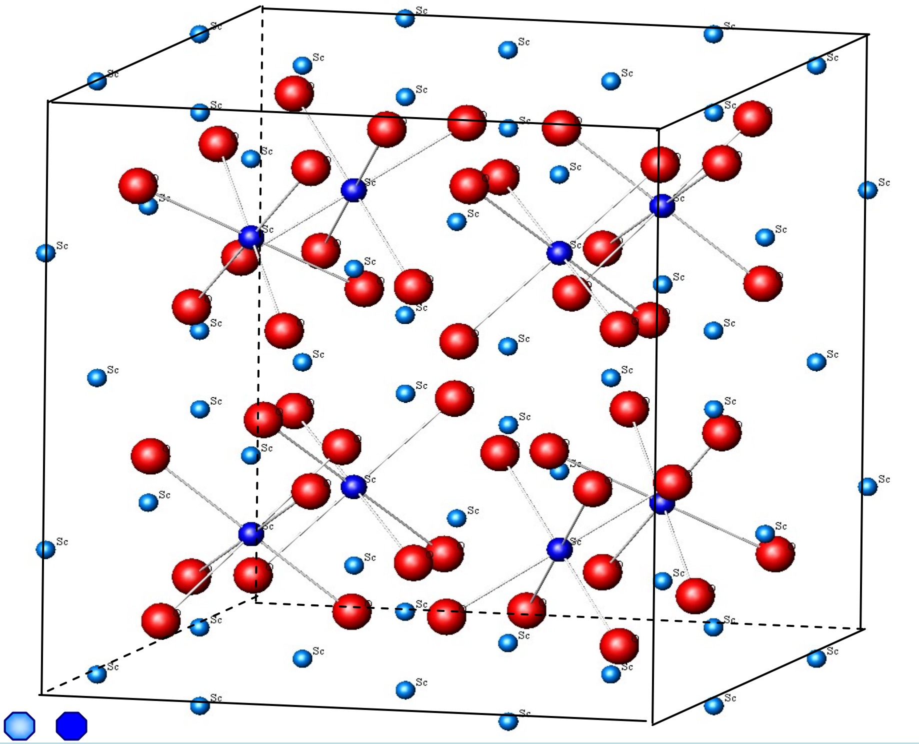
In collaboration with M.Hong, National Tsing Hua University

Sc_2O_3 structure

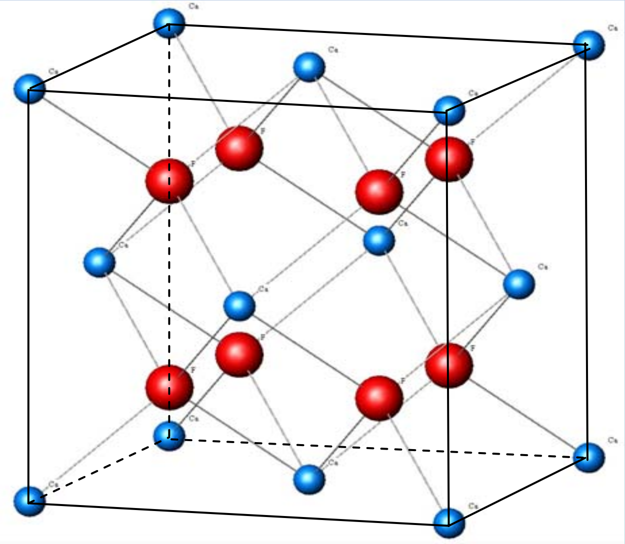
Bulk Sc_2O_3 has the cubic bixbyite structure

a=9.845Å (Ia$\underline{3}$)

Can be considered as 16 “fluorite”-like unit cell (a=4.9225Å) with 2 off 8 O atoms missing and two distinct Sc positions



Sc ⬢ ⬢
O ⬢



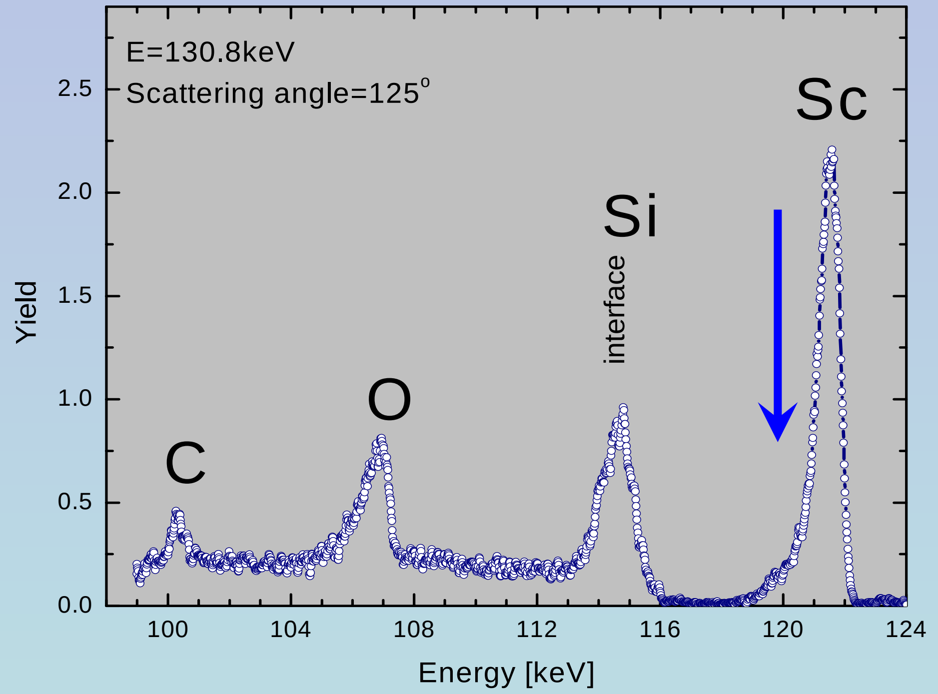
CaF_2

Ca ⬢ F ⬢

Lattice mismatch with Si ~10%

defined as $(2\times a_{Si}-a_{Sc2O3})/a_{Sc203} = 0.107$

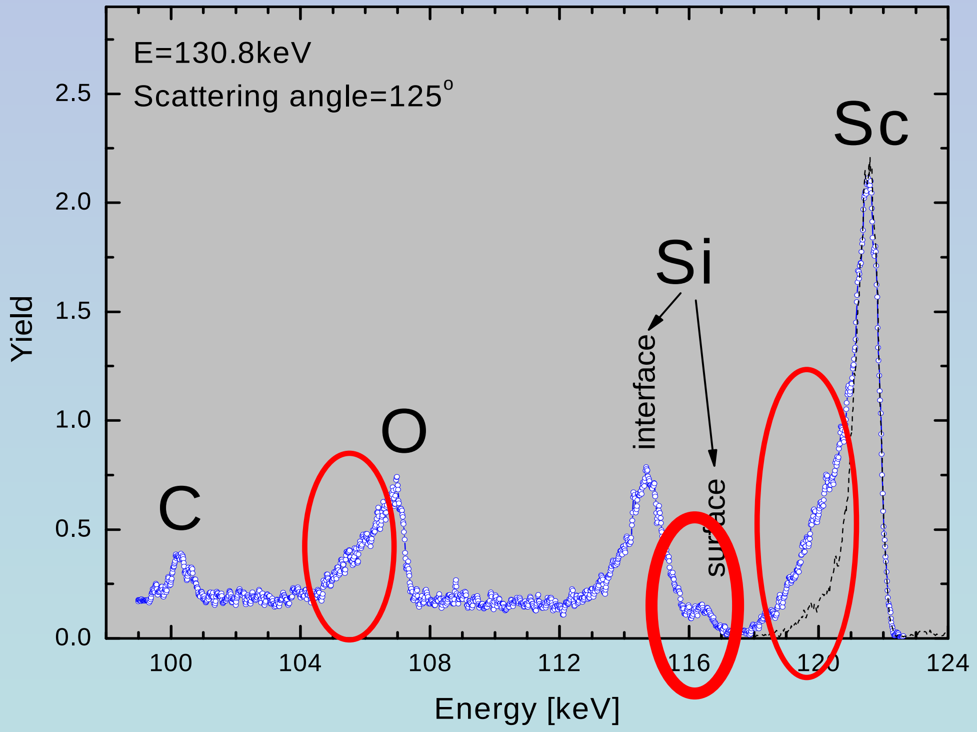
MEIS experimental data
50Å Sc_2O_3(111)/Si(111)



- χ = $Yield_{cryst}/Yield_{amorph}$ = 4%, indicating good film crystalline quality;
- no interface Sc and O are observed;
- fractional number of silicon atoms ⇒ crystallinity of the interface and predominant deformation of Si lattice

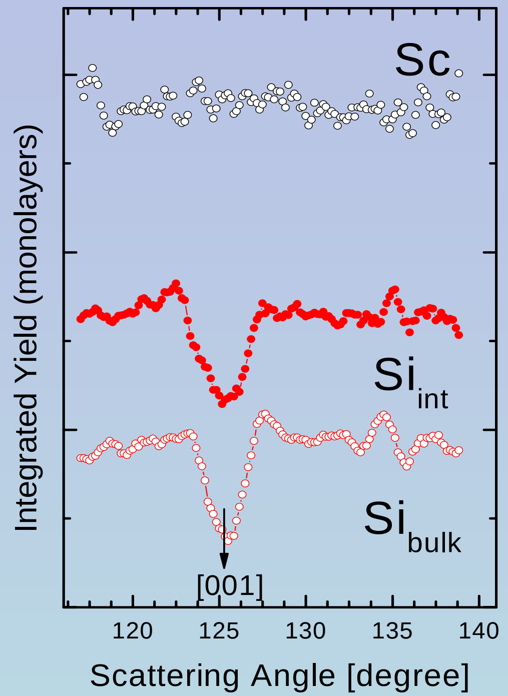
Lower growth temperature

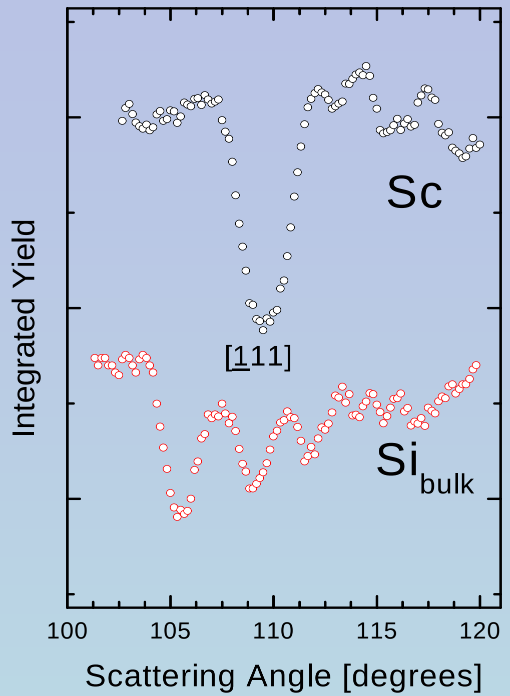
80Å Sc_2O_3(111)/Si(111)



- Crystalline film, however quality deteriorates
- Surface Si peak: formation of void in the film that leave some of the substrate exposed, or Si enriched grain boundaries

Angular Distribution Analysis





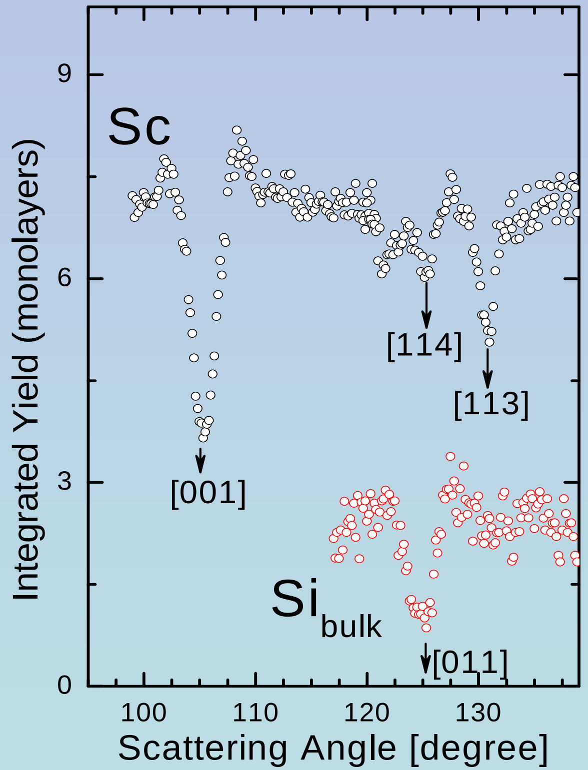
- No minima for Sc in the Si blocking geometry

- Detector shift to a different angle range reveals blocking minima in Sc yields

- Sc blocking minimum can be related to the stereographic projection of the (111) faced cubic crystal and corresponds to the $[\underline{2}11]$ scattering plane.

$(111)Sc_2O_3$ // (111)Si and $[\underline{2}11]Sc_2O_3$ // $[\underline{11}2]$ Si

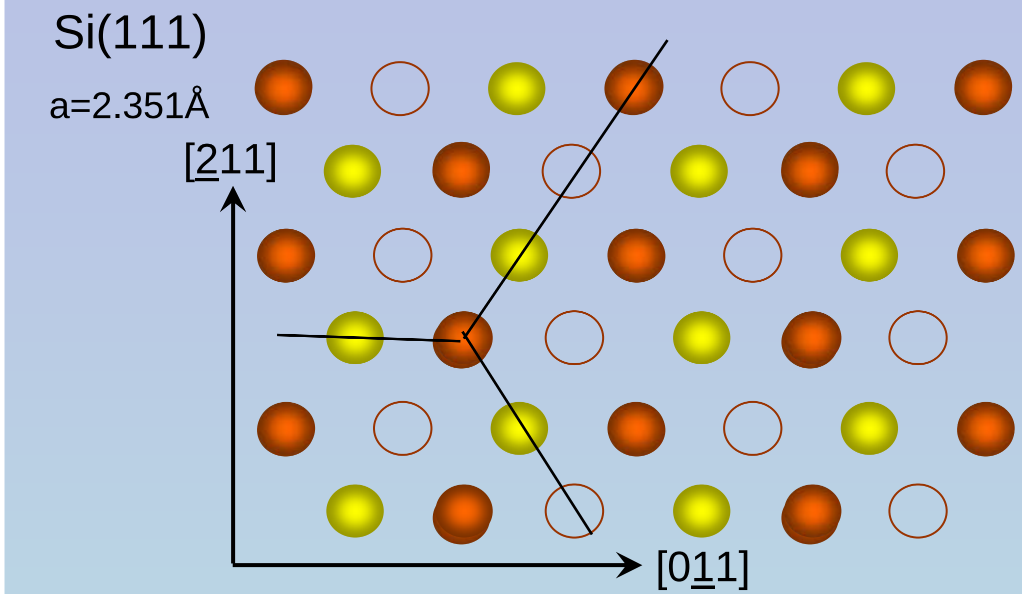
Alternative Scattering direction: [211] channeling

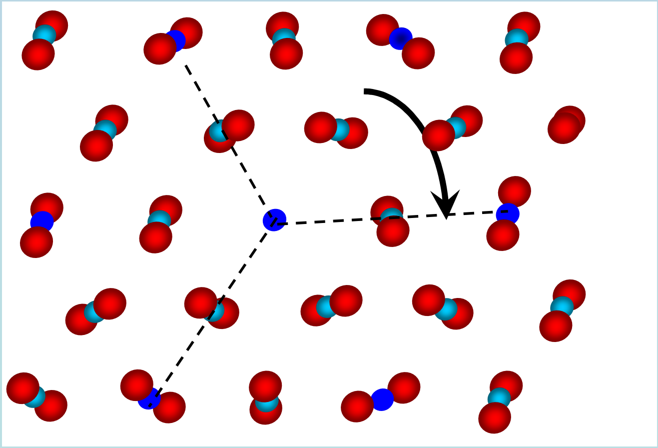


To confirm the azimuth orientation of the epitaxial film sample was rotated by 60^{o}.

- The [211] channeling direction and the $[\underline{2}11]$ Si scattering plane were used and the alternative blocking directions were probed.
- Si yields show a blocking minimum at 125^{o}, which corresponds to [011] direction.
- Sc angular distribution has minima at ~105^{o}, 125^{o} and 131^{o}, that can be identified as the [001], [114] and [113] blocking directions in the $[\underline{11}2]$ scattering plane.

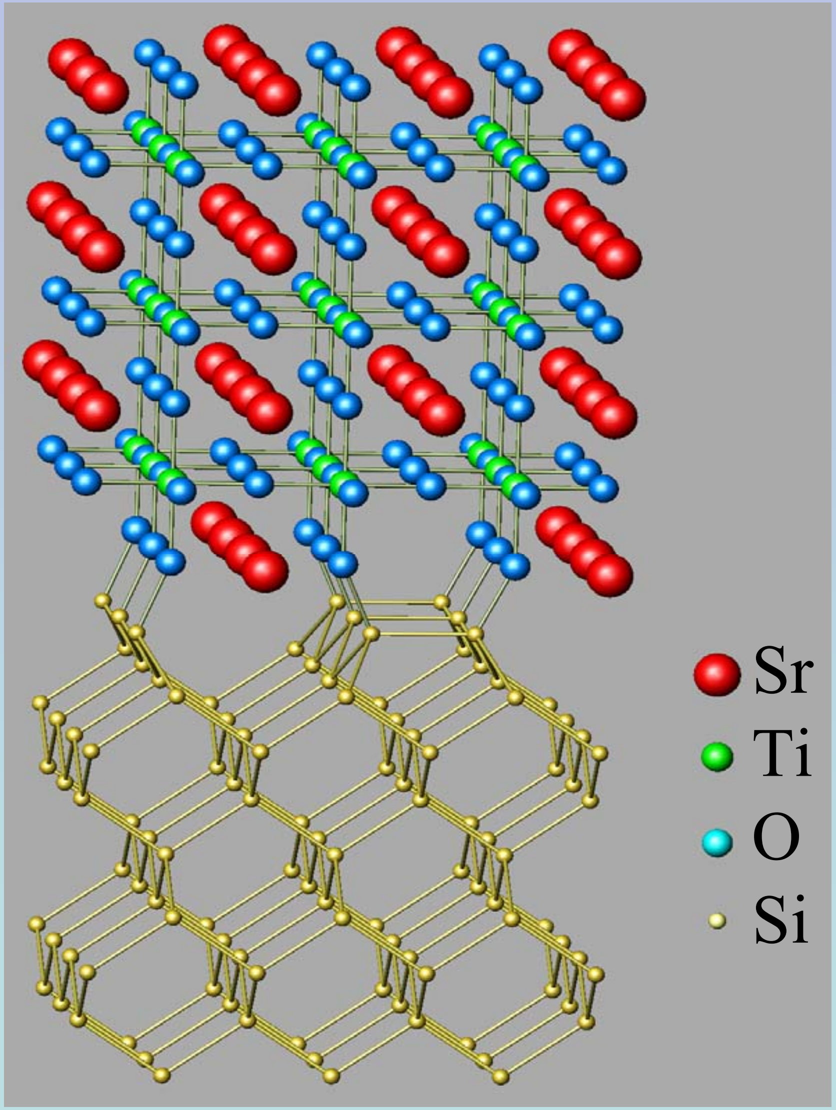
Growth and structure of the interface





- Both Si(111) and Sc_2O_3(111) surfaces exhibit 3-fold rotational axis symmetry
- (7x7) Si(111) surface was used to initiate Sc_2O_3 growth (a=16.457Å)
- Unique positions of oxygen atoms in Sc_2O_3 film relatively to (7x7)Si(111) surface favor 60^o ($=180^0$) rotation
- Possible sub-oxide formation at the interface

$SrTiO_3$/Si(001): Film fabrication



Solution: multi-step epitaxy

- initial formation of $SrSi_2$ to:
  - (i) provide template for epitaxy;
  - (ii) avoid Si oxidation;
  - (iii) avoid Ti contact with Si
- further growth by alternating cycles of low-T Sr and Ti co-deposition in O_2, and re-crystallization at high T

- how does interface change during high-T step (due to Ti, Sr, Si, O diffusion/ reaction)?

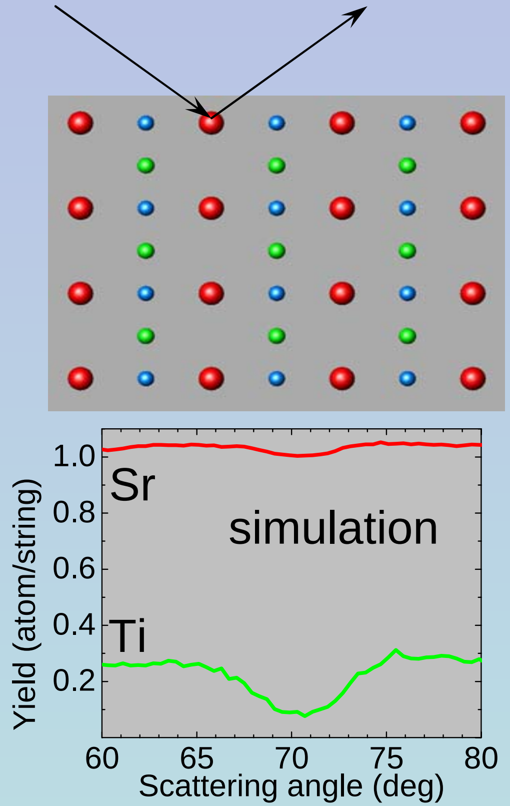
- optimization of re-crystallization conditions

Top surface termination

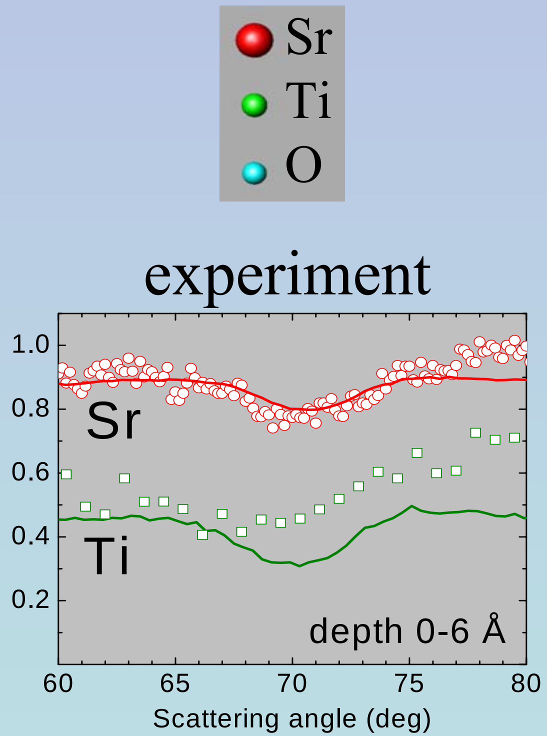
Sr termination

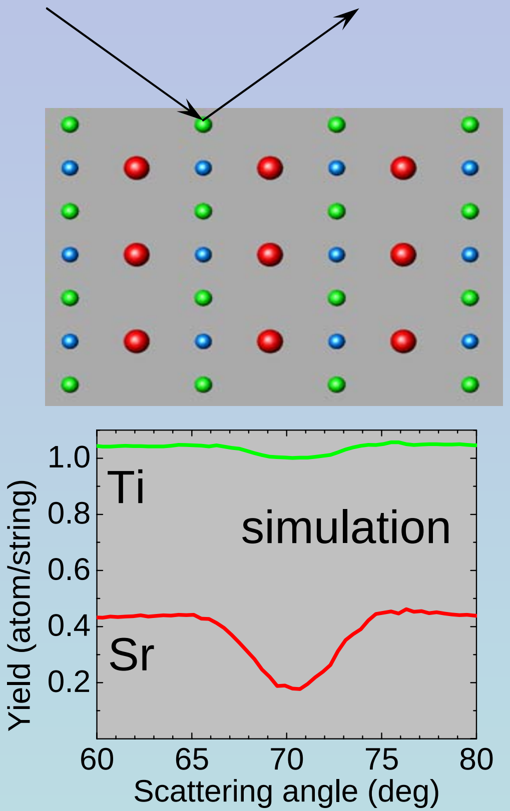
(110) scattering plane,
54.74° → 54.74°

Ti termination



×0.8





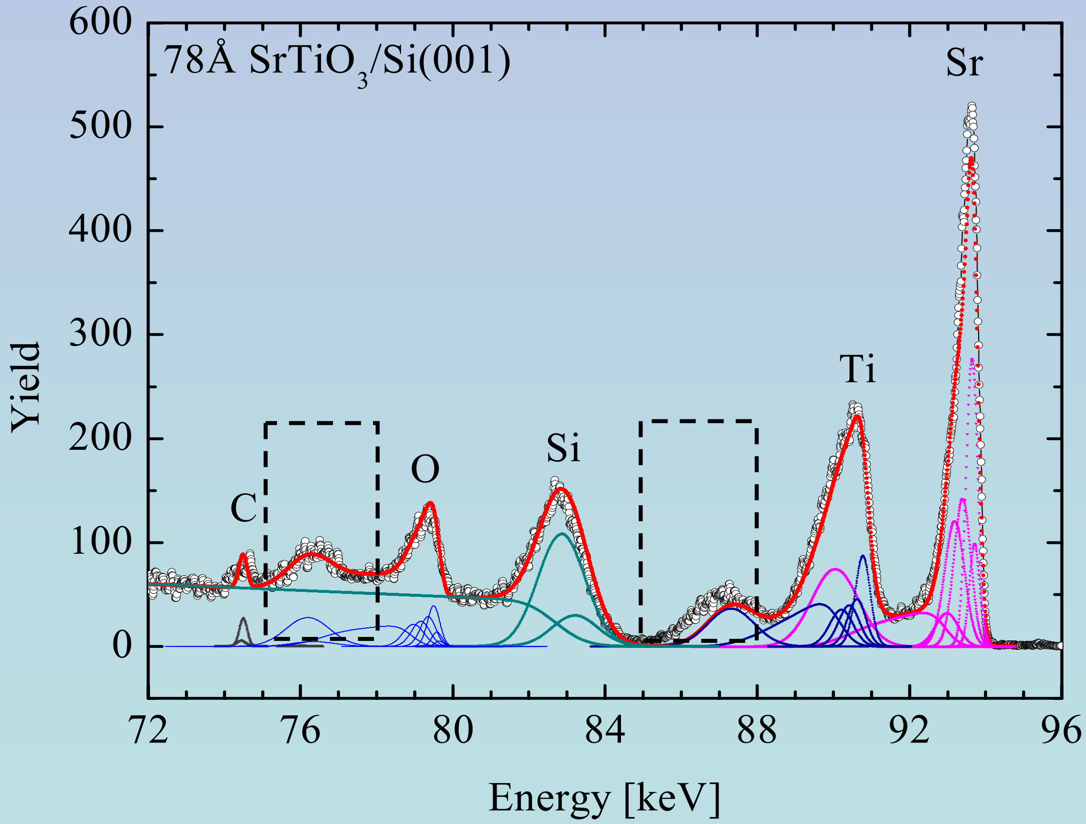
×0.2

- predominantly Sr termination, but better quantitative agreement by invoking 20% Ti-terminated patches

Interface composition

Normal incidence, 98keV H^+, scattering angle 125° (substrate Si blocking)
$SrTiO_3/SrTiSi_xO_y/Si(001)$

Sr, Ti and O are observed in the interface region - they are visible to the ion beam (not blocked) in this scattering geometry

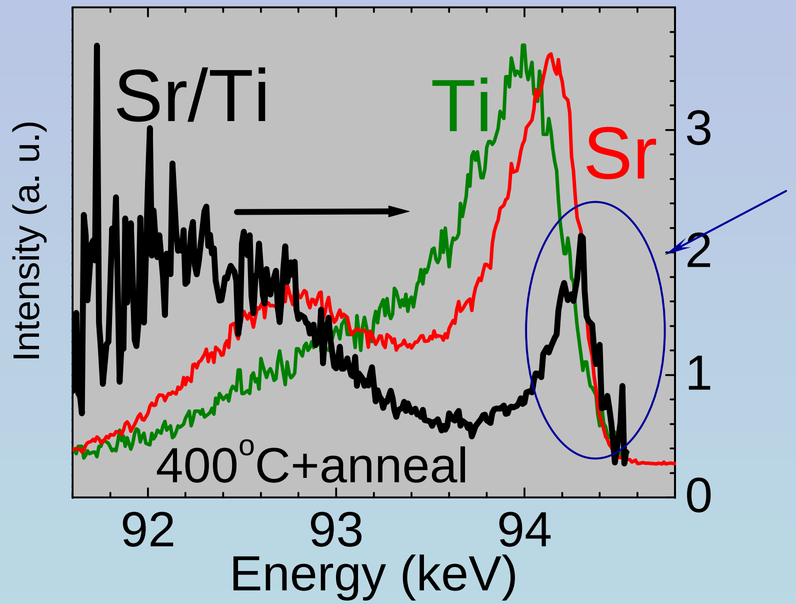


$SrTiO_3$	78Å
SrO	2Å
$TiSi_xO_y$	6Å
Si(001)	

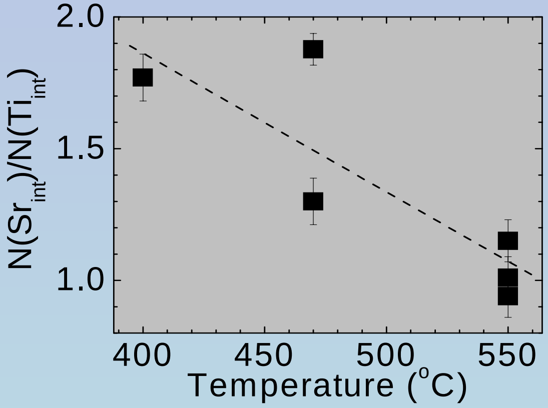
or

$SrTiO_3$	78Å
$Ti_{1-x}Sr_xSi_yO_z$	8Å
Si(001)	

Interfacial peak analysis

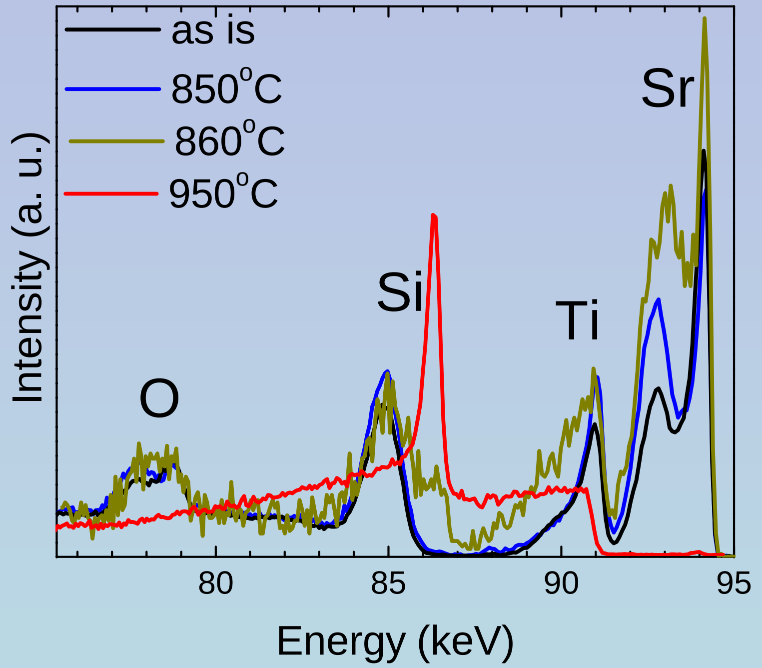


confirms Sr termination



- lowering re-crystallization temperature results in reduction of visible interfacial Ti, consistent with Sr silicide/silicate interface

Thermal stability issues

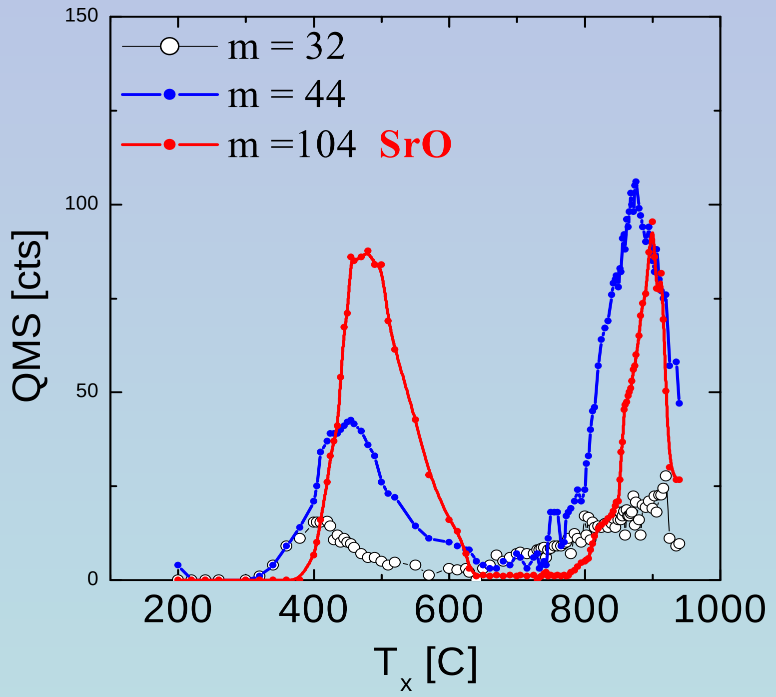


- no change after annealing up to 750°C
- disordering starts at interface at 850°C, eventually results in $TiSi_2$ formation and removal of Sr and O

$$2Si + SrTiO_3 \rightarrow TiSi_2 + SrO(g) + O_2(g) + SiO(g)$$

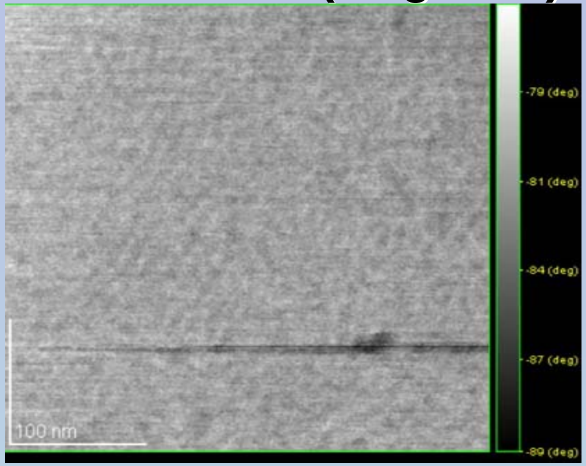
Thermal decomposition

TPD (temperature desorption spectra) for 35Å $SrTiO_3/Si(001)$ (heating rate of 1.5K s^{-1})

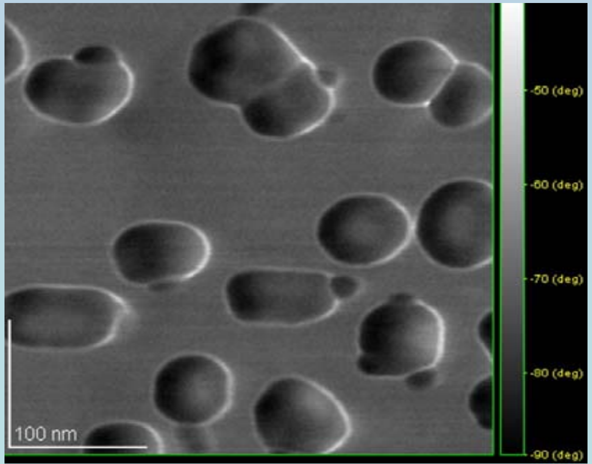


- SrO and SiO (?) desorption at T>800°C
- Complete decomposition and formation of large $TiSi_x$ islands (l=50-100nm, h~10nm)

AFM before (as grown)



Annealed to 950°C

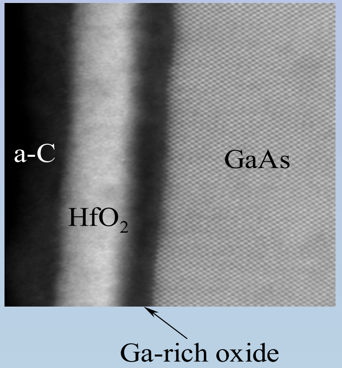
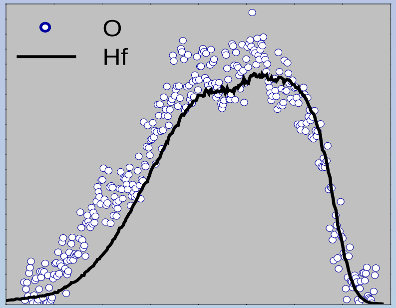
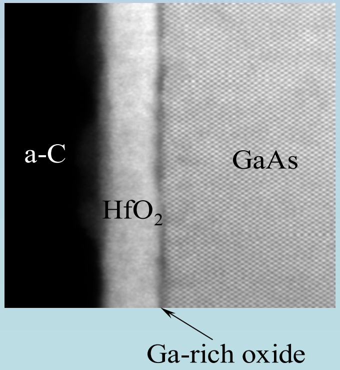
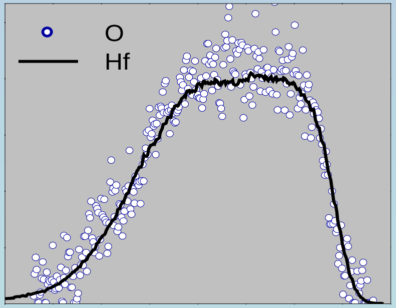


350nm

Why GaAs (or Ge)?

- Potentially great advantages over Si-based devices for both high-speed and high-power applications
- The electron mobility of GaAs is 5x that in Si
- **Much thinner interfacial oxide**

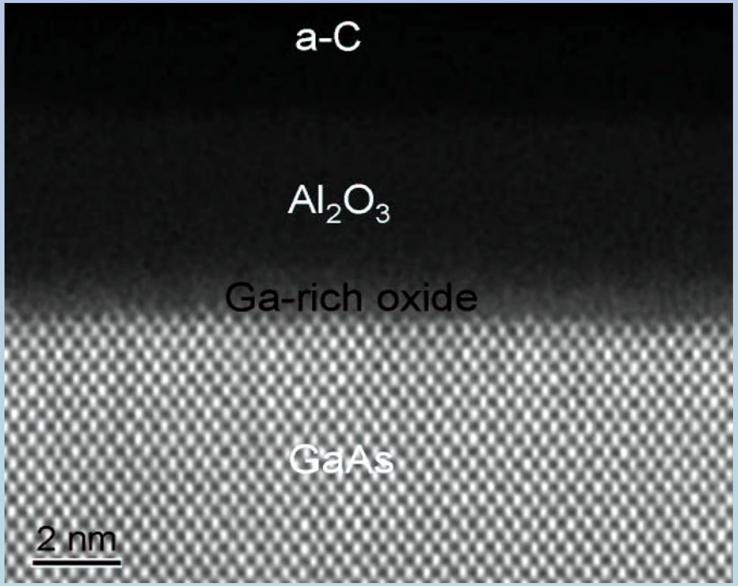
HfO_2 on GaAs: MEIS and TEM comparison

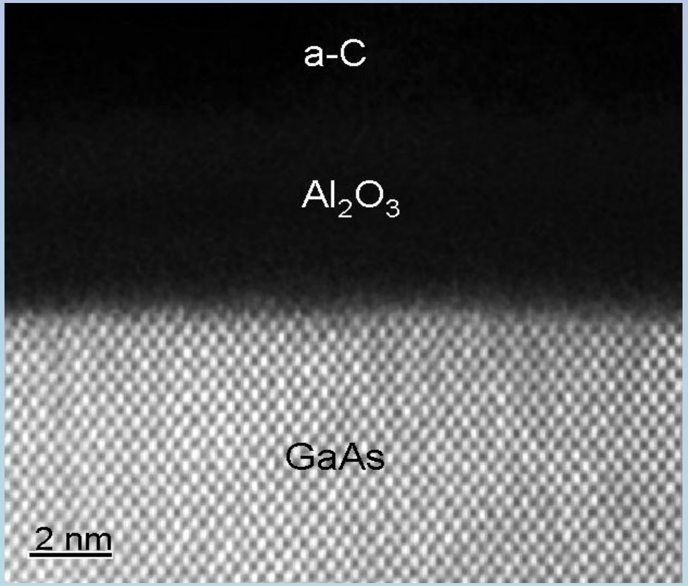
	TEM[*]	MEIS
No etch		
HF etch		

[*] Grazul & Muller, Cornell

- TEM and MEIS results are consistent

TEM of $\mathbf{Al_2O_3}$ on GaAs


No etch


HF etch

(J. Grazul and D. Muller, Cornell)

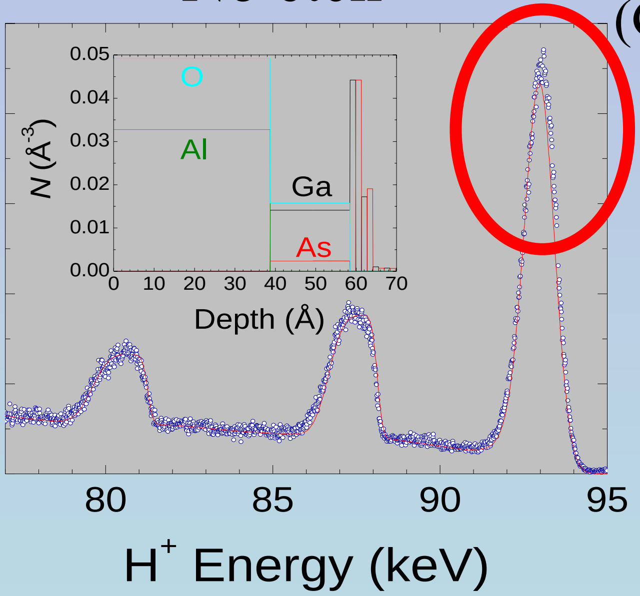
- no contrast between Al_2O_3 and Ga_xAs_yO

MEIS data of **Al_2O_3** on GaAs: one-parameter fitting

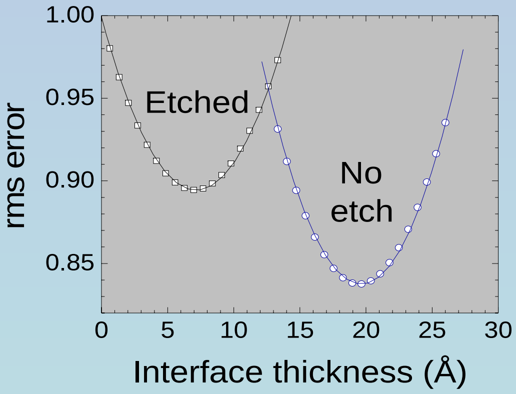
<u>Interfacial oxide:</u>

$(Ga_2O_3)_{0.37}(Ga_2O)_{0.63}(As_2O_3)_{0.17}$, porous oxide: $\rho = 0.5\ \rho_{bulk}$

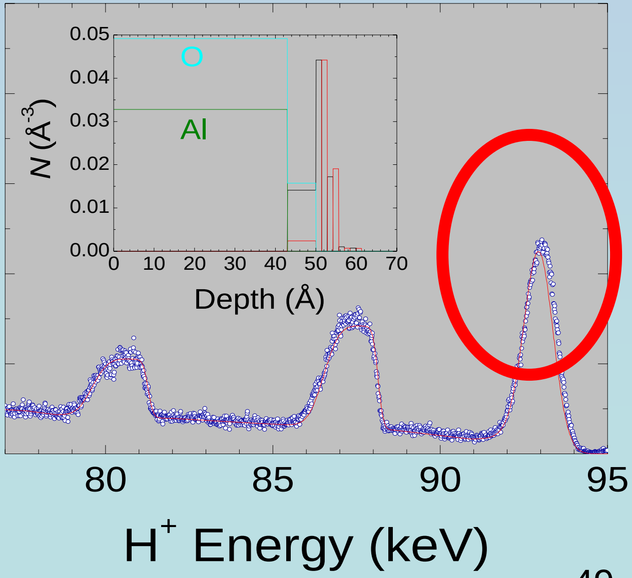
No etch



	n(Ga+As), Å^{-2}	*n(Al), Å^{-2}*	*n(O), Å^{-2}*	*n(O)/n(Al)*
HF etch	0.33	1.48	2.23	1.51
No etch	0.55	1.30	2.22	1.70



HF etch



- interfacial oxide is much thinner for the HF-etched sample

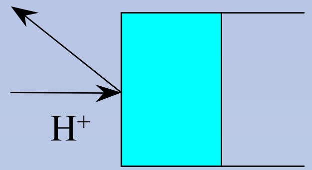
Summary

- Highly ordered epitaxial growth.
- Epitaxial growth of Sc_2O_3 was accompanied by 60° in-plane rotation of the film relatively to substrate
- Low leakage current and a high breakdown field show promising electrical characteristics
- Composition of $SrTiO_3$ on Si(001) interface can be controlled by recrystallization temperature
- $SrTiO_3$ film decompose under UHV anneal above 850°C with formation of $TiSi_x$ islands

Conclusions

- Oxygen mobility in high-k films is a serious issue. Interesting material dependence!
- High-k films compositionally layered, usually with SiO_2 at interface on Si. Methods to monitor SiO_2 content developed.
- Crystalline films on Si show promising (or at least interesting) properties. Composition and structure have been determined.

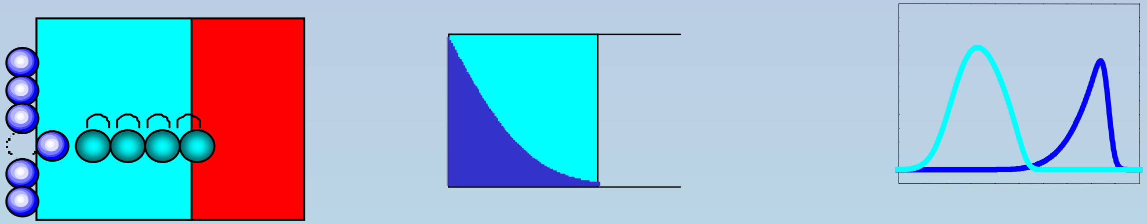
Oxygen transport mechanisms examined by ion scattering



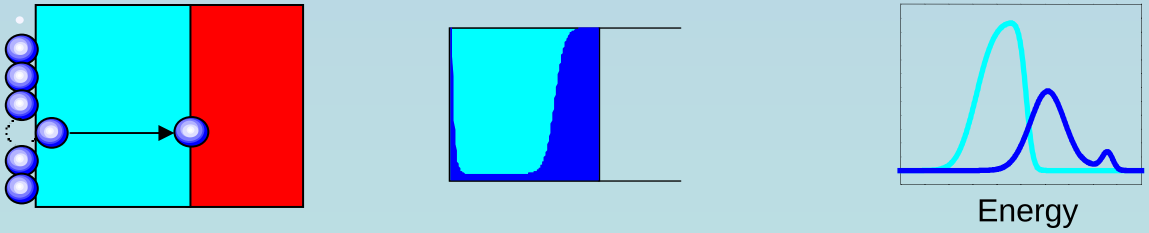
▭ ^{16}O marker

■ ^{18}O tracer

Oxygen lattice transport (O or vacancy exchange)



Direct oxygen “short circuit” transport to interface (via grain boundary?)



Concentration vs depth profile of all isotopes in film

“Raw” ion scattering spectra (for two isotopes