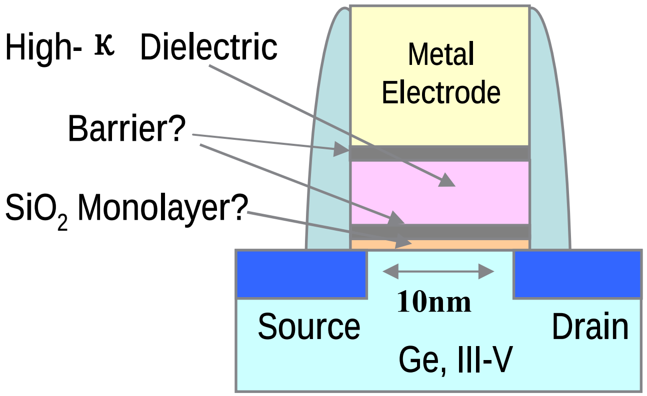
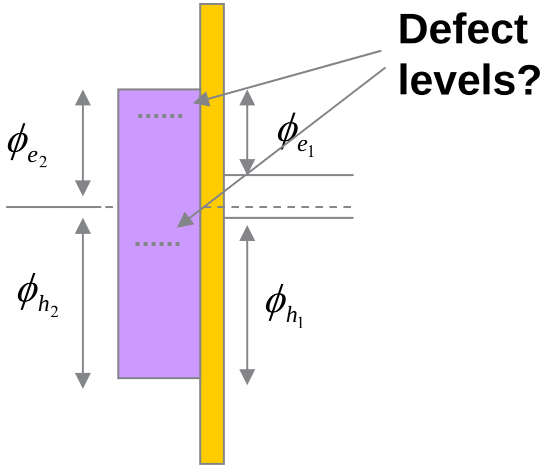
Materials stability, band alignment and defects in CMOS nanoelectronics



CMOS gate ~2010?



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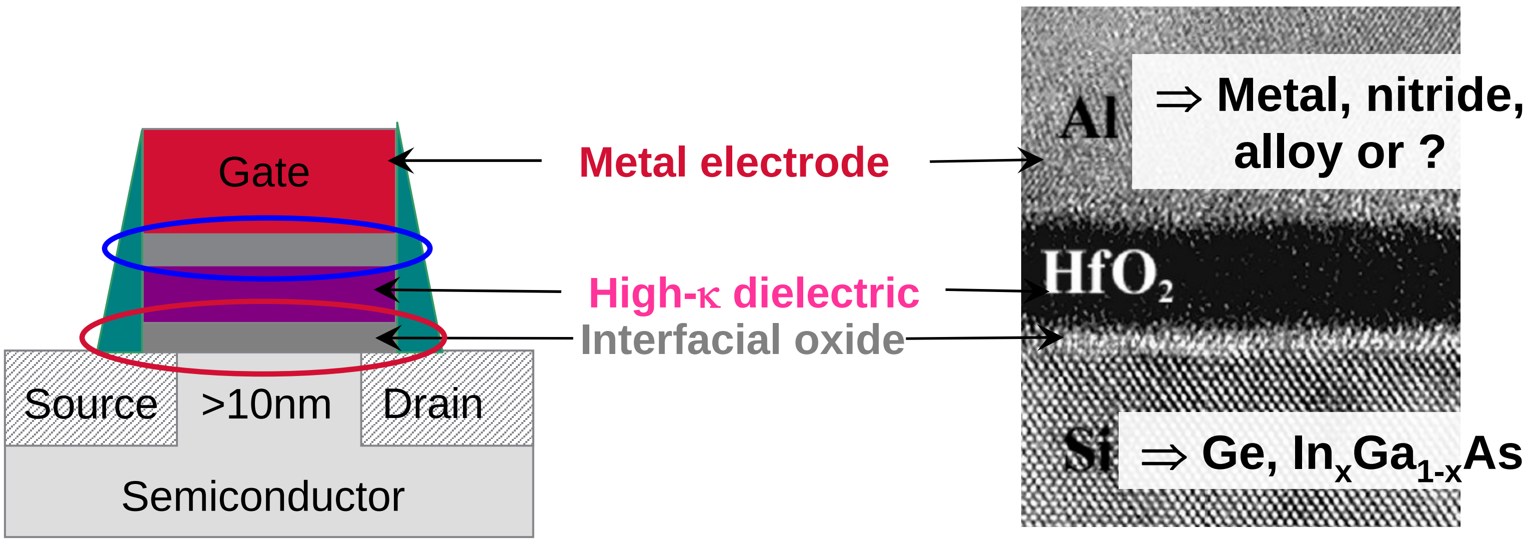
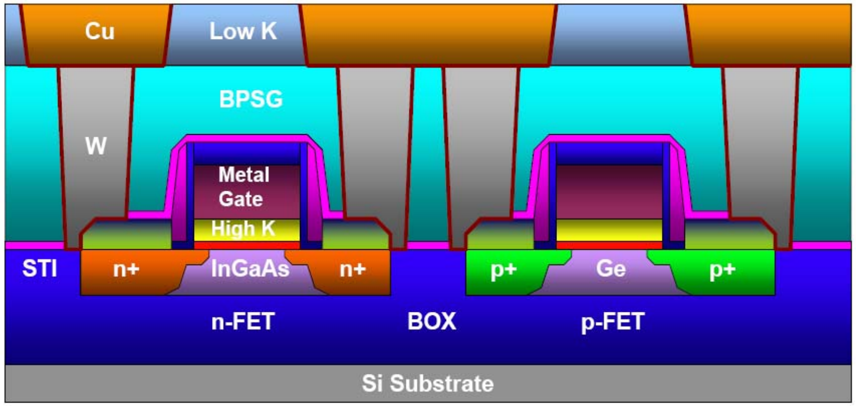
Collaboration: Vanderbilt, Sematech, NIST, Intel, IBM, IMEC, NCSU, Penn State, Stanford, UT-Dallas, UT-Austin, Albany….

Materials issues and electrical behavior



H. Kim, *et al.*, *JAP* **96** (2004) 3467

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



IBM

- **Defects at high-κ/semiconductor interfaces, in interface layers, or in films**
- **Interfacial oxide formation at high-κ/metal gate interface**
- **Thermal stability and interdiffusion**

Use high resolution characterization methods 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

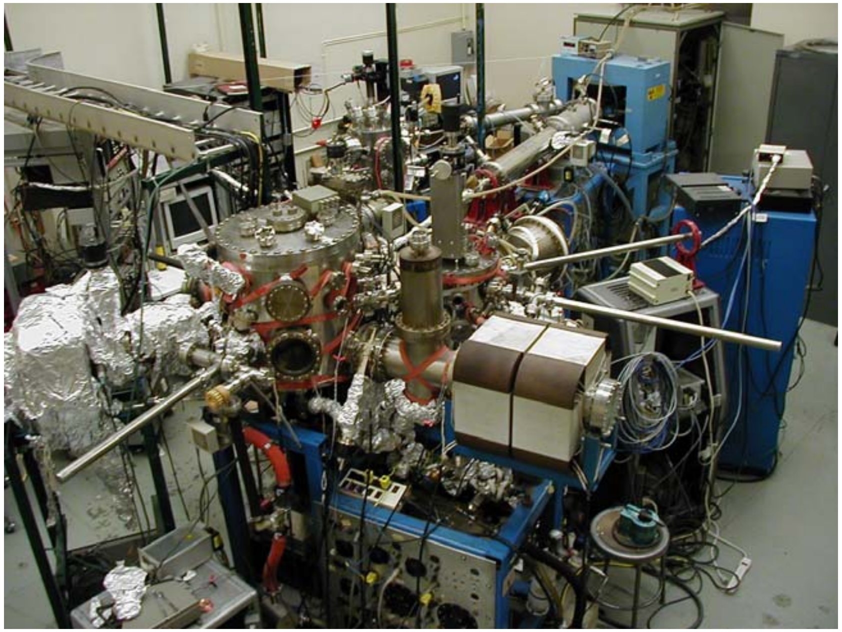
Outline

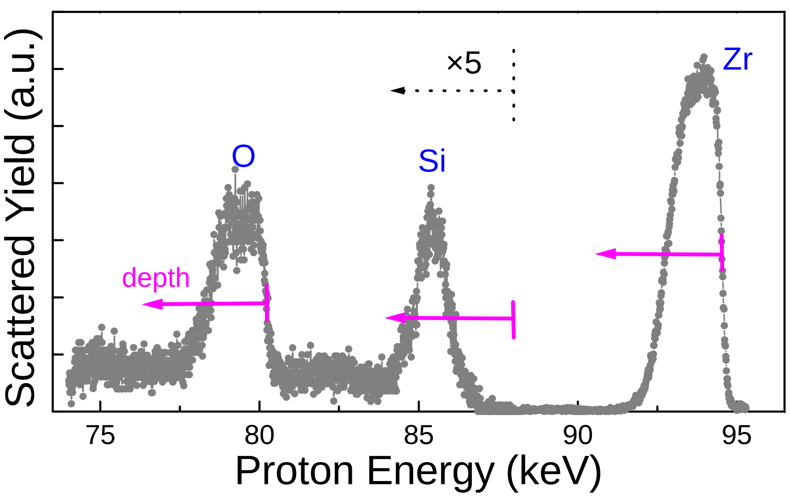
1. Experimental Methods
   - compositional depth profiling – MEIS, XPS, RBS…
   - electronic structure – PES, IPE, optical and electrical methods…
2. High-k on Si, Ge and III-V substrates (new materials, defects and radiation damage)
   - HfO_2 on InGaAs (passivation issues)
   - Metal gate effects and interface interactions

Defects – understand and control critical for high-K integration

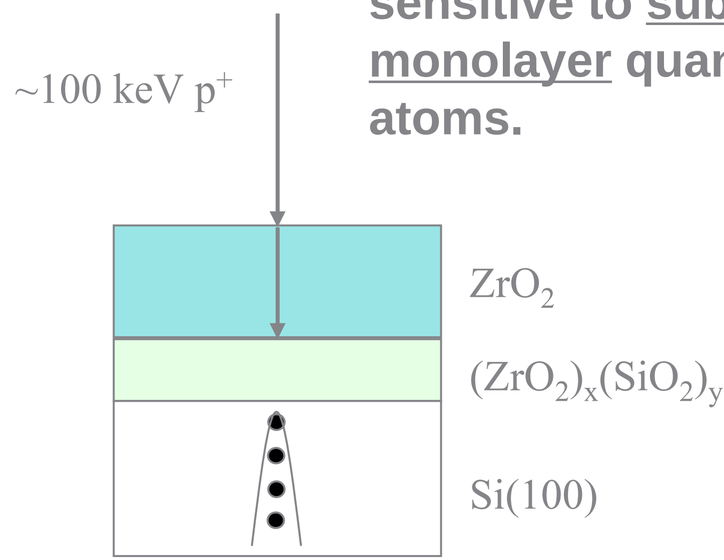
- What defects are in as-grown high-K stacks?
  - vacancies - O, Hf or Si
  - impurities - H, Si, Ti, Zr, Hf, N, C, Cl, F etc.
  - interstitials - O, Hf and Si
  - Thermo/kinetic (stable/metastable);
- When formed during processing?
  - During high-K dep, stressing, metallization and/or post-growth anneals
- How best to minimize?
  - During or following anneals
- Does high-E radiation create defects or just permit the population of preexisting ones?

Medium energy ion scattering: high resolution, low energy variant of RBS.



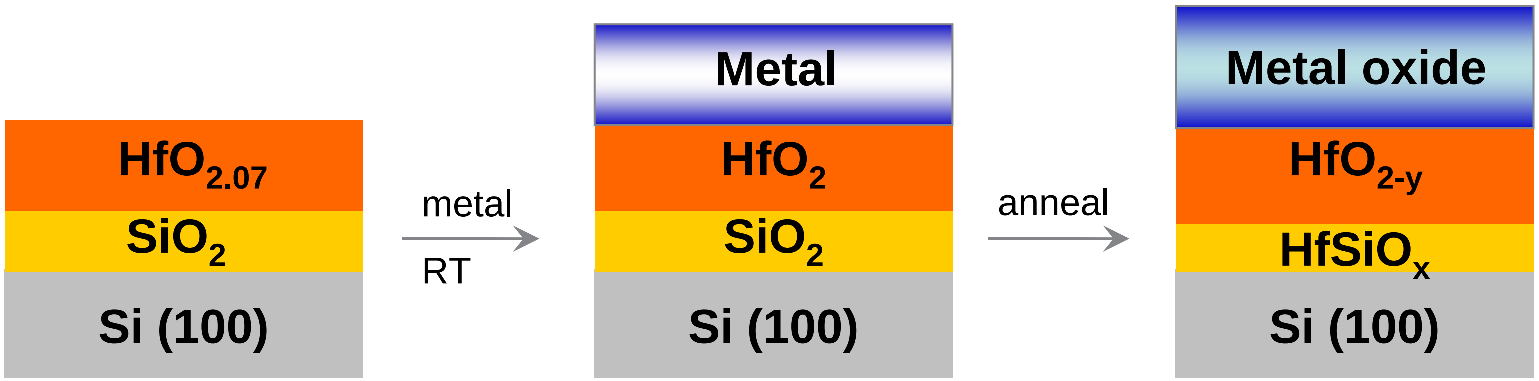


MEIS is a <u>quantitative</u> technique with <u>sub-nm</u> depth resolution, sensitive to <u>sub-monolayer</u> quantities of atoms.

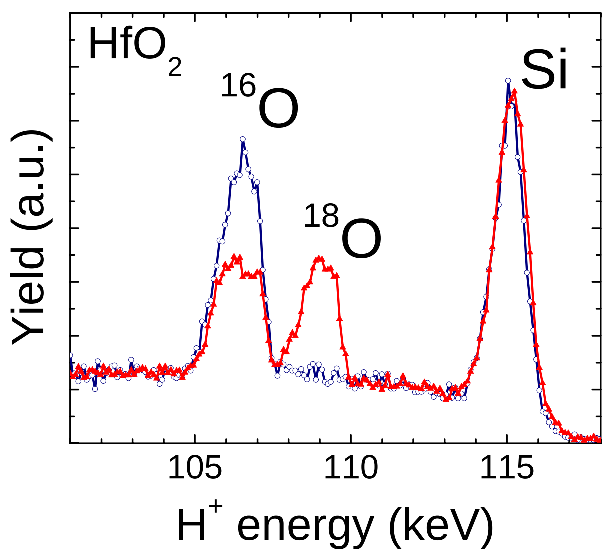


w/Gustafsson

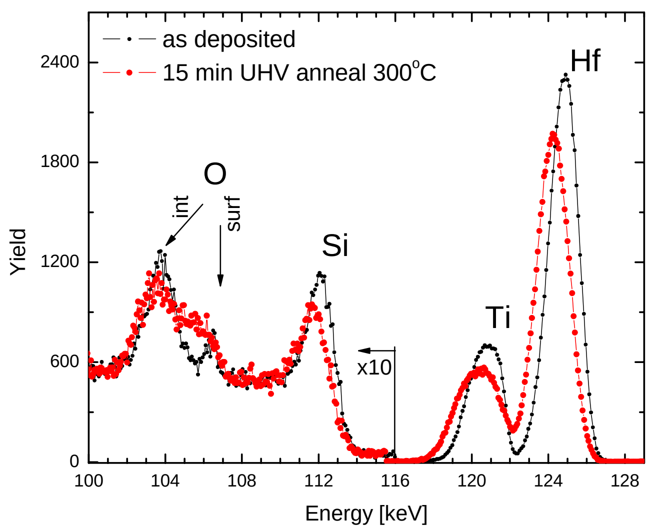
Gate metal effect on chemical stability of dielectrics



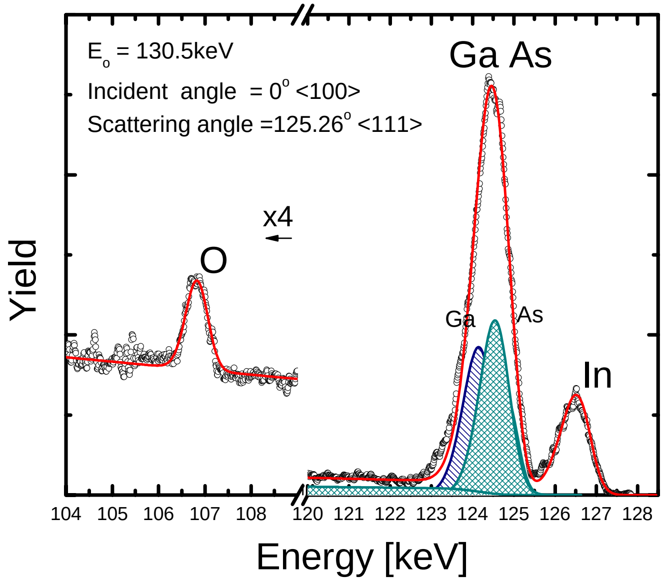
metallization

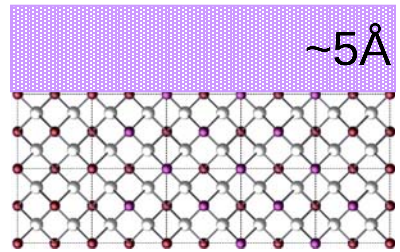


isotope studies



Oxides of InGaAs: surface characterization

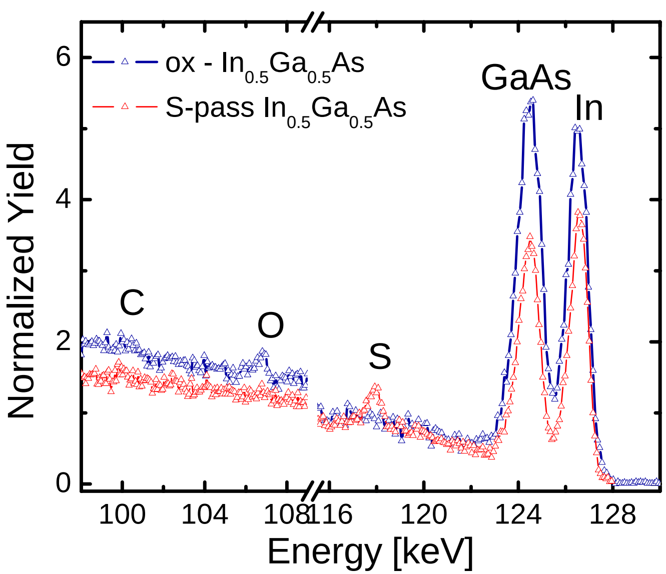




~5Å $(In_{0.36}Ga_{1.64}O_3)_{0.6} : (As_2O_3)_{0.4}$

InGaAs(001)

- Top layer contains thin oxide
- O areal density = 2.3×10^{15} atoms/cm^2
- Separation of Ga and As peak is poor



S passivation procedures:

1.(a) HF etch; (b) $(NH_4)_2S$ (40%; 80°C, 15min)

2.(a) no HF ; (b) $(NH_4)_2S$ (10%; 80°C, 15min)

➢ Thin native oxide layer on InGaAs before S pass.

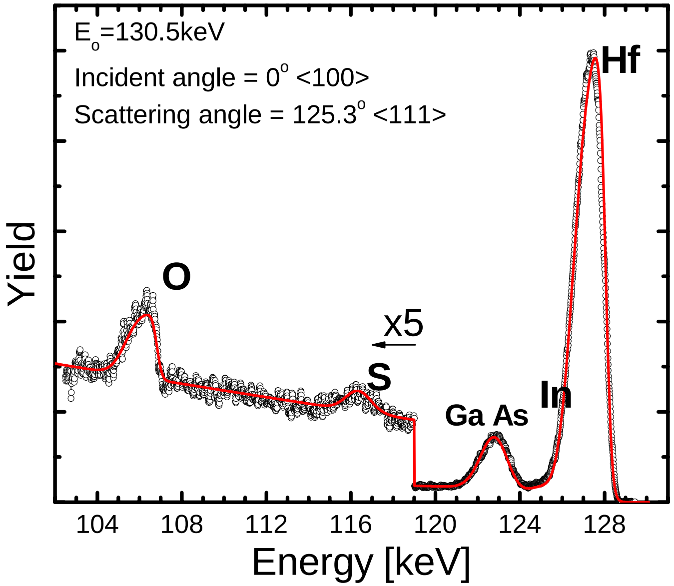
➢ After passivation: oxygen is removed; S peak appears; change in surface $In_{0.5}Ga_{0.5}As$ composition

$In/(Ga + As)_{\text{before passivation}} = 0.85$

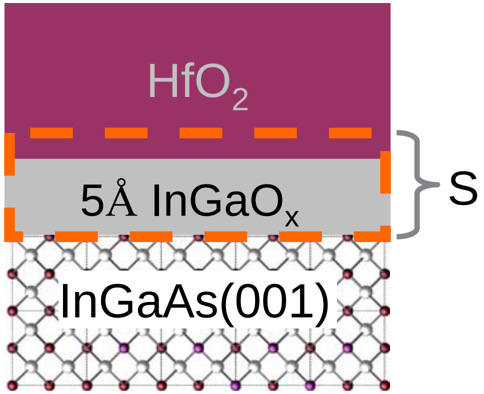
$In/(Ga + As)_{\text{after passivation}} = 1.17$

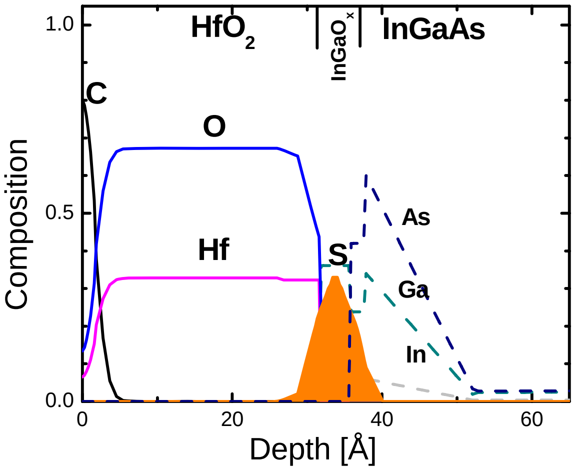
➢ **Roughness issue**!!!

HfO_2 deposition on S-passivated InGaAs(001)

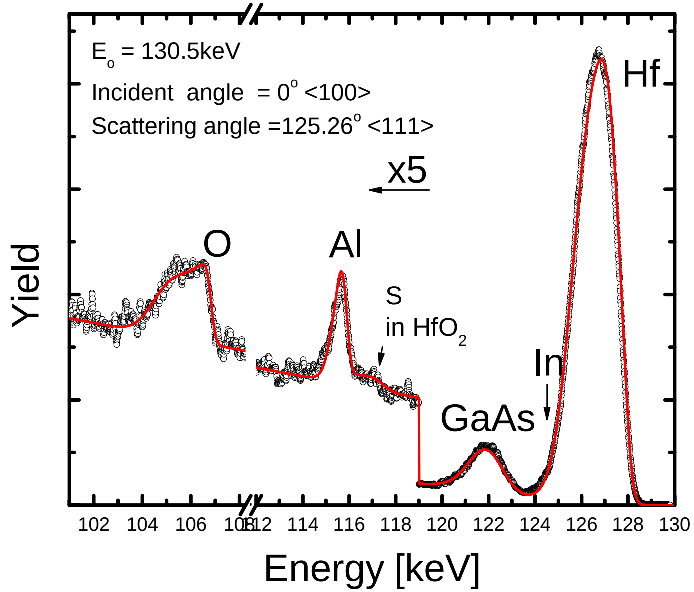


- Sulfur (1.3×10^{15}atms/cm^2) is distributed at the HfO_2/InGaAs interface
- HfO_2 layer has small oxygen excess;
- Thin Ga-rich interfacial $In_{0.13}Ga_{0.87}O_{x:}S$ layer is present

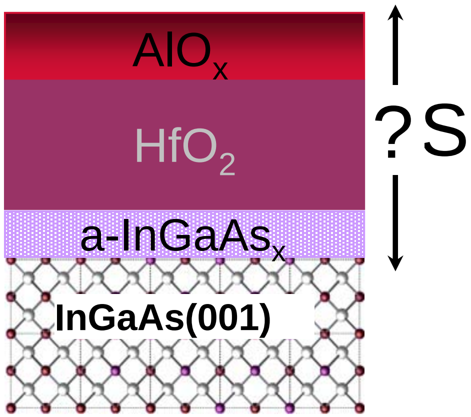


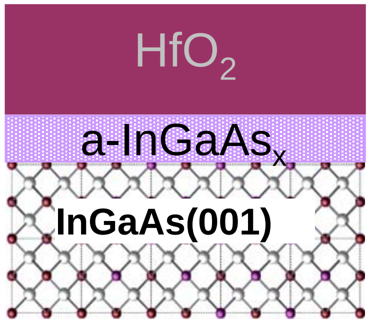


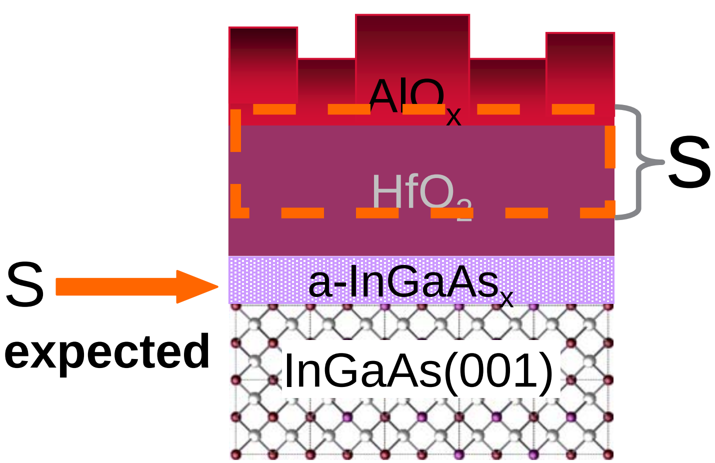
Depth profiling of Al/HfO_2/S-passivated InGaAs(001)

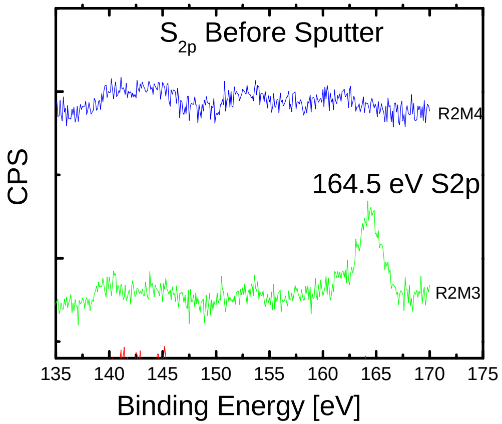


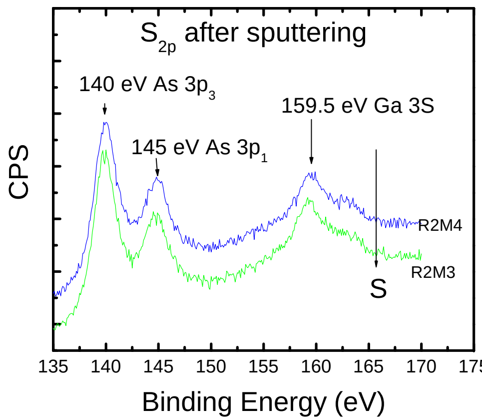
XPS results:







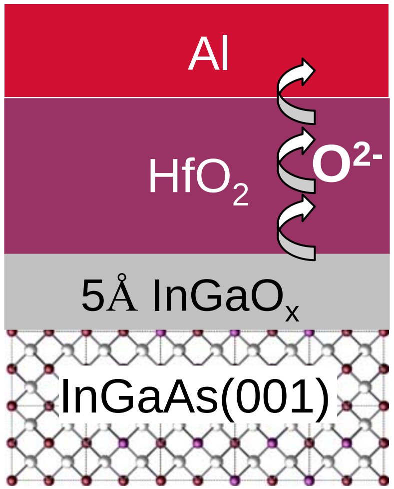




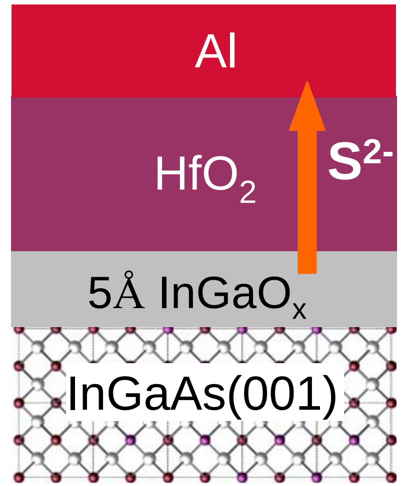
Conclusion: XPS confirms MEIS – S moves!

Diffusion and reaction processes in the films

Oxygen diffusion



Sulfur diffusion



- No interfacial layer
- Oxygen gettering was observed for Ti or Al/HfO_2/Si(001)

- After Al deposition S distribution is within the HfO_2 layer, not at HfO_2/InGaAs interface

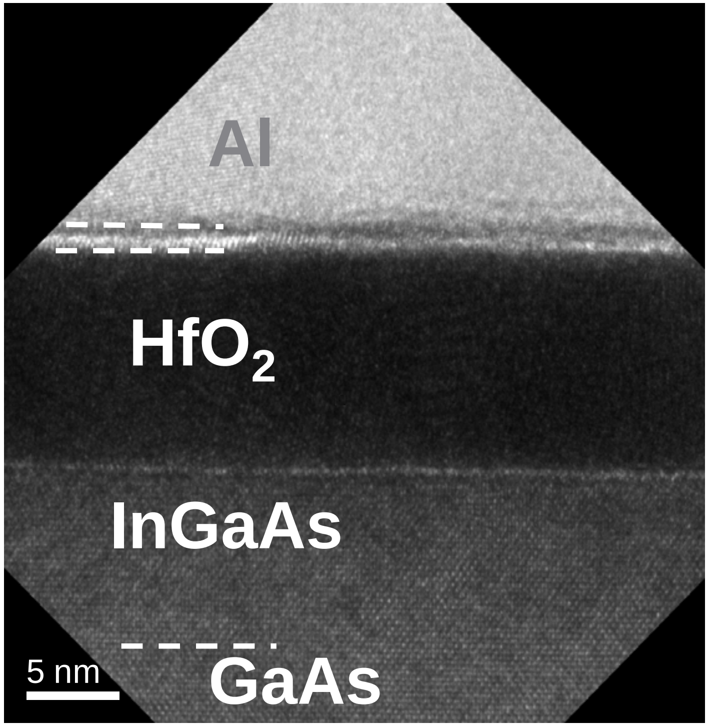
Comparison of free energy of formation from I.Barin, *Thermochem. data of pure substances*, 1995

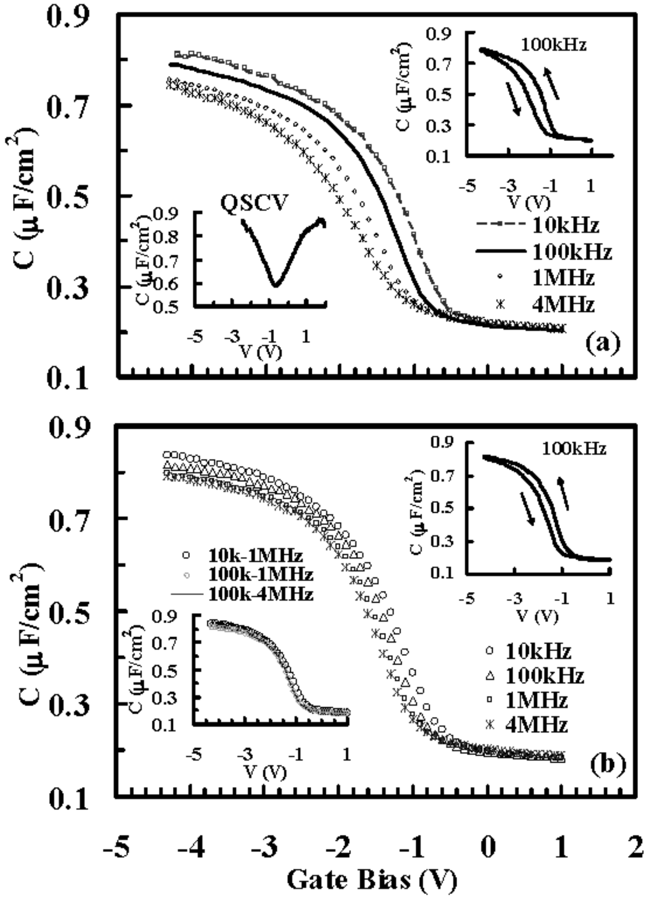
ΔG^f_{300K}, kJ/mol	M_2O_3	M_2S_3	ΔG^f_{300K}, kJ/mol	M_2O_3	M_2S_3
In	-830.04	-341.17	Hf (HfO_2)	-1087.9	*
Ga	-997.77	-505.61	Al	-1581.7	-713.24
As	-576.16	-166.16	* Data not available		

Al/HfO_2/InGaAs: TEM and electrical

- Thickness of Al/HfO_2 interface is ~12 Å.
- From CV data the interfacial oxide has k < 9
- Thicker HfO_2 films are crystalline

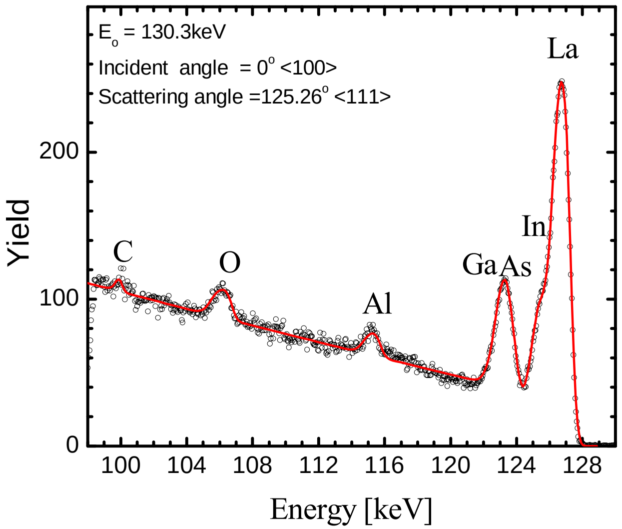
Sulfur passivation of InGaAs improves the frequency dispersion in room temperature C-V measurements



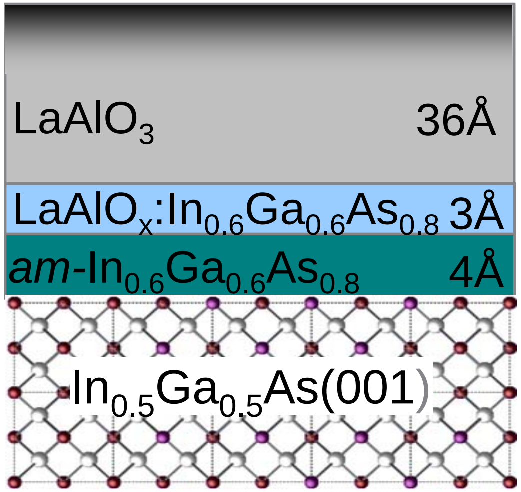


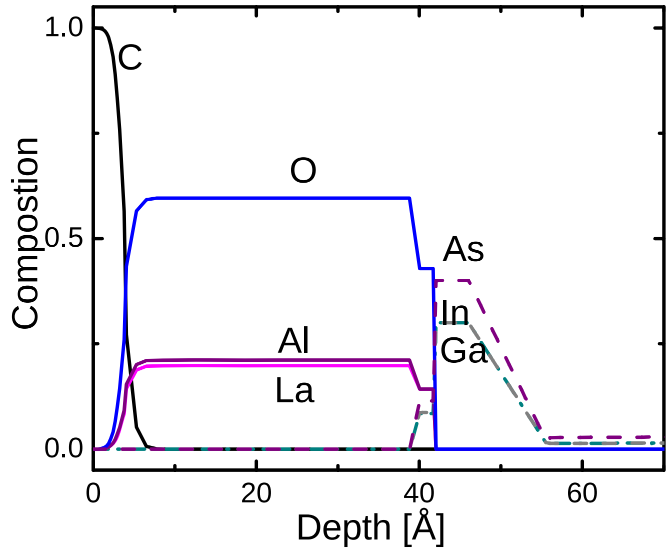
N. Goel, et al, *Appl. Phys. Lett.* **89** (2006) 163517

Post HfO_2 dielectrics: $LaAlO_3$ / InGaAs



- No **interfacial** $In_{0.4}Ga_{0.6}AsO_3$ layer
- Possible interdiffusion on $LaAlO_3$/InGaAs interface
- Relatively large **C peak** ⇒ surface La carbonates..?
- Some interface reactions at ~500C





Alternative channel - partial summary:

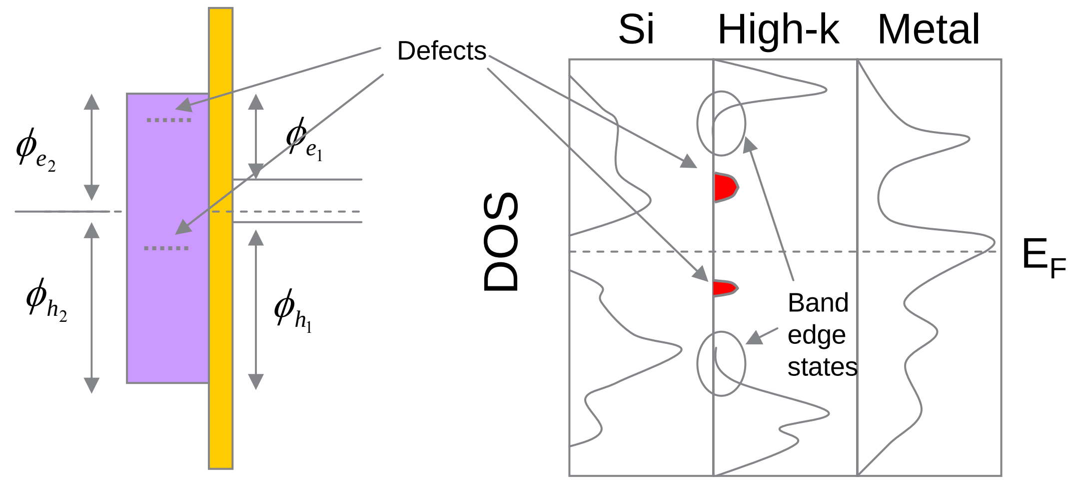
- High-K films on Ge and III-Vs compositionally layered.
- Oxides of Ge and GaAs less stable than SiO_2, hence potentially easy to remove thermally or chemically.
- Sulfur passivation helps in some systems. Roughness from etching an issue.
- Sulfur movement during high-K deposition and metallization, but some still in film.
- Si monolayers at interface appear helpful in minimizing defects.
- Metallization materials and processes effect film/interface – oxygen depletion.
- Possible inter-mixing of Hf at the interface during post deposition anneal (Hf in InGaAs - E_f pinning?)
- Nitride layers still help control interdiffusion.
- ALD growth initiation issues (again).

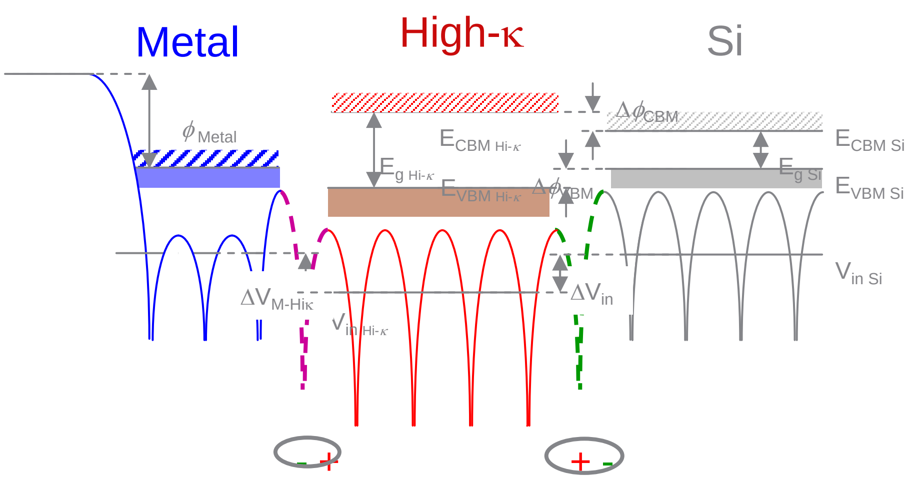
Electronic structure, band alignment and defects

- Band edge energies determined in many ways: mainly electrical and optical spectroscopy

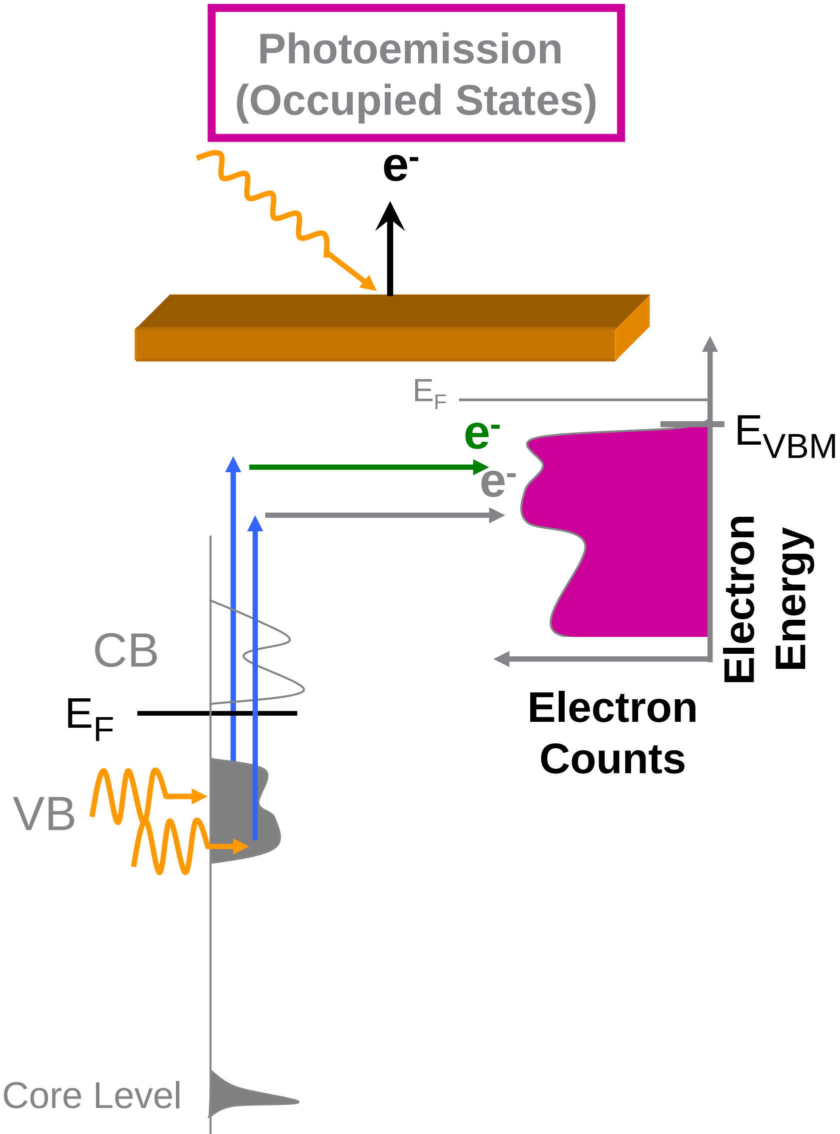
Can we use spectroscopies to:

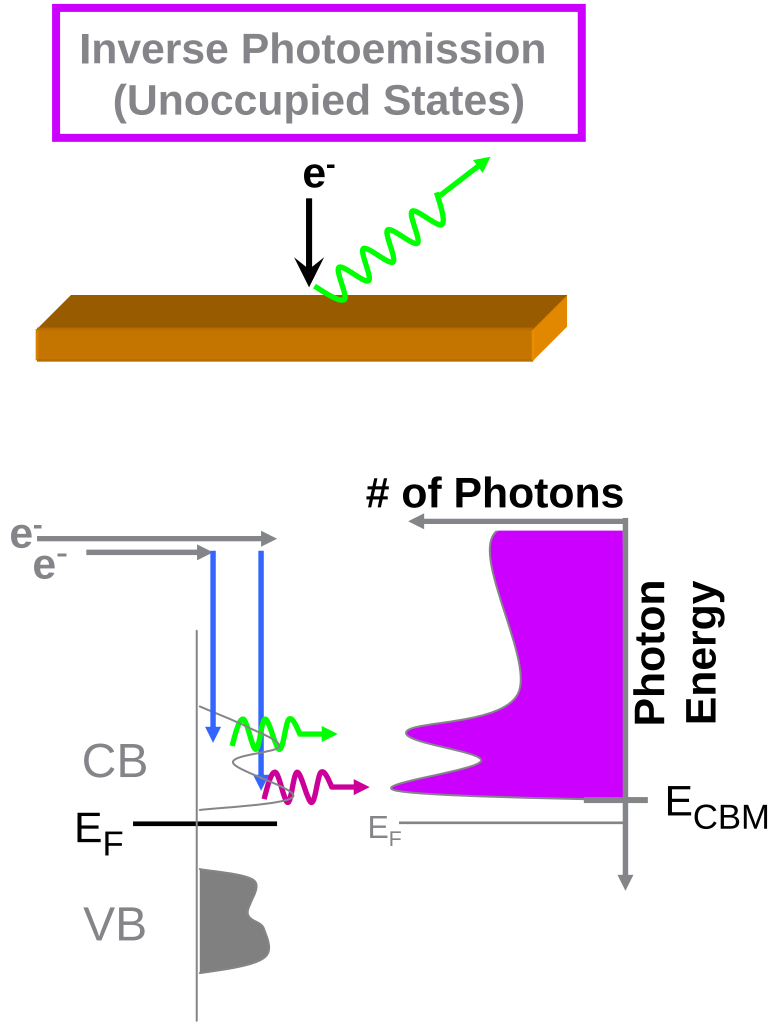
- measure energies and LDOS more precisely,
- see and quantify defects,
- determine interface dipoles and band alignment, and
- use interface engineering to control effective work function…





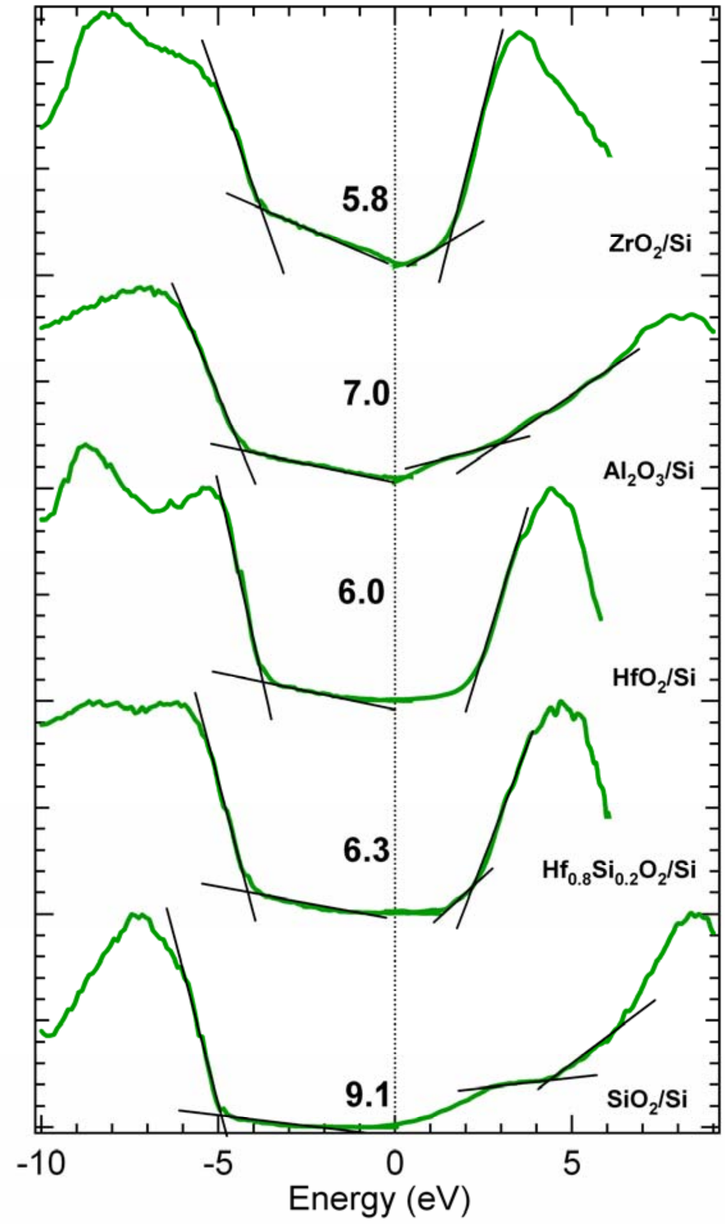
Experimental methods of band alignment





w/Bartynski

Densities of states and band gaps from various high-K dielectrics on Si

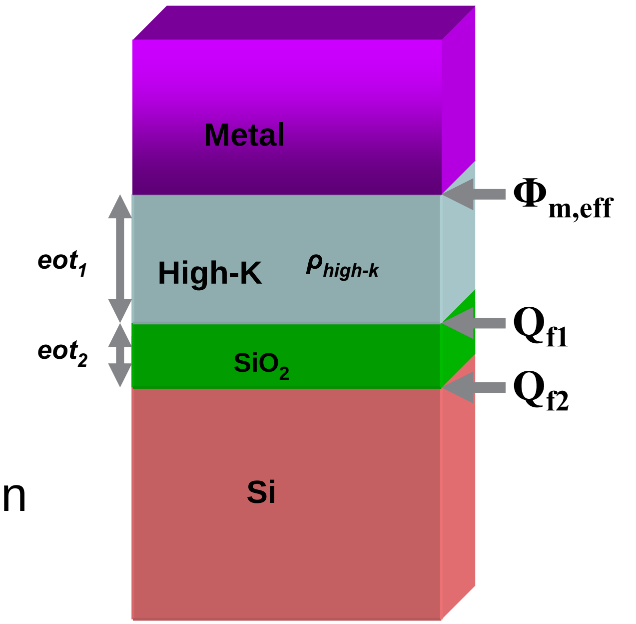


Work function – real and linguistic issues

- Work function (or vacuum work function) – minimum energy to remove an electron from a solid to >1nm.
  work function $\neq$ electrochemical potential

$$\left(E_N - E_{N-1}\right) \rightarrow \left(\frac{\partial A}{\partial n}\right)_{T,V} = \bar{\mu}$$

- Many ways to measure work function: UPS, kelvin probe, thermionic emission….
- "Effective work function" in devices – fictitious quantity, qualitatively assumed to be related to the real work function, that is used to explain band alignment between solids – defects that can charge and interface dipoles must be included in model



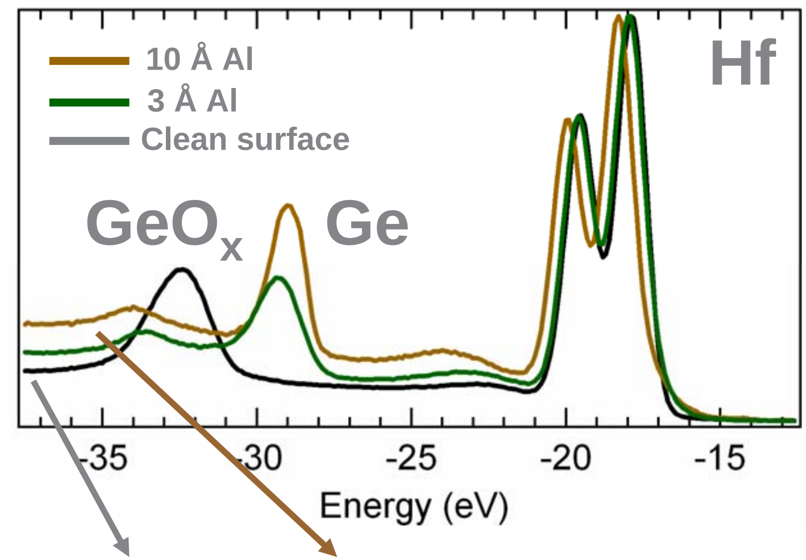
$$\Phi_{m,eff} = \Phi_{m,vac} + \Delta\Phi_{m,charge} + \Delta\Phi_{m,MIGS,dipoles,reaction}$$

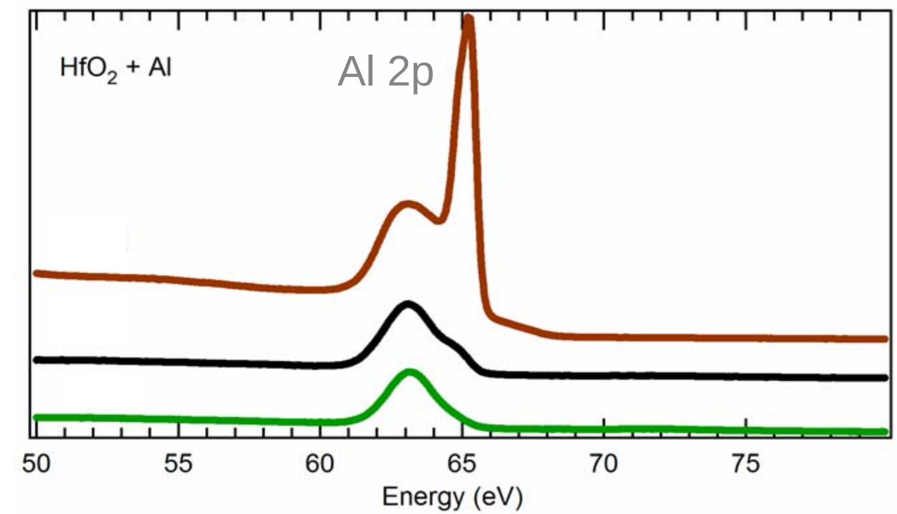
$$V_{FB} = \Phi_{m,eff-s} + \frac{1}{\varepsilon_{OX}}\left(Q_{f1} eot_2\right) - \frac{1}{\varepsilon_{OX}}\left(Q_{f1} + Q_{f2}\right) eot$$

$$V_{fb} = (\underline{\underline{\Phi'_{ms}}} - \frac{Q_i * EOTh}{\varepsilon_{ox}} - \frac{\rho_b * (\varepsilon_h / \varepsilon_{ox}) * EOTh^2}{2 * \varepsilon_{ox}} + \underline{\underline{\Delta D + \Delta Q}}) - \frac{Q_f * EOT}{\varepsilon_{ox}}$$

Rutgers, UTAustin, Sematech, NCSU, etc.

Interface Chemistry - Al/HfO_2/GeO_x/Ge and Al/HfO_2/SiO_x/Si



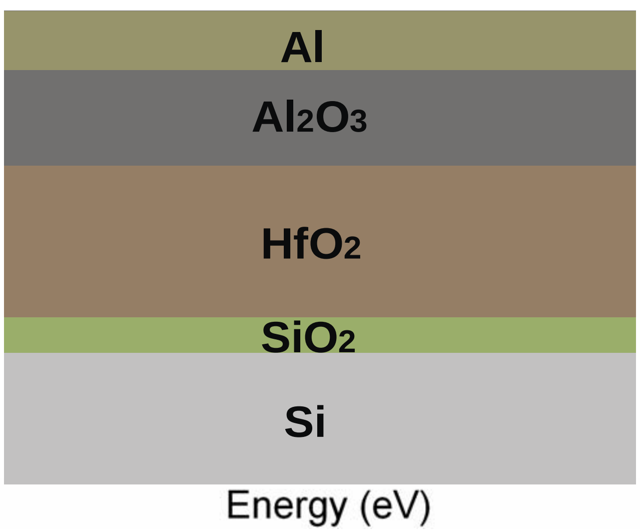


Hf4f and VB shift

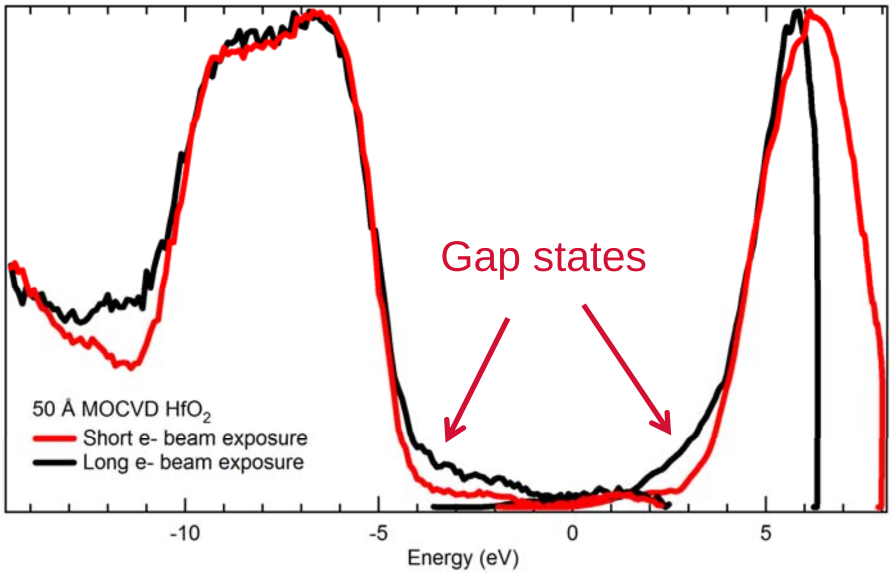
No significant reduction of HfO_2 in Hf4f

Interfacial oxide reduction at 300 K

Oxidation of Aluminium
Formation of a Al_2O_3 layer

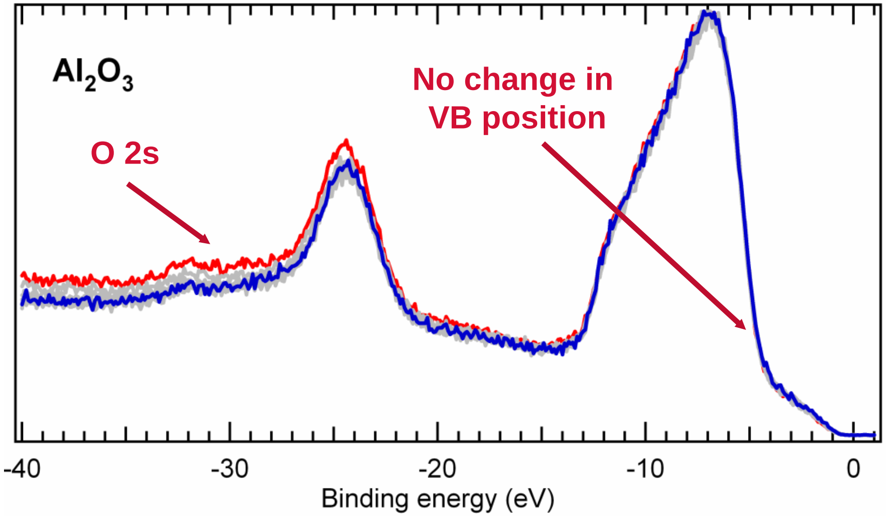


High-K oxides under low-energy radiation

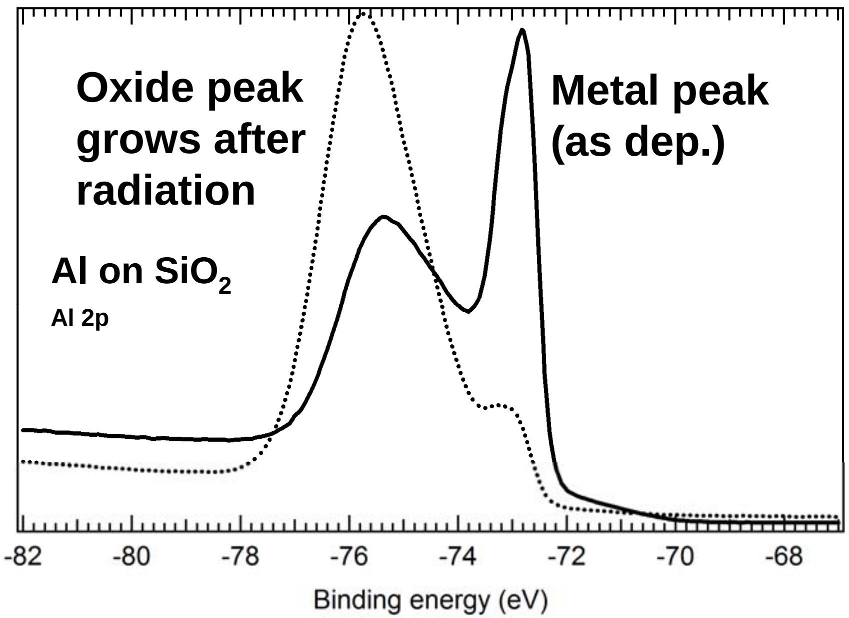


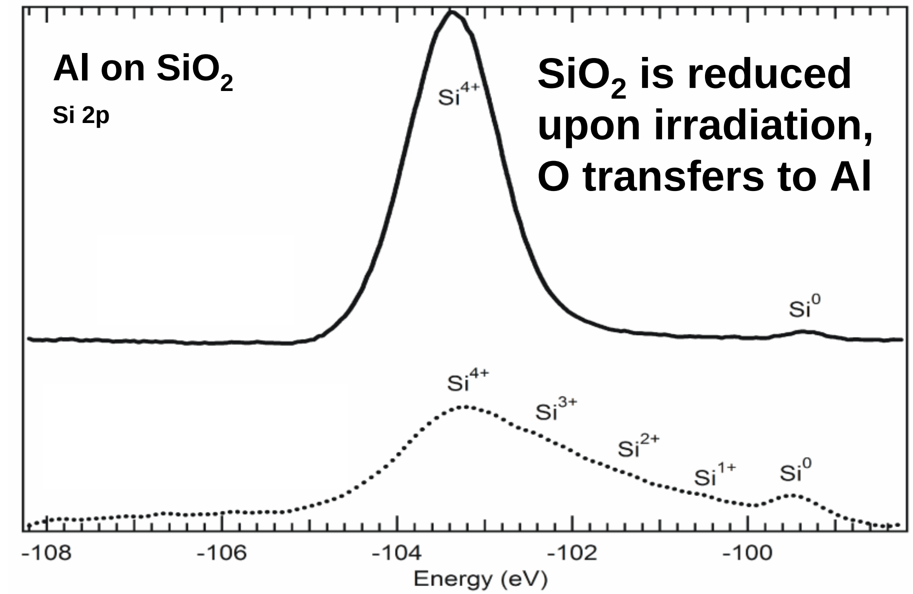
- **Gap states creation in HfO_2 upon electron beam exposure (less pronounced w/photons).**
- **20eV electrons; ~10^{15}/cm^2**
- **Electron-stimulated oxygen desorption?**
- **K-F mech?**

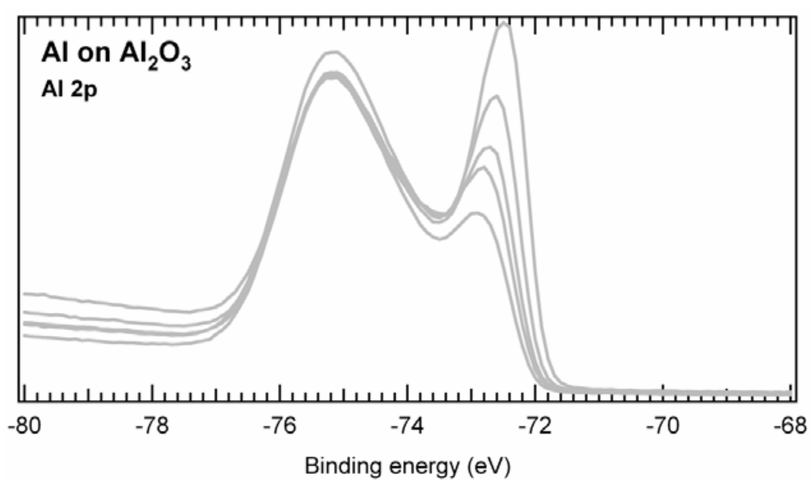
Hints of oxide reduction in Al_2O_3 as a function of x-ray exposure (from red to blue), but much less extensive than in HfO_2.



Metal / oxide interaction upon x-ray exposure







Radiation induced interface chemistry!

Several monolayers of oxygen move.

Plans

- **Pursue high-K/metal gate integration on III-Vs and Ge**
- **Correlate physical measurement results with electrical methods (vis a vis defects).**
  - **Thermal and chemical stability of passivation layers on III-V surfaces and relation to defect conc: Si, S, etc.**
  - **Correlate S content and location with electrical properties**
- **Explore E_f pinning and relation to interface composition in alt. channel materials**
- **Monitor H/D concentration and profiles in alternative channel materials, and explore radiation induced defect generation.**
- **Explore defects in Ge nanowire FETs**

Students and PDs:

Lyudmila Goncharova, Chien-Lan Hsueh, Weirong Jiang, Ozgur Celik, Ken Bratland, Lauren Klein, Tong Wang, Chi-yueh Kao, Gloria Gottardi, Safak Sayan, Mateus Dalponte, Sylvie Rangan, Tian Feng, Eric Bersch

Selected Recent MURI-related Publications (past year):

- L. V. Goncharova, M. Dalponte, T. Gustafsson, O. Celik, E. Garfunkel, P. S. Lysaght and G. Bersuker; *Metal-gate-induced reduction of the interfacial layer in Hf oxide gate stacks*, J. Vac. Sci. Tech. A **25**, 261 (2007).
- C.M. Osburn, T. Gustafsson, E. Garfunkel, et al; *Materials and Processes for High k Gate Stacks: Results from the FEP Transition Center, ECS Transactions*, **3**, (3) 389 (2006).
- E. Garfunkel, T. Gustafsson, P. Lysaght, S. Stemmer, R. Wallace; *Atomic Scale Materials Characterization Challenges in Advanced CMOS Gate Stacks*, Future FAB International **21**, 126 (2006).
- L.V. Goncharova, D.G. Starodub, E. Garfunkel, T. Gustafsson, V. Vaithyanathan, J. Lettieri, D.G. Schlom; *Interface structure and thermal stability of epitaxial SrTiO3 thin films on Si(001)*, J. Appl. Phys. **100**, 014912 (2006).
- L.V. Goncharova, M. Dalponte, D.G. Starodub, T. Gustafsson, E. Garfunkel, P.S. Lysaght, B. Foran, J. Barnett, G. Bersuker; *Oxygen diffusion and reactions in Hf-based dielectrics*, J. Appl. Phys. **89**, 044108 (2006).
- R. Barnes, D. Starodub, T. Gustafsson, E. Garfunkel; *A medium energy ion scattering and x-ray photoelectron spectroscopy study of physical vapor deposited thin cerium oxide films on Si(100)*, J. Appl. Phys. **100**, 044103 (2006).
- B. Chen, R. Jha, H. Lazar, N. Biswas, J. Lee, B. Lee, L. Wielunski, E. Garfunkel, V. Misra; *Influence of Oxygen Diffusion Through Capping Layers of Low Work Function Metal Gate Electrodes*, IEEE Electron Device Letters **27**, (4) p. 228 (2006).

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