Advanced Gate Stacks and Substrate Engineering

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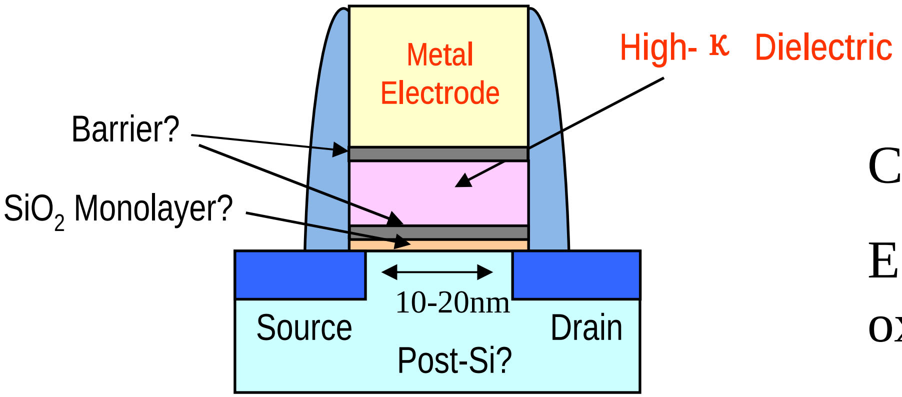
Key interactions:

- Gustafsson, Bartynski, Chabal – Rutgers
- Gennadi Bersuker – Sematech
- Rich Haight, Supratik Guha – IBM

Other collaborators: M. Green – NIST; E. Gusev - Qualcomm; W. Tsai – Intel; J. Chambers, H. Niimi – TI

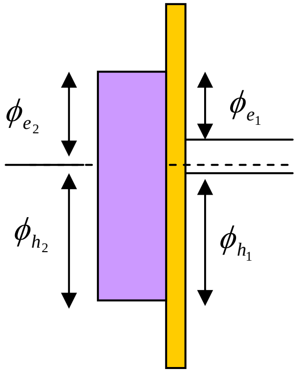
Goal: develop understanding of interaction of radiation with CMOS materials



CMOS transistor ~2010?

$C \propto A\varepsilon/d$

EOT - effective oxide thickness



- New materials: metal electrodes, high-K dielectrics, semiconducting substrates
- Electronic structure, defects, mobility, reliability, failure
- Look for specific physical and chemical signatures of radiation induced defects – create atomic picture of defects

Rutgers CMOS Materials Analysis

Use high resolution characterization methods to:

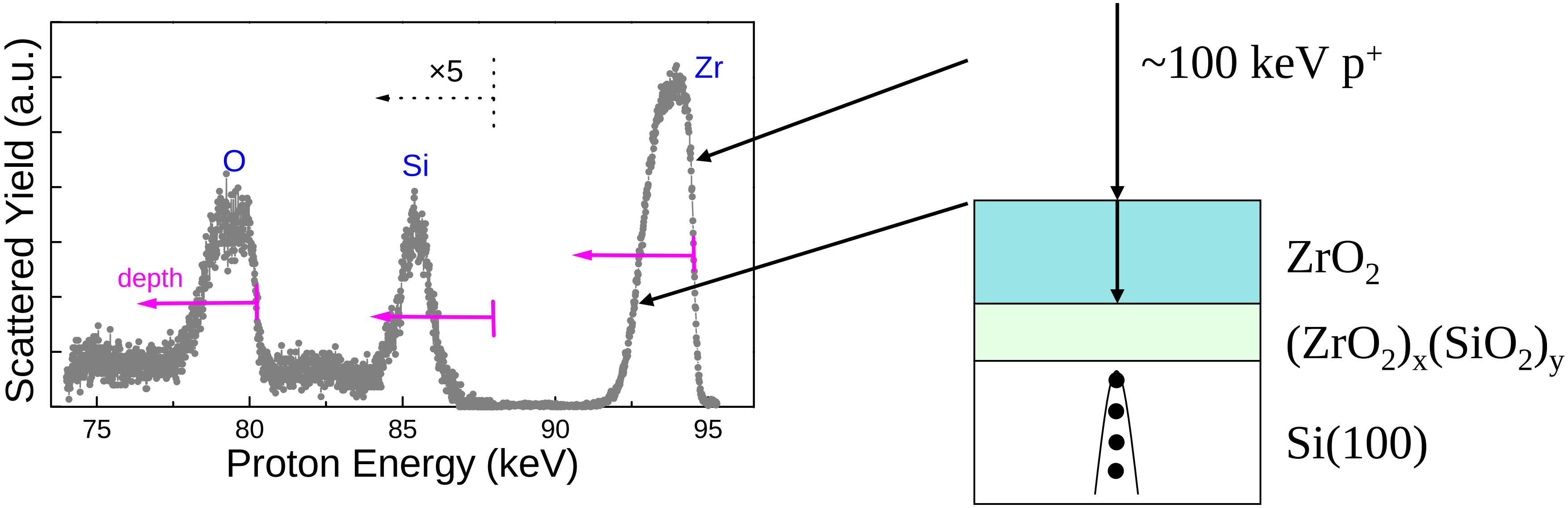
1. Determine composition, structure and electronic properties gate stacks that use new (post-Si) materials
2. Help determine physical and chemical nature of radiation induced defects

- Scanning probe microscopy – topography, surface damage, electrical defects
- Ion scattering: RBS, MEIS, NRA, ERD – composition, crystallinity, depth profiles, H/D
- Direct, inverse and internal photoemission – electronic structure, band alignment, defects
- FTIR, XRD, TEM
- Electrical – IV, CV
- Growth – ALD, CVD, PVD

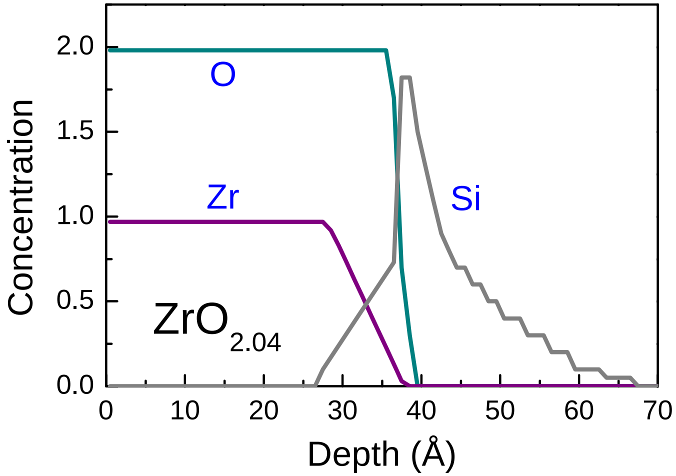
Results

- Generated thin films with high-K dielectrics (HfO_2) and metal gate electrodes (Al, Ru).
- Performed ion scattering, photoemission, internal and inverse photoemission on selected systems.
- Had samples irradiated by Vanderbilt group (Feldman), as well as at Rutgers.
- Performed conductive tip SPM measurements of defects on selected systems

MEIS depth profiling



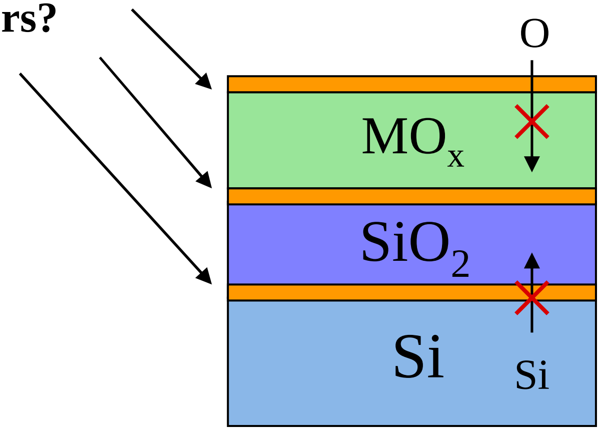
depth profile

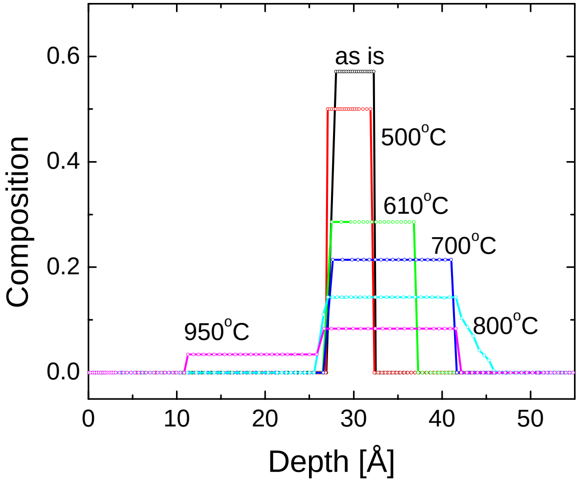


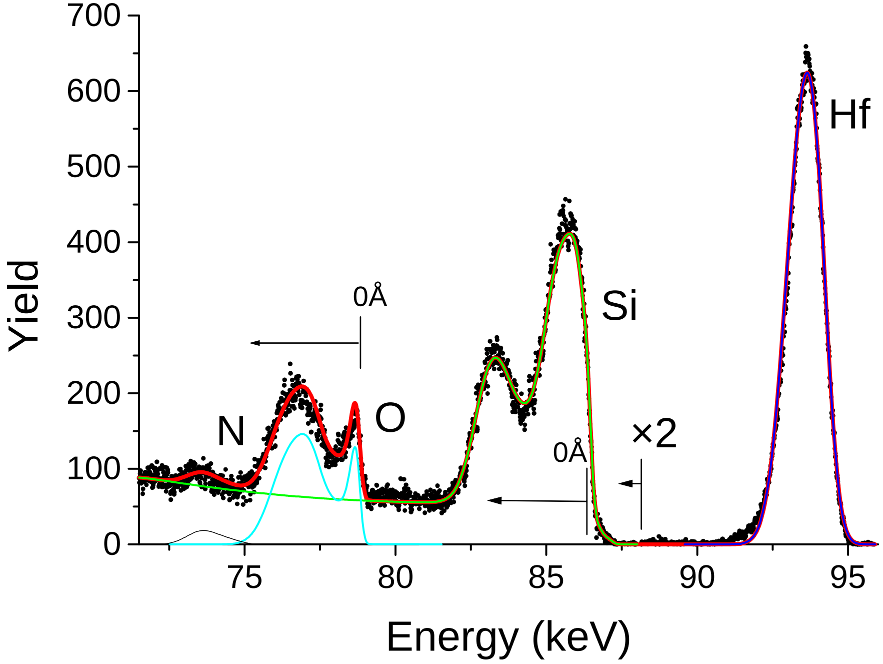
- **Sensitivity**:
  ≈ 10^{+12} atoms/cm^2 (Hf, Zr)
  ≈ 10^{+14} atoms/cm^2 (C, N)
- **Accuracy** for determining total amounts:
  ≈ 5% absolute (Hf, Zr, O), ≈ 2% relative
  ≈ 10% absolute (C, N)
- **Depth resolution**: (need density)
  ≈ 3 Å near surface
  ≈ 8 Å at depth of 40 Å

Nitride barrier monolayers to minimize diffusion

Nitride barrier layers?





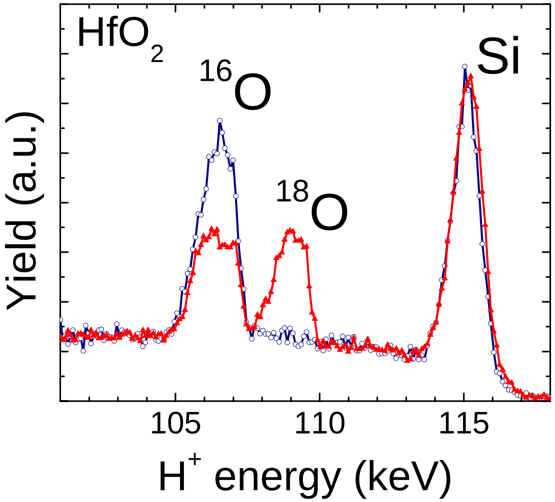


- **Nitride barrier layers helpful to slow O, Si and dopant diffusion, as well as silicate formation and other interface reactions.**
- **Nitridation also raises crystallization temperature.**

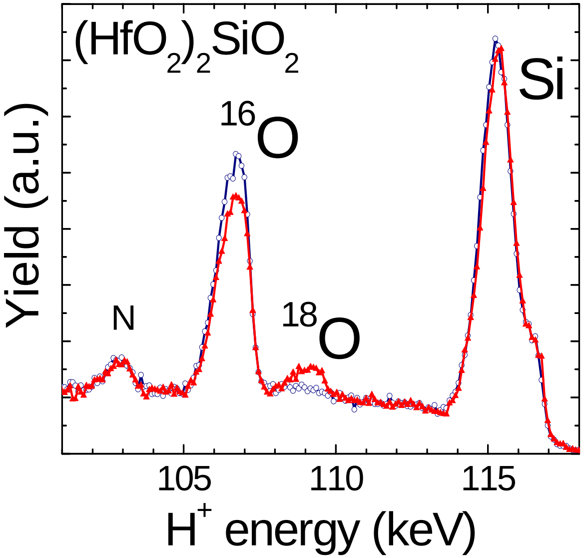
Isotope reactions and diffusion in silicates

Relation between composition and O incorporation

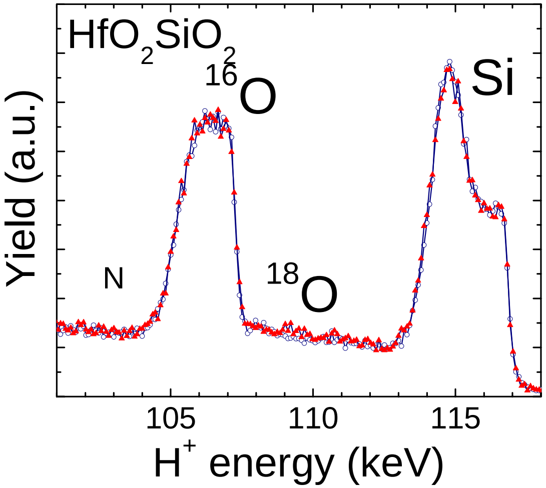
HfO$_2$(SiO$_2$)$_x$ re-oxidation in ^{18}O: 500° C, 10^{-2} Torr, 30 min



x = 0%



33%

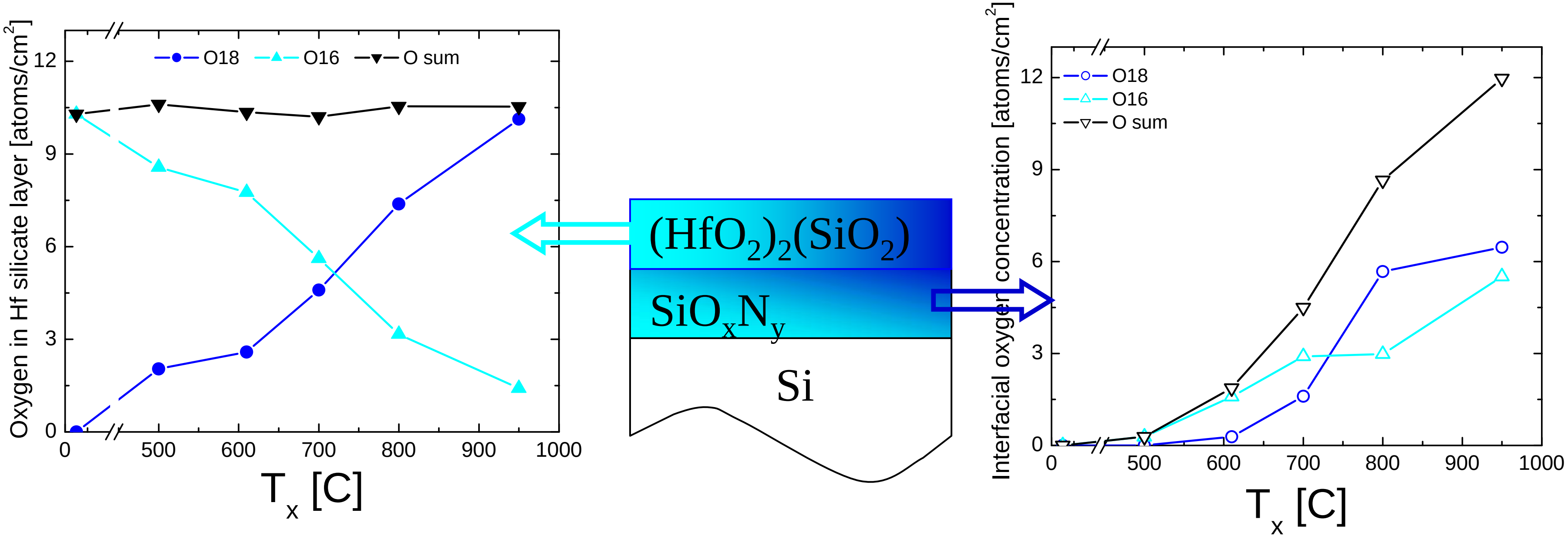


50%

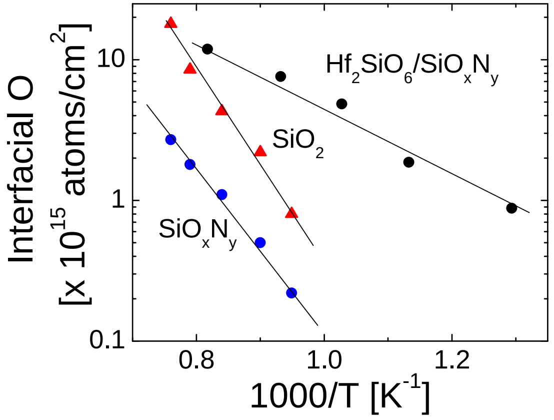
- strong exchange reaction even at 500°C: ^{16}O loss, with same total O conc.
- no change in width of ^{16}O and Si peaks (no formation of interfacial oxide)
- exchange rate decreases with increase of SiO$_2$ fraction x
- 50:50 mix of SiO$_2$:HfO$_2$ is enough to suppress oxygen exchange (in this case)

Rutgers/Sematech

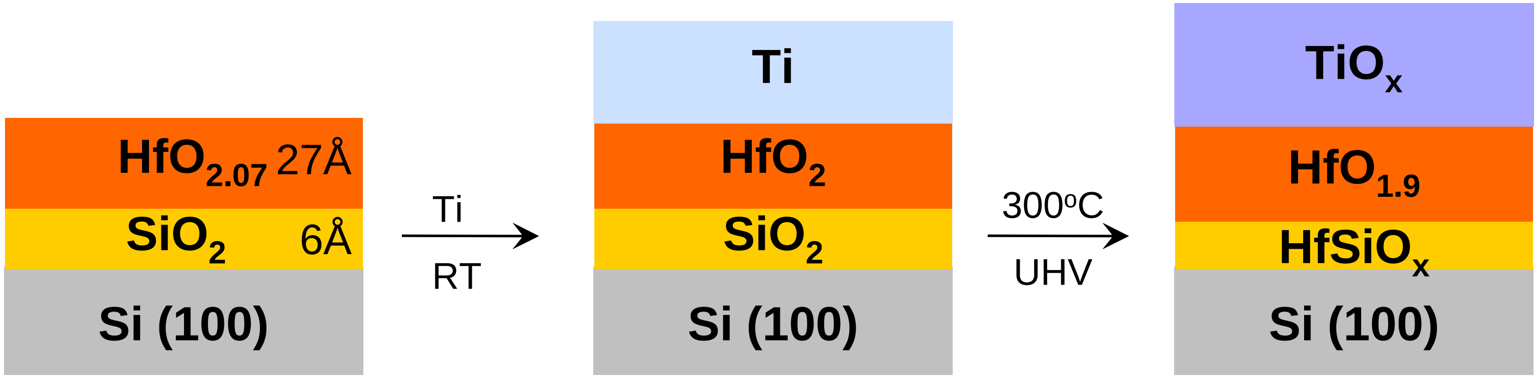
Exchange and growth T-dependence



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



Interaction of metal overlayers with dielectric



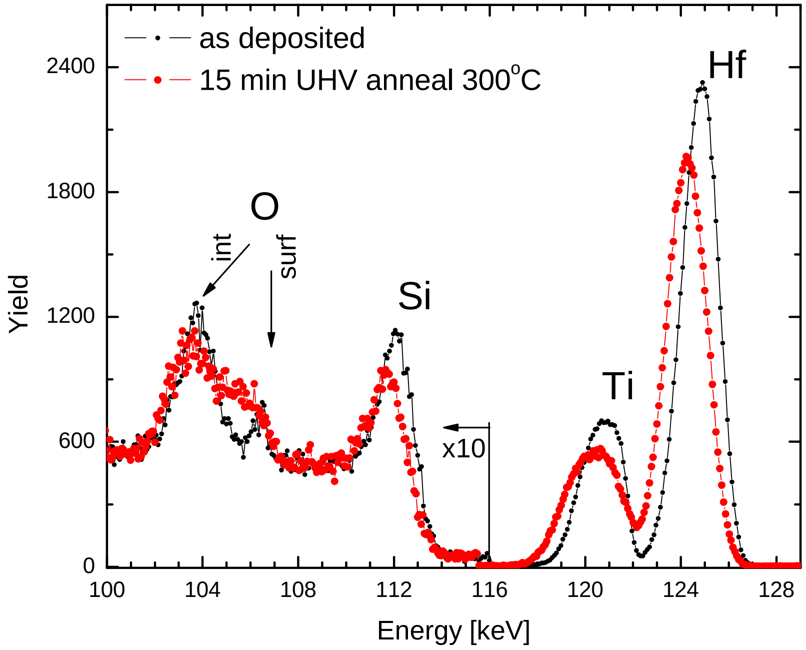
$HfO_{2.07}$ 27Å
SiO_2 6Å
Si (100)

$\xrightarrow[\text{RT}]{\text{Ti}}$

Ti
HfO_2
SiO_2
Si (100)

$\xrightarrow[\text{UHV}]{300^oC}$

TiO_x
$HfO_{1.9}$
$HfSiO_x$
Si (100)



- As-deposited amorphous HfO_2 film has small amount of interfacial SiO_2 (~6-7Å) and excess of oxygen (~$HfO_{2.07}$)
- Deposited Ti forms uniform layer, no strong intermixing with HfO_2;
- Oxygen concentration in Ti layer is small (TiO_x, $x<0.10$)

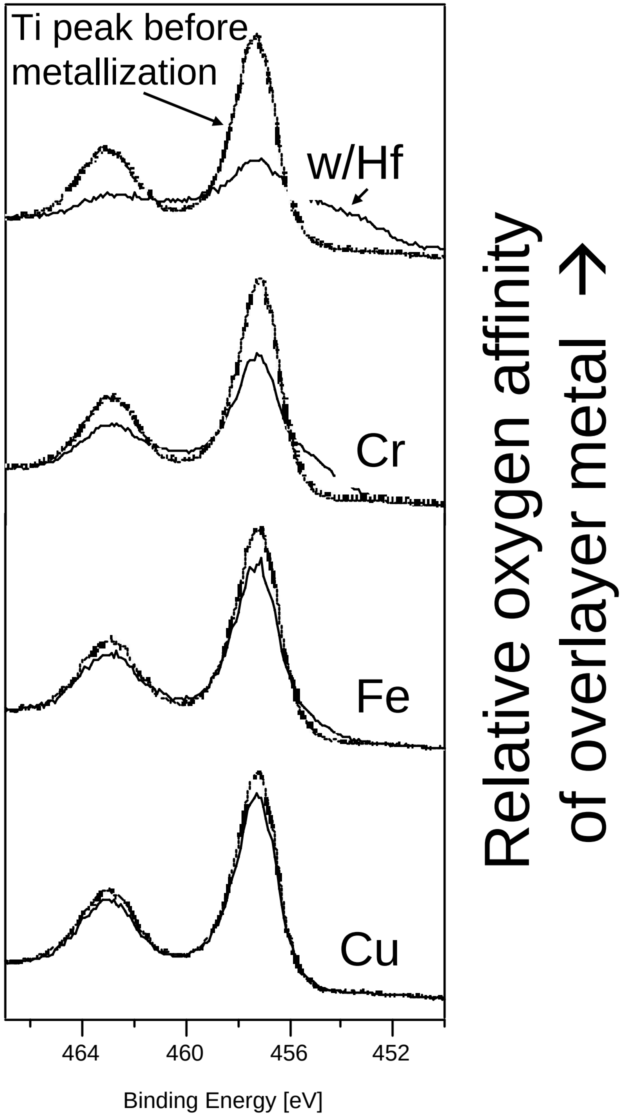
After UHV anneal at 300ºC for 15 min:

- Lowering and broadening of Ti peak
- Hf and Si peak shift and O peak change

⇒ Ti layer oxidation

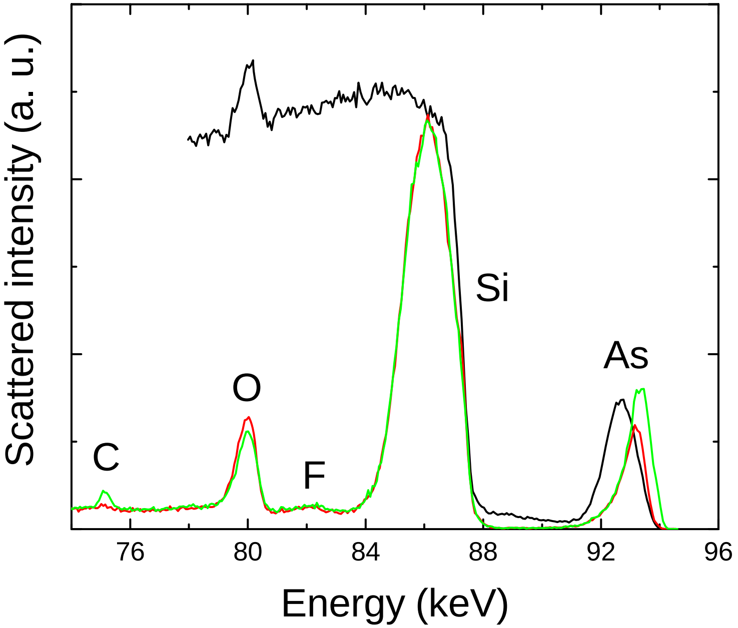
Interface chemical stability: Heats of oxide formation of most stable oxides and XPS results demonstrating interface reactivity

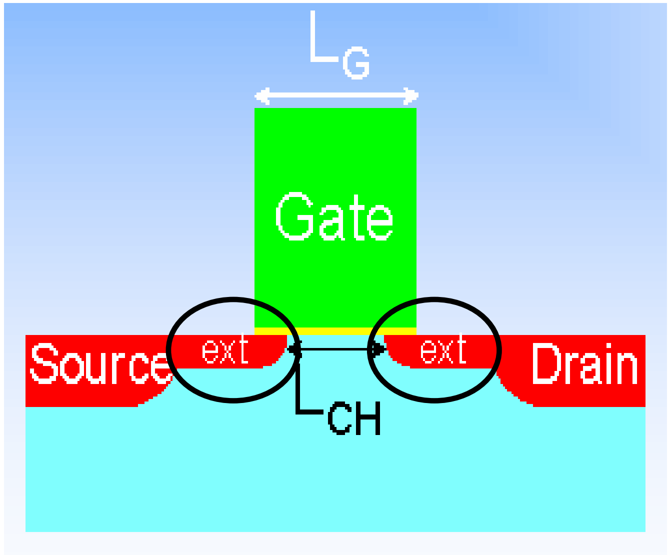
-ΔH formation in kJ per mol O	Metal
<0	Au
0 - 50	Ag, Pt
50 - 100	Pd
100 - 150	Rh
150 - 200	Ru, Cu
200 - 250	Re, Co, Ni, Pb
250 - 300	Fe, Mo, Sn, W, Ge
300 - 350	Rb, Cs, Zn
350 - 400	K, Cr, Nb, Mn
400 – 450	Na, V
450 – 500	Si
500 - 550	Ti, U, Ba, Zr
550 - 600	Al, Sr, Hf, Ce, La
600 - 650	Sm, Mg, Th, Ca, Sc, Y

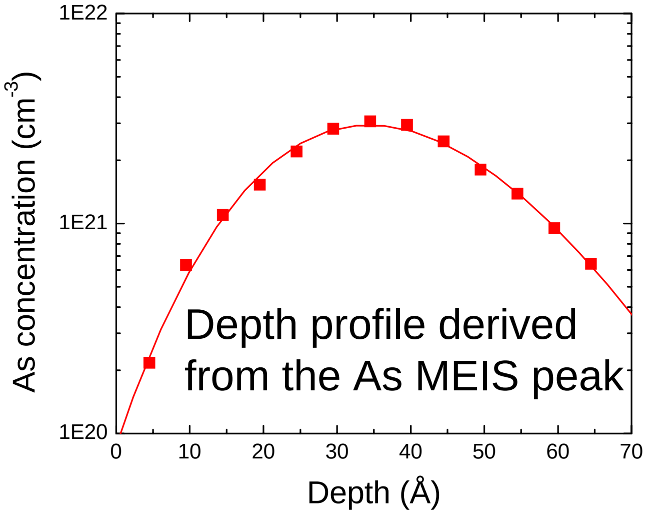


Surf. Sci. 333 (1995) 845; Surf Sci. Rep, 27, 1997

MEIS spectra of low energy dopant implants: ultrashallow junctions







Depth profile derived from the As MEIS peak

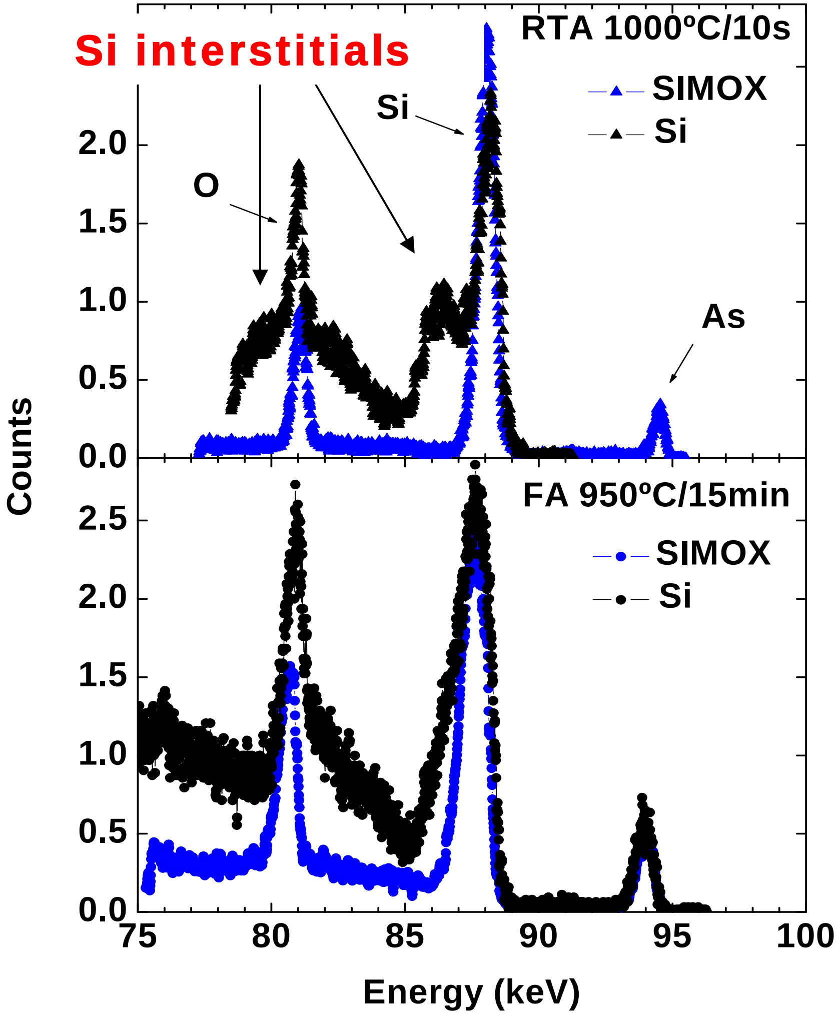
Depth profile of As in Si from a low energy implant (1kV, ~10^{15} As/cm^2)

Arsenic (As) behavior in SIMOX vs. bulk-Si

Interaction of As with vacancies following higher E implants…

After annealing:

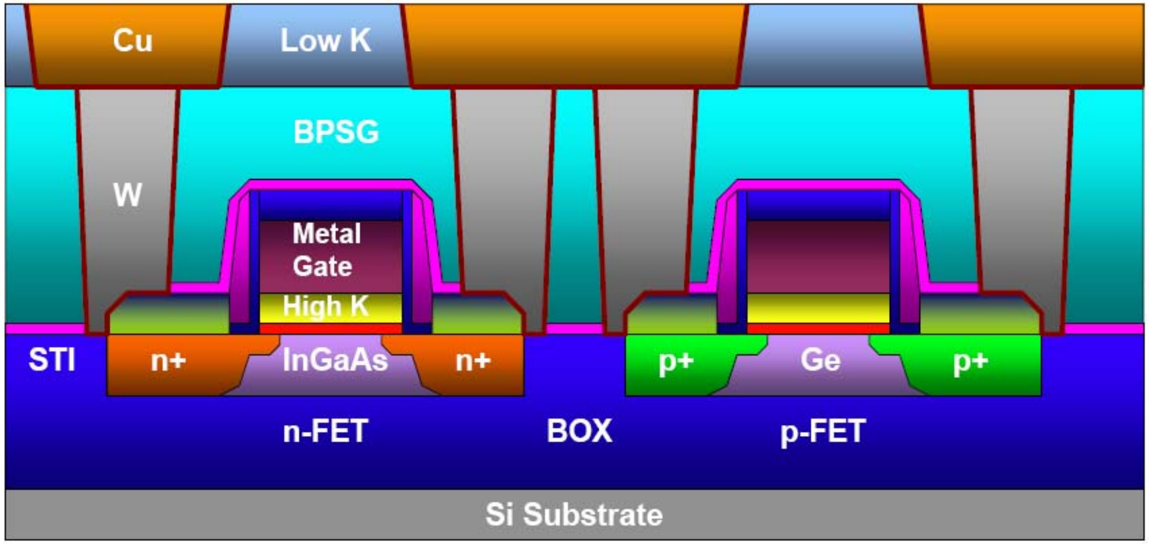
- Si interstitials remain in bulk-Si, but NOT in SIMOX
- excess vacancies annihilate Si interstitials in SIMOX
- SIMOX crystal quality is excellent, especially for RTA



Alternative Channel Materials

- Mobility improves by straining Si, but CMOS scaling demands further improvements….try other semiconductors!
- Key challenge for alternative channel materials is the dielectric – need low interface and bulk defect concentration
- Also need high I_{on}/I_{off} ratio, appropriate integration, high thermal stability, appropriate band alignment with no E_f pinning, etc.
- Ge and SiGe studied extensively for years - IBM, Intel…
- III-V compound semiconductors now being seriously considered for CMOS – Motorola/Freescale, Agere, Intel, IBM, IMEC…

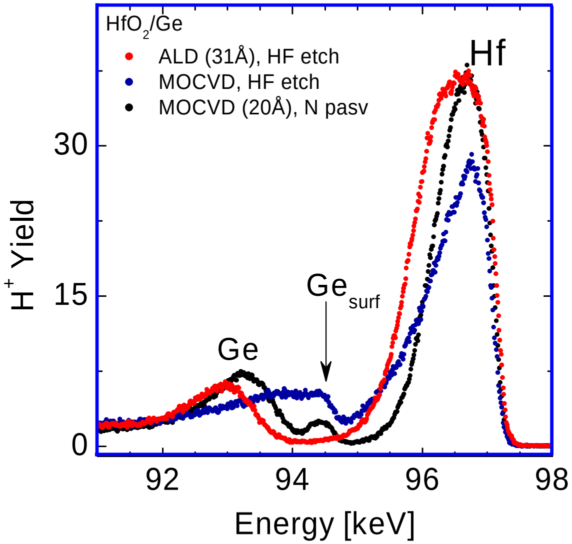
- InGaAs-on-insulator: NFET (surface channel)
- Ge-on-Insulator: PFET (surface channel)

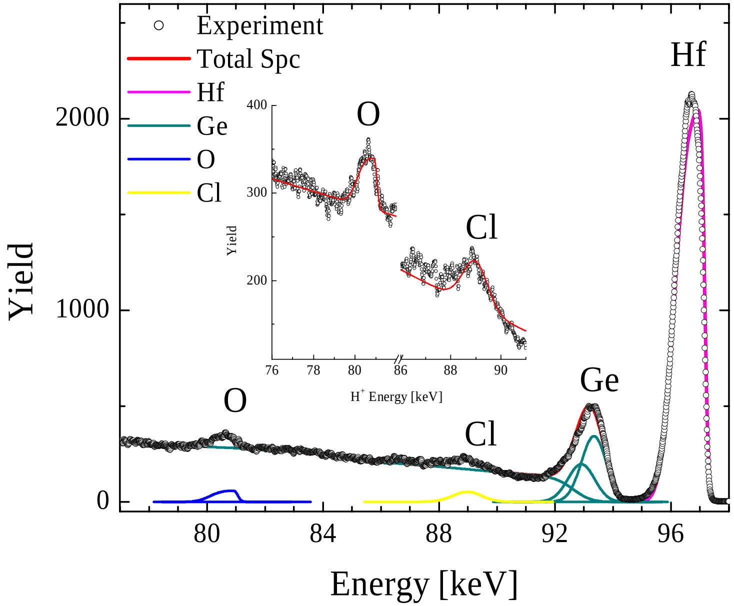


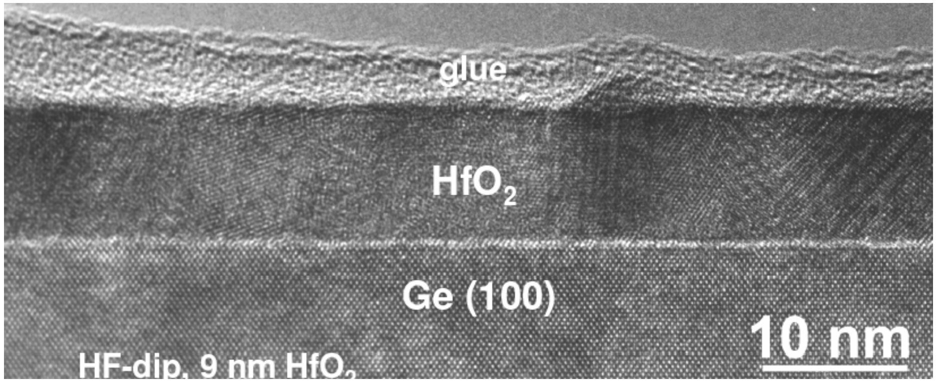
from IBM

HfOx/Ge (ALD and MOCVD)

Film properties very gowth dependent



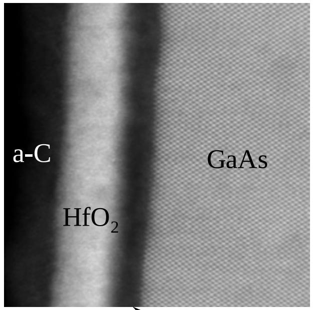
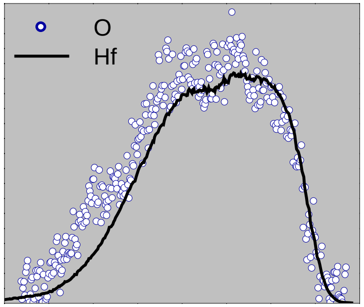
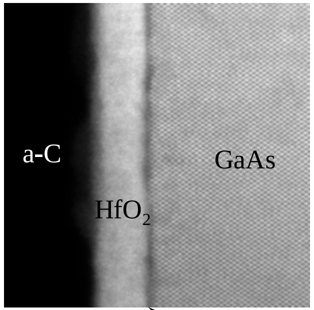
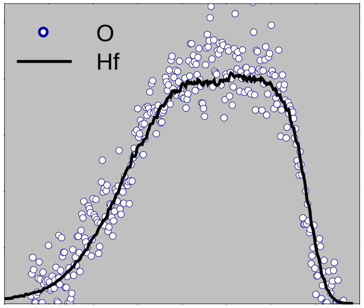




ALD little interfacial GeO$_x$ (within sensitivity of the measurements)
some Cl accumulation at the interface
some epitaxial growth

MOCVD HfGe and HfGeO$_x$ intermixing (condition dependent)
surface Ge (supressed by Ge nitridation)

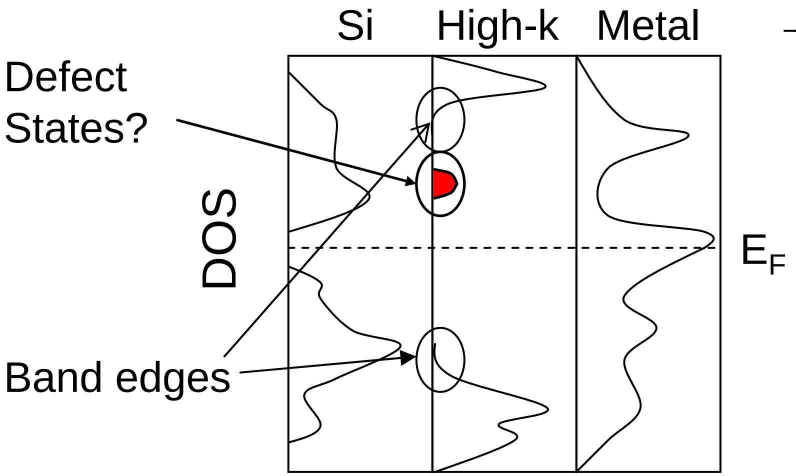
HfO_2 on GaAs: MEIS and TEM comparison

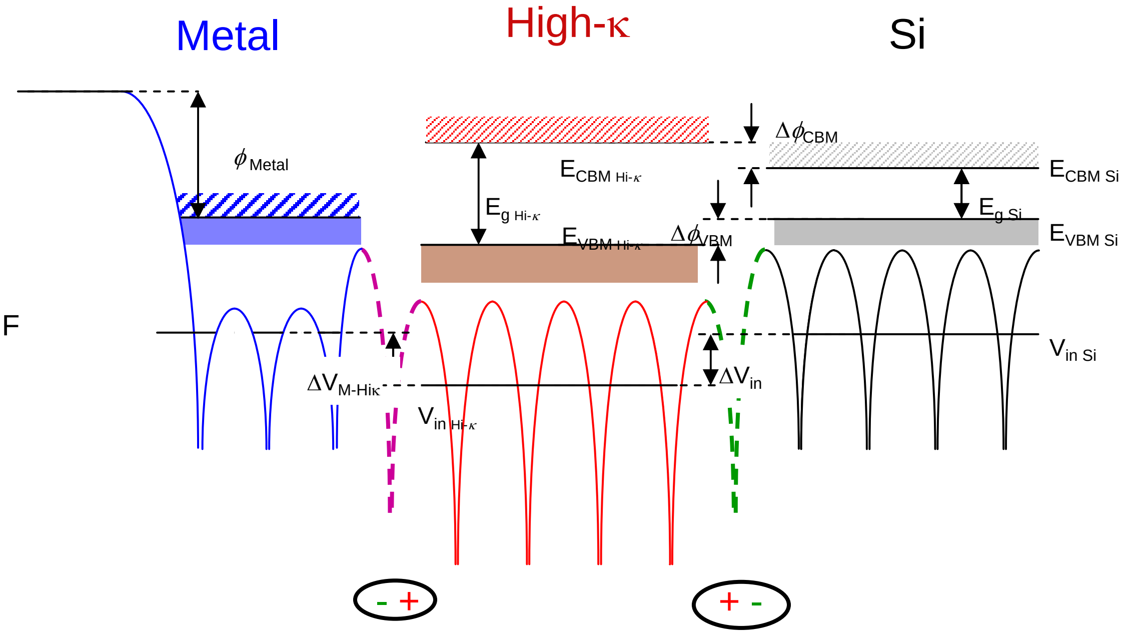
	TEM*	MEIS
No etch	 Ga-rich oxide	
HF etch	 Ga-rich oxide	

- TEM and MEIS results are consistent;
- native oxide ≈ 20 Å;
- As:Ga ≈ 0.17, (Ga+As):O ≈ 1.04

w/Agere

Electronic structure in multilayer stacks

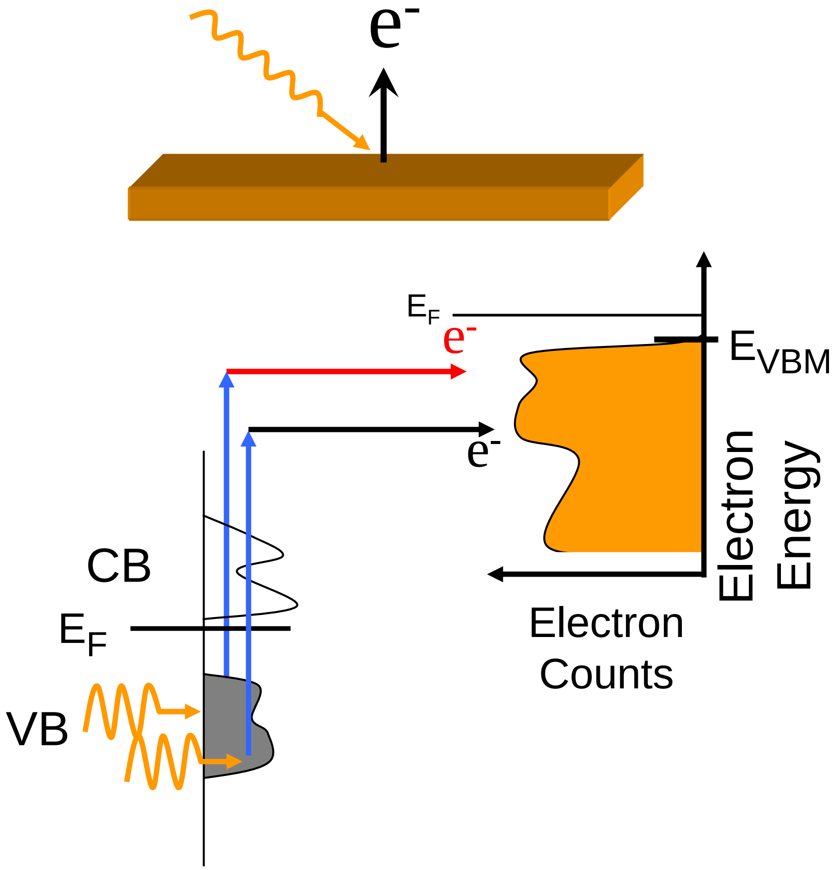




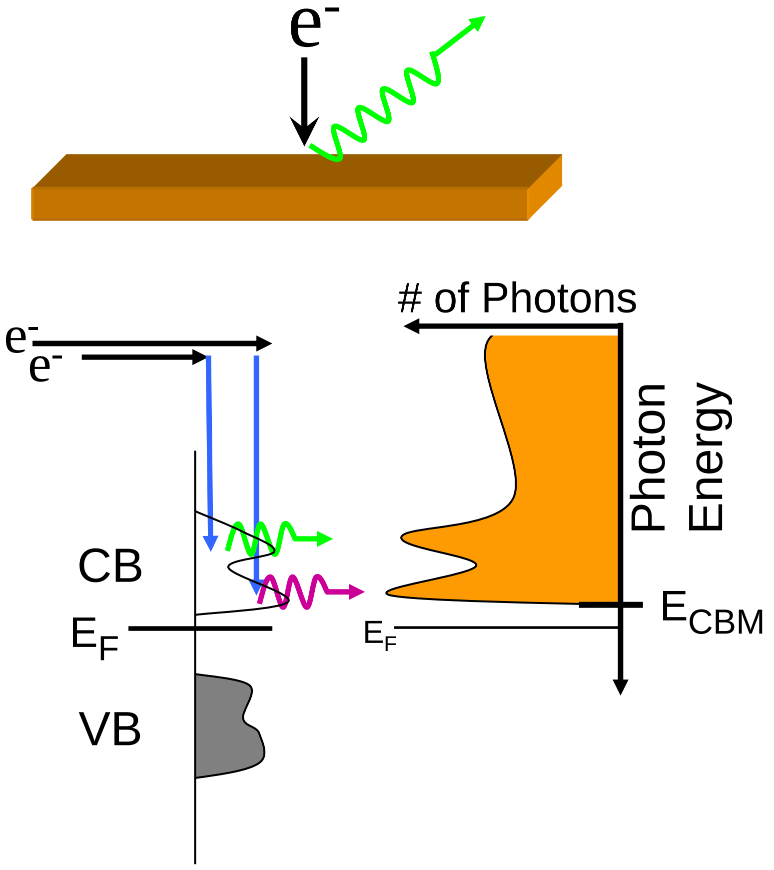
- Band edge energies determined in many ways – elec. and optical spec.
- Can we use spectroscopies to (i) measure energies and LDOS more precisely, (ii) determine interface dipoles and band alignment, and (iii) use interface engineering to control effective work function…

Experimental tools to examine electronic structure

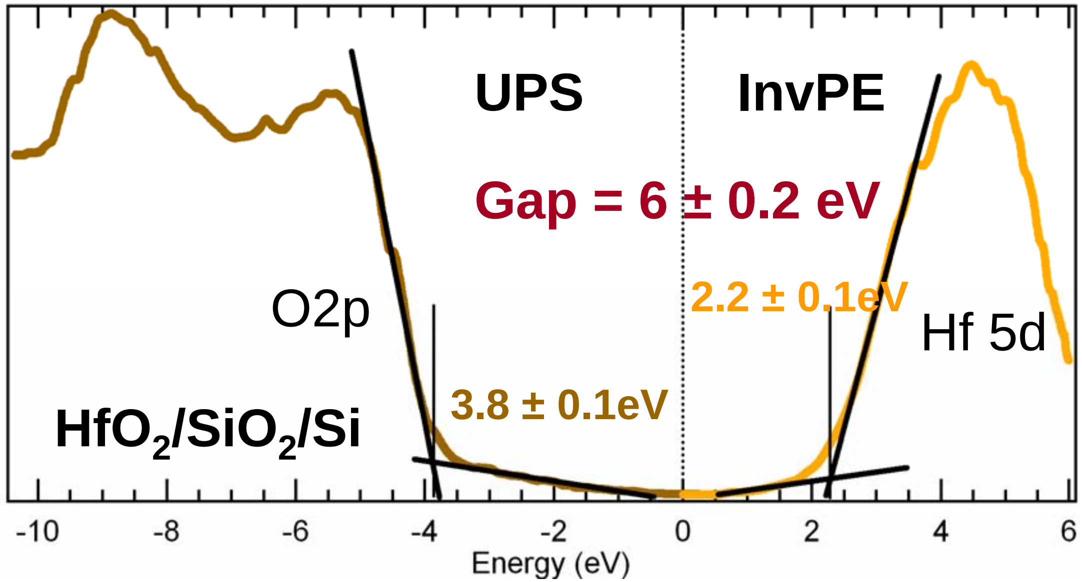
Photoemission (Occupied States)



Inverse Photoemission (Unoccupied States)



Direct Gap Determination



Single chamber measurments

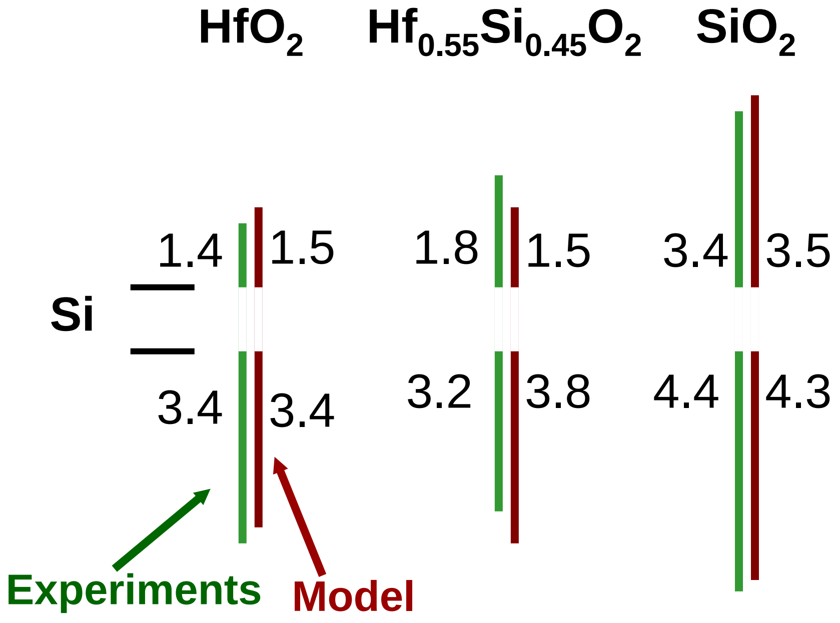
Underlying silicon states visibles

Band tail states

Defects states

Thicker oxides may charge - use care!

Band offsets with Si for $Hf_xSi_{1-x}O_2$



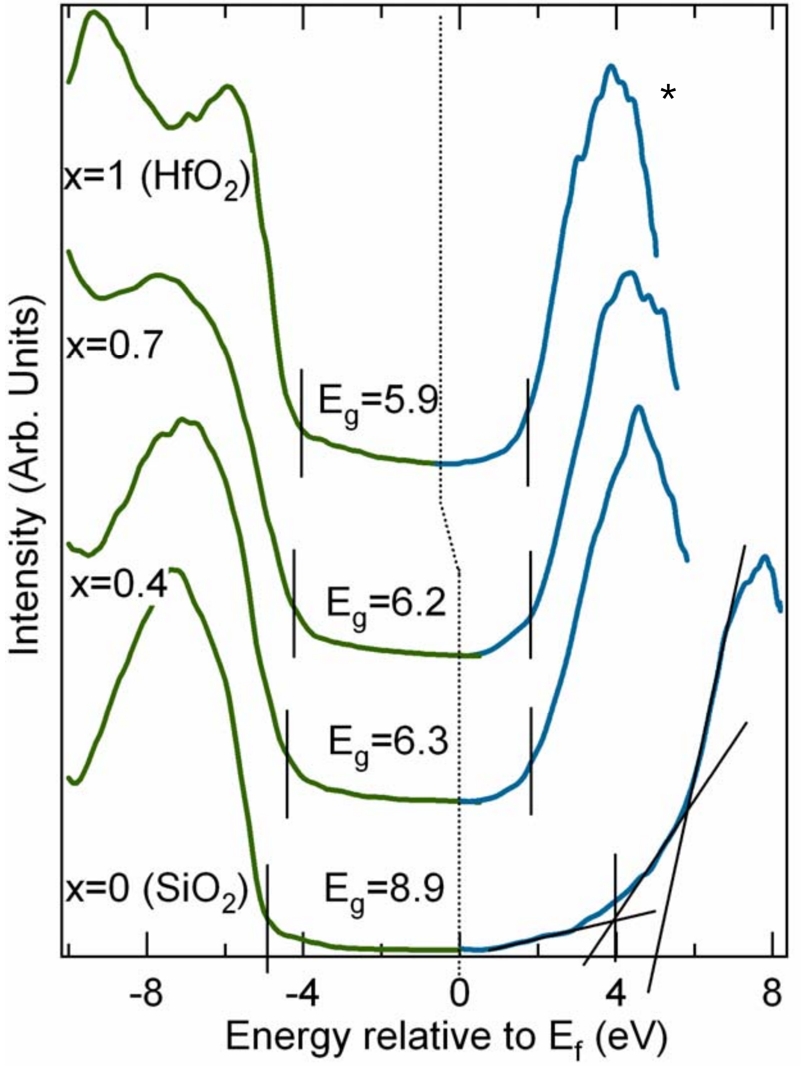
HfO_2 $Hf_{0.55}Si_{0.45}O_2$ SiO_2

Si

1.4 1.5 1.8 1.5 3.4 3.5

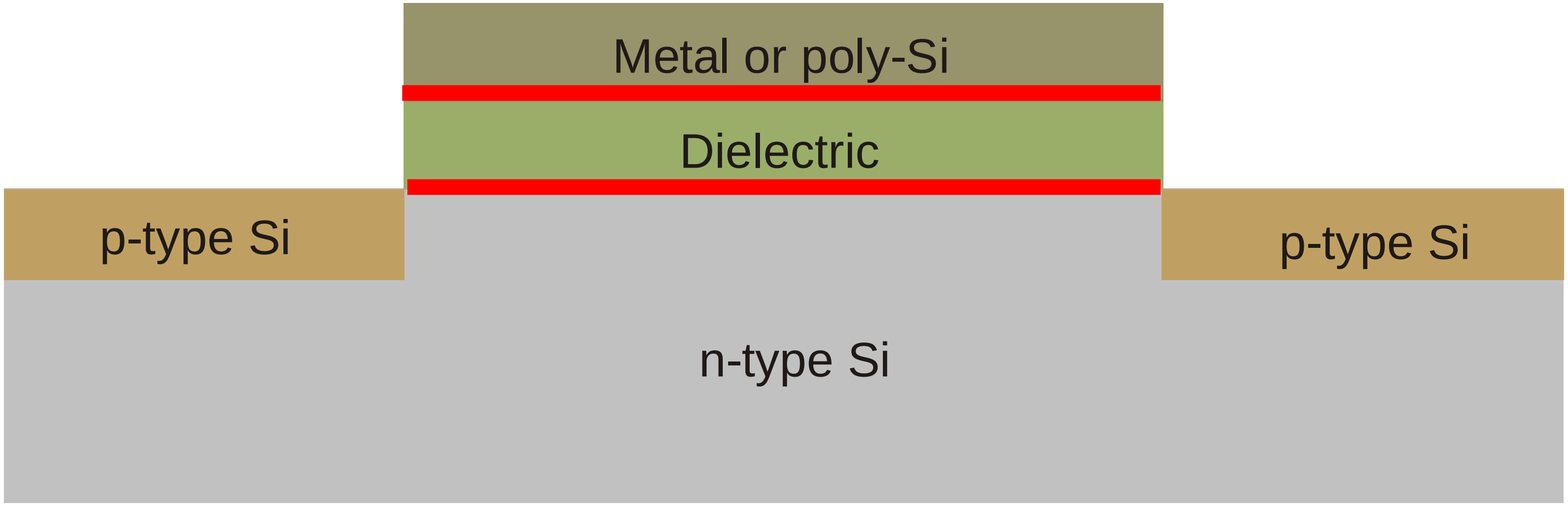
3.4 3.4 3.2 3.8 4.4 4.3

Experiments **Model**



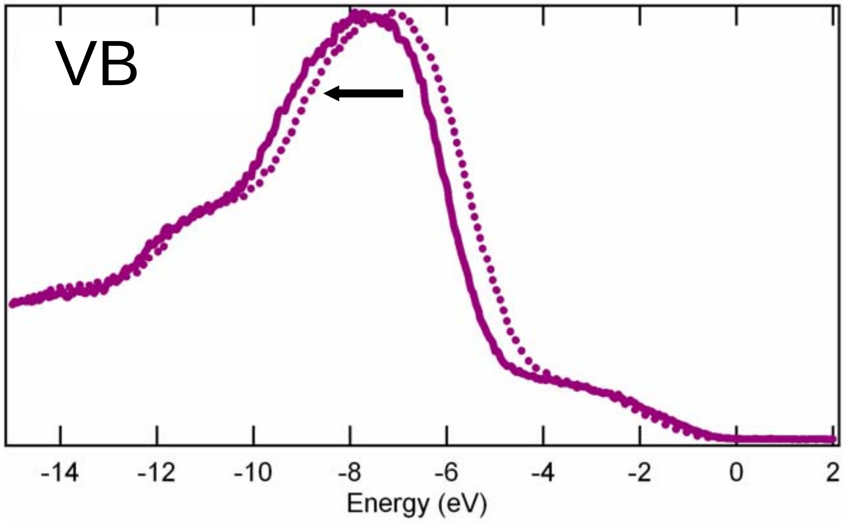
***Ef position corrected to account for the Si doping**

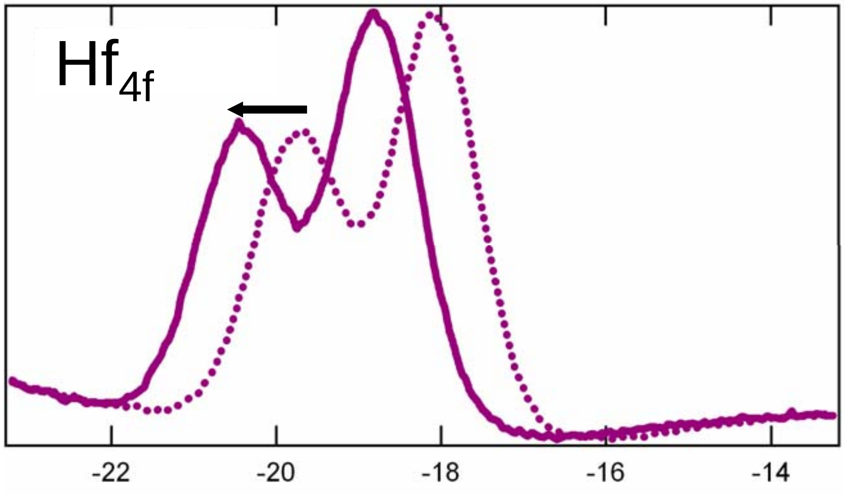
Oxide/semiconductor and metal/oxide interfaces

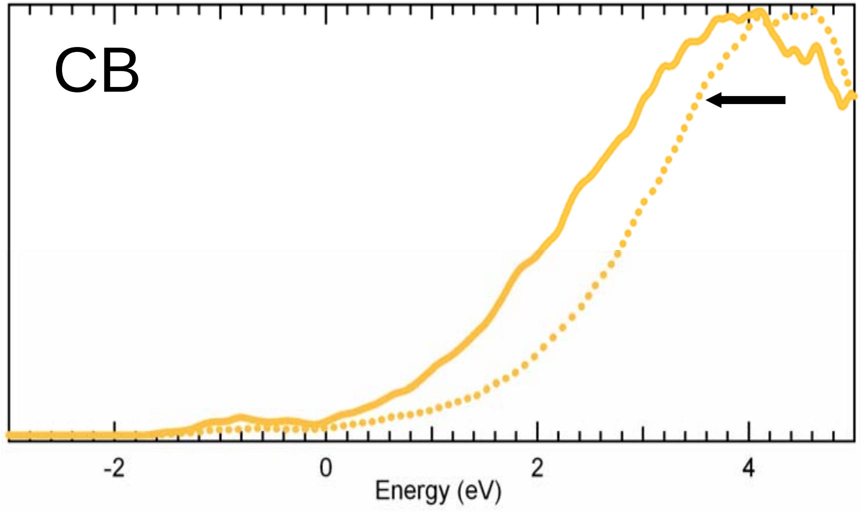


Dielectric		
SiO_2 →	**$Hf_xSi_{1-x}O_2$** →	**HfO_2**
Metal electrode	**Ru**	**Al**
Workfunction	**5.2 eV**	**4.2 eV**
Chemistry	**Low Reactivity** **~ Noble Metal**	**High Reactivity** **Stable Oxide**

Energy shifts upon metallization



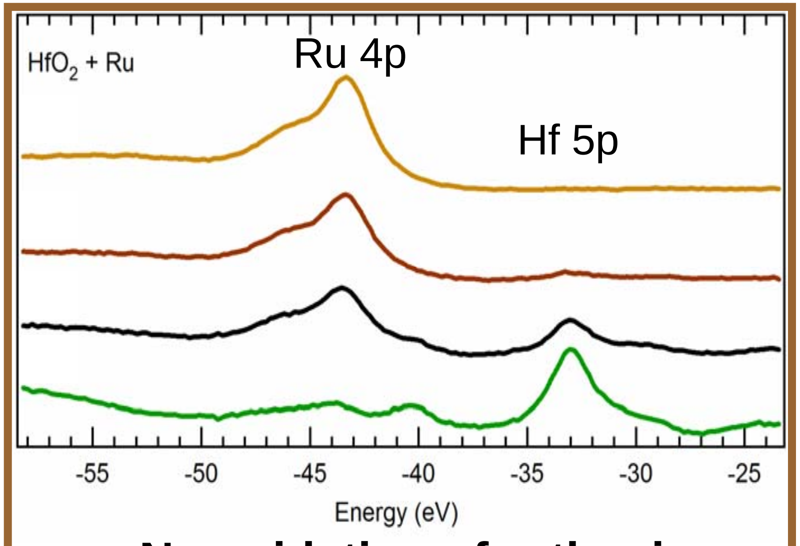




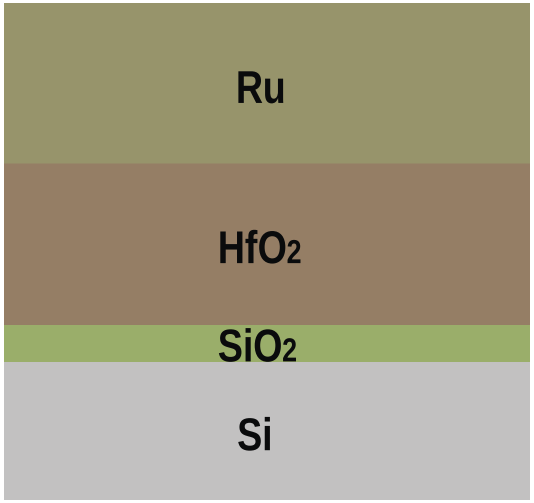
$Al/Hf_{0.55}Si_{0.45}O_2$

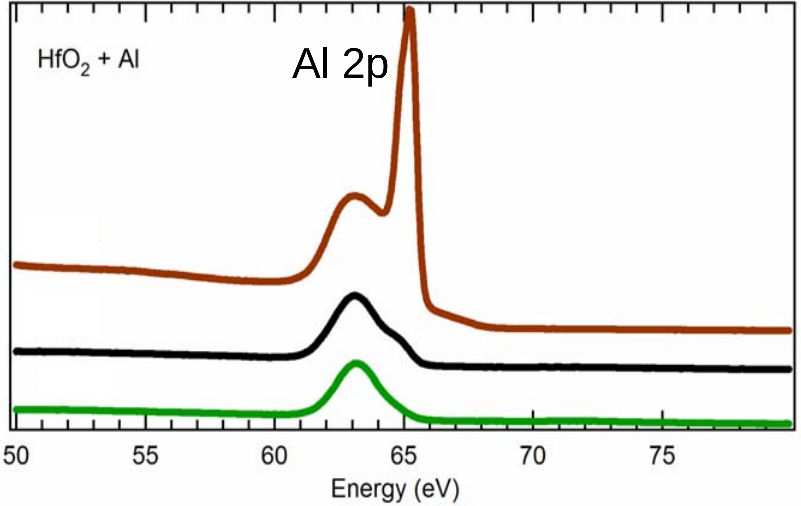
VB, CB and core levels are shifting the same way by the same amount

Metal interaction with the substrate

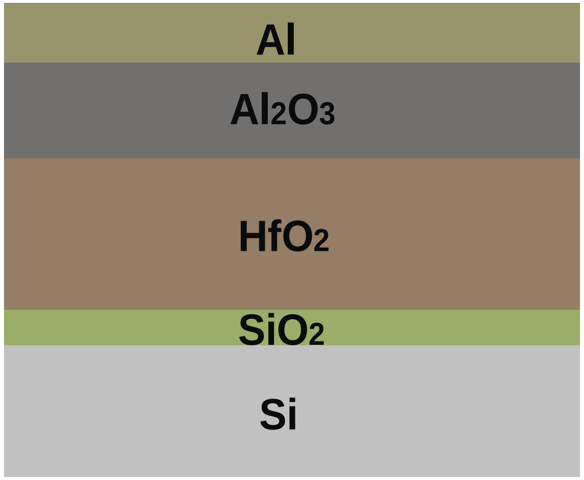


No oxidation of ruthenium

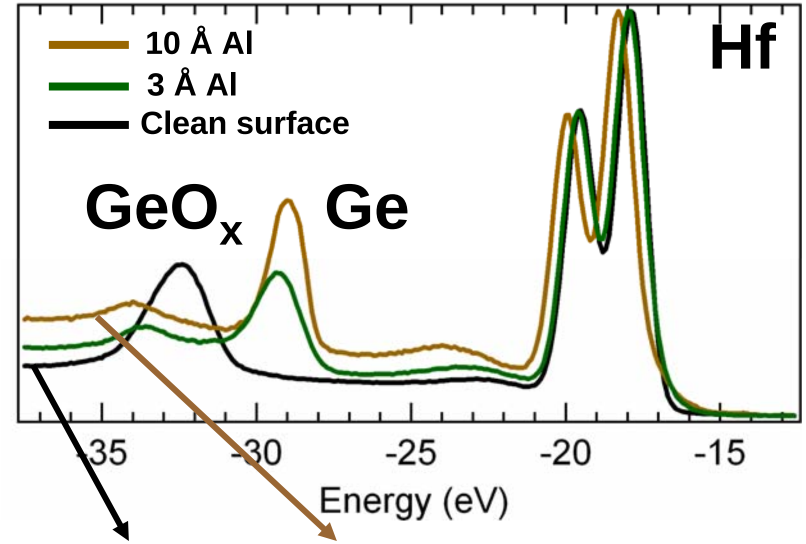


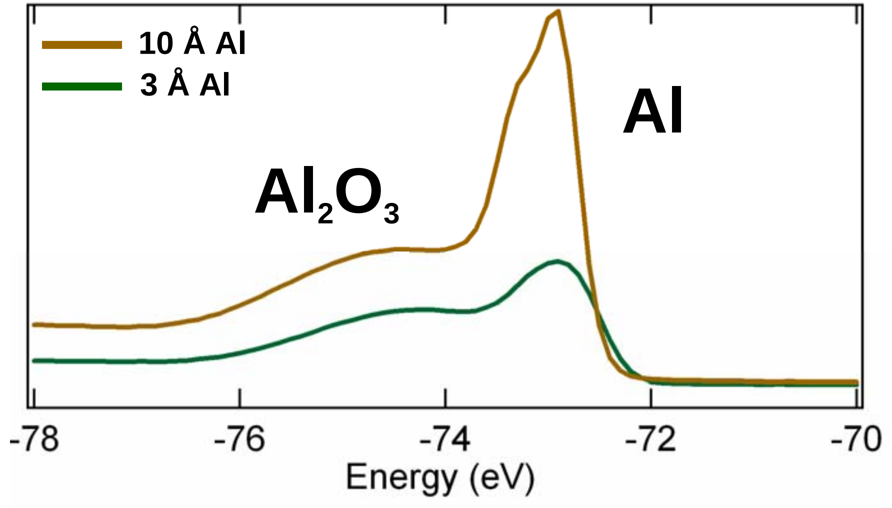


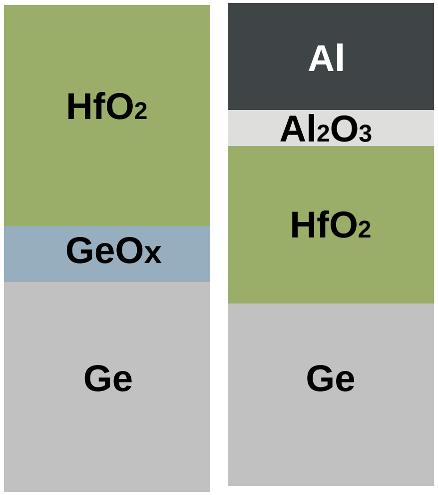
Oxidation of Aluminium
Formation of a Al_2O_3 layer



Al/HfO_2/GeO_x/Ge



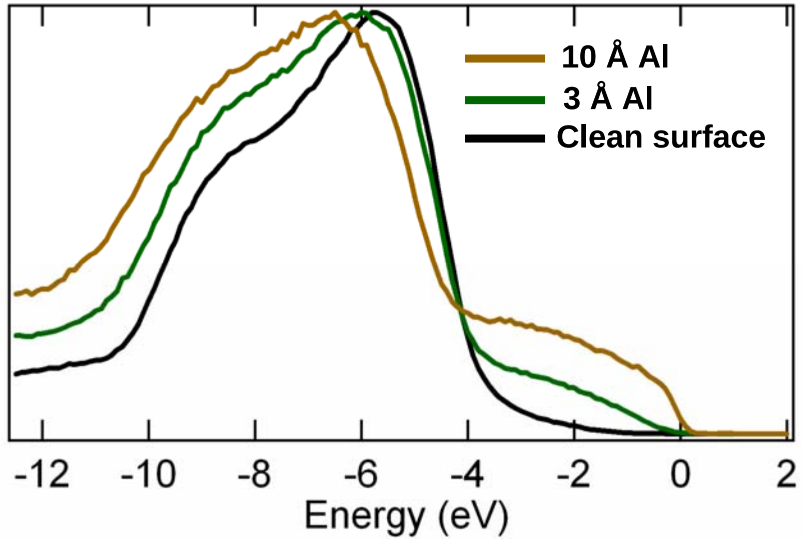




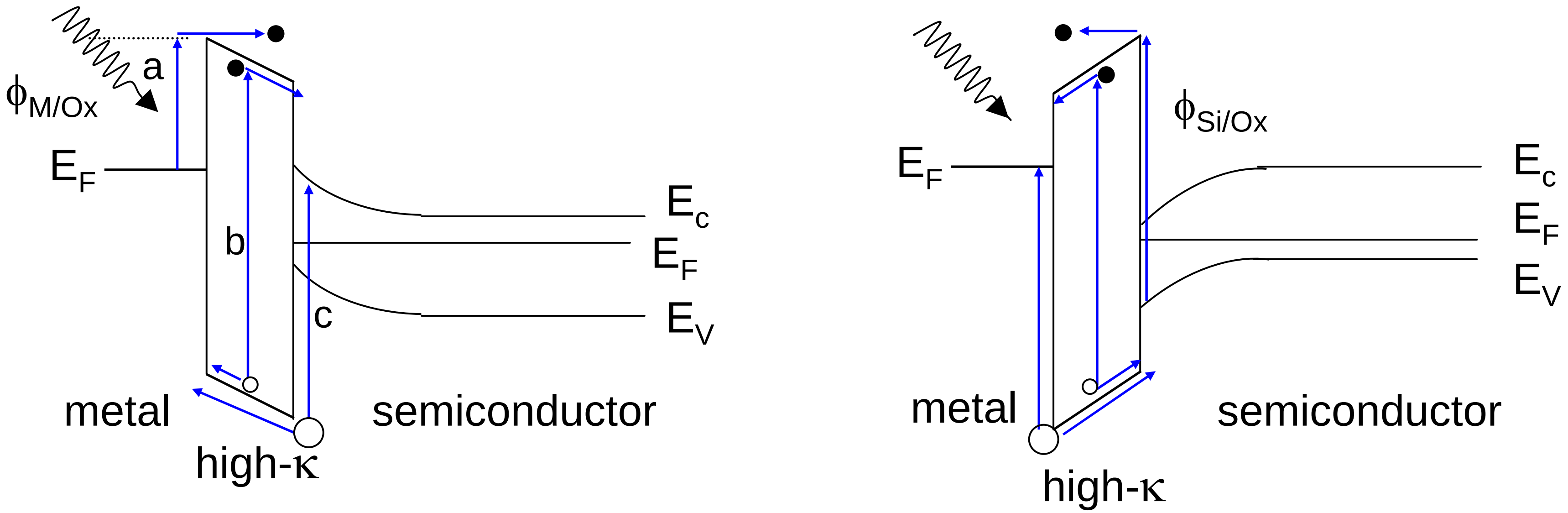
Hf4f and VB shift

No significant reduction of HfO_2 in Hf4f

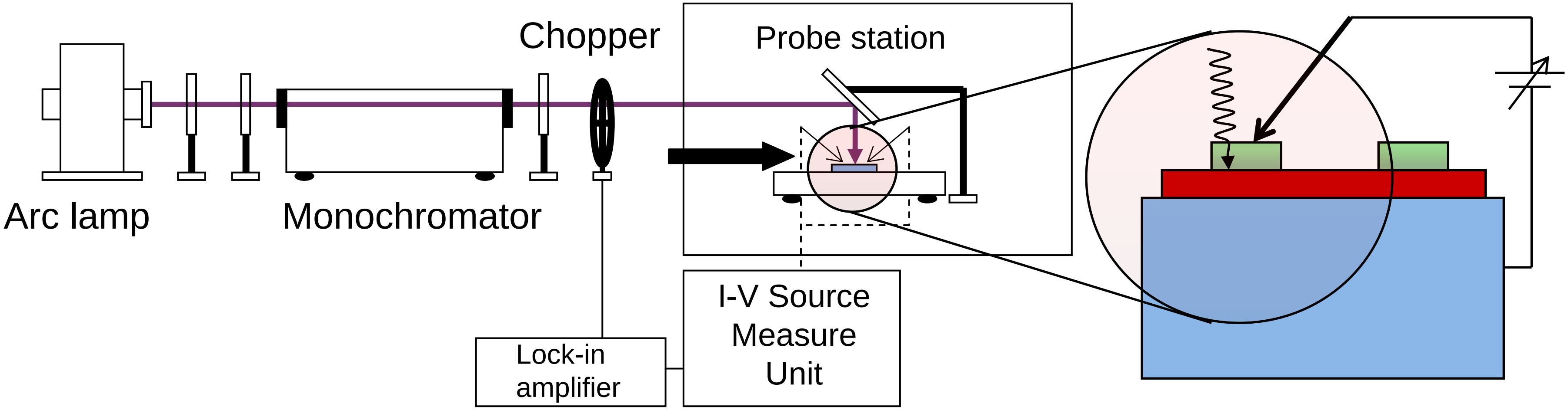
Interfacial oxide reduction at 300 K



Internal Photoemission (IntPES)

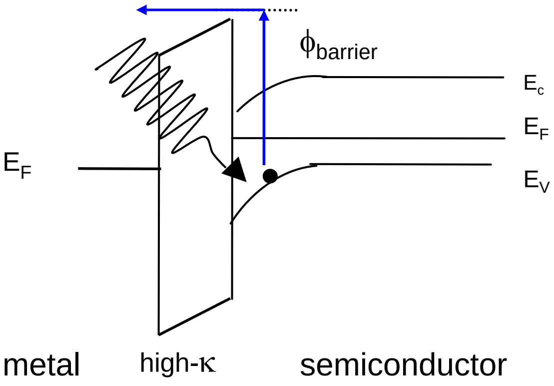


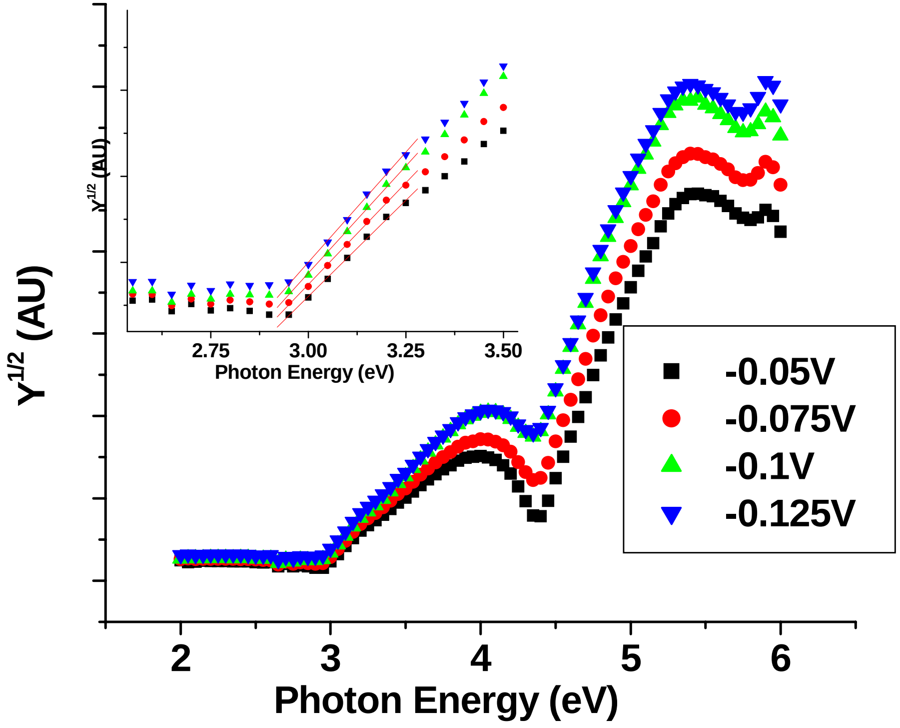
(a) E_c(Hiκ)-E_F(met.) e-IntPES; (b) photo-excitation; optical band gap; (c) E_c(sc)-E_v (Hiκ) h-IntPES

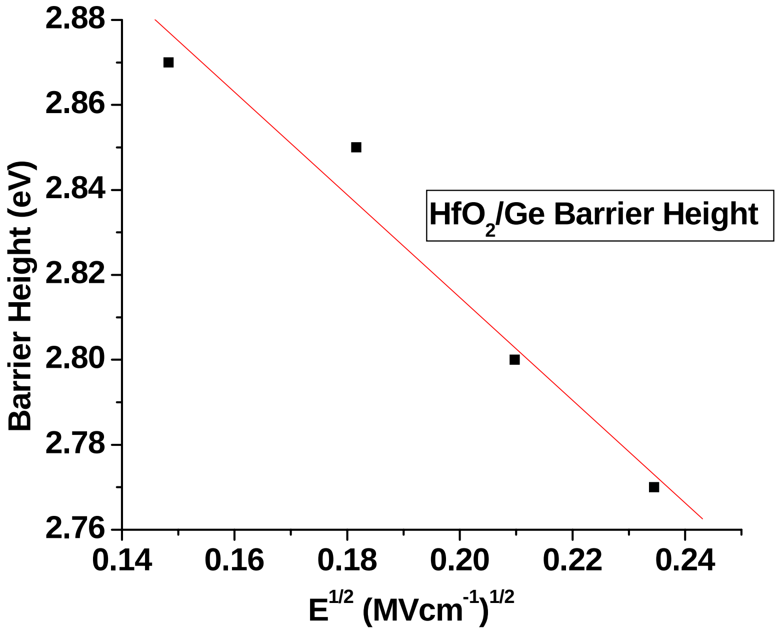


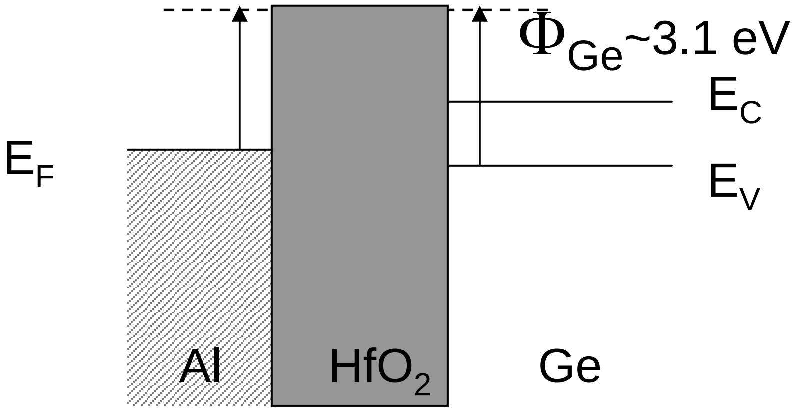
IntPES: Al / HfO_2 / Ge

Negative Bias on Ge, $\Phi_{Ge/\ HfO2}$: ~3.1 eV









Scanning probe measurements of topography and dielectric properties

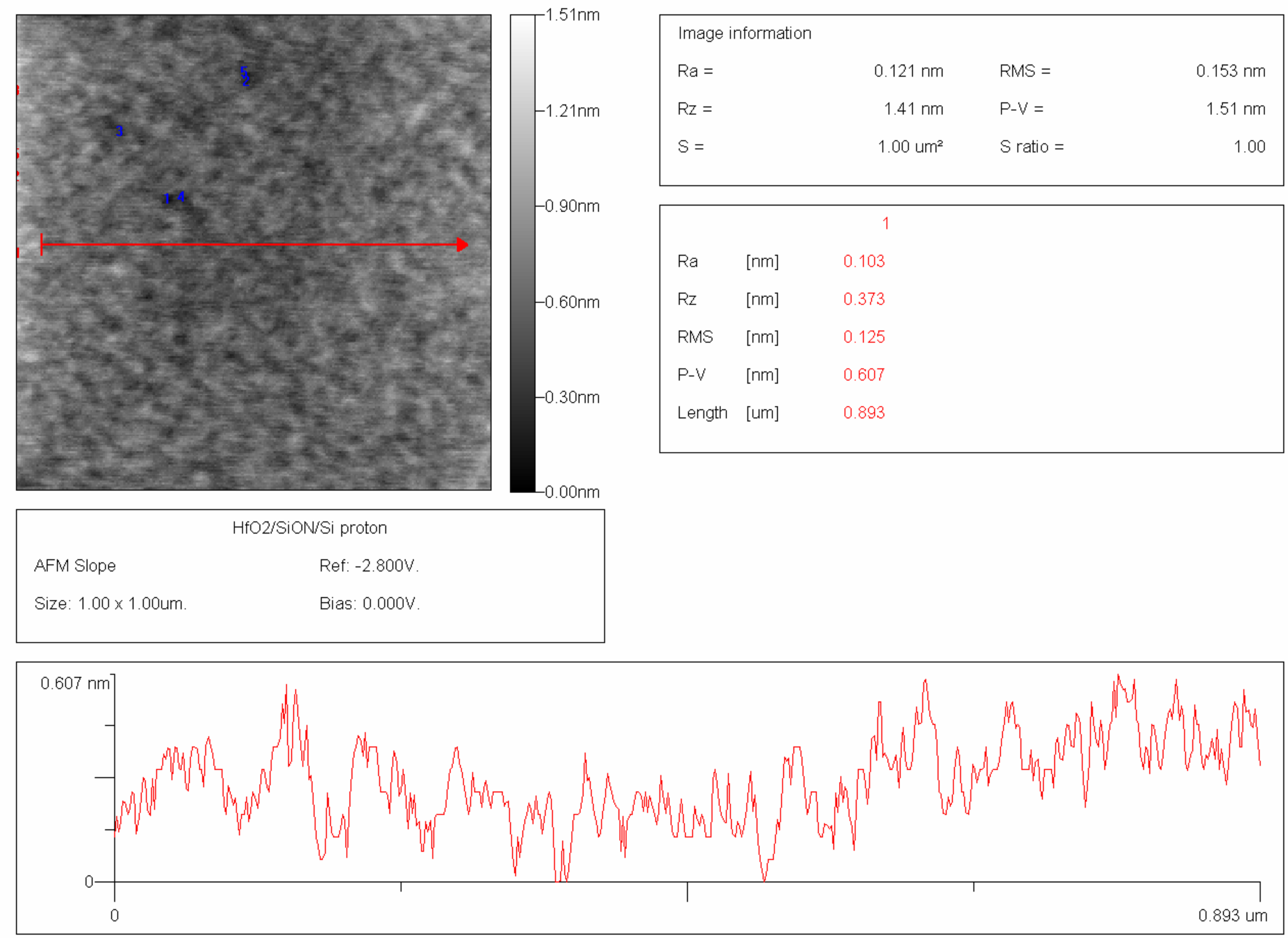


Image information

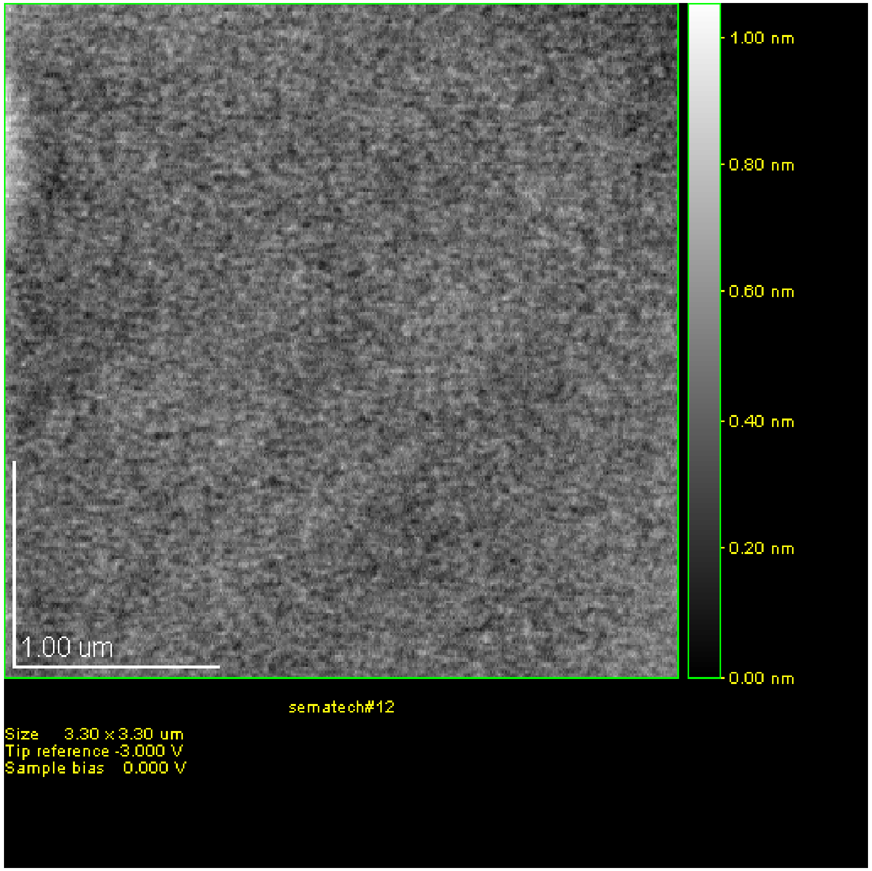
Ra =	0.121 nm	RMS =	0.153 nm
Rz =	1.41 nm	P-V =	1.51 nm
S =	1.00 um²	S ratio =	1.00

		1
Ra	[nm]	0.103
Rz	[nm]	0.373
RMS	[nm]	0.125
P-V	[nm]	0.607
Length	[um]	0.893

HfO2/SiON/Si proton

AFM Slope	Ref: -2.800V.
Size: 1.00 x 1.00um.	Bias: 0.000V.

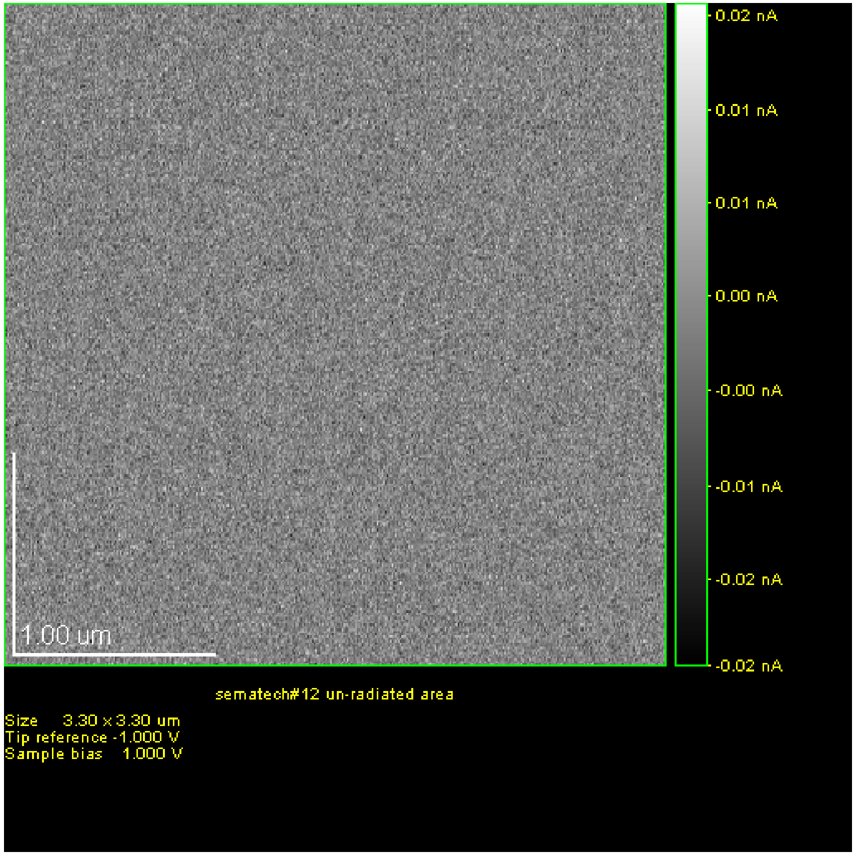
AFM and current image of unirradiated $Hf_xSi_yO_z/Si$ film



sematech#12

Size 3.30 x 3.30 um
Tip reference -3.000 V
Sample bias 0.000 V

tapping mode



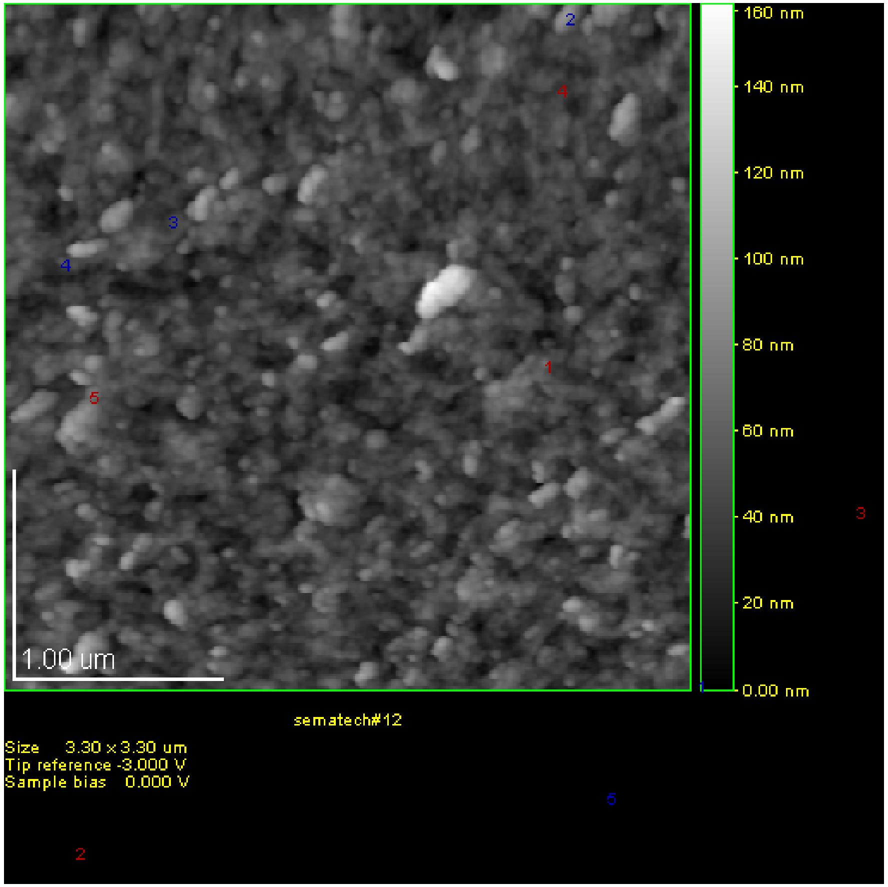
sematech#12 un-radiated area

Size 3.30 x 3.30 um
Tip reference -1.000 V
Sample bias 1.000 V

current image

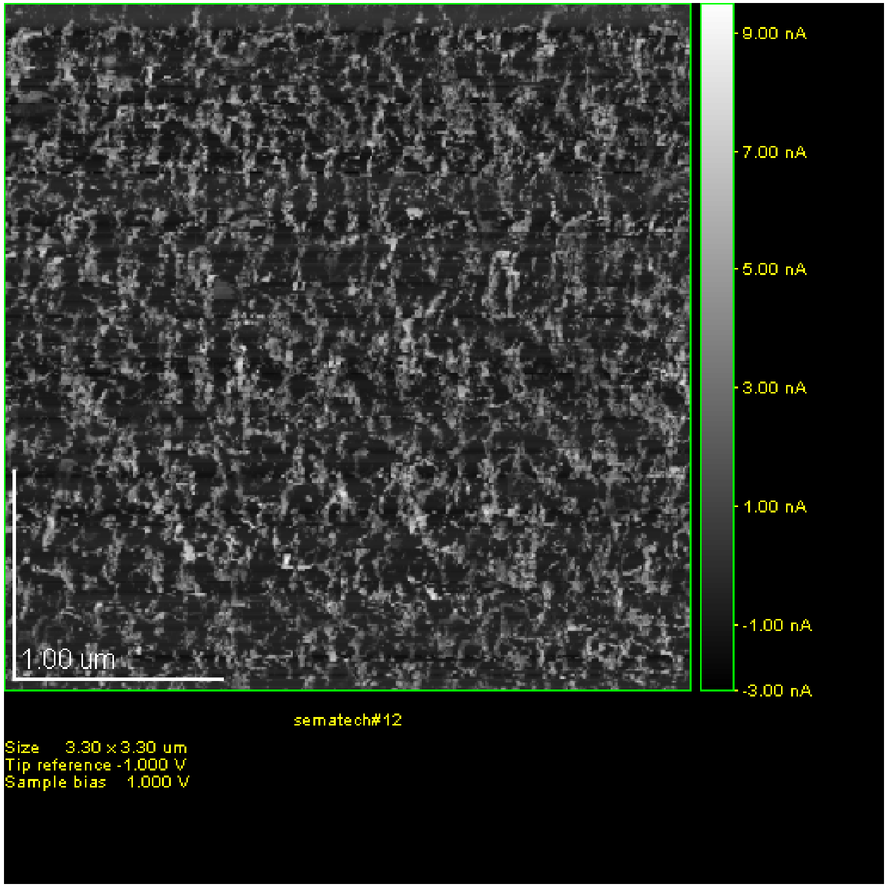
AFM and current image of irradiated HfO_2/Si film

flux is ~$2x10^{15}$ H^+/cm^2 H^+~100keV



Size 3.30 x 3.30 um
Tip reference -3.000 V
Sample bias 0.000 V

Left: tapping mode

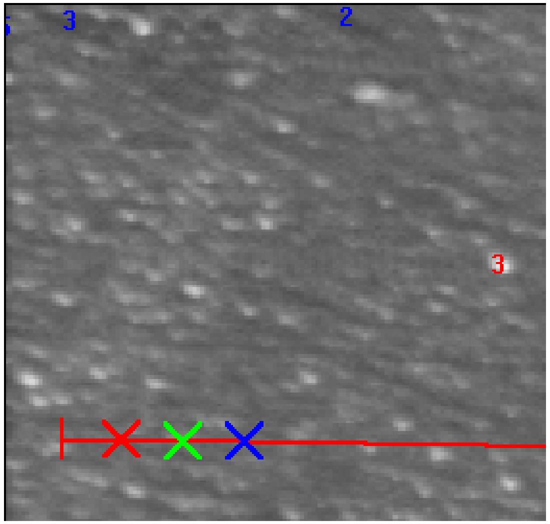


Size 3.30 x 3.30 um
Tip reference -1.000 V
Sample bias 1.000 V

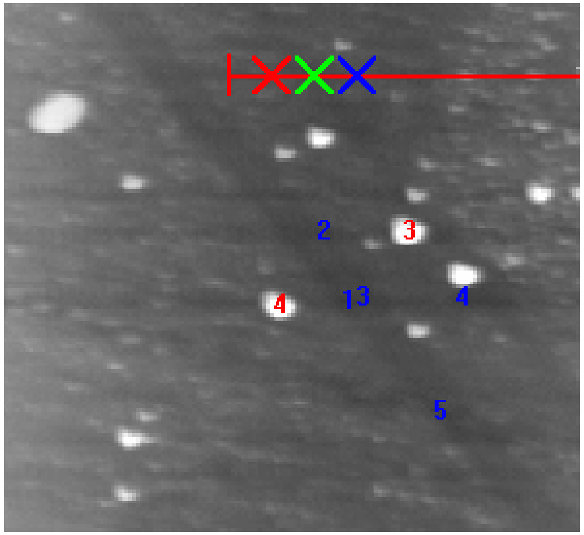
Right: current image

AFM images of HfO_2/SiON/Si

Before (a) and after (b) radiation exposure ~10^{15} ~ 200keV He^{2+}



(a)



(b)

Conductive Tip AFM Image and I-V Behavior of a Ru/HfO_2/Si Stack

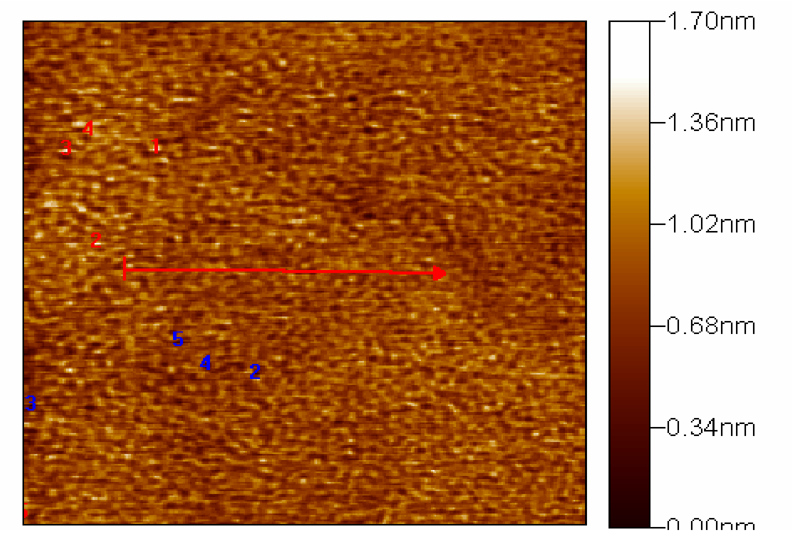
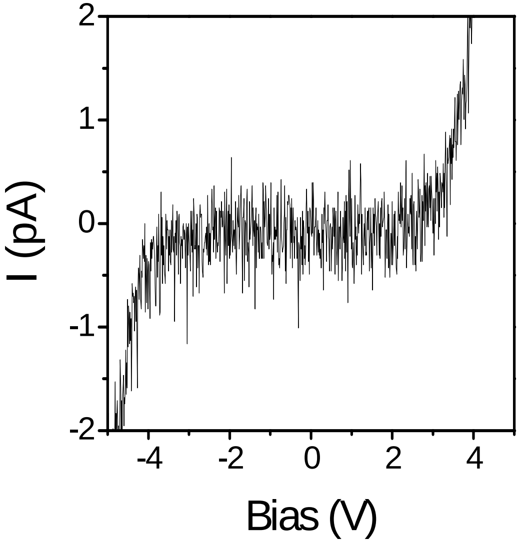
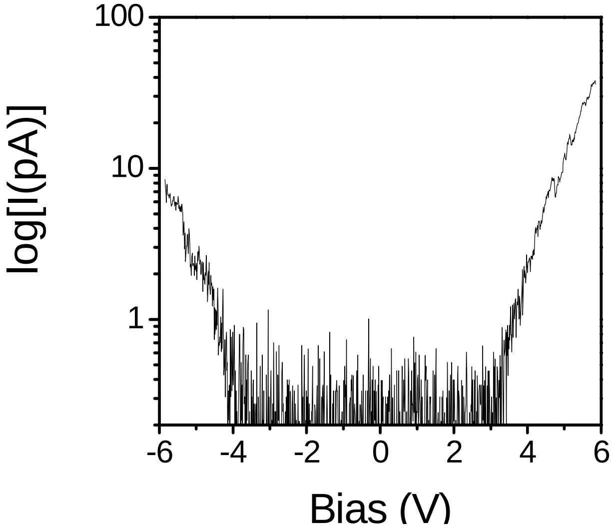
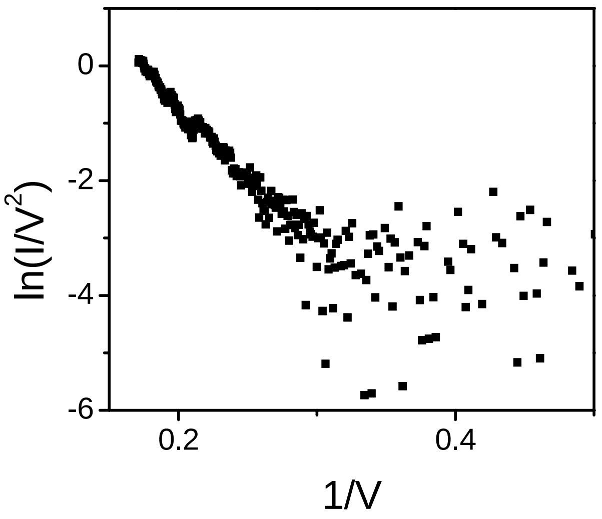


Image physical and spectroscopic behavior of radiation induced defects

For simple F-N tunneling with an electron effective mass of 0.18, the HfO_2/Si conduction band barrier height is 1.4eV







Plans

- Generation broader range of films and devices with high-K dielectrics (HfO_2) and metal gate electrodes (Al, Ru, Pt).
- Interface engineering: SiO_xN_y (vary thickness and composition)
- Expand physical measurements of defects created by high energy photons and ions using SPM and TEM
- Correlate physical measurement results with electrical methods.
- Develop quantitative understanding of behavior as a function of particle, fluence and energy.
- Monitor H/D concentration and profiles, and effects on defect generation (by radiation) and passivation.
- Determine if radiation induced behavior changes with new channel materials (e.g., Ge, InGaAs), strain, or SOI
- Explore effects of processing and growth on radiation behavior.
- Correlate with first principles theory.