Materials stability, band alignment and defects in CMOS nanoelectronics

Team members: L. Yu, T. Feng, H.D. Lee, C.L. Hsueh, A. Wan, Q. Jiang, L. Goncharova, S. Rangan, D. Mastrogiovanni, E. Bersch, O. Celik, R. Bartynski, L. Feldman, T. Gustafsson and E. Garfunkel
Departments of Physics and Chemistry
Rutgers University, Piscataway, NJ

Collaborators:

Vanderbilt team; Sematech team - Bersuker, et al.

plus researchers at NIST, NCSU, Stanford, IMEC, UT-A, UT-D, Penn State, UCSB, IBM, Intel, AMAT, TI, Freescale, Taiwan ….

Support: Vanderbilt MURI (AFOSR) and SRC

Motivation: Help develop a fundamental understanding and control of radiation induced defects in future CMOS materials.

Rutgers team uses high resolution characterization tools to:

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

Experimental studies of High-k on Ge and III-V substrates:

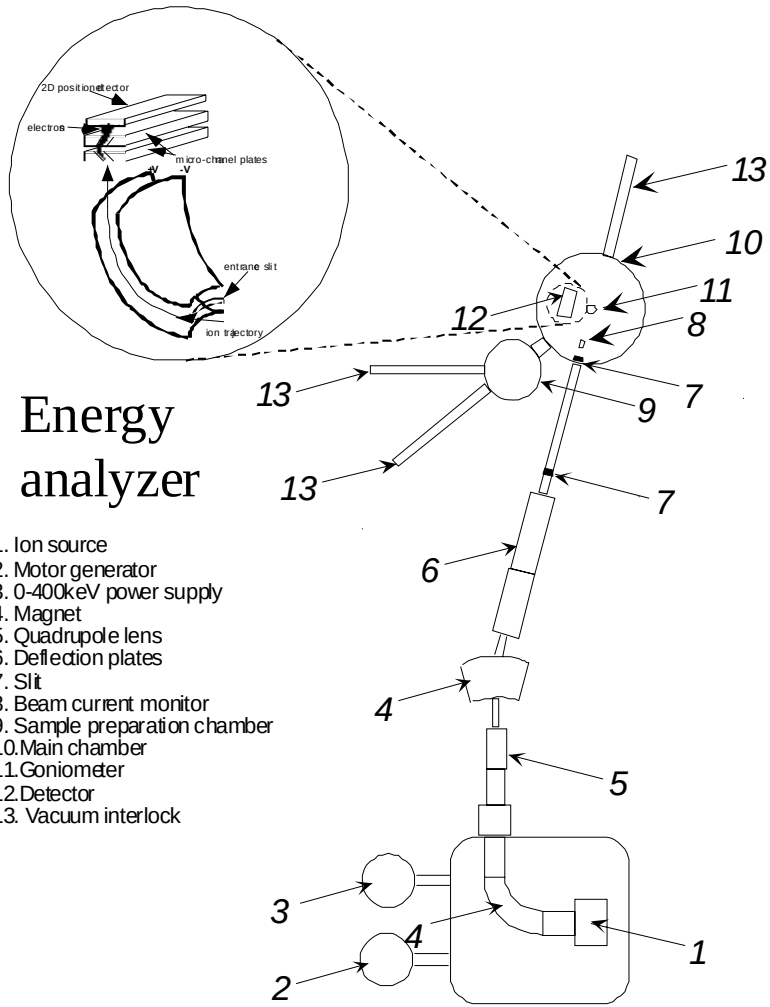
- Composition and depth profiling –XPS, MEIS, RBS, SPM…
- Electronic structure – PES, IPE, optical and electrical methods
- Surface/interface passivation chemistry and relation to defects

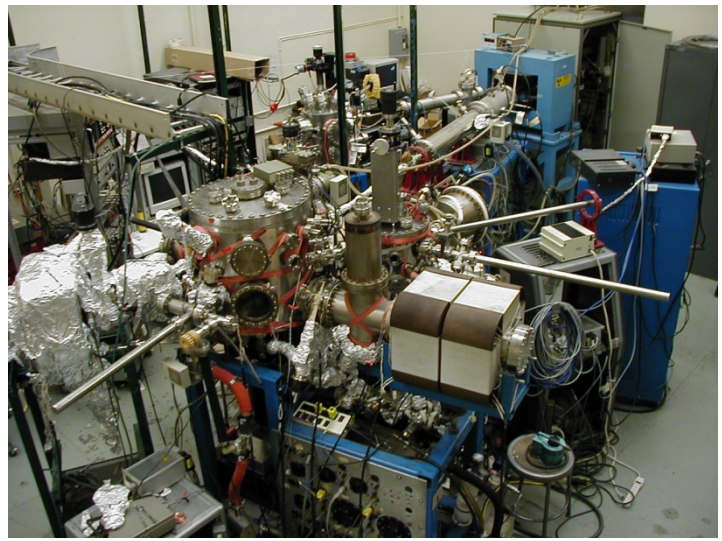
Current Rutgers work on CMOS gate stacks

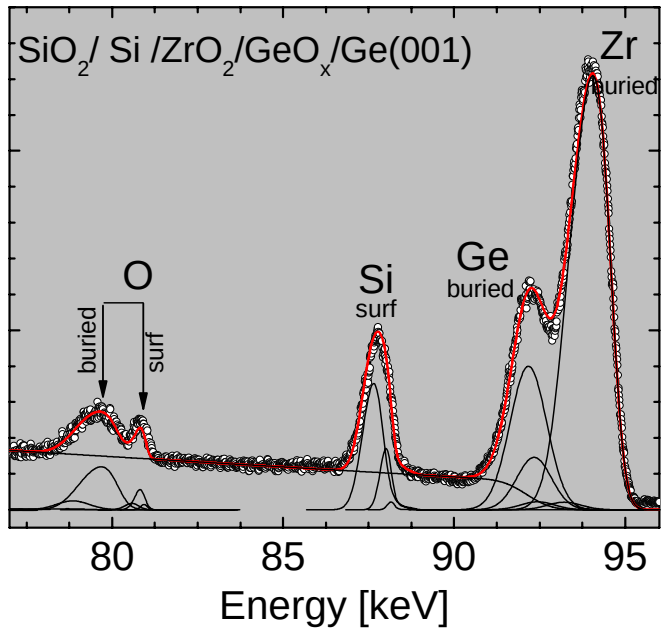
- Ion scattering - MEIS, RBS, LEIS
- Electronic structure – XPS, UPS, InvPES, IntPES
- Microscopy - TEM, SEM, AFM….
- Alternative substrates: Ge, GaAs, InGaAs
- Defect – radiation induced, processing induced, etc.
- Etching chemistry and roughness
- Film stoichiometry and thickness for multilayer structures
- Diffusion/atomic mobility (O, Si, N, metal, etc…)
- Dopant profiling and diffusivity – As, Sb, Bi, In, Ga
- Film initiation and growth (esp. for ALD growth)
- Influence of interface layers (diffusion barrier, growth initiator, work function engineering)
- Metal gate/high-κ dielectric film and interface stability
- Impurity concentration/profile – C, H, …
- Epitaxial oxides - e.g. STO/Si, La compounds

MEIS (Medium Energy Ion Scattering)

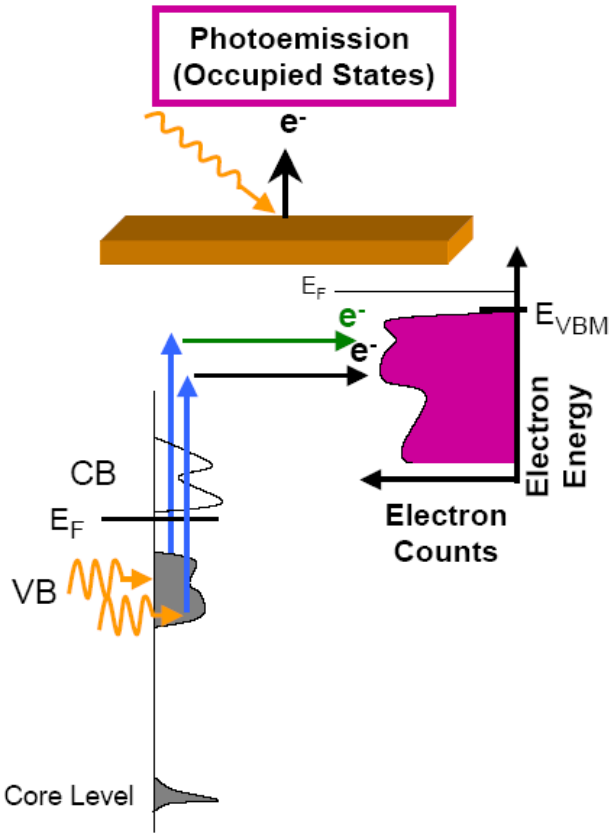
Low-energy version of RBS with high depth resolution (~ 3 Å vs. ~100 Å)

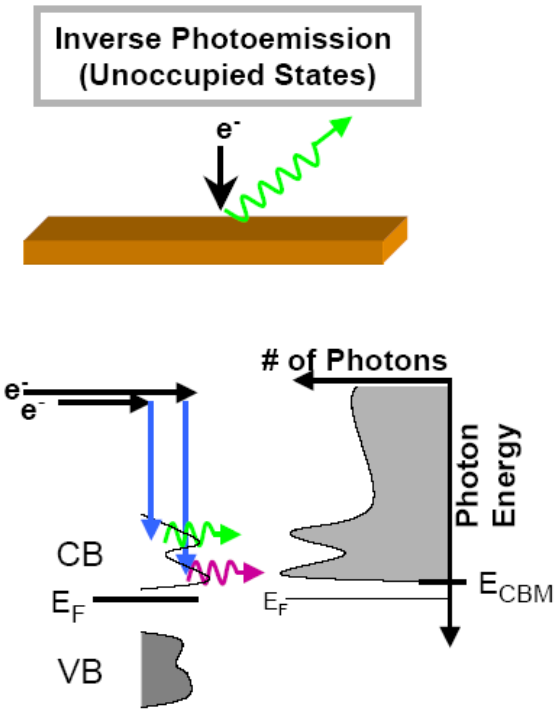


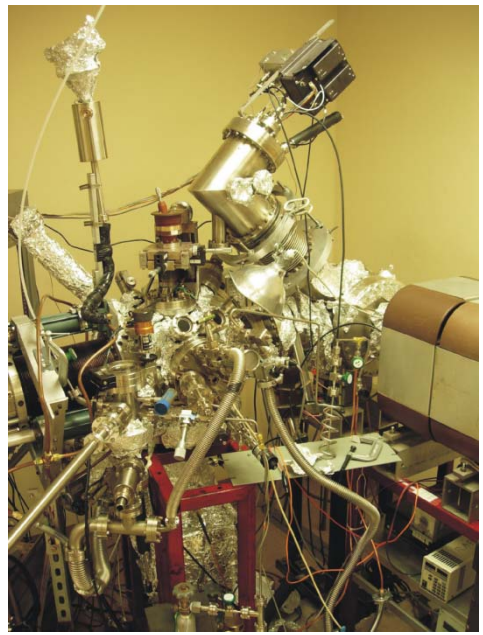




Electronic structure and band alignment



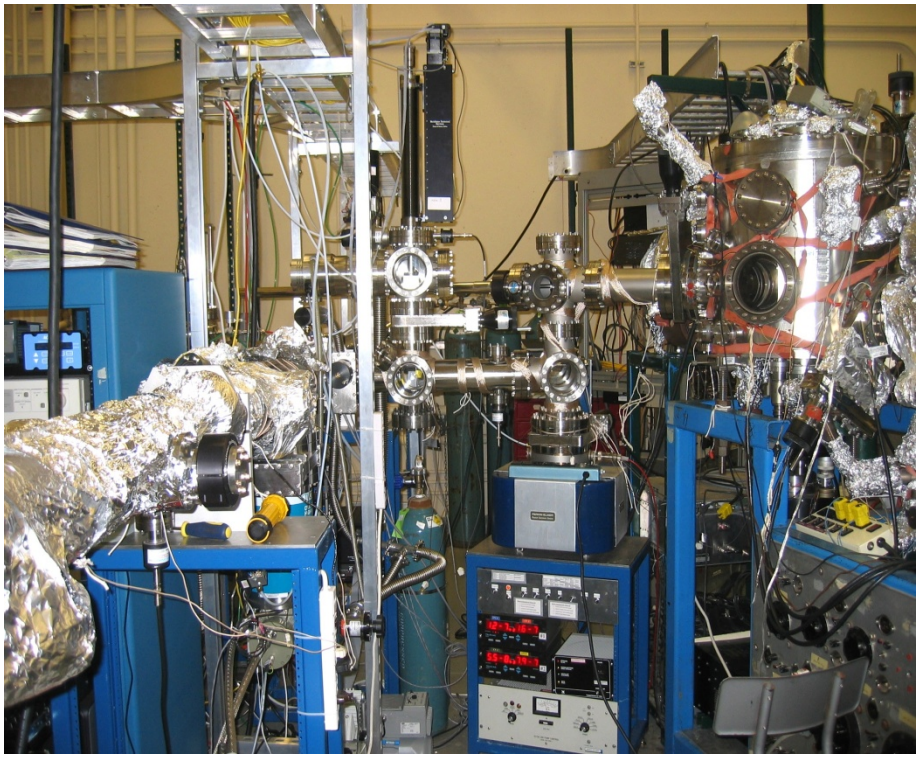


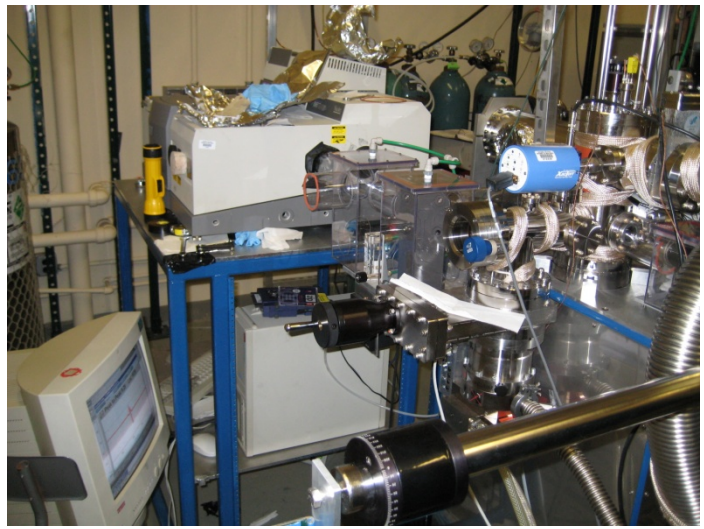


w/Bartynski

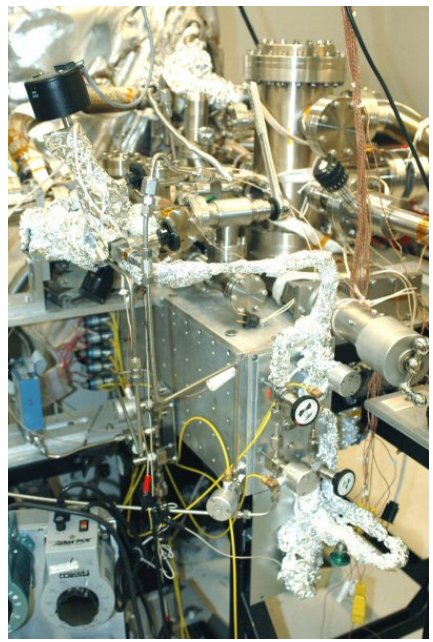
Other newly installed/commissioned equipment

UHV transfer system for growth and film analysis





Several ALD growth systems



Not shown: New photoemission system (XPS and UPS); new electrical testing system (Keithley 4200)

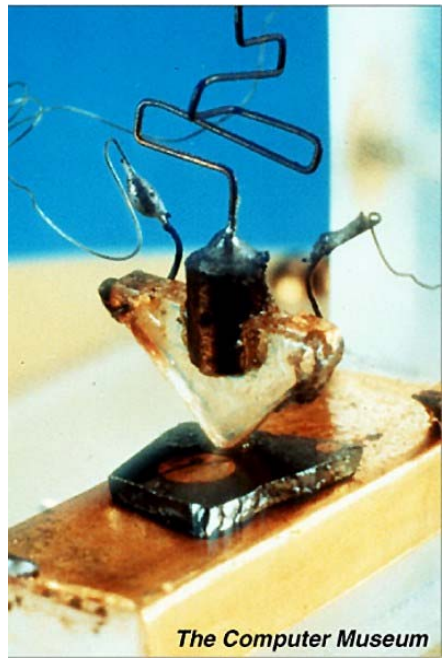
Several Ge MOSFET issues

- Unlike SiO_2, GeO_2 is relatively unstable and dissolves in water. GeO is less water soluble, but more defective.

- Film defects, interfacial GeO_x, and impurities such as CH_x and GeC increase defect density and degrade device performance. How to create an optimal interface?

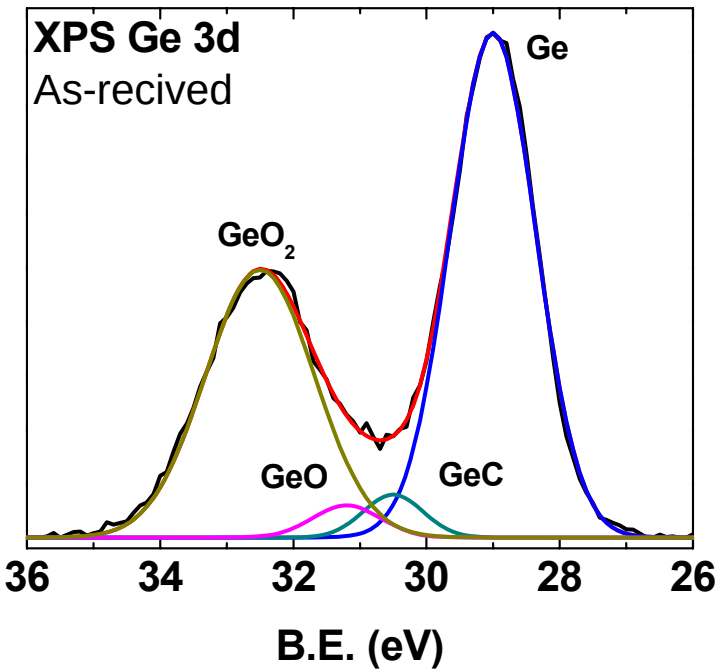
- Can a high-K dielectric be integrated on a Ge channel?

- Ge good for PMOS and NMOS?



Native oxides and carbon on Ge

None of the reported wet-chemical cleaning methods leads to an impurity-free Ge surface. Alternative approach: Convert hard-to-remove species into other chemical species which are easier to remove.



Some chemistries explored:

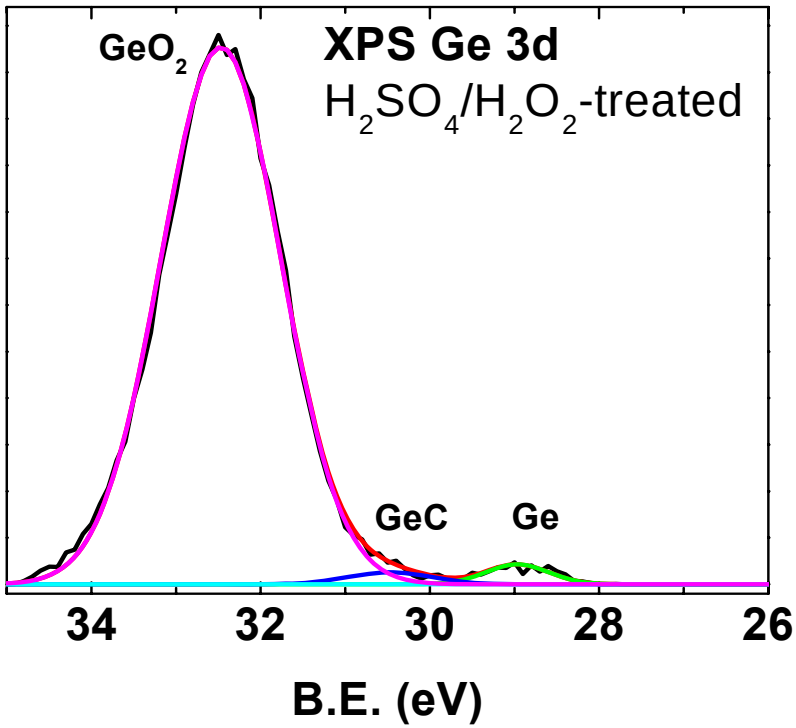
- **De-ionized water; HF; DIW/H_2O_2**
- **HF/DIW/H_2O_2**
- **NH_4OH/H_2O_2**
- **HCl/H_2O_2**
- **H_2SO_4**

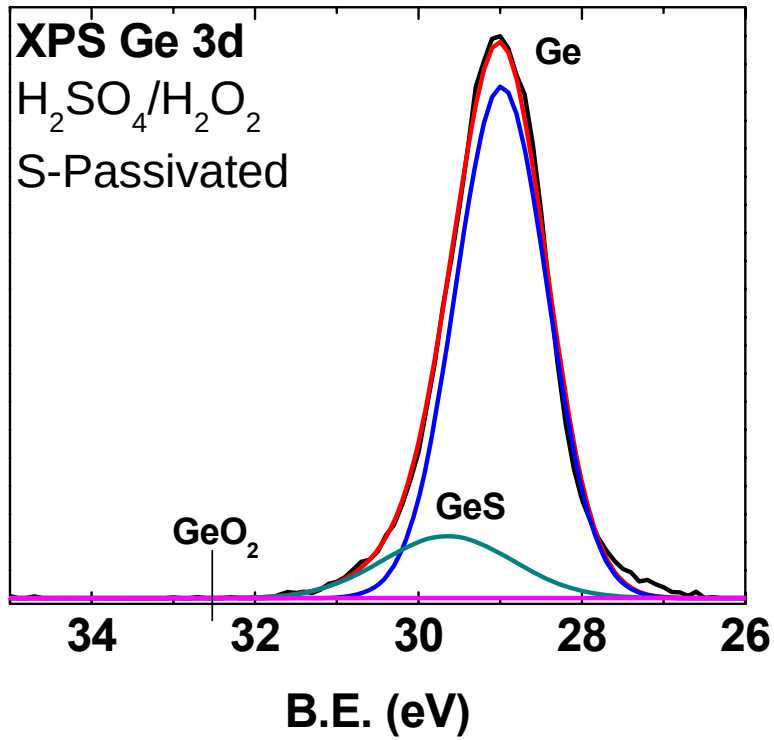
Sulfur-passivation in hot $(NH_4)_2S$ on H_2SO_4/H_2O_2-treated Ge

- **$(NH_4)_2S$ etches oxide**
- **Thin GeO_xS_y layer remains**
- **H_2SO_4/H_2O_2 and $(NH_4)_2S$ treatment results in low C**

- Starting surface has GeO, GeO_2, hydrocarbon, carbon….
- Some chemistries leave a thick oxide or sulfide.

Ge cleaning / oxidation

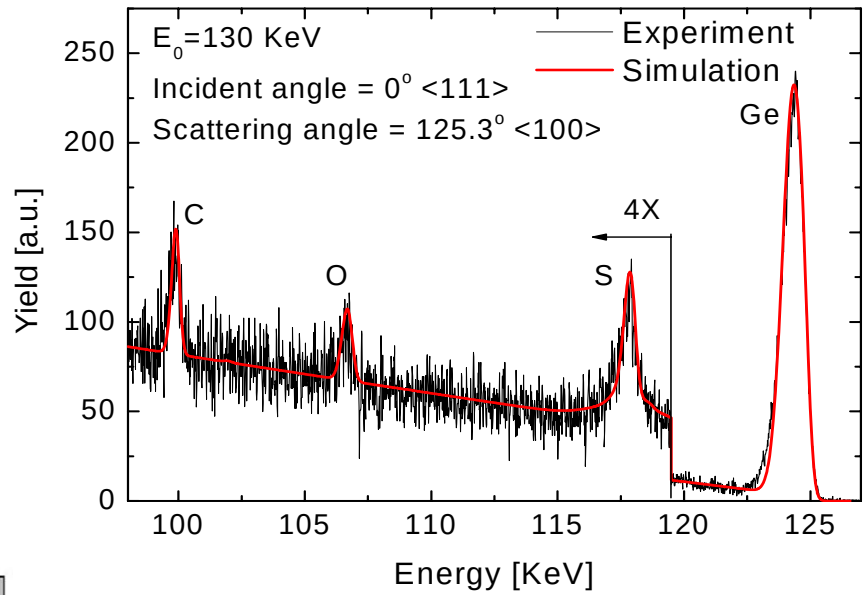


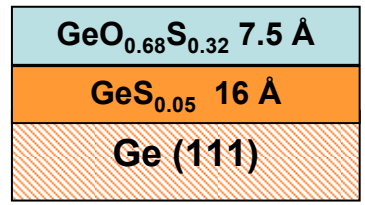


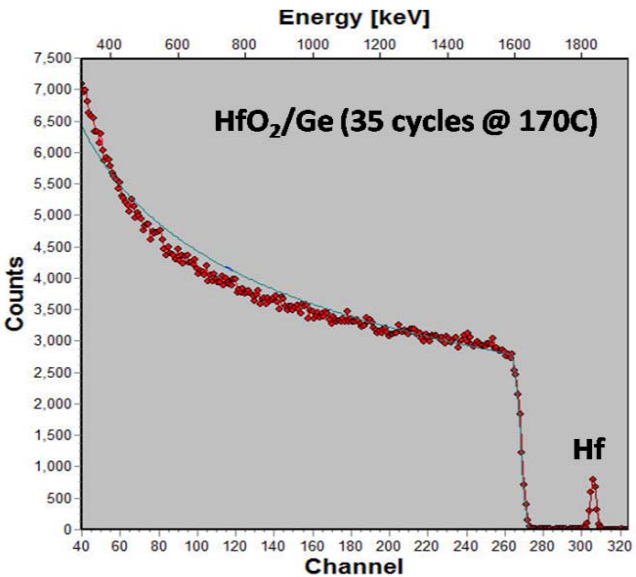
- XPS of Ge3d and C1s spectra of oxidized and S-passivated samples.
- No chemistry resulted in a C-free surface, but optimal ones lower the carbon and other impurities significantly.

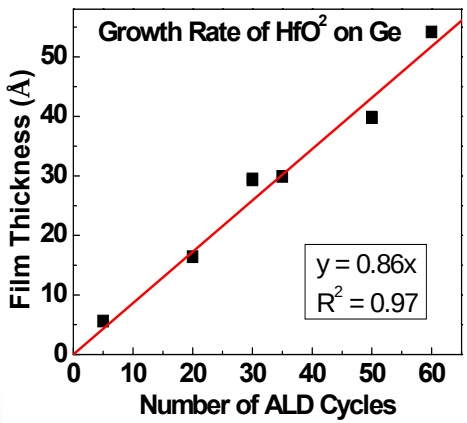
Ion Scattering (MEIS and RBS)

MEIS for composition and depth profile of the S-passivated layer.





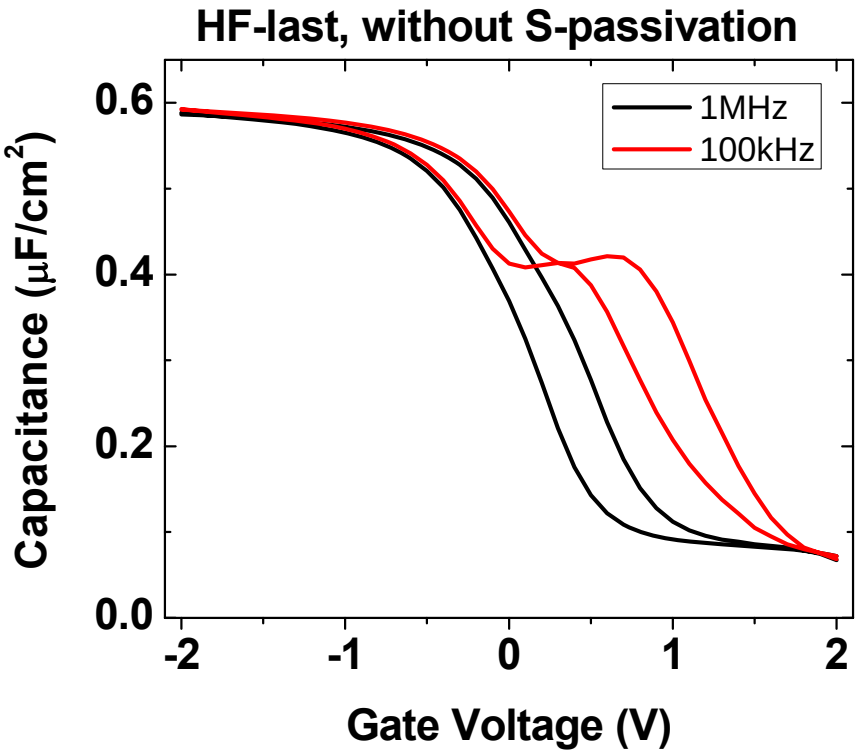




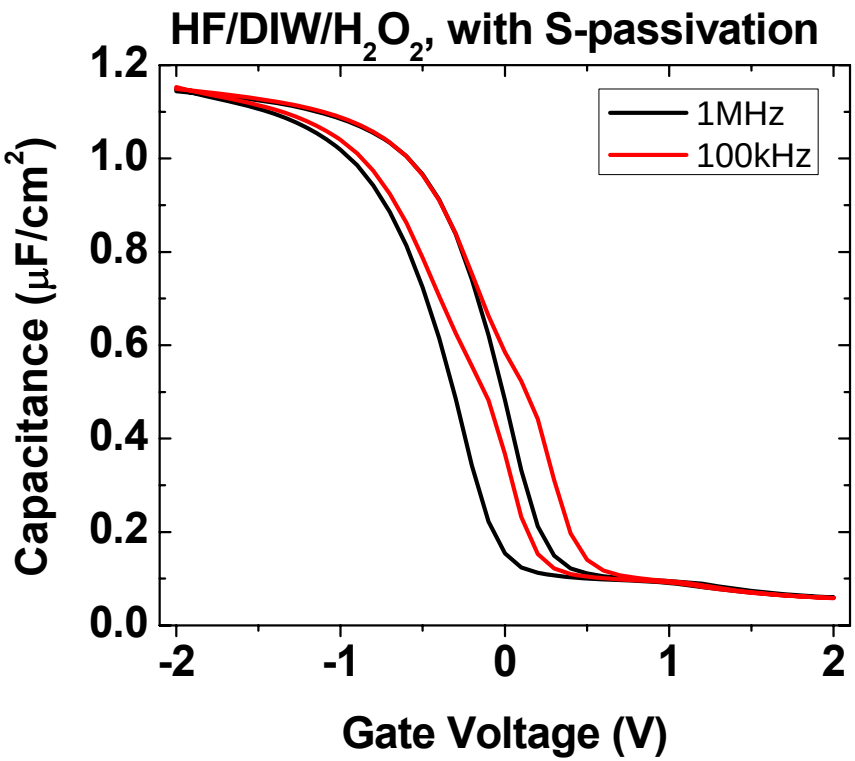
HfO_2 Growth conditions:

- Substrate temperature: ~150°C
- Hf Precursor ($Hf(N(CH_3)(C_2H_5))_4$)
- Growth Rate: ~0.86 Å/cycle

S-Passivation Improves the Interface

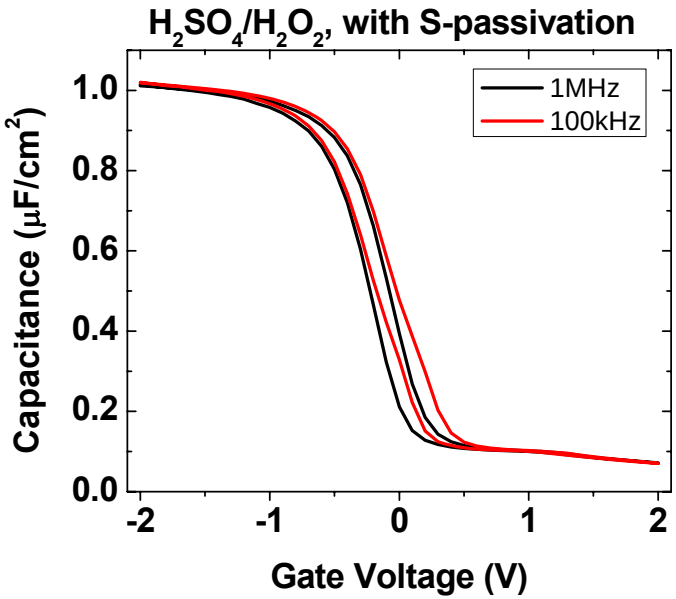


Q_i/e (cm^{-2})	4.00×10^{13}
Q_{HS}/e (cm^{-2})	1.15×10^{13}
ΔV_{FB_HS}(V)	0.31
D_{it} (eV^{-1} cm^{-2})	3.80×10^{12}



Q_i/e (cm^{-2})	4.17×10^{12}
Q_{HS}/e (cm^{-2})	2.09×10^{12}
ΔV_{FB_HS}(V)	0.29
D_{it} (eV^{-1} cm^{-2})	1.66×10^{11}

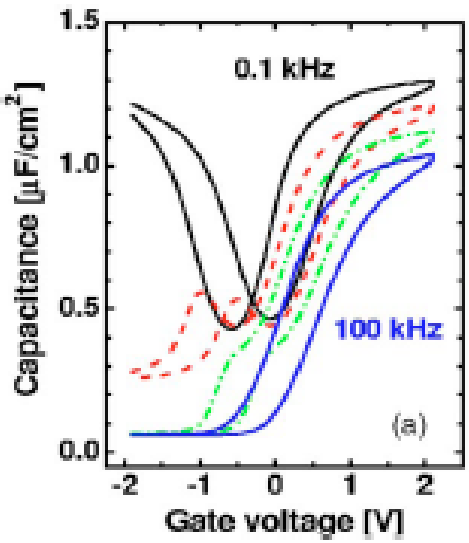
Cleaning	HF	HF/DIW/H_2O_2	H_2SO_4/H_2O_2 HF	H_2SO_4/H_2O_2
S-passivation	No	Yes	Yes	Yes
Q_i/e (cm^{-2})	$4.00x10^{13}$	$4.17x10^{12}$	$3.56x10^{12}$	$3.19x10^{12}$
Q_{HS}/e (cm^{-2})	$1.15x10^{13}$	$2.09x10^{12}$	$1.5x10^{12}$	$9.72x10^{11}$
ΔV_{FB_HS}(V)	0.31	0.29	0.22	0.15
D_{it} (eV^{-1} cm^{-2})	$3.80x10^{12}$	$1.66x10^{11}$	$8.91x10^{10}$	$6.23x10^{10}$



HfO_2 40Å, hysteresis is ~0.15V.
Ge surface was first H_2SO_4/H_2O_2 treated.
No HF used before sulfiding in $(NH_4)_2S$.

Prior work (lit.)

Current work (Hsueh, et al)



77Å HfO_2, hysteresis is ~0.5V.
10% HF etching for 10mins before sulfiding in $(NH_4)_2S$.
APL 89, 112905 (2006)

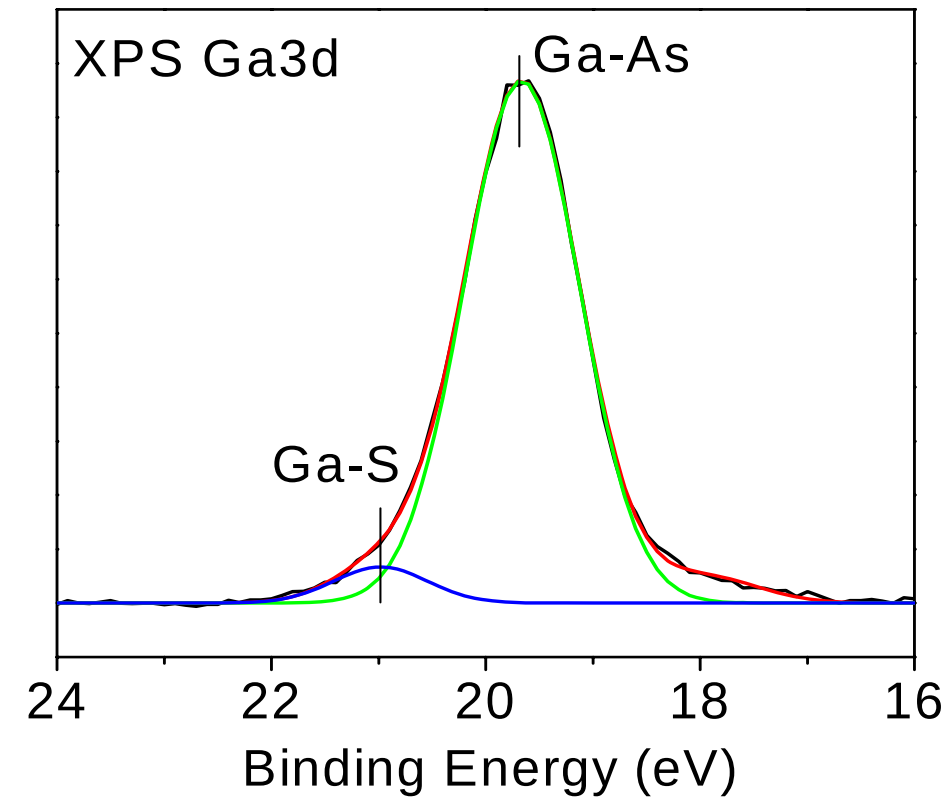
Summary Ge results

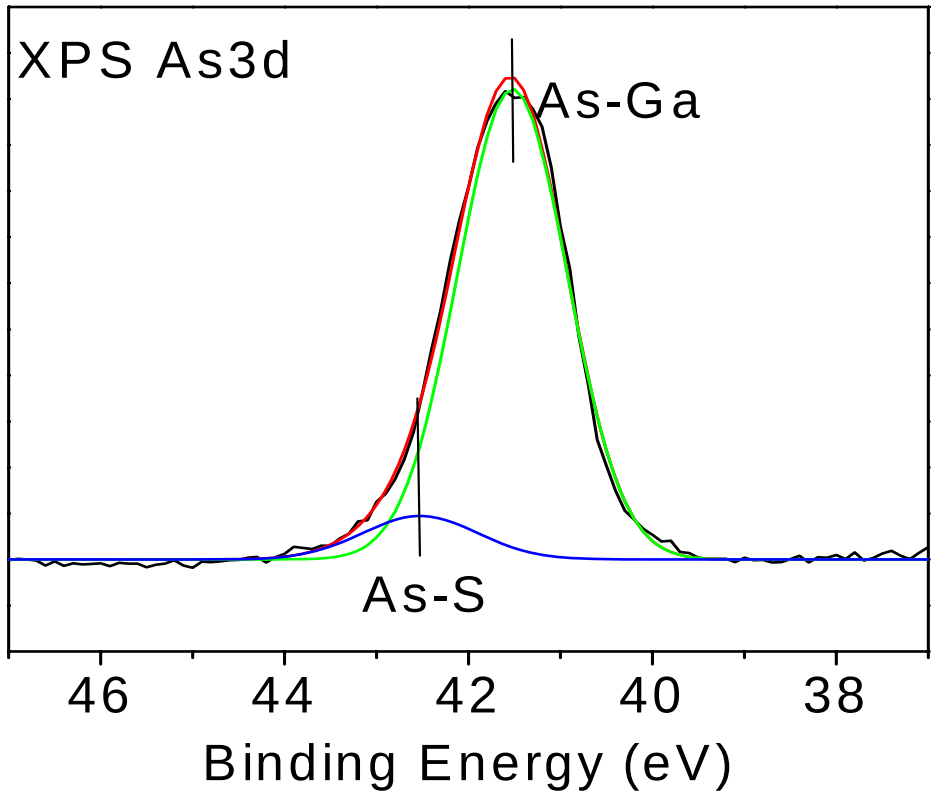
- Ge based high-k dielectric MOSCAPs have been grown and show very good electrical properties.
- MOSCAP properties are a strong function of surface cleaning and passivation. Wet chemistry is critical, and must be controlled with reproducible conditions (purity, temperature, concentration, pH, time etc.).
- Variations in surface treatment and ALD growth show up clearly in physical characterization (XPS, MEIS, etc.) and can be correlated with defects such as interface state density.

GaAs – based stacks

- How best to grow a high-K/metal electrode gate stack on GaAs-based channels with high quality interface?
- Can we use cleaning and passivation chemistries on GaAs that were found to produce optimal Ge/high-K gate stacks?
- Do ALD high-K growth chemistries and conditions that work on Si and Ge also work on III-V films?
- Do we need SiO_2, nitride, Al_2O_3 or other interlayer materials and structures to minimize defect density and produce viable gate stacks?

S Passivation of GaAs-based compounds

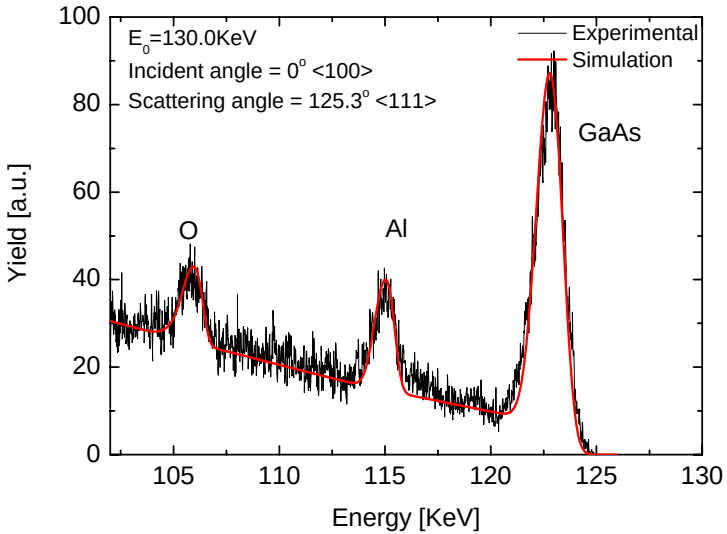




Using new wet chemical treatments, we can produce a film in which there is no native oxide on the GaAs surface and a relatively passive sulfide layer

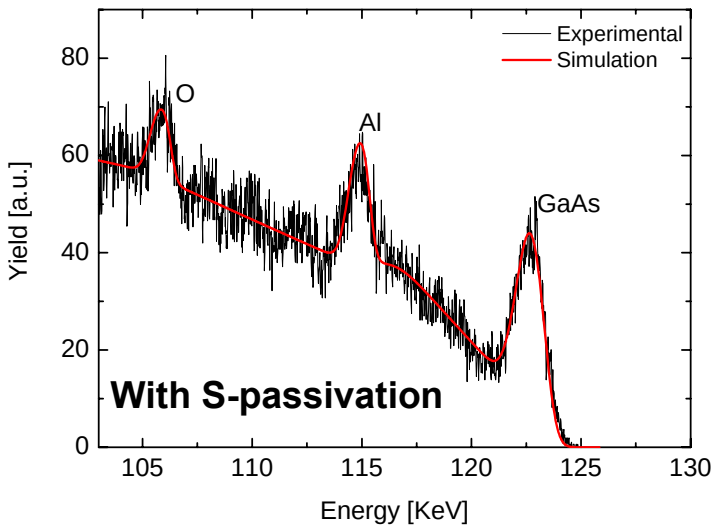
MEIS of ALD-grown Al_2O_3/GaAs

In-situ Al_2O_3/GaAs(001) without S-passivation



- One single uniform layer of $Al_{1.7}O_3$ (20Å, a little off-stoichiometry) on the surface fits the data well; the data indicate little roughness on this film.
- Native oxides on GaAs result in an interface GaAs peak larger than one on a passivated sample (see below).

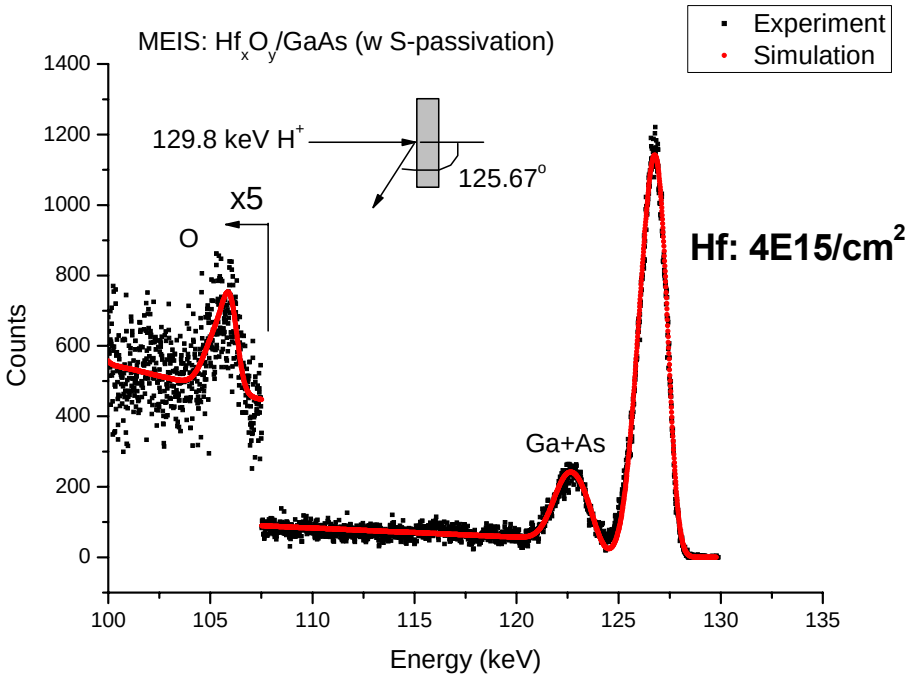
Element	Concentration $\times 10^{15}$[atoms/cm^2]
Al	8.7
O (not including native oxide)	15.0

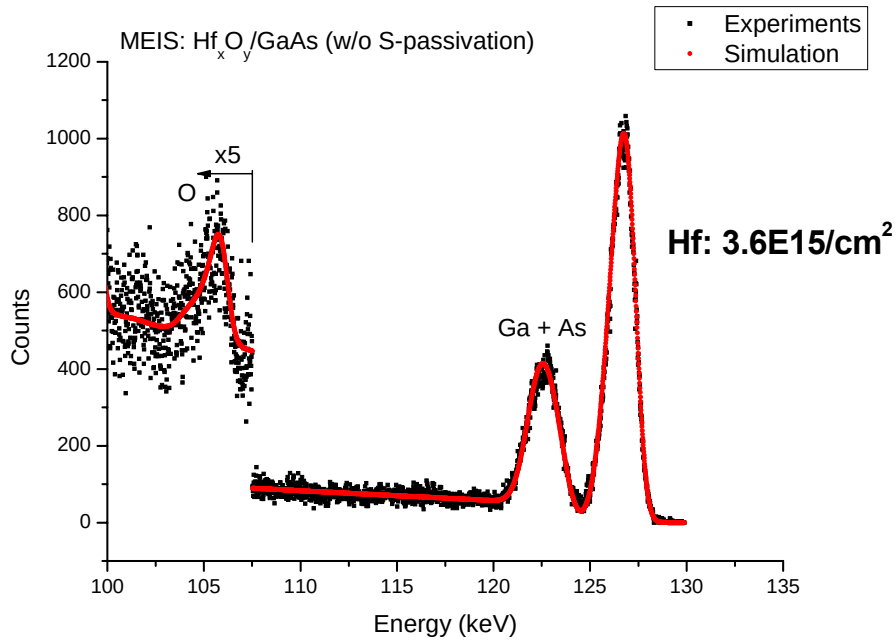


- One single uniform layer of Al_2O_3 (20Å, 20 cycles) on the surface fits the data well, indicating little roughness.
- High background due to poor
- No S observed.

Element	Concentration $\times 10^{15}$[atoms/cm^2]
Al	9.4
O	14.2

MEIS of ALD-grown HfO_2/GaAs

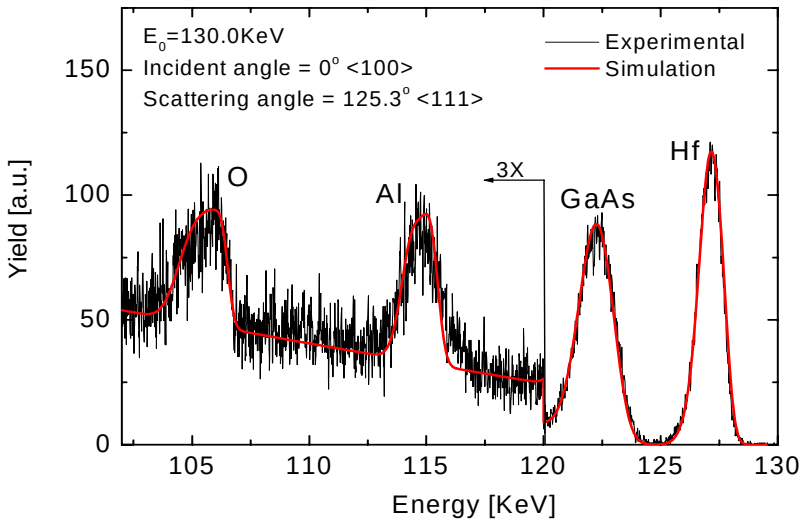




- **No S remains on the S-passivated sample**
- **Film not perfectly flat (non-uniform initial nucleation).**
- **More oxide at the interface of HfO_2/GaAs w/o S-passivation**

Multilayer $HfO_x/Al_2O_3/GaAs$ gate stack MEIS

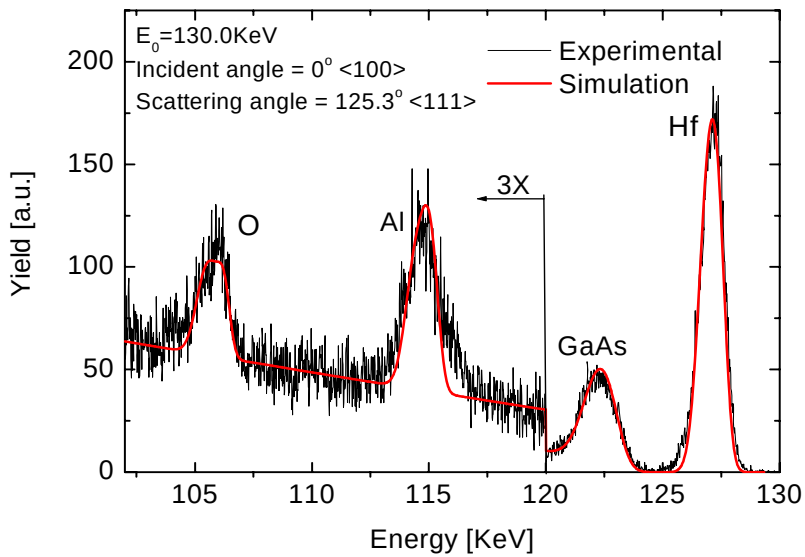
without sulfur passivation



- HfO_x ~ 20Å (20cycles), Al_2O_3 ~ 15Å (15cycles), interface $GaAsO_x$ ~ 30Å.
- The HfO_x layer appears somewhat rough: Al has to be included in HfOx layer to fit both Hf and Al peaks with a uniform-layer model.

Element	Concentration $\times 10^{15}$[atoms/cm^2]
Hf	1.74
Al	10.54
O (not including native oxide)	20.67

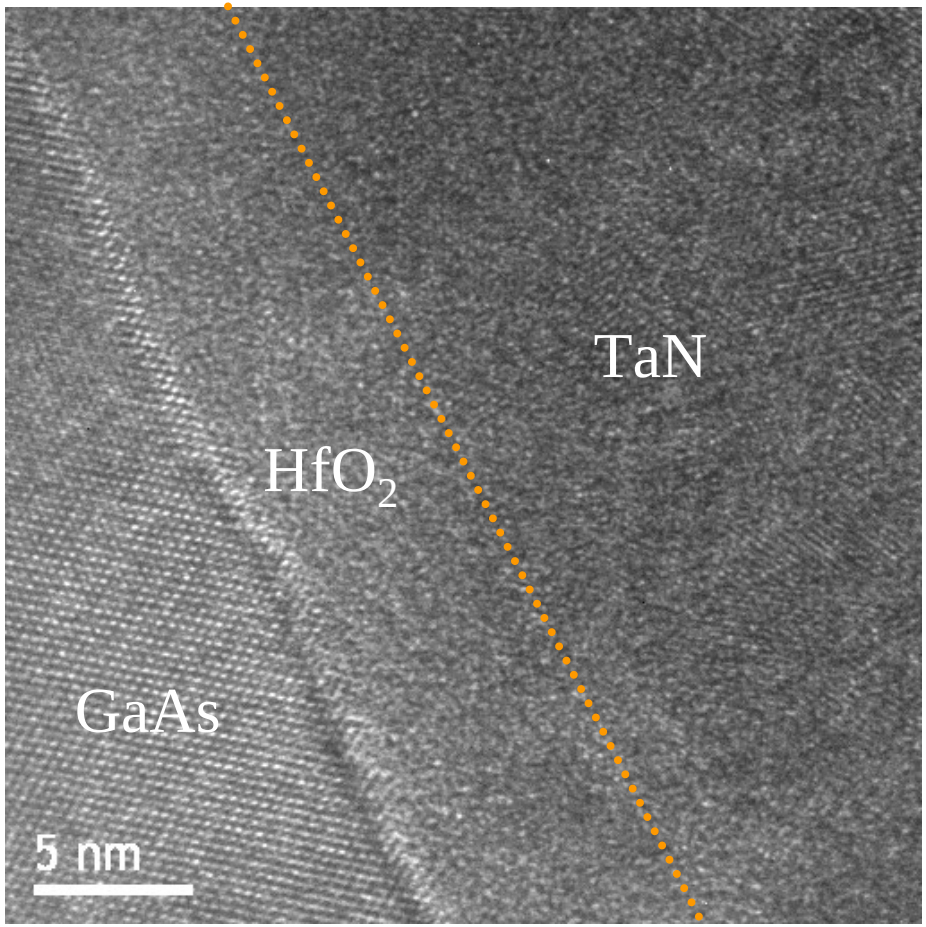
with sulfur passivation



- Similar rough structure as non-passivated sample.
- No S observed in this passivated sample.
- Reduced height of GaAs peak might be due to the removal of native GaAs oxide during etching, resulting in better crystalinity of GaAs.

Element	Concentration $\times 10^{15}$[atoms/cm^2]
Hf	1.8
Al	10.44
O	16.14

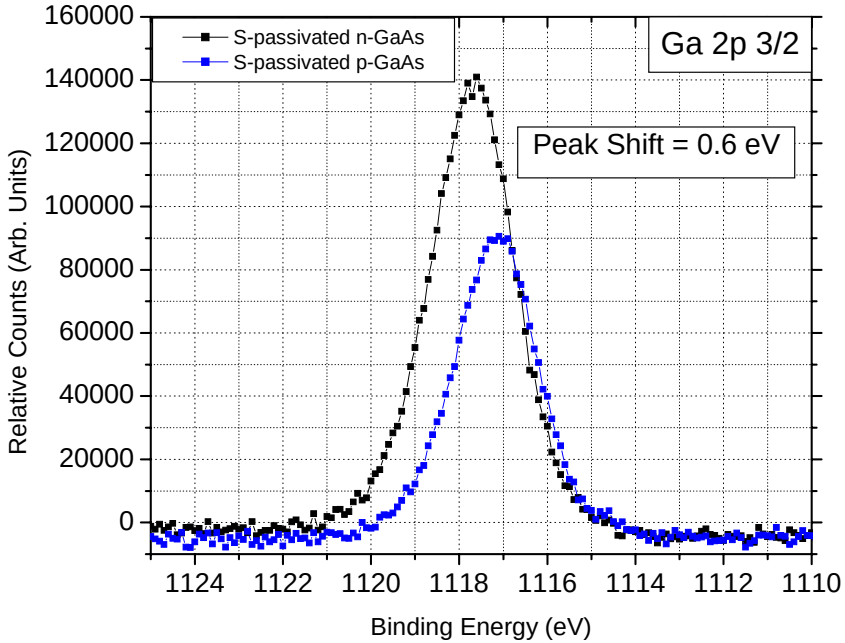
TEM for GaAs/HfO_2/TaN Gate Stack

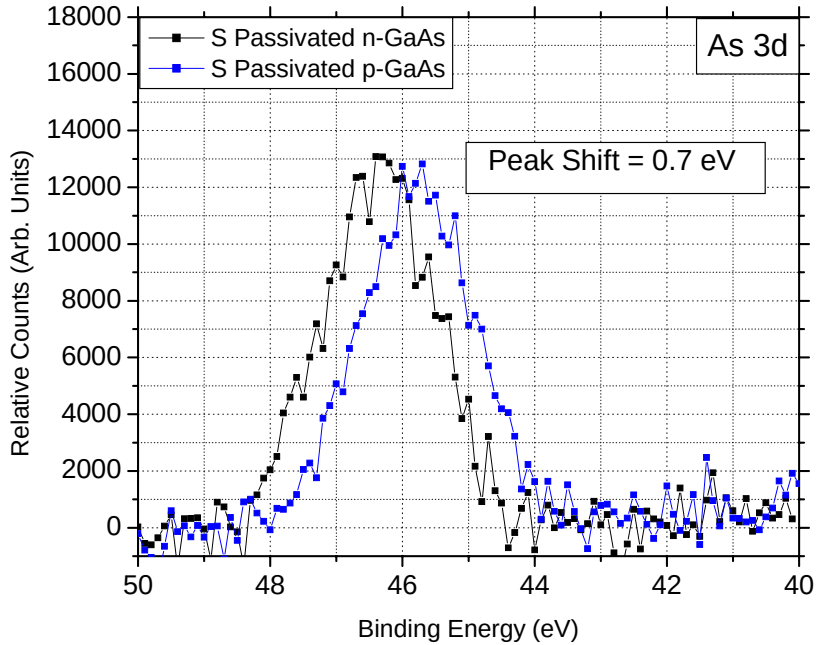


A TEM image of a GaAs sample with following process: native oxide etched, sulfur passivated, HfO_2 grown by ALD, TaN metal grown by PVD.

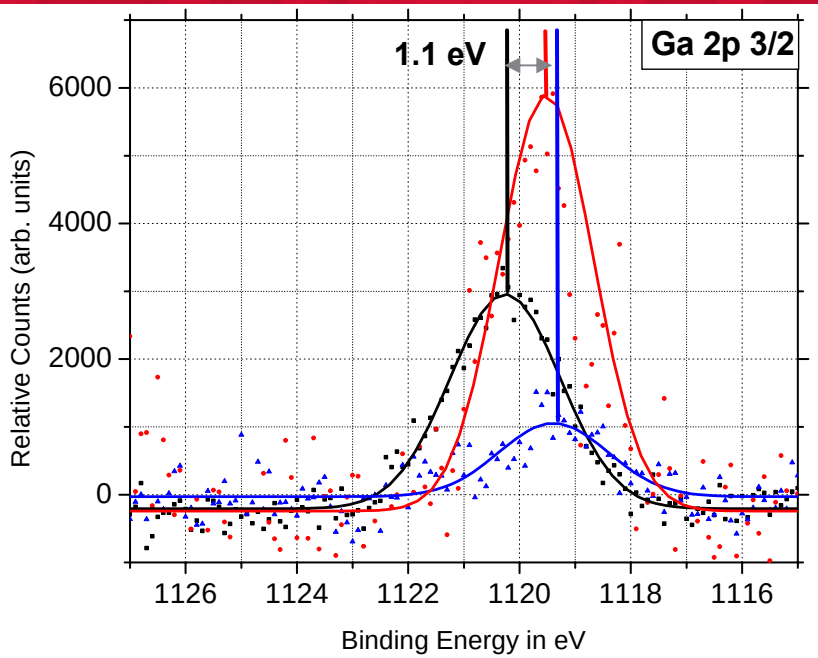
From TEM images (and microscopic elemental analysis, AFM, etc.), we find that the interface roughens after this specific chemical oxidation and passivation

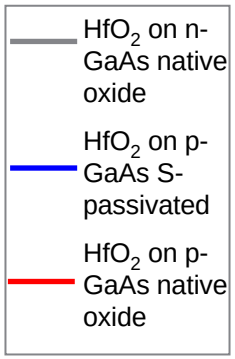
GaAs with S-passivation XPS band alignment (highly doped n and p-type)

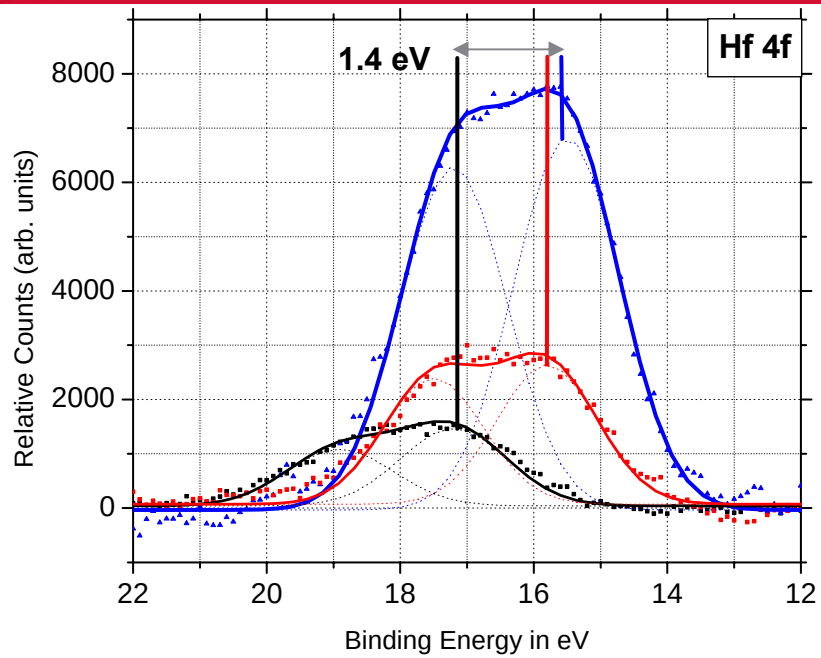


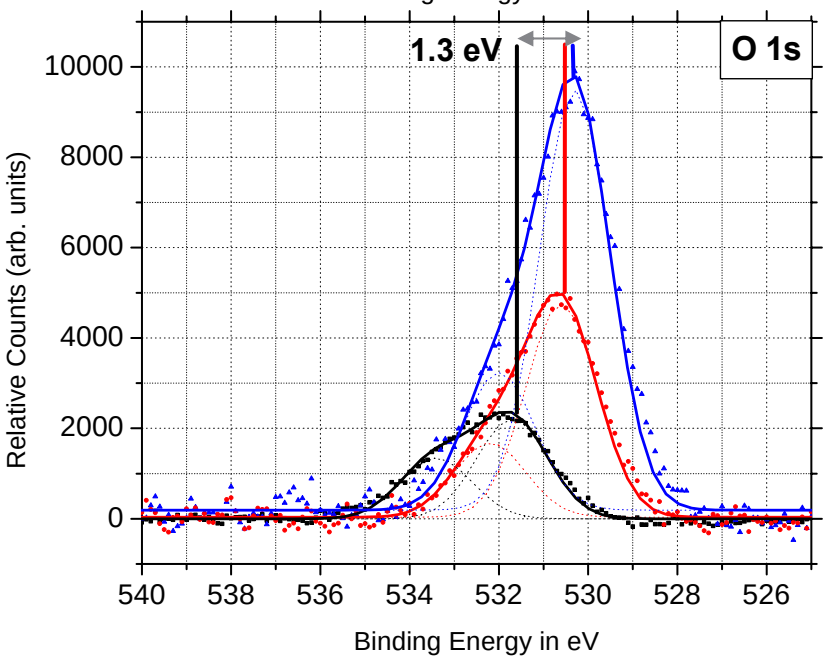


- **Partial pinning of the Fermi level at S-passivated surface**
- **Results imply a ~0.4±0.05 eV upward band bending for n-GaAs, ~0.4±0.05 eV downward band bending for p-GaAs**



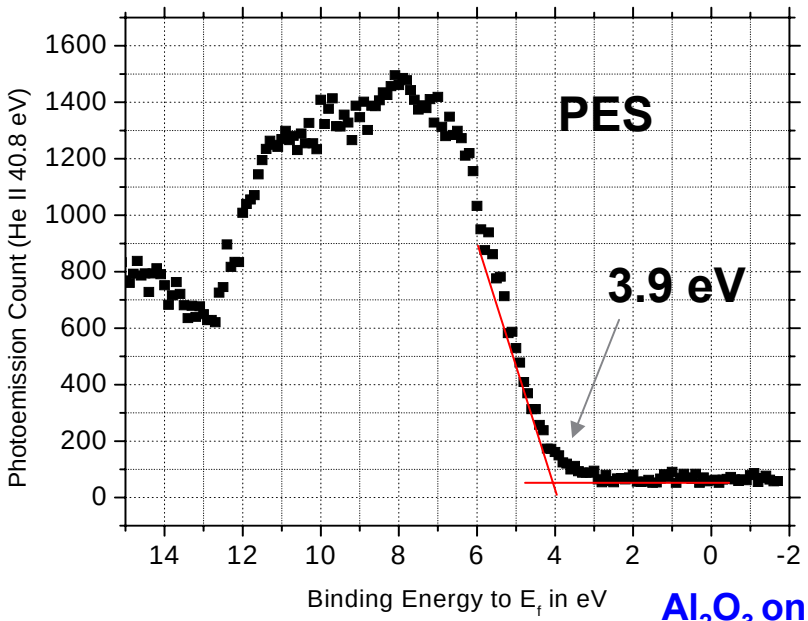


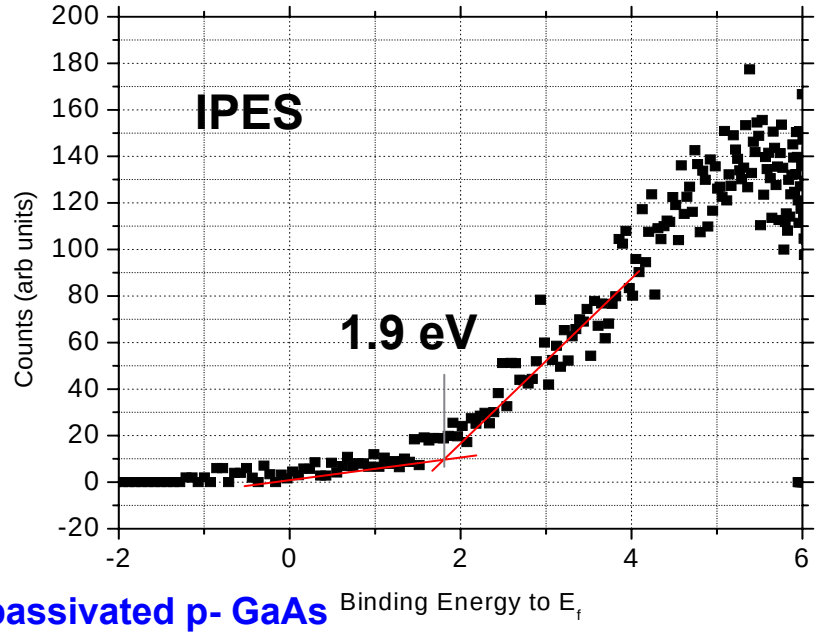




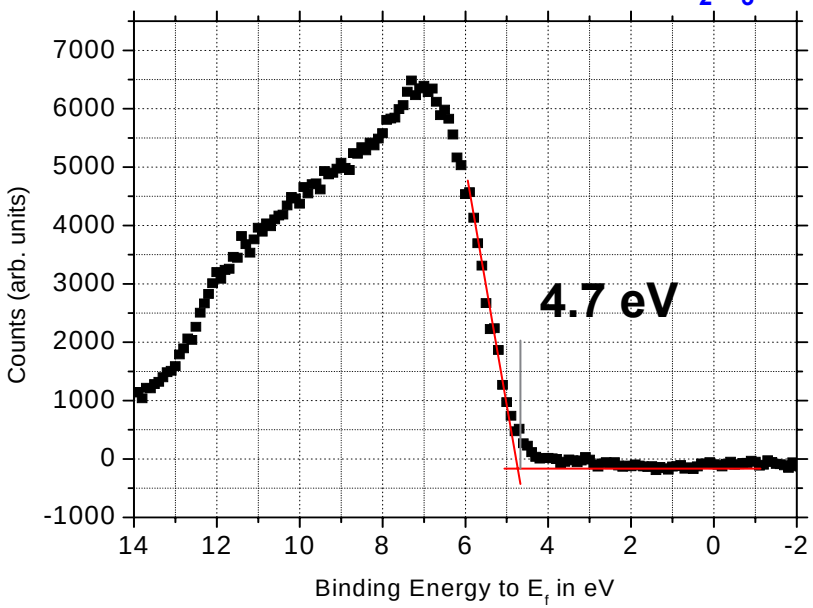
- **Little difference in interface chemistry between HfO_2 on S-passivated and HfO_2 on native oxide sample.**
- **Ga 2p is single Gaussian (consistent with GaAs), no GaO_x or AsO_x in O 1s signal**
- **Shift between n-type and p-type samples ~1.2-1.4 eV means *the Fermi level is not strongly pinned.***
- **Results imply that the interfacial O and S are likely removed during high-K growth.**

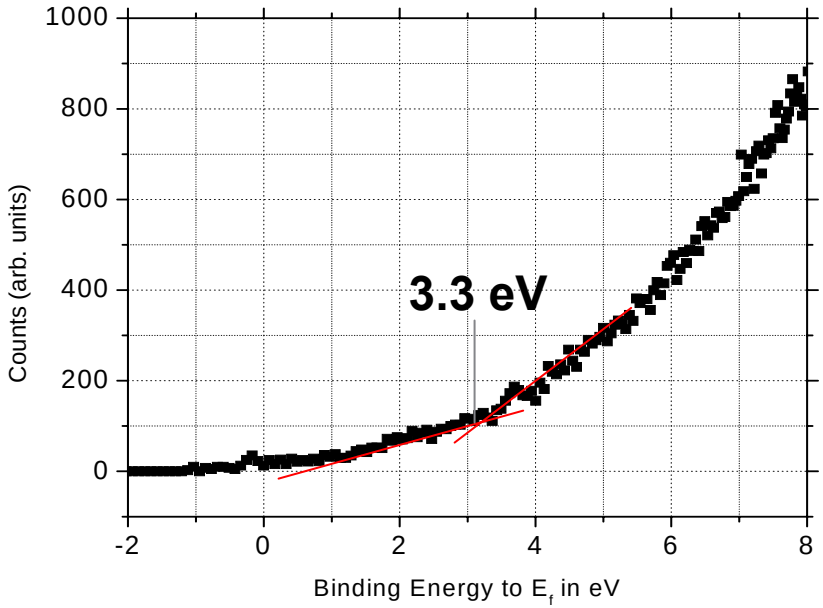
HfO_2 on S-passivated n- GaAs



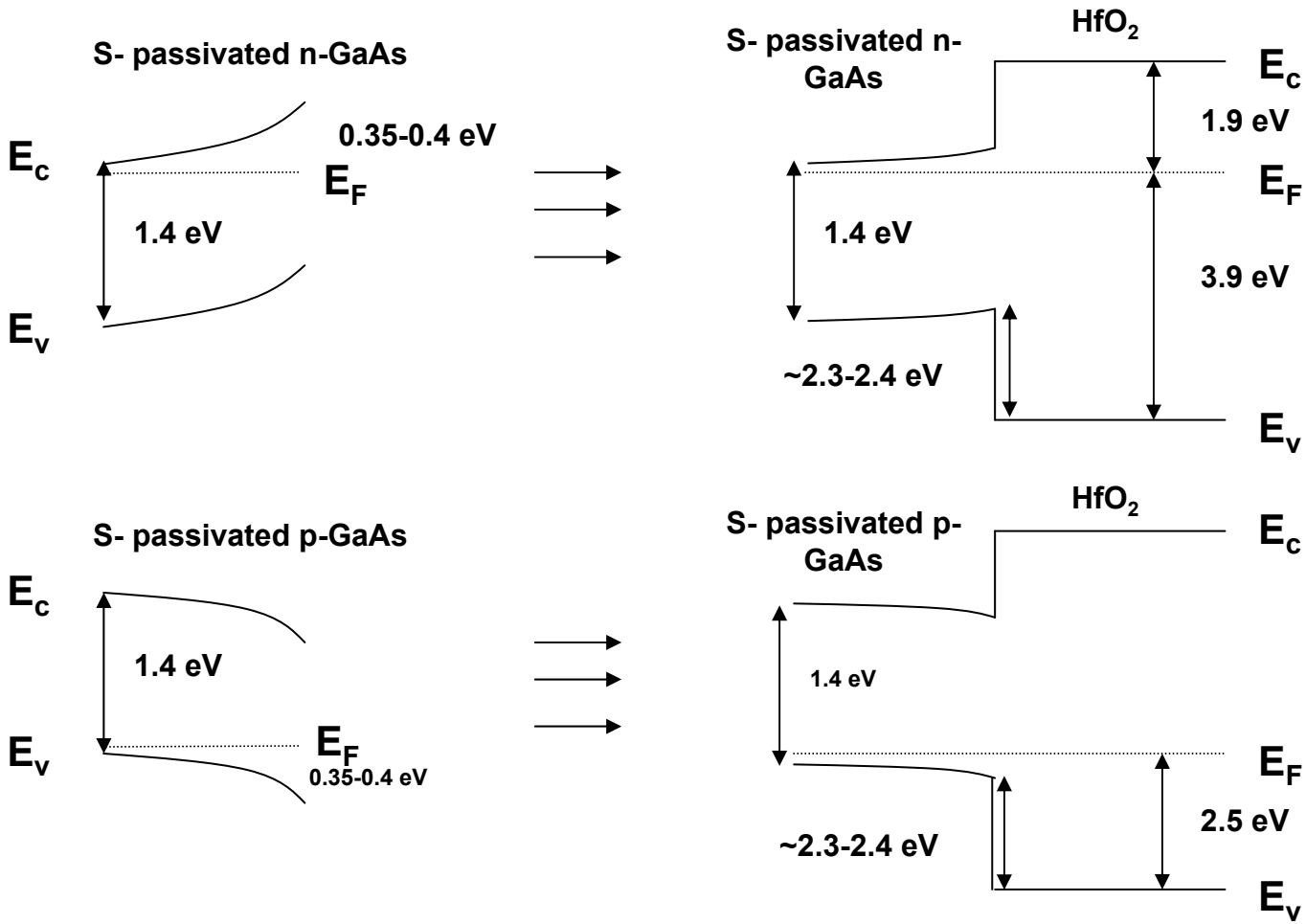


Al_2O_3 on S-passivated p- GaAs





- S-passivated film Fermi levels partially pinned.
- After HfO_2 growth, little pinning.
- Conduction and valance band offsets agree with literature.



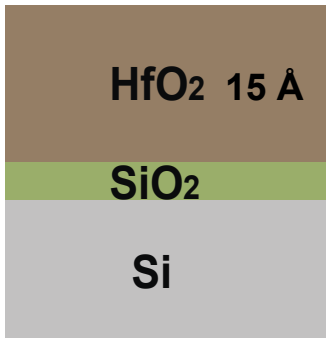
Summary GaAs results

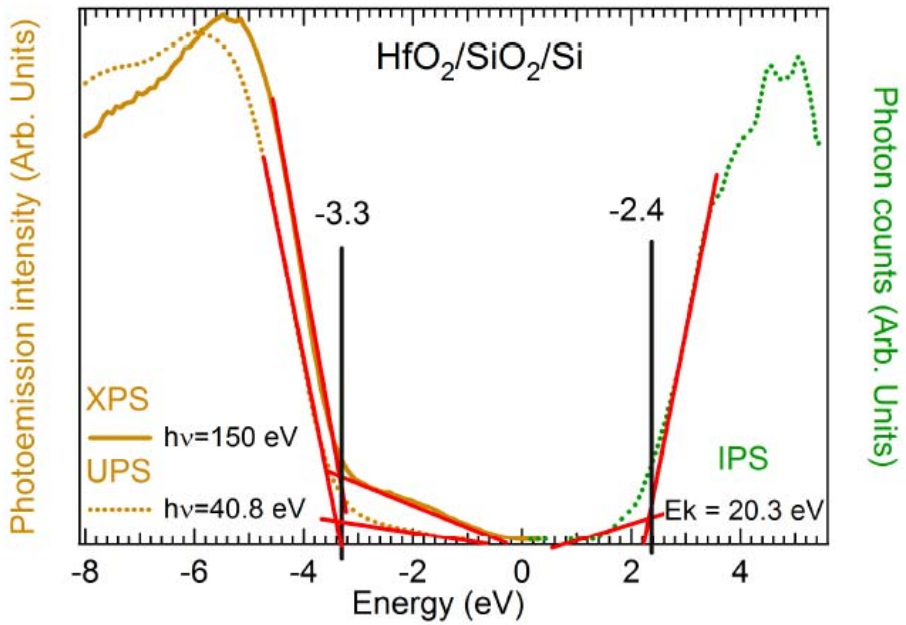
- Electronic structure of various films and interface passivation routes examined. The removal of the native oxide and passivation of GaAs surface is effective.
- Appropriate band alignment and little Fermi level pinning found for some passivation and film growth conditions.
- Exploring new routes to decrease roughening during the wet chemistry
- Device measurement in progress

Band Edge Determination

Single chamber

UHV measurements





Calculated bulk Fermi level

Experimental Fermi level

↓

Band bending

Substrate band edges determination

↓

Band offsets

Gap determination

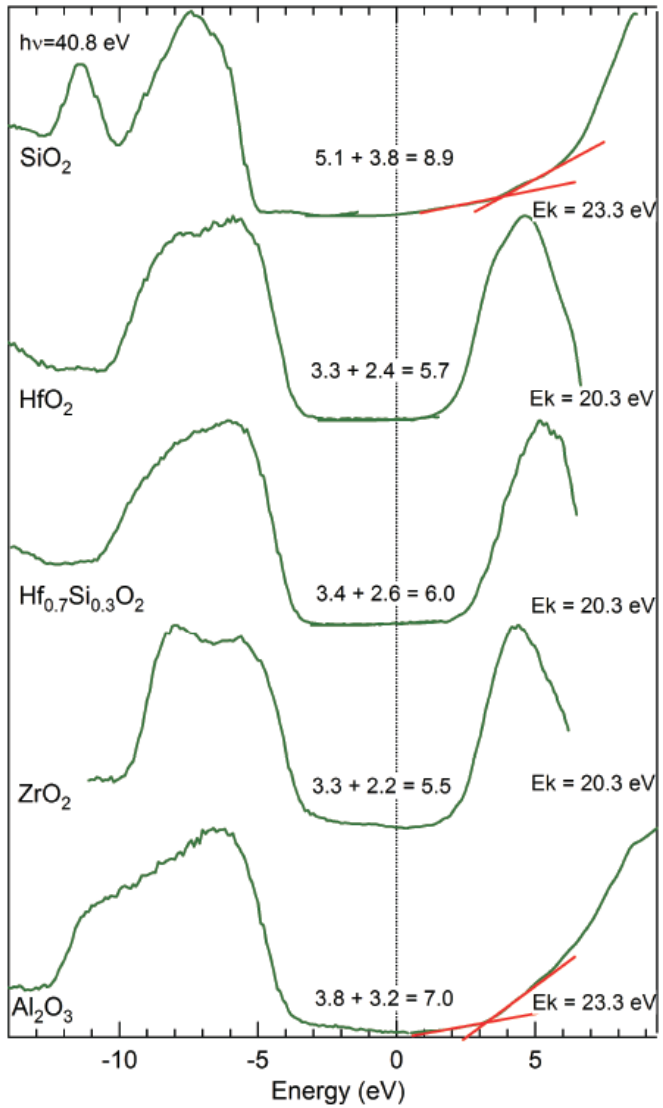
w/Rangan, Bartynski, et al.

Band Gap Measurements

Single chamber measurements

Spectra shifted to set at zero
The silicon midgap

Gaps and band offsets
comparable to literature



Comparison To Literature

Method	Gap	VBO	CBO
XPS, energy loss[8]	6.95	3.75	2.08
XPS, energy loss[15]	6.52	3.03	2.37
XPS, energy loss[26]	6.7	2.9	2.7
IntPE[12]	6.2	2.95	2.15
SE[27]	6.26	—	—
BEEM[28]	—	—	2.8
This work	7.0	3.2	2.7

Al_2O_3

Method	Gap	VBO	CBO
XPS, energy loss[14]	5.7	3.10	1.48
XPS, energy loss[15]	5.25	2.22	1.91
XPS, IPS[16]	5.86	3.28	1.46
XAS, XPS[17]	5.1	3.0	1.0
UPS[18]	—	2.75	—
IntPE[19]	5.6	2.5	2.0
XAS[20]	6.0	—	$\geq$1.2
EELS[21]	5.8	—	—
SE[22]	5.8	—	—
This work	5.7	2.7	1.9

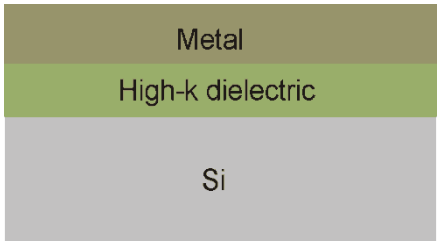
HfO_2

Method	Gap	VBO	CBO
XPS, energy loss[25]	5.65	3.65	0.88
XPS, energy loss[8]	5.50	3.35	1.03
XPS, energy loss[26]	5.6	2.5	2.0
XPS, UPS[11]	5.7	3.4	1.2
XPS, IPS[23]	5.68	3.40	1.16
IntPE[12]	5.4	2.3	2.0
EELS[21]	5.0	—	—
This work	5.5	2.8	1.6

ZrO_2

Method	Gap	VBO	CBO
XPS, energy loss[8]	8.95	4.49	3.34
XPS, UPS[11]	9.0	4.4	3.5
IntPE[12]	—	—	3.15
XPS[10]	—	4.35	—
XPS[?]	8.95	4.54	3.28
This work	8.9	4.5	3.3

SiO_2

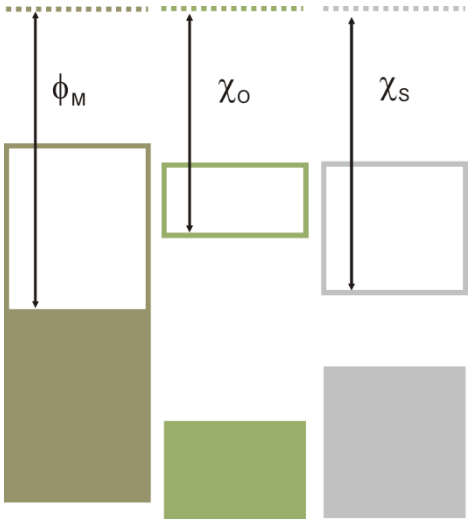


Band Alignment Models

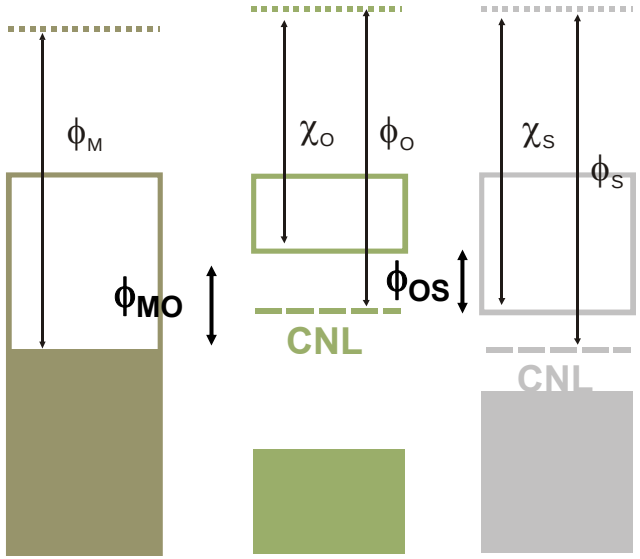
Schottky limit

S = 1

→ No pinning



Induced Gap State Model



$$\phi_{MO} = S\,(\phi_M - \phi_O) + (\phi_O - \chi_O)$$

$$\phi_{OS} = (\chi_O - \phi_O) - (\chi_s - \phi_s) + S\,(\phi_O - \phi_S)$$

S = pinning parameter

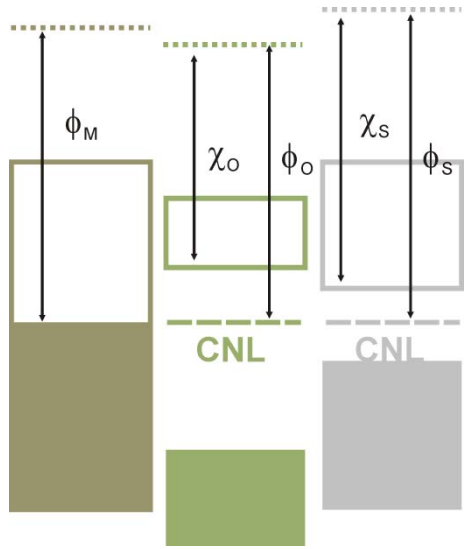
Reality is in between

Alignment of the CNL modified by S

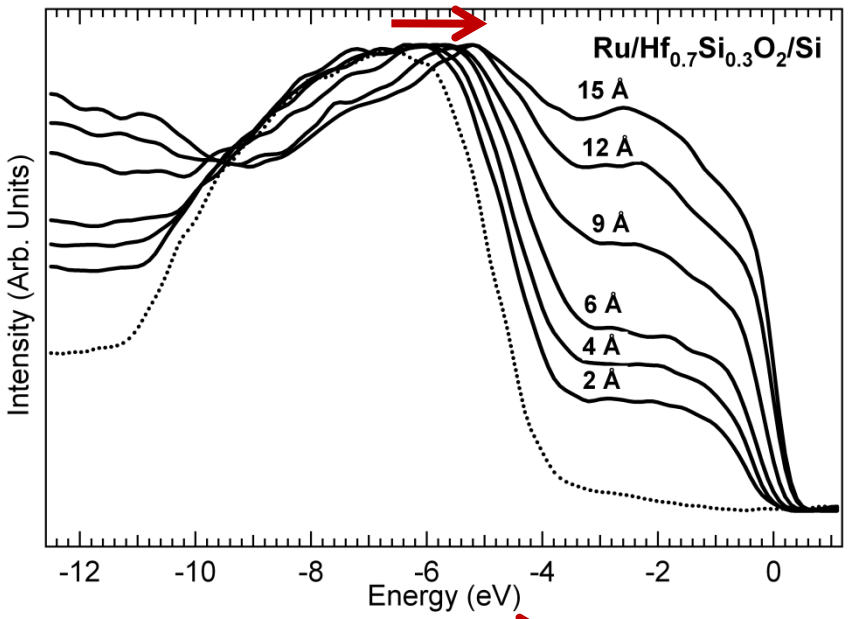
Bardeen limit

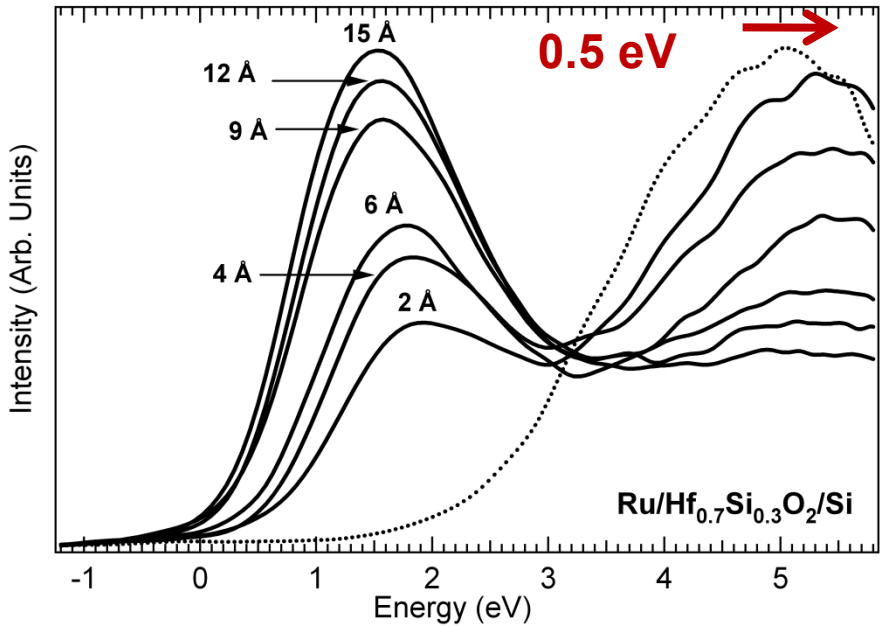
S = 0

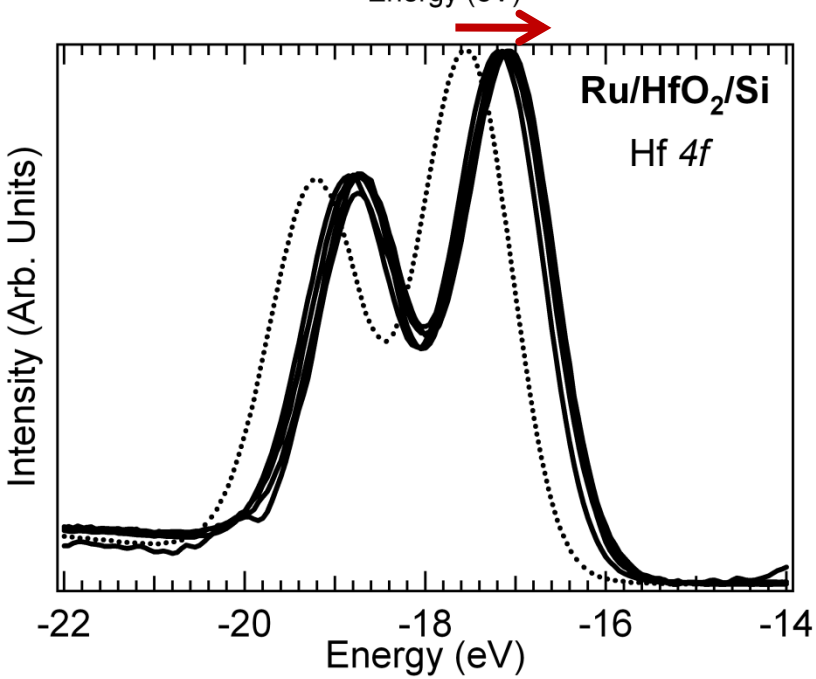
→ Strong pinning

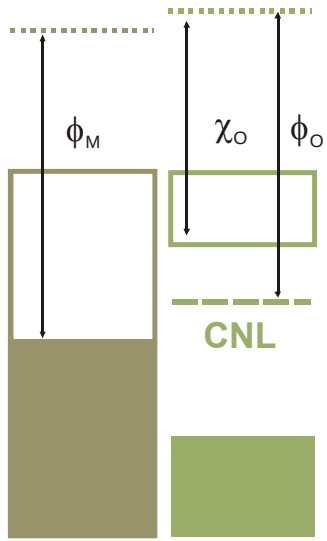


Ru/HfO$_2$/Si









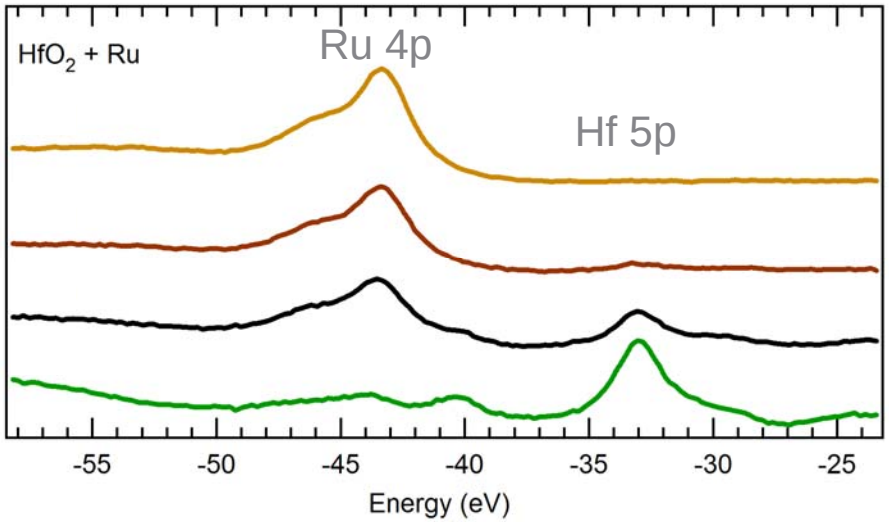
$\phi_{MO} = S\,(\phi_M - \phi_O) + (\phi_O - \chi_O)$

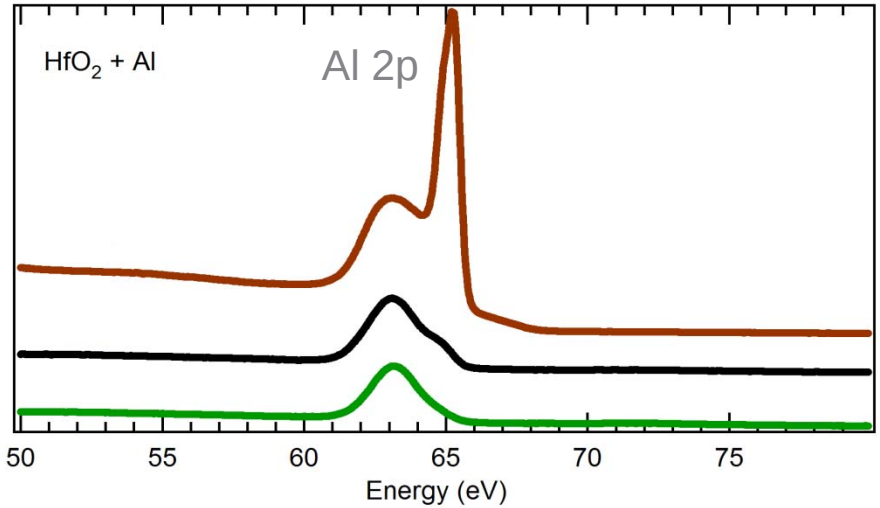
S=0.53 CNL=3.7

Robertson, JVSTB,18,1785, 2000

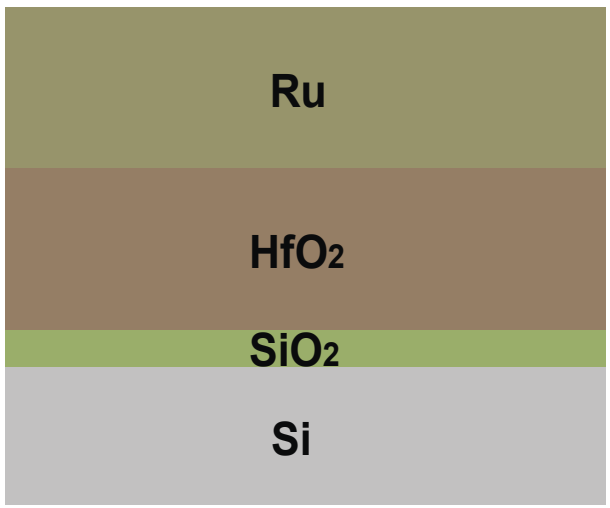
Theoretical shift: 0.4 eV

Metal Interaction with the Substrate

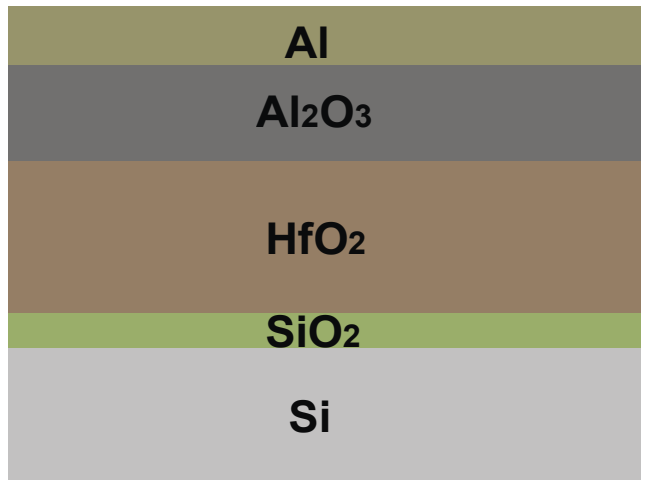




No oxidation of ruthenium



Oxidation of aluminium
Formation of a Al_2O_3 layer



Summary

Ge and GaAs based high-k dielectric MOSCAPs have been grown. Electronic and chemical structure of various films and interface passivation routes examined.

Ge MOSCAPs show good electrical properties. Electrical properties are a strong function of surface cleaning and passivation. Wet chemistry is critical, and must be controlled with reproducible conditions (purity, temperature, concentration, pH, time etc.).

Variations in surface treatments also show up clearly in physical characterization (XPS, MEIS, etc.) of both Ge and GaAs, and can be correlated with defects such as interface state density.

Favorable band alignment found for some passivation and film growth conditions. Fermi level pinning (of interface defects?) appears not to be critical if film grown properly.

Plans

- **Pursue high-K/metal gate integration on III-V's and Ge.**
  - **Correlate defect generation rate with E_{gap} and e-h pair generation probability of semiconductor and metal layers adjoining dielectric**
  - **Correlate physical and electrical measurements of "intrinsic" and "radiation induced/enhanced" defects**
  - **Thermal and chemical stability of passivation layers on III-V surfaces and relation to defect conc: Si, S, N, Al, etc.**
  - **Explore E_f pinning and relation to interface composition in Ge and III-V's**
  - **Monitor H/D concentration/profiles in post-silicon materials and radiation induced changes in them**

- **Explore radiation induced defects in organic, nanowire, MEMS other novel devices.**

Recent MURI-related publications:

- L.V. Goncharova, et al; *Metal-gate-induced reduction of the interfacial layer in Hf oxide gate stacks*, J. Vac. Sci. Tech. A **25**, 261 (2007).
- N. Goel, et al; *Band offsets between amorphous $LaAlO_3$ and InGaAs*, Appl. Phys. Lett. **91**, 113515 (2007).
- M. Dalponte, et al. *MEIS study of antimony implantation in SIMOX and vacancy-rich Si,* J. Phys. D: Appl. Phys. **40**, 4222, (2007).
- S. Rangan, et al, *GeO_x interface layer reduction upon Al-gate deposition on a $HfO_2/GeO_x/Ge$ stack,* Appl. Phys. Lett. **92**, 172 (2008).
- E. Garfunkel, G. Bersuker and J. Gavartin, *Defects in CMOS Gate Dielectrics*, to be published (2008).

These and other papers can be downloaded at:
http://rutchem.rutgers.edu/faculty/garf/publications.html